Bounds to electron-repulsion energies

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Abstract. A review of rigorous bounds to electron-repulsion integrals for atoms and molecules is presented. Inequalities involving direct (classical) as well as indirect (quantal) Coulomb energies are discussed. This is followed by an account of two-electron integrals in a Hartree–Fock context over Gaussian basis-sets. Novel rigorous bounds to these integrals are derived and tested for some organic molecules. Connections are established with the density-based inequalities presented earlier. The present results are expected to enhance the efficiency of a general *ab initio* Gaussian program and yet have a sound theoretical footing.

Keywords. Electron-repulsion integrals; Coulomb integrals; Gaussian basis-sets; density-based inequalities.

1. Introduction

Quantum chemical calculations on atoms and molecules at Hartree–Fock and more refined levels (viz. CI, MCSCF etc.) have now become feasible due to the advent of high-speed computers. These calculations need evaluation of one- and two-electron integrals over suitably chosen basis functions. Among the required integrals, the computation of electron repulsion energies is the most expensive part and forms a real bottleneck to further progress in this area. For example, use of N basis functions in a Hartree–Fock program (e.g. primitive Gaussian) requires $\sim N^4/8$ two-electron integrals. Thus, for example $N \sim 10^3$ necessitates enumeration of a huge number of ($\sim 10^{11}$) two-electron integrals. Evaluation and storage of these integrals requires large CPU time and disk-space respectively. However, it has been shown (Christoffersen 1972; Clementi and Mehl 1974) that for large molecular systems, a rather large fraction of the two-electron integrals is negligibly small in magnitude. Clementi (1972) demonstrated, with the example of a guanine-cytosine complex, that computer time can be considerably reduced if one avoids evaluation of numerically small integrals with a negligible loss in total energy. Many approximate criteria for discarding insignificant two-electron integrals have been used in the literature (see § 4 for further details). However, Ahlrichs (1974) was the first to derive a rigorous upper bound to the electron-repulsion integral for s-type Gaussians. With the application of this bound, integrals numerically smaller than a pre-set threshold value, can be identified and neglected without actually computing them. In fact, Ahlrichs demonstrated with the example of the C_2H_4 molecule that if a cutoff value of 10^{-7} a.u. is chosen, then there is no loss in the optimal value of the SCF energy. However, this approach was not extended to other types of orbitals, e.g. $p, d, \ldots$ types of Gaussians.

Of late, the density functional theory (DFT) (for a comprehensive review, see Dreizler and Providencia 1985) has been extensively applied to a wide variety of

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atomic, molecular and solid-state problems. The crux of DFT is contained in the celebrated Hohenberg–Kohn (1964) theorem which proves that the ground state properties of these systems are unique functionals of the corresponding electron density, ρ. In particular,

$$E[\rho] = \int v(\mathbf{r})\,\rho(\mathbf{r})\,d\mathbf{r} + F[\rho], \tag{1}$$

where, v is the external potential and $F[\rho]$ the universal Hohenberg Kohn functional. $F[\rho]$ comprises two parts: the kinetic energy functional $T[\rho]$ and the electron repulsion energy functional, $U[\rho]$. The direct, or the Coulomb part $J[\rho]$ and the indirect part $E_{xc}[\rho]$ together make up the total electron-repulsion energy, U. A practical method for implementing the density functional calculations is offered by the Kohn–Sham (1965) procedure. The chief problem with DFT is that the universal functional $F[\rho]$ may never be known. However, towards an affirmative end, one may be able to develop bounding properties to this functional or its ingredients. In the past decade or so, a variety of rigorous bounds to these functionals have become available (for prototype results see Gadre *et al* 1979, Lieb and Oxford 1981, Sahni and Levy 1986, and references therein).

The purpose of the present work is two-fold. Firstly, we present an extensive review of the *rigorous* inequalities to electron-repulsion energies which are either density- or orbital-based. This is followed by a derivation of completely new tight bounds derived to electron repulsion integrals over Gaussian basis-sets.

The organization of this article is as follows. The bounds to the direct, or the Coulomb part are reviewed in §2. A compilation of the bounds to the indirect part, exchange energy etc. will be presented and discussed in §3. We work within the extra-field-free, non-relativistic, time-independent domain. Hartree atomic units $(m_e = e = \hbar = 1)$ are employed throughout the article. Section 4 contains a review of the rigorous and approximate work done so far with Gaussian basis-sets. New rigorous upper bounds to electron repulsion energies which are more general and tighter than those so far available in the literature will be derived in §5, wherein lower bounds to these integrals will be presented for the first time. Also, connections with the results presented in §§2 and 3 will be developed. Numerical tests and conclusions follow in §6.

2. Bounds to direct (Coulomb) energies

Schrader and Prager (1962) were the first to employ electrostatic variation principles for quantum chemical molecular energy calculations. In their work, the Thomson and Dirichlet principles of electrostatics have been used to obtain lower and upper bounds to electron-repulsion integrals in molecular calculations. For the Coulomb interaction

$$J = (1/2)\int [\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)/r_{12}]\,d\mathbf{r}_1\,d\mathbf{r}_2.$$

Consider minimization of $(1/8\pi)\int E^2\,d\mathbf{r}$ subject to $\nabla \cdot \mathbf{E} = 4\pi\rho$. This variational problem leads to the requirement that $\mathbf{E} = -\nabla V$ for some scalar function V. Noting that the second variation of $\int E^2\,d\mathbf{r}$ is always positive, one obtains

$$J \leqslant (1/8\pi)\int |\mathbf{E}|^2\,d\mathbf{r}, \tag{2}$$

for all $\mathbf{E}$ satisfying $\mathbf{E} = -\nabla V$.

A lower bound to J may be obtained by minimizing

$$W[V] = \int [2\rho V - (1/4\pi)(\nabla V)^2] \, dr,$$

where V is an arbitrarily chosen scalar function. The minimizing condition is provided by $\nabla^2 V = -4\pi\rho$, the Poisson equation. Noting that the second variation of W is always nonpositive, leads to a lower bound to J

$$J \geqslant \int [\rho V - (1/8\pi)(\nabla V)^2] \, dr, \tag{3}$$

which is essentially the Dirichlet principle that has enjoyed a long history in the computation of capacitances etc. Equation (3) attains equality if V is the electrostatic potential due to the charge density.

The above results (1) and (2) can be employed to obtain a bound

$$(1/2)\int [\rho_1(\mathbf{r}_1)\rho_2(\mathbf{r}_2)/r_{12}] \, dr_1 \, dr_2$$
$$\geqslant (1/8)\{ \int [2(\rho_1 + \rho_2)V - (1/4\pi)(\nabla V)^2] \, dr - (1/8\pi)\int E^2 \, dr\} \tag{4}$$

where $\nabla \cdot \mathbf{E} = 4\pi(\rho_1 - \rho_2)$. The inequalities were tested on the H_2 molecule and found to be fairly tight.

In a work by Weinstein *et al* (1975), numerical tests on a number of atoms indicate that, within the Hartree–Fock approximation, the spherically averaged ground state $\rho(\mathbf{r}) \equiv \rho(r)$ is indeed a monotone decreasing function. No rigorous proof of this observation exists to date. It is, however, possible to show rigorously that $\Phi(r)$, the total electrostatic potential for an atom is also monotone decreasing. Writing

$$\Phi(r) = Z/r - \int \rho(\mathbf{r}') \, d\mathbf{r}'/|\mathbf{r} - \mathbf{r}'|, \tag{5}$$

with the use of Poisson's equation $\nabla^2 \Phi = 4\pi\rho_{\text{(electronic)}}$ and employing spherical symmetry, one is led to

$$\Phi'' + (2/r)\Phi' = 4\pi\rho \geqslant 0, \tag{6}$$

which prohibits $\Phi'' < 0$ at the r-value where $\Phi' = 0$. Thus, $\Phi(r)$ is a monotone nonincreasing function. Thus, $\Phi' < 0$, for spherically averaged atomic electron density.

Bounds to Coulomb energies have been provided by Thulstrup and Linderberg (1979) in their pioneering work. The integral approximation method suggested by Harris and Rein (1966) has been further developed and applied. Thulstrup and Linderberg also noted that the first-ever use of Sobolev type inequalities in this context was reported by Okninski (1974). Here, one uses a result (Rosen 1971) in which the optimum form of the Sobolev inequality has been obtained, viz,

$$4\pi J = \int |\nabla\Phi|^2 \, dr \geqslant 3(\pi/2)^{4/3} (\int |\Phi|^6 \, dr)^{1/3}. \tag{7}$$

Note that

$$J[\rho] = (1/2)\int \rho(\mathbf{r}) \Phi(\mathbf{r}) \, dr, \tag{8}$$

where $\rho(\mathbf{r})$ is the charge density, and Φ, the electrostatic potential. Applying Hölder's inequality, one is led to

$$J[\rho] \leqslant (\int \rho^{6/5} \, dr)^{5/6} (\int |\Phi|^6 \, dr)^{1/6}/2. \tag{9}$$

Combining (1) and (3) leads to

$$J[\rho] \leqslant (4/3)(2/\pi)^{1/3} \left(\int \rho^{6/5}\, d\mathbf{r}\right)^{1/3}. \tag{10}$$

The constant in the above bound turns out to be approximately 1.147.

A more flexible form is suggested by a further application of the Hölder inequality, yielding

$$\int \rho^{6/5}\, d\mathbf{r} = \int |f(\mathbf{r})|\, d\mathbf{r}\, \rho^{6/5}(\mathbf{r})/|f(\mathbf{r})|$$

$$\leqslant \left(\int |f|^m\, d\mathbf{r}\right)^{1/m} \left(\int \rho^{6n/5} f^{-n}\, d\mathbf{r}\right)^{1/n} \tag{11}$$

with $1/m + 1/n = 1$ and $m > 1$.

A variety of bounds to $J[\rho]$ can be generated by using (10) and (11) with appropriate choices of f. However bounds can be made tighter by optimizing the numerical constants in these bounds for each choice of f, e.g.,

$$J[\rho] \leqslant C_1 N^{4/3} \left(\int \rho^2\, d\mathbf{r}\right)^{1/3}. \tag{12}$$

The best possible constant C_1 is determined by variational calculus $\delta \{ J[\rho]/[(\int \rho\, d\mathbf{r})^{4/3} (\int \rho^2\, d\mathbf{r})^{1/3}] - \mu \int \rho\, d\mathbf{r} \} = 0$, and where μ is the Lagrange multiplier, turns out to be:

$$C_1 \simeq 1.5/\pi^{1/3} \simeq 1.0242.$$

Further discussion of these and related bounds as well as some test examples was carried out in detail (Thulstrup and Linderberg 1979). The results of this paper have been exploited by Gadre *et al* (1979) to obtain bounds to $J[\rho]$ in the form

$$J[\rho] \leqslant K \int \rho^{4/3}\, d\mathbf{r}. \tag{13}$$

These bounds are of interest since the most popular approximation to exchange viz. the Slater–Dirac exchange is of the form given by the RHS of (13) but with a negative constant multiplier. Golden (1980) has employed the result due to Thulstrup and Linderberg (1979). Assuming that the spin summations have been carried out, one is led to [via (11) above]

$$\int d\mathbf{r}_1\, d\mathbf{r}_2 |\psi_k(\mathbf{r}_1)|^2 |\psi_k(\mathbf{r}_2)|^2/|\mathbf{r}_1 - \mathbf{r}_2|$$

$$\leqslant C \int \{ |f_k(\mathbf{r})|^{5/2} \}^{2/3}\, d\mathbf{r} \int |\psi_k(\mathbf{r})|^4\, d\mathbf{r}/|f_k(\mathbf{r})|^{5/3}.$$

Here, $C = (2^{10/3})/(3\pi^{1/3})$,

$$\tag{14}$$

by choosing $f_k(\mathbf{r}) = \{ \psi_k(\mathbf{r}) \}^{6/5}/\rho_\uparrow^{1/5}(\mathbf{r})$,

$$\tag{15}$$

where

$$\rho_\uparrow(\mathbf{r}) = \sum_{n=1}^{N\uparrow} |\psi_n(\mathbf{r})|^2. \tag{16}$$

This leads to

$$\sum_{n=1}^{N\uparrow} \int d\mathbf{r}_1\, d\mathbf{r}_2 |\psi_n(\mathbf{r}_1)|^2 |\psi_n(\mathbf{r}_2)|^2/|\mathbf{r}_1 - \mathbf{r}_2|.$$

$$\leqslant C \int \rho^{4/3}\, d\mathbf{r}. \tag{17}$$

Employing a result derived earlier by Golden (1979), a bound on the indirect part of the electron repulsion energy was also derived. This bound resembles that due to

Lieb to be discussed in the following section. However, it may be noticed that these results (Golden 1979, 1980) are confined to the realm of the Hartree–Fock theory. The results due to Lieb, on the other hand, are more general.

The work of Thulstrup and Linderberg (1979) was extended by Gadre *et al* (1979). The motivation was provided by a local density functional model derived earlier (Parr *et al* 1979)

$$E[\rho] = (3/5)A_0 \int \rho^{5/3} \, \mathbf{dr} + (3/4)B_0 N^{2/3} \int \rho^{4/3} \, \mathbf{dr} + \int v\rho \, \mathbf{dr}. \tag{18}$$

The form was derived assuming that the kinetic and electron–electron repulsion energies are represented by local functionals of the form $K(N)\int \rho^l \, \mathbf{dr}$, where $K(N)$ includes the function of the number of electrons, N, as well as constants. The constant l was uniquely fixed by the use of elegant scaling arguments (Szasz *et al* 1975). In this work (Parr *et al* 1979), various fits to the $J[\rho]$ and $K[\rho]$ evaluated from near Hartree–Fock quality (Clementi and Roetti 1974) densities were presented. Some of the fits carried out may be represented as:

$$J[\rho] = B_0 N^{2/3} \int \rho^{4/3} \, \mathbf{dr},$$

$$K[\rho] = B_1 \int \rho^{4/3} \, \mathbf{dr},$$

$$J[\rho] = (B_0 N^{2/3} + B_1) \int \rho^{4/3} \, dr,$$

and

$$V_{ee}[\rho] = (B_0 N^{2/3} + B_1) \int \rho^{4/3} \, \mathbf{dr}. \tag{19}$$

Gadre *et al* (1979) derived a theorem that all densities $\rho(\mathbf{r})$ which are finite everywhere and $\to 0$ as $|\mathbf{r}| \to \infty$ *must* satisfy

$$J[\rho] = (1/2)\int [\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)/r_{12}] \, \mathbf{dr}_1 \, \mathbf{dr}_2$$

$$\leqslant 1.0918 \, N^{2/3} \int \rho^{4/3}(\mathbf{r}) \, \mathbf{dr}. \tag{20}$$

The proof begins with the inequality (11) above.
Putting $f = \rho^{2/5}$, $m = 5/2$ and $n = 5/3$, one gets

$$J \leqslant CN^{2/3} \int \rho^{4/3} \, \mathbf{dr} \tag{21}$$

where C is obtained by minimizing

$$F[\rho] = J[\rho]/[(\int \rho \, \mathbf{dr})^{2/3} \int \rho^{4/3} \, \mathbf{dr}]. \tag{22}$$

By the use of the solution of a Lane–Emden type equation, it turns out that $C \simeq 1.0918$ (see also Lieb and Oxford 1981).

Some lower bounds to $J[\rho]$ were also obtained by the use of Dirichlet's principle as pointed out by Schrader and Prager (1962), viz,

$$J \geqslant (1/2)[\rho(\mathbf{r})V(\mathbf{r}) - (1/4\pi)|\nabla V(\mathbf{r})|^2 \, \mathbf{dr}], \tag{23}$$

where the equality is attained when $V = \Phi$, the classical electrostatic potential arising from the charge density $\rho(\mathbf{r})$. Gadre *et al* (1979) derived various lower bounds to J, which are rather complicated in form since they involve gradients of the electron density, e.g.,

$$J \geqslant \pi(\int \rho^{4/3} \, dr)^3 / \{9N T_2[\rho]\}, \tag{24}$$

where $T_2[\rho]$ is one-ninths of the Weizsäcker correction.

The upper and lower bounds obtained in this work were tested on the atomic near Hartree–Fock densities (Clementi and Roetti 1974). An immediate interesting application of these bounds was made by Perdew and Zunger (1981) to estimate the self-interaction correction within the X_α theory. They employed the bound (3) in the sense of an equality and estimated the correction to be $\cong 0.16 \sum_{\alpha\sigma} \int \rho_{\alpha\sigma}(\mathbf{r})^{4/3} d\mathbf{r}$.

Here, α and σ denote orbital and spin indices. Gadre and Bendale (1983) investigated the possibility of modelling the Coulomb (J) and total electron repulsion energy (V_{ee}) by simple functionals of one-electron density.

The forms explored by them were:

$$N^{2/3} \int \rho^{4/3} d\mathbf{r}, \left(\int \rho^{6/5} d\mathbf{r} \right)^{5/3}, N^{4/3} \left(\int \rho^2 d\mathbf{r} \right)^{1/3} \text{ and } N^{3/2} \left(\int \rho^3 d\mathbf{r} \right)^{1/6}.$$

They found that these forms lead to remarkably linear fits to J and V_{ee} when employed in conjunction with near Hartree–Fock data.

Gadre and Pathak (1981a) carried out variational calculations on the He atom and the H_2 molecule by replacing $J[\rho]$ by the RHS of (20). They noted that the total energy thus obtained is higher by a mere 0.3% for the He atom w.r.t. the near Hartree–Fock wavefunction. The H_2 molecule shows binding at around the true Hartree–Fock minimum: the sacrifice in energy being less than 0.2%.

Further, along these lines, Pathak *et al* (1982) developed a first-ever approximate density functional model for atoms in momentum space. The total electron-repulsion energy was modelled by them as $BN^{2/3} \int \rho^{4/3} d\mathbf{r}$. However, semiclassical phase-space considerations lead to a result that $\int \rho^{4/3} d\mathbf{r}$ is proportional to $\langle p \rangle$, the linear momentum expectation value (Pathak and Gadre 1981; Gadre and Pathak 1981b). This enabled Pathak *et al* (1982) to obtain a remarkably simple form for atomic momentum densities and rather quick predictions of atomic momentum space properties.

Coulomb energy, total X-ray scattering intensities and average electron densities were connected via rigorous bounds by Chakravorty and Gadre (1987). In this work, a number of relationships among the Coulomb energy, total x-ray scattering intensities, $\langle r^n \rangle$ values and $\langle \rho \rangle$ were derived.

The classical Coulomb energy, $J[\rho]$, is given by

$$J[\rho] = (1/2) \int d\mathbf{r} \, \rho(\mathbf{r}) \left[\int \rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'| \right] d\mathbf{r}'. \tag{25}$$

By using the definition

$$f(\mathbf{k}) = \int \rho(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} \, d\mathbf{r}, \tag{26}$$

and the Faltung (convolution) theorem, one readily obtains

$$J[\rho] = \left(\int d\mathbf{k} \, I(\mathbf{k})/|\mathbf{k}|^2 \right)/(2\pi)^2, \tag{27}$$

where $I(\mathbf{k}) = |f(\mathbf{k})|^2$.

For atomic densities which are centrosymmetric, one obtains

$$J[\rho] \leqslant (N/\pi) \int_0^\infty f(k) \, dk, \tag{28}$$

and employing a well-known identity (Silverman and Obata 1963), viz.

$$\langle r^{-1} \rangle = (2/\pi) \int_0^\infty f(k) \, dk, \tag{29}$$

one gets

$$J[\rho] \leqslant (1/2) N \langle r^{-1} \rangle = (1/2) |V_{ne}| N/Z. \tag{30}$$

It was shown (Chakravorty and Gadre 1987) that a number of lower bounds to $J[\rho]$ could be obtained by employing the recent results of Galvez and Dehesa (1987); Dehesa and Galvez (1985), e.g.,

$$J[\rho] \geqslant \pi^2 \langle r^{-1} \rangle^3 / (18 \langle r^{-2} \rangle). \tag{31}$$

This can be simplified further by using $\langle r^{-2} \rangle \leqslant 8 T_w$ and $T_w \leqslant T$ to

$$J[\rho] \geqslant \pi^2 \langle r^{-1} \rangle^3 / (144 \, T). \tag{32}$$

We have attempted to present an exhaustive review of the density-based rigorous bounds to the direct part of the electron repulsion energies in the present section. The indirect part will be treated in the following section.

3. Bounds to indirect Coulomb energies

Analogous to the work by Gadre *et al* (1979), an upper bound to the exchange integral

$$I_{ij} \equiv \int u_i^*(\mathbf{r}) u_j^*(\mathbf{r}') u_i(\mathbf{r}') u_j(\mathbf{r}) |\mathbf{r} - \mathbf{r}'|^{-1} \, d\mathbf{r} \, d\mathbf{r}' \tag{33}$$

(the $\{u_i\}$ being the orthonormal canonical Hartree–Fock orbitals), was derived by Pathak (1984). Defining the "differential overlap" $F_{ij}(\mathbf{r}) = u_i^*(\mathbf{r}) u_j(\mathbf{r})$, the exchange integral can be cast into

$$I_{ij} = (1/4\pi) \int d\mathbf{r} \, |\nabla \Phi_{ij}(\mathbf{r})|^2, \tag{34}$$

with Φ_{ij}, the complex "potential", identified as

$$\Phi_{ij}(\mathbf{r}) = \int F_{ij}^*(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1} \, d\mathbf{r}'. \tag{35}$$

Application of the three-dimensional Sobolev inequality in conjunction with the Cauchy–Schwarz inequality leads to:

$$I_{ij} \leqslant (8/3)(2/\pi)^{1/3} \left[\int d\mathbf{r} \, |F_{ij}(\mathbf{r})| \right]^{2/3} \left[\int d\mathbf{r} \, |F_{ij}(\mathbf{r})|^{4/3} \right], \tag{36}$$

with

$$\int d\mathbf{r} \, |F_{ij}(\mathbf{r})| = \int d\mathbf{r} \, |u_i(\mathbf{r})| \, |u_j(\mathbf{r})|$$

$$\leqslant \left[\int d\mathbf{r} \, |u_i(\mathbf{r})|^2 \right]^{1/2} \left[\int d\mathbf{r} \, |u_j(\mathbf{r})|^2 \right]^{1/2} = 1, \tag{37}$$

one finally arrives at

$$I_{ij} \leqslant (8/3)(2/\pi)^{1/3} \int d\mathbf{r} \, |F_{ij}(\mathbf{r})|^{4/3}. \tag{38}$$

Further, summing over the indices i and j along with the factor $(-1/2)$ yields a *lower* bound to the Hartree–Fock exchange energy. Thus, the Hartree–Fock exchange energy is connected in terms of an *inequality* to the Hartree–Fock orbitals partaking in the exchange.

In a more general context, an interesting general lower bound to the indirect or purely quantal part of the electron–electron repulsion energy V_{ee}, for a general system of charges $e_1, e_2, e_3 \ldots e_N > 0$ (or *all* < 0) obeying arbitrary dynamics and

statistics was derived by Lieb (1979). He obtained a lower bound to the quantity E given by

$$E = V_{ee} - D[\rho, \rho]$$

$$= \left\langle \sum_{\substack{i=1, j=1 \\ i<j}}^{N\ N} e_i e_j |\mathbf{r}_i - \mathbf{r}_j|^{-1} \right\rangle - \int \rho(\mathbf{r}) \rho(\mathbf{r}')(2|\mathbf{r}-\mathbf{r}'|)^{-1}\, d\mathbf{r}\, d\mathbf{r}'. \tag{39}$$

The functional $D[\rho, \rho]$ represents the classical Coulomb repulsion energy for the charge density $\rho(\mathbf{r})$. A major ingredient of E, viz. the exchange energy, is popularly approximated by the Dirac–Slater exchange (Dirac 1930; Slater 1951), viz.

$$E_{exch} \approx -C_{ex}|e|^{2/3} \int \rho^{4/3}(\mathbf{r})\, d\mathbf{r} \tag{40}$$

with $C_{ex} = \text{const} > 0$. However, (40) is not a rigorous "bound". For an N-electron closed-shell system, $C_{ex} = (3/4)(3/\pi)^{1/3}$ in Hartree atomic units.

Lieb's proof hinges on two theorems applied in succession. Defining $\mathbf{X} = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ representing the spatial degrees of freedom, and setting,

$$f(\mathbf{X}) = \sum_{\alpha} |\Psi(\mathbf{X}, \alpha)|^2, \tag{41}$$

Ψ being the many-particle wavefunction, and α, any other degrees of freedom apart from the spatial ones (e.g. spin). One observes that $\int f(\mathbf{X})\, d\mathbf{X} = 1$ and the density due to the ith particle, ρ_Ψ^i, emerges as

$$\rho_\Psi^i(\mathbf{r}_i) = e_i \sum_{\alpha} \int f(\mathbf{X})\, d\mathbf{r}_1 \ldots d\mathbf{r}_{i-1}\, d\mathbf{r}_{i+1} \ldots d\mathbf{r}_N,$$

and one readily has the *total* density derived from Ψ, viz. ρ_Ψ, given by

$$\rho_\Psi(\mathbf{r}) = \sum_{i=1}^{N} e_i \rho_\Psi^i(\mathbf{r}).$$

The expectation value

$$I[\Psi] \equiv \left\langle \Psi \left| \sum_{i<j} e_i e_j / |\mathbf{r}_i - \mathbf{r}_j| \right| \Psi \right\rangle, \tag{42}$$

is the total Coulomb repulsion for the state Ψ. Further, setting $D[h, g] = (1/2) \int h(\mathbf{r}) g(\mathbf{r}') |\mathbf{r}-\mathbf{r}'|^{-1}\, d\mathbf{r}\, d\mathbf{r}'$, Lieb established that

$$E_{ind}[\Psi] \equiv I[\Psi] - D[\rho_\Psi, \rho_\Psi]$$

$$\geqslant -C \left\{ \int \rho_\Psi^{4/3}(\mathbf{r})\, d\mathbf{r} \right\}^{1/4} \cdot \left\{ \int \left[\sum_{i=1}^{N} e_i^{2/3} \rho_\Psi^i(\mathbf{r}) \right]^{4/3} d\mathbf{r} \right\}^{3/4}. \tag{43}$$

For electrons,

$$C = \pi^{1/12} 3^{11/12} 2^{3/2} \simeq 8.52 \text{ and}$$

$$E_{ind} \geqslant -C|e|^{2/3} \int \rho_\Psi^{4/3}(\mathbf{r})\, d\mathbf{r}. \tag{44}$$

The following criticism on Lieb's elegant work is in order. It is gratifying that, in arriving at the inequality (44), Lieb derived an important general inequality, a lower bound to the *operator* $\hat{V}_{ee}$: $\hat{V}_{ee} \equiv \sum_{i<j} e_i e_j r_{ij}^{-1}$, namely,

$$\sum_{i<j} e_i e_j / r_{ij} \geqslant -D[\rho, \rho] + \sum_i (2D[\rho, \mu_i] - D[\mu_i, \mu_i]), \qquad (45)$$

where $\mu_i(\mathbf{r})$ are arbitrary functions satisfying (i) $\mu_i(\mathbf{r}) \geqslant 0$; (ii) $\mu_i(\mathbf{r}) \equiv \mu_i(|\mathbf{r} - \mathbf{r}_i|)$ i.e. they are spherically symmetric around $\mathbf{r}_i$ and (iii) $\int \mu_i \, d\mathbf{r} \leqslant e_i$. Note that the dependence of the RHS of (45) on the vectors $\mathbf{r}_i$: $i = 1, 2, \ldots, N$ comes implicity through the functions μ_i. To derive the inequality (43), Lieb has chosen the following prescription for μ_i:

$$\mu_i(\mathbf{r}, \mathbf{r}_i) = \bar{\rho}_\Psi(\mathbf{r}) \theta(R_i(\mathbf{r}_i) - |\mathbf{r} - \mathbf{r}_i|), \qquad (46)$$

where $\bar{\rho}_\Psi(\mathbf{r})$ is the spherical average of ρ_Ψ around $\mathbf{r} = \mathbf{r}_i$; i.e.

$$\bar{\rho}_\Psi(\mathbf{r}) = (1/4\pi) \int \rho_\Psi(\mathbf{r} - \mathbf{r}_i) \, d\Omega_{\{(\mathbf{r} - \mathbf{r}_i), |\mathbf{r} - \mathbf{r}_i|\}}$$

and $R_i(\mathbf{r}_i)$, by the virtue of the Heaviside unit step-function θ, the finite radii such that $\int \rho_\Psi(\mathbf{r}') \theta(R_i(\mathbf{r}_i) - |\mathbf{r}' - \mathbf{r}_i|) \, d\mathbf{r}' = e_i$, meaning that a sphere of radius R_i centred at $\mathbf{r} = \mathbf{r}_i$ is chosen such that it encompasses a total charge e_i. It is, however, not clear whether this choice for μ_i is the best one in a lower bound sense. Another important step towards the inequality (43) is the introduction of the "maximal function"

$$Mg(\mathbf{r}) \equiv \mathrm{Sup}(4\pi R^3/3)^{-1} \int |g(\mathbf{r}')| \theta(R - |\mathbf{r} - \mathbf{r}'|) \, d\mathbf{r}',$$

which is a sort of *macroscopic average charge density* in a sphere of radius R centred at r. It may be remarked that the maximal function for a hydrogenic system at $r = 0$, would be

$$Mg(0) = \mathrm{Sup}(4\pi R^3/3)^{-1} \int \rho_H(\mathbf{r}') \, d\mathbf{r}' \, |\theta(R - |\mathbf{r}'|)$$

$$= \mathrm{Sup}(4\pi R^3/3)^{-1} (Z^3/\pi) \int_0^R e^{-2Zr'} 4\pi r'^2 \, dr'$$

$$= \mathrm{Sup}(4\pi R^3/3)^{-1} \{1 - e^{-2ZR}(1 + 2RZ + 2Z^2 R^2)\};$$

with ρ_H, the hydrogenic charge density for nuclear charge $+Ze$. Evidently, as $R \to 0$, $Mg(0) \to \infty$: finiteness of the maximal function is thus not ensured. However, according to Lieb (private communication), this is not a problem and can always be circumvented. Also, the negative-semidefiniteness of $E_{ind}[\Psi]$ i.e. $E_{ind}[\Psi] \leqslant 0$ is not always guaranteed. However, for atoms and molecules, it is expected to be negative, as is desirable. Subsequent to Lieb's work, a study due to Lieb and Oxford (1981) improved the numerical constant in the inequality (44) from 8·52 to 1·68 thus making it tighter. Also, the use of the maximal function was by-passed.

Lieb and Oxford (1981) started with the inequality (45) with a prescription on $\mu \geqslant 0$ as: $\mu_\mathbf{r}(\mathbf{r}') \equiv \lambda^3 \rho_\Psi(\mathbf{r}) \mu(\lambda \rho_\Psi^{1/3}(\mathbf{r}) |\mathbf{r}' - \mathbf{r}|)$ along with $\mu(s) = 0$ if $s > 1$ and $\int \mu(\mathbf{r}') \, d\mathbf{r}' = 1$. The positive scaling constant was suitably determined later. The inequality (7) was rewritten as

$$\sum_{i<j} e_i e_j / r_{ij} \geqslant -D[\rho_\Psi, \rho_\Psi] + 2 \sum_{i=1}^{N} D[\rho_\Psi, e_i \delta_{r_i}]$$

$$-2\left(\sum_{i=1}^{N} D[\rho_\Psi, e_i \delta_{r_i} - e_i \mu_{r_i}] + D[e_i \mu_{r_i}, e_i \mu_{r_i}]\right), \tag{47}$$

with $\delta_{r_i}(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_i)$, the Dirac δ-distribution function representing a point-charge density centred on $\mathbf{r}_i$, totalling a unit positive charge.

The introduction of the δ-distribution leads to ρ_Ψ upon taking its expectation value for the state Ψ. Thus

$$I[\Psi] \geqslant D[\rho_\Psi, \rho_\Psi] - \left(\sum_{i=1}^{N} \int 2D[\rho_\Psi, \delta_{r_i} - \mu_{r_i}] \rho_\Psi^i(\mathbf{r}_i) d\mathbf{r}_i + \right.$$

$$\left. + \sum_{i=1}^{N} \int D[\mu_{r_i}, \mu_{r_i}] e_i \rho_\Psi^i(\mathbf{r}_i) d\mathbf{r}_i\right). \tag{48}$$

Using characteristic functions such as $\chi_a(\mathbf{s}) = \theta[\rho_\Psi(\mathbf{s}) - a]$ and certain scaling properties, Lieb and Oxford (1981) established that the first term in the large parentheses in (48) is bounded above by $(3/\lambda^2) K \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}$ where K is a constant depending on the choice of μ. The second term in the large parentheses is also seen to be bounded, noting that the $\mathbf{r}_i$ now become dummy integration variables:

$$\sum_{i=1}^{N} \int D[\mu_{r_i}, \mu_{r_i}] e_i \rho_\Psi^i(\mathbf{r}) d\mathbf{r}$$

$$= \lambda D[\mu, \mu] \sum_{i=1}^{N} e_i \int \rho_\Psi^i(\mathbf{r}) \rho_\Psi^{1/3}(\mathbf{r}) d\mathbf{r}$$

$$\leqslant \lambda D[\mu, \mu] \left[\int \left(\sum_{i=1}^{N} e_i \rho_\Psi^i(\mathbf{r})\right)^{4/3} d\mathbf{r}\right]^{3/4} \left[\int \rho_\Psi^{4/3}(\mathbf{r}) d\mathbf{r}\right]^{1/4}.$$

The λ-dependencies in both the upper bounds to the respective terms in the large parentheses of (47) were then optimized leading finally to a *lower* bound (because of the negative sign)

$$E_{ind}[\Psi] \geqslant -1.68 \left[\int \left(\sum_{i=1}^{N} e_i \rho_\Psi^i(\mathbf{r})\right)^{4/3} d\mathbf{r}\right]^{1/2} [\int \rho_\Psi^{4/3}(\mathbf{r}) d\mathbf{r}]^{1/2}. \tag{49}$$

For a many-electron system, with $e_i = e$ for all i, the lower bound gives, in Hartree units $(e_i = -|e| = -1$

$$E_{ind}[\Psi] \geqslant -1.68 \int \rho_\Psi^{4/3}(\mathbf{r}) d\mathbf{r}. \tag{50}$$

This lower bound is not a very tight one; the present coefficient of -1.68 is numerically far larger than the Slater-coefficient of $-(3/4)(3/\pi)^{1/3} \simeq -0.7386$ for the exchange energy estimate. However, the Lieb–Oxford bound gives us a marked improvement over Lieb's earlier result [inequality (44)].

Kinoshita (1959), in his illuminating paper, obtained several inequalities connecting the kinetic and potential energies of a two-electron system such as the helium atom. In particular, he obtained inequalities concerning the expectation value

$$\langle f(\mathbf{r}_1,\mathbf{r}_2)\,|\,1/r_{12}\,|f(\mathbf{r}_1,\mathbf{r}_2)\rangle \text{ for } any \text{ } well\text{-}behaved \text{ } real \text{ function } f.$$

Setting $\mathbf{u}=\mathbf{r}_1-\mathbf{r}_2$, $\hat{V}_{12} \equiv 1/r_{12}=1/u$

and noting that

$$\nabla_{\mathbf{u}}(\hat{u}f^2)=f^2(\nabla_{\mathbf{u}}\cdot\hat{u})+2\hat{u}\cdot f\nabla_{\mathbf{u}}f=2f^2/u+2\hat{u}\cdot f\nabla_{\mathbf{u}}f,$$

with Kinoshita (1959), we observe vide the Cauchy–Schwarz inequality that

$$\langle f|\,V_{12}\,|f\rangle = -\int(\hat{u}f)\cdot(\nabla_{\mathbf{u}}f)\,d\mathbf{r}_1\,d\mathbf{r}_2$$

$$\leqslant \langle[\int d\mathbf{r}_1\,d\mathbf{r}_2\,f^2]^{1/2}\,[\int d\mathbf{r}_1\,d\mathbf{r}_2\,(\nabla_{\mathbf{u}}f)^2]^{1/2}. \tag{51}$$

Next, with transformation to the 'centre-of-mass' and the 'relative' coordinates,

$$\mathbf{R}=(\mathbf{r}_1+\mathbf{r}_2)/2;\; \mathbf{u}=\mathbf{r}_1-\mathbf{r}_2.$$

one has

$$\nabla_1 f = \nabla_{\mathbf{R}} f + \nabla_{\mathbf{u}} f, \quad \nabla_2 f = \nabla_{\mathbf{R}} f + \nabla_{\mathbf{u}} f, \tag{52}$$

whence

$$(\tfrac{1}{2})(\nabla_1 f)^2 + (\tfrac{1}{2})(\nabla_2 f)^2 = (\tfrac{1}{2})(\nabla_{\mathbf{R}} f)^2 + (\tfrac{1}{2})(\nabla_{\mathbf{u}} f)^2 \geqslant \tfrac{1}{2}(\nabla_{\mathbf{u}} f)^2. \tag{53}$$

From the previous three relations (51), (52), (53) it follows that

$$\langle f|\,\hat{V}_{12}\,|f\rangle \leqslant \langle f|\,\hat{K}\,|f\rangle^{1/2}, \tag{54}$$

with $\hat{K} = -(\tfrac{1}{2})(\nabla_1^2+\nabla_2^2)$, the kinetic energy operator for the two-electron system.

Kinoshita's work can be easily generated to an N-particle system: multiply (4) by N_{C_2} throughout; leading to

$$V_{ee} \leqslant [N^{1/2}(N-1)\,T^{1/2}/2]. \tag{55}$$

With $T=-E$ for ground states of Coulomb systems, (55) yields a bound connecting V_{ee}, the total electron repulsion energy to the total energy. This bound, however, is not expected to be a tight one especially for large values of N.

Pathak and Bartolotti (1985) employed the three-dimensional Sobolev inequality and the Hölder inequality and derived certain interconnections among the terms in the gradient expansion of the kinetic- and exchange-correlation energy functionals for atomic systems. The ones involving the major ingredient of the exchange-correlation energy functional, viz. K_0, the Dirac–Slater approximation to the exchange $-K_0[\rho] \equiv -C_{ex}\int\rho^{4/3}(\mathbf{r})\,d\mathbf{r}$;

$$C_{ex}=(3/4)(3/\pi)^{1/3} \simeq 0.7386,$$

$$1 \leqslant (1/2)\pi^2\,(8/3)^{3/2}(C_{\text{TF}}^2/C_{ex})\,N^{1/2}\,K_0\,T_w^{3/2}/T_0^2, \tag{56}$$

with $C_{\text{TF}}=(3/10)(3\pi^2)^{2/3}$ occurring in $T_0[\rho]=C_{\text{TF}}\int\rho^{5/3}(\mathbf{r})\,d\mathbf{r}$, the 'Thomas–Fermi'

contribution to the kinetic energy functional $T[\rho]$ and $T_w[\rho] = \int (|\nabla \rho|^2/\rho)\,dr/8$, the "full Weizsäcker correction".

The rigorous inequalities

$$1 \leqslant (8/(3(2\pi^2)^{2/3}))(C_{TF}^{5/3}/C_{ex}^{4/3})\,K_0^{4/3}\,T_w/T_0, \tag{57}$$

and

$$1 \leqslant (C_{TF}^2/C_{ex})\,N\rho(0)\,K_0/T_0^2, \tag{58}$$

were obtained. This last one is valid for atomic systems with spherical symmetry wherein it is assumed that the density has its maximum value at $r=0$, i.e. at the nucleus (Weinstein *et al* 1975). Another study on inequalities involving the kinetic and the exchange-correlation contributions was carried out by Dehesa and Galvez (Dehesa and Galvez 1985; Galvez and Dehesa 1987). They established that

$$W_n = \int [\rho(\mathbf{r})]^n\,d\mathbf{r} \text{ is bounded from below as}$$

$$W_n \geqslant [nk/((k+3)n-3)] \times$$
$$\times A^n\{k[(3n-3)/(k+3)n-3]^{3/k}/4\pi B(n/n-1,3/k)\langle r^k\rangle^{3/k}\}^{n-1}, \tag{59}$$

for $k = 1, 2, \ldots,$

where $B(x, y) = \Gamma(x)\Gamma(y)/\Gamma(x+y)$ is the usual beta-function,

$$A = \int \rho(\mathbf{r})\,d\mathbf{r},$$

and $\langle r^k\rangle = (1/A)\int r^k \rho(\mathbf{r})\,d\mathbf{r}.$

It was shown in their work that

$$W_n \geqslant [nk/(n(3-k)-3)] \times$$
$$\times A^n\{[k[(n(3-k)-3)/(3n-3)]\langle r^{-k}\rangle]^{3/k}/4\pi B(3/k-1/n-1,n/n-1)\}^{n-1}, \tag{60}$$

provided $k = 1, 2, \ldots,$ and that $k < (3n-3)/n.$

Also an *upper* bound to the Dirac–Slater exchange energy was found by Dehesa and Galvez, viz.

$$E_{ex} = -(3/4)(3/\pi)^{1/3}\int \rho^{4/3}(\mathbf{r})\,d\mathbf{r}$$

$$\leqslant -(3/4)(3/\pi)^{1/3}\,K_k\,A^{4/3}/\langle r^k\rangle^{1/k},$$

$$k = 1, 2, 3, \ldots,$$

and

$$K_k = (4k/(4k+3))\{k[3/(4k+3)]^{3/k}/4\pi B(4, 3/k)\}^{1/3}. \tag{61}$$

Similar bounds for the same quantities in nuclei were also derived and analyzed by these authors.

In a density functional context, inequalities concerning the exchange and correlation energies were derived by Sahni and Levy (1986). In their work, bounds to correlation energy and an inequality involving the correlation potential were obtained. Consider the following definitions

$$E_c[\rho] = E[\rho] - E_{xo}[\rho], \tag{62}$$

where

$$E[\rho] = \langle \Psi | \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v(\mathbf{r}_i) | \Psi \rangle, \quad \text{comes from } \Psi \text{ which is the}$$

interacting ground-state wavefunction,

$$E_{xo}[\rho] = \langle \Phi | \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v(\mathbf{r}_i) | \Phi \rangle, \tag{63}$$

where Φ is the single determinantal wavefunction made from Kohn–Sham orbitals which also leads to ρ, the ground-state (g.s.) density, and minimizes the expectation value in (63).

Similarly, let

$$E_c'[\rho] = E[\rho] - E_{xo}[\rho].$$

Here, $E_{xo}'[\rho] = \langle \Phi' | \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v(\mathbf{r}_i) | \Phi' \rangle. \tag{64}$

Φ' is that single determinant which is constrained to be the g.s. of some noninteracting Hamiltonian $\hat{T} + \sum_{i=1}^{N} v_s(\mathbf{r}_i)$, which minimizes the expectation-value in (64). The ground state density obtained from Φ' is, in general, different from ρ.

Also, let $E_c^{HF}[\rho] = E[\rho] - E_{xo}^{HF}$,

$$E_{xo}^{HF}[\rho] = \langle \Phi^{HF} | \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v(\mathbf{r}_i) | \Phi^{HF} \rangle. \tag{65}$$

Φ^{HF} is a single determinant which minimizes the expectation value in (4) with no further restriction. The g.s. density from Φ^{HF} is $\rho^{HF} \neq \rho$, in general.

By constructing Φ as a single determinant that minimizes $\langle \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v(\mathbf{r}_i) + \sum_{i=1}^{N} v_c(\mathbf{r}_i) \rangle$ and is simultaneously restricted to be the g.s. of some noninteracting Hamiltonian $\hat{T} + \sum_{i=1}^{N} v_s(\bar{r}_i)$, one is led therefore to

$$\langle \Phi' | \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v(\mathbf{r}_i) | \Phi' \rangle > \langle \Phi | \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v(\mathbf{r}_i) | \Phi \rangle, \tag{66}$$

and

$$E_{xo}[\rho] - E_{xo}[\rho] = \delta_1 > 0, \tag{67}$$

unless $v_c(\mathbf{r}_i)$ is constant.

Also it follows that

$$\langle \Phi' | \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v(\mathbf{r}_i) + \sum_{i=1}^{N} v_c(\mathbf{r}_i) | \Phi' \rangle -$$

$$- \langle \Phi | \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v(\mathbf{r}_i) + \sum_{i=1}^{N} v_c(\mathbf{r}_i) | \Phi \rangle = \delta_2 > 0. \tag{68}$$

Adding (66) and (68), one obtains

$$\int [\rho'(\mathbf{r}) - \rho(\mathbf{r})] v_c(\mathbf{r}) d\mathbf{r} = \delta_1 + \delta_2 > 0. \tag{69}$$

From (67) and (69),

$$E_{xo}[\rho] - E'_{xo}[\rho] = \int [\rho'(\mathbf{r}) - \rho(\mathbf{r})] v_c(\mathbf{r}) d\mathbf{r} - \delta_2 > 0, \tag{70}$$

is obtained. Therefore,

$$0 < E'_c[\rho] - E_c[\rho] < \int [\rho'(\mathbf{r}) - \rho(\mathbf{r})] v_c(\mathbf{r}) d\mathbf{r}. \tag{71}$$

Also, one obtains

$$E_c[\rho] < E'_c[\rho] < E_c^{HF}[\rho]. \tag{72}$$

These bounds are indeed rigorous, however, a practical use of these results is rather hard to demonstrate. Also, these authors define the correlation energy and exchange energy in a physically tangible way, but in a manner different from the conventional one.

Within the Hohenberg–Kohn–Sham–Levy framework (Hohenberg and Kohn 1964; Kohn and Sham 1965; Levy 1979), Levy and Perdew (1985) derived the inequality

$$E_{xc}[\rho] + \int \rho(\mathbf{r})\mathbf{r} \cdot \nabla v_{xc}([\rho], \mathbf{r}) d\mathbf{r}$$

$$= -T_s[\rho] - T[\rho] = -T_c[\rho] \leqslant 0, \tag{73}$$

where $E_{xc}[\rho]$ is the Kohn–Sham (1965) exchange-correlation energy functional, T and T_s being the "interacting" and the "noninteracting" (single-particle) kinetic energies (Kohn and Sham 1965) and $V_{xc}([\rho]; \mathbf{r})$ is the functional derivative $\delta E_{xc}[\rho]/\delta\rho(\mathbf{r})$. Further they proved that

$$E_c[\rho] + \int \rho(\mathbf{r})\mathbf{r} \cdot \nabla v_c([\rho]; \mathbf{r}) = -T_c[\rho] \leqslant 0, \tag{74}$$

where E_c is the "correlation energy function", obtained as $E_c = E_{xc} - E_x$, E_x being the exchange energy. All these functionals are universal functionals of the density (Hohenberg and Kohn 1964; Kohn and Sham 1965). Numerous interacting results were obtained by Levy and Perdew (1985) by exploring the repercussion of a "parametrized external potential" $V_\lambda(\mathbf{r})$ and the "scaled electron–electron interaction $\lambda \hat{V}_{ee}$". Noteworthy is the fact that $\langle \hat{V}_{ee} \rangle_\lambda$ becomes a monotone decreasing function of λ. Also

$$\gamma V_{ee}[\rho] - V_{ee}[\rho_\gamma] > \gamma^2 T[\rho] - T[\rho_\gamma], \ (\gamma < 1), \tag{75}$$

and

$$\gamma V_{ee}[\rho] - V_{ee}[\rho_\gamma] < \gamma^2 T[\rho] - T[\rho_\gamma], \ (\gamma > 1), \tag{76}$$

were obtained for the *exact* functionals.

4. Electron repulsion integrals over Gaussian basis-sets

Some work on the estimation of electron repulsion integrals over Gaussian basis-sets has been reported in the literature. Ahlrichs (1974) derived an upper bound to

the repulsion integrals

$$\langle ij|kl\rangle = \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, u_i^*(\mathbf{r}_1) \, u_j(\mathbf{r}_1) \, u_k^*(\mathbf{r}_2) \, u_l(\mathbf{r}_2)/r_{12}$$

exclusively for s-type Gaussians. This bound is based on the result that $F(x) = x^{-1/2} \, erf(x^{1/2}) \leqslant 2\pi^{-1/2}$. As seen in §1, the bound was employed by Ahlrichs (1974) to neglect certain electron repulsion integrals (without a precise evaluation) which fall below a pre-set threshold. However, no attempt was made by him to extend this approach to p- and d-type Gaussians. Also, no rigorous lower bounds to $\langle ij|kl\rangle$ have as yet been derived. Cremer and Gauss (1986) have, in their direct SCF program, utilized these bounds by Ahlrichs (1974) over s-type Gaussians to estimate the electron-repulsion integrals. It was found that this formula is also useful for approximate estimation of the integrals over a p- and d-type Gaussian though it is not any longer a rigorous bound. It has been recently pointed out by Häser and Ahlrichs (1988) that the Ahlrichs bound is just a special case of the Schwarz inequality:

$$|\langle ij|kl\rangle| \leqslant Q_{ij} \, Q_{kl}, \tag{77}$$

where $Q_{ab} = \langle ab|ab\rangle^{1/2}$. This bound is optimal since the equality holds for the case $(i, j) = (k, l)$.

Almlöf *et al* (1982) adopted a different approach for this purpose. They based their estimates on radial overlap integrals. Häser and Ahlrichs (1988) tested the bound (1) applied to the batches of integrals. They employed the data for the molecule $C_{14}H_{10}O_2$, also used earlier by Cremer and Gauss (1986) for testing purposes in their direct SCF approach. Some test runs in P_5H_5 in C_1 symmetry were also carried out by them. They noticed a 15% reduction in computer time with the use of more precise integral bounds for pre-screening purposes. The application of these bounds would also result in tremendous savings in secondary (disk/tape) storage. In fact, for large molecules, many of the electron repulsion integrals in an SCF calculation are negligible.

Clementi *et al* (1973) studied the computer time needed for evaluation of various types of integrals, viz. $\langle aa|aa\rangle$, $\langle aa|ab\rangle$, $\langle ab|ab\rangle$, $\langle aa|ab\rangle$ ... etc. for the case of staggered ethane. Even for this small molecule, the three- and four-centre integrals need more than 60% of CPU time. Clementi (1972) reported typical computational times for large molecular systems, viz. $Na(H_2O)_n$, cytosine, guanine, cytosine–guanine complex etc. For the largest system analysed, the number of integrals is $\sim 10^9$. The computer time can be drastically reduced by (i) computing with full numerical accuracy only those integrals larger than a given threshold T_1; (ii) computing with intermediate accuracy only those integrals which lie between T_1 and $T_2 (T_1 > T_2)$, (iii) neglecting those which lie below a threshold $T_3 (T_3 \ll T_2)$. Integrals in category (ii) are evaluated by replacing the contraction by a single primitive Gaussian (termed by Clementi as 'adjoint basis-set'). He commented that with these strategies, the "bottleneck of the integral computation is broken ....".

An exhaustive analysis of the distribution of the numerical magnitudes of these electron-repulsion integrals was carried out by Clementi and Mehl (1974) and by Habitz and Clementi (1982). It was pointed out by Clementi and Mehl (1974) that for a large molecule, a vast number of integrals must be smaller (in absolute value) than a given threshold ε and a large number should be nearly equal to zero, i.e. smaller than another threshold ε', where $\varepsilon' \ll \varepsilon$. An analysis of the integral

distribution of a test example, viz. the guanine–cytosine complex ($C_6N_5OH_5$-$C_4N_3OH_5$) with 136 electrons with a pre-chosen basis-set revealed that out of the 8.06×10^8 integrals, 74% are numerically less than 10^{-10} a.u., 12% lie in the range 10^{-10} to 10^{-5} and 14% are numerically greater than 10^{-5}. The adjoined and dynamic-basis sets were examined in this context.

Habitz and Clementi (1982) analysed in detail the statistical distributions of the matrix elements for chemical systems. They examined the distribution of overlap integrals and their products, such as S_{AB} and $|S_{AB}S_{CD}|$, $|S_{AA}S_{BC}|$ ... etc. They also analysed two-electron integrals statistically and found that many of the integrals of the form $\langle AA|AA \rangle$ are numerically significant. However, the numerically insignificant fraction increases as one proceeds to a multi-centre situation e.g. $\langle AA|BB \rangle \rightarrow \langle AA|BC \rangle \rightarrow \langle AB|CD \rangle$. The molecules examined in this study included S-P-S-G (S = sugar, P = phosphate, G = guanine), S-P-S, benzopyrene and $[Zn(NH_3)_2OH]^+$. The general conclusions noted above were seen to be valid for all these molecules as well. More recently, Dupuis *et al* (1976) discussed evaluation and storage strategies for electron-repulsion integrals based on estimations of their numerical values.

In this section, a brief resumé of the work done on derivation and estimation of rigorous or semirigorous bounds to electron-repulsion integrals has been presented. However, it may be seen that rigorous upper bounds to $\langle 1/r_{12} \rangle$ exist only for s-type Gaussian basis-functions (Ahlrichs 1974, and private communication). The estimation of the integrals made by Clementi and others is done in a similar spirit (Clementi 1988) but is not based on completely rigorous grounds. We present in the following section general rigorous upper bounds to $\langle ij|kl \rangle$ for s, p as well as d-type Gaussians. Some numerical tests of these bounds using some organic molecules as test examples will be presented therein. A novel *lower* bound to the electron-repulsion integral over s-type Gaussians will also be derived and discussed.

5. Rigorous upper and lower bounds to electron-repulsion integrals over Gaussian basis-sets

Gaussian-basis sets (Boys 1950; Shavitt 1965) were first introduced systematically in quantum chemistry by Boys in 1950. Over the years, they have become extremely popular and more than 90% *ab initio* level computations employ Gaussian basis-sets. The advantage with Gaussians is that the matrix elements of the Hamiltonian can be evaluated in a closed form over them. However, the number of primitive Gaussians required in a large molecular Hartree–Fock calculation is extremely large. The number of electron-repulsion integrals that must be computed in such a calculation is $\sim N^4/8$ where N is the number of primitive Gaussians. As discussed in § 1, this requires large computer time as well as secondary storage, as has been summarized well by Clementi and Mehl (1974) who call it "a long bottleneck" of quantum chemistry.

The electron-repulsion integrals $\langle ij|kl \rangle$ over Gaussian basis-sets are rather simply obtained by suitable differentiation/s of integrals involving s-type Gaussians, viz. $\langle s_As_B|s_Cs_D \rangle$. The expressions for these integrals involve exponentials and special functions $F_m(t) = \int_0^1 u^{2m} e^{-tu^2} du$ (Boys 1950). Evaluation of these special functions requires a good deal of computer time.

Let us begin by derivation of an upper bound to

$$\langle s_A s_B | s_C s_D \rangle = F_0 \left[(a+b)(c+d) \overline{PQ}^2/(a+b+c+d) \right] (16abcd)^{3/4} \cdot 2\pi^{5/2} \cdot \times$$
$$\times \exp \left[-(ab\overline{AB}^2/(a+b)) - (cd\overline{CD}^2/(c+d)) \right] \div$$
$$\div \left[\pi^3 \cdot (a+b)(c+d)(a+b+c+d)^{1/2} \right]. \tag{78}$$

Employing a rather elementary bound, viz. $F_0(t) \leqslant 1$, presented in the appendix for all values of t, one is led to

$$\langle s_A s_B | s_C s_D \rangle \leqslant ((16abcd)/\pi^4)^{3/4} \cdot 2\pi^{5/2} \cdot \exp \left[-(ab\overline{AB}^2/(a+b)) - (cd\overline{CD}^2/(c+d)) \right] \div$$
$$\div \left[(a+b)(c+d)(a+b+c+d)^{1/2} \right]$$
$$\equiv K \cdot (16abcd/\pi^4)^{3/4} \tag{79}$$

with obvious notations. In (78) and (79), a, b, c, d are exponents of normalized Gaussians s_A, s_B, s_C and s_D respectively; A, B, C, D being the corresponding centres; $\mathbf{P} = (a\mathbf{A} + b\mathbf{B})/(a+b)$; $\mathbf{Q} = (c\mathbf{C} + d\mathbf{D})/(c+d)$. This bound does not depend on the argument of F_0 and is universal and has earlier been derived by Ahlrichs (1974).

It is instructive to discuss special cases of relation (79) for the case of the self-repulsion of a single orbital. It turns out, using bound (79) that

$$\langle aa | aa \rangle \leqslant 2(a^{1/2})/\pi^{1/2}, \tag{80}$$

where a is the orbital exponent.

The general and tight bound due to Gadre *et al* (1979) discussed earlier, viz. $\langle aa | aa \rangle < 2 \cdot 1836 \int \rho_a^{4/3} \, dr$ yields

$$\langle aa | aa \rangle < (1 \cdot 0918 \; 3^{3/2} \; a^{1/2})/(2^{3/2} \; \pi^{1/2}). \tag{81}$$

Comparison of (80) and (81) shows that (80) is tighter than (81) only by about 0·3%. An interesting aspect of bounds (80) and (81) is that they obviously *do not* involve overlap-type terms. Also, as pointed out by Gadre *et al* (1979) and by Perdew and Zunger (1981), these bounds are quite tight and may be used to *approximate* the Coulomb repulsions. Hence, since a, the orbital exponent ranges from 10^{-2} to 10^3, the self-repulsion terms are normally expected to be significant. This is in good agreement with the results of Clementi and Mehl (1979) which show that almost all self-repulsion integrals are non-negligible. One may also compare the results obtained by employing the bound (79) for the exchange integral $\langle ij | ji \rangle$ with those provided by the inequality

$$I_{ij} = \langle ij | ji \rangle \leqslant (8/3)(2/\pi)^{1/3} \int |F_{ij}|^{4/3} \, dr \tag{82}$$

due to Pathak (1984). Inequality (79) yields

$$I_{ij} = \langle ij | ji \rangle \leqslant (4a_i a_j)^{3/2} \cdot 2^{1/2} \cdot \exp(-2a_i a_j \overline{AB}^2/(a_i + a_j))/[\pi^{1/2} (a_i + a_j)^{5/2}]. \tag{83}$$

The results may be compared to those obtainable from Pathak's (1984) inequality, viz.

$$I_{ij} \leqslant 2^{7/3} \cdot 3^{1/2} \cdot a_i \cdot a_j \exp \left[-4a_i a_j \overline{AB}^2/(3a_i + 3a_j) \right]/[\pi^{3/2} \cdot (a_i + a_j)]. \tag{84}$$

It may be noticed from (83) and (84) that the former bound is tighter than the latter at large separations AB. However, the best bound due to Pathak yields

$$I_{ij} \leqslant 2^{10/3} \; 3^{1/2} \; (a_i a_j)^{3/2} \exp \left[-2a_i a_j \overline{AB}^2/(a_i + a_j) \right]/[(a_i + a_j)^{5/2} \; \pi^{5/6}],$$

which is quite comparable to the inequality (83). The statistical distribution of the exchange integrals is thus expected to be rather more diffuse than the self-repulsion type $\langle aa|aa \rangle$ integrals.

We have so far considered rigorous upper bounds to the electron repulsion integral $\langle ij|kl \rangle$ and some special cases thereof for s-type Gaussians. These bounds are *rigorous* and fairly tight ones as may be noticed from the test examples presented in the following section. It is also possible to derive rigorous *lower* bounds to these integrals. The derivation hinges upon a rather elementary result, viz., $F_0(t) \geqslant e^{-t}$, derived in the appendix.
This yields

$$\langle s_a^- s_b | s_c s_D \rangle \geqslant (16abcd)^{3/4} 2 \cdot \exp\left[-(ab\overline{AB}^2/(a+b)) - (cd\overline{CD}^2/(c+d)) - t \right] \div$$

$$\div \left[\pi^{1/2} (a+b)(c+d)(a+b+c+d)^{1/2} \right], \tag{85}$$

where $t = (a+b)(c+d)\overline{PQ}^2/(a+b+c+d).$ \hfill (86)

As a special case

$$\langle aa|aa \rangle \geqslant 2a^{1/2}/\pi^{1/2} \tag{87}$$

in which the lower bound actually attains the true value given by (80). It is also obvious that the exchange-type integral $\langle ab|ba \rangle$ is also bounded from below by its exact value, viz.

$$(2ab)^{1/2} \exp\left[-(2ab\,\overline{AE}^{\,?}/(a+b)) \right]/(a+b)^{1/2}. \tag{88}$$

Tighter bounds to $\langle ij|kl \rangle$ may also be derived using tighter bounds to F_0, e.g. for $t > 0$,

$$F_0(t) > [1 - \exp(-t)]/t \tag{89}$$

derived in the appendix (vide (A2)). This yields

$$\langle s_A s_B | s_C s_D \rangle \geqslant (16abcd)^{3/4} \cdot \exp\left[-(ab\overline{AB}^2/(a+b)) - (cd\overline{CD}^2/(c+d)) \right] \times$$

$$\times [1 - \exp(-t)]/[t \cdot \pi^{1/2} (a+b)(c+d)(a+b+c+d)^{1/2}], \tag{90}$$

wherein t is expressed by (88).

Bounds derived in this section are rigorous and tight ones and do not require computation of $F_0(t)$ which is the most expensive step (Shavitt 1965; Ahlrichs 1974) in the computation of $\langle s_A s_B | s_C s_D \rangle$. Only the weak bound (79) has been derived by Alhrichs. In fact, with this work, *lower* bounds to the electron-repulsion integrals appear in the literature for the first time. One may employ the new bounds derived in this work to estimate electron-repulsion integrals without actually computing them: Computation of exponentials suffices for their enumeration. The bounds to self-repulsion and exchange integrals obtained as a special case almost match the earlier results in the literature (Gadre *et al* 1979; Pathak 1984) employing the Sobolev inequality.

The technique employed in this section, viz. to obtain rigorous bounds to $F_0(t)$, may be further generalized to extract bounds to $F_m(t)$ where $F_m(t) = \int_0^1 u^{2m} e^{-tu^2} du$. These bounds can be used to yield rigorous upper bounds to integrals involving s, p and d-type Gaussians (e.g. (A5), (A6) and (A7) discussed in the appendix). We have derived inequalities to all the possible combinations of s, p_x, p_y, p_z orbitals and some prototype ones involving d-orbitals. We report below some of these results.

$$|\langle s_A s_B | s_C p_{x,D}\rangle| \leqslant (16abcd/\pi^4)^{3/4}\, 2d^{1/2}\, K \cdot \{c|C_x - D_x|/(c+d) +$$
$$+ |P_x - Q_x|L/[3(c+d)]\}, \quad (91)$$

where $K = 2\pi^{5/2}\exp\{-(ab\overline{AB}^2/(a+b)) - (cd\overline{CD}^2/(c+d))\} \div$

$$\div [(a+b)(c+d)(a+b+c+d)^{1/2}]$$

and

$$L = (a+b)(c+d)/(a+b+c+d), \quad \mathbf{P} = (a\mathbf{A}+b\mathbf{B})/(a+b); \quad \mathbf{Q} = (c\mathbf{C}+d\mathbf{D})/(c+d).$$

$$|\langle s_A p_{x,B} | s_C p_{x,D}\rangle| \leqslant (16abcd/\pi^4)^{3/4}\cdot 4(bd)^{1/2}\cdot K \cdot \{ac|A_x - B_x|\cdot|C_x - D_x| +$$
$$+ L[a\cdot|A_x - B_x|\cdot|P_x - Q_x| + c\cdot|C_x - D_x|\cdot|P_x - Q_x| +$$
$$+ 1/2]/3 + L^2(P_x - Q_x)^2/5\}, \quad (92)$$

$$|\langle s_A s_B | p_{x,C} p_{x,D}\rangle| \leqslant (16abcd/\pi^4)^{3/4}\cdot 4(cd)^{1/2}\cdot K \cdot$$

$$\{cd(C_x - D_x)^2 + \tfrac{1}{2}(c+d) + L[|C_x - D_x|\cdot|P_x - Q_x|\cdot|c - d| +$$
$$+ 1/2]/3 + L^2(P_x - Q_x)^2/5\}/(c+d)^2. \quad (93)$$

These bounds are based on inequalities $F_1(t) \leqslant 1/3$ and $F_2(t) \leqslant 1/5$ which are derived in the appendix. However, tighter bounds, viz. $F_1(t)$ and $F_2(t)$ both less than $(1 - e^{-t})/2t$, may also be used (refer to appendix for the derivation).

This approach can be readily extended to electron-repulsion integrals involving d-type Gaussians as well. For instance,

$$\langle ss | sd_{x^2}\rangle \leqslant K \cdot (16abcd/\pi^4)^{3/4}\cdot (32/3)^{1/2}\cdot d \cdot [(c^2\cdot CD_x^2/v^2) +$$

$$+ (c\cdot L\cdot CD_x PQ_x/(3v^2)) + (2cd/v) + (PQ_x\cdot c\cdot CD_x\cdot L/3v) +$$

$$+ (L/6v) + (PQ_x^2\cdot L^2/5v^2)]. \quad (94)$$

Here, $v = c+d$, $CD_x = |C_x - D_x|$ and $PQ_x = |P_x - Q_x|$.

The upper and lower bounds derived in this section can be meaningfully employed to predict whether an electron-repulsion integral is numerically significant or can be neglected with almost no loss of accuracy in total electronic energy. We present numerical tests of the bounds for s-type Gaussians for some organic molecules in the following section.

6. Numerical tests of the bounds and discussion

Numerical computations of two-electron repulsion integrals involving s-type primitive Gaussians as a test case, were carried out for the molecular systems diborane, cyclopropene, *trans*-butadiene and naphthalene. The 4-31G** basis set tabulated by Snyder and Basch (1972) was employed for this purpose. This basis set is essentially of the double-zeta quality, however, the general conclusions drawn in this section are expected to be qualitatively independent of the basis. The basis set employed for the present study comprises ten s-type primitive Gaussians for the atoms carbon and boron, while for hydrogen, four s-type orbitals are used. The best upper and lower bounds to these s-type repulsion integrals, given respectively by the inequalities (79) (with (A5)) and (90), were also computed. In all these computations, the coefficients accompanying a given Gaussian to form a

contraction were included. The computation of upper and lower bounds hardly needs any significant computer time, since evaluation of F_0 is completely eliminated.

Analysis for gainfully employing the bounds can be carried out as follows: Define the two-electron repulsion integral Q by

$$Q \equiv f_A f_B f_C f_D | <s_A s_B | s_C s_D> |,$$

(f_A denoting the coefficient accompanying the primitive Gaussian S_A etc.). Choose a cut-off value say, G (which is usually set to be $\sim 10^{-8}$ to 10^{-6}, Ahlrichs 1974). Let U and L denote, respectively, the upper and lower bounds to Q: evidently, $L \leqslant Q \leqslant U$. We now make different bins for the values of Q as shown: if $10^1 \geqslant Q > 10^0$ then Q lies in the first bin, if $10^0 \geqslant Q > 10^{-1}$ then Q lies in the second bin and so on. If, in a particular evaluation of the integral Q, it turns out that

(A) the upper bound, U_1, itself is *less* than the cut-off G, it follows naturally that Q_1 is negligible since $Q_1 \leqslant U_1$;

(B) on the other hand, if the lower bound, L_2 is *greater* than the cut-off G, then the corresponding integral viz. Q_2 is *not* negligible and must be evaluated since $Q_2 \geqslant L_2 \geqslant G$.

These bounds may be employed for a quick estimation of electron-repulsion integrals without actually computing them. For this purpose, one may follow either or both of the above strategies. Figure 1 depicts the above two cases schematically, for a hypothetical cut-off value $G = 10^{-8}$.

Figure 2a portrays a histogram, giving the number of integrals Q in a given bin for the case of diborane, containing 44 primitive Gaussians. Figures 2b and c do the same for the lower and upper bounds, respectively. In figures 3, 4 and 5 analogous
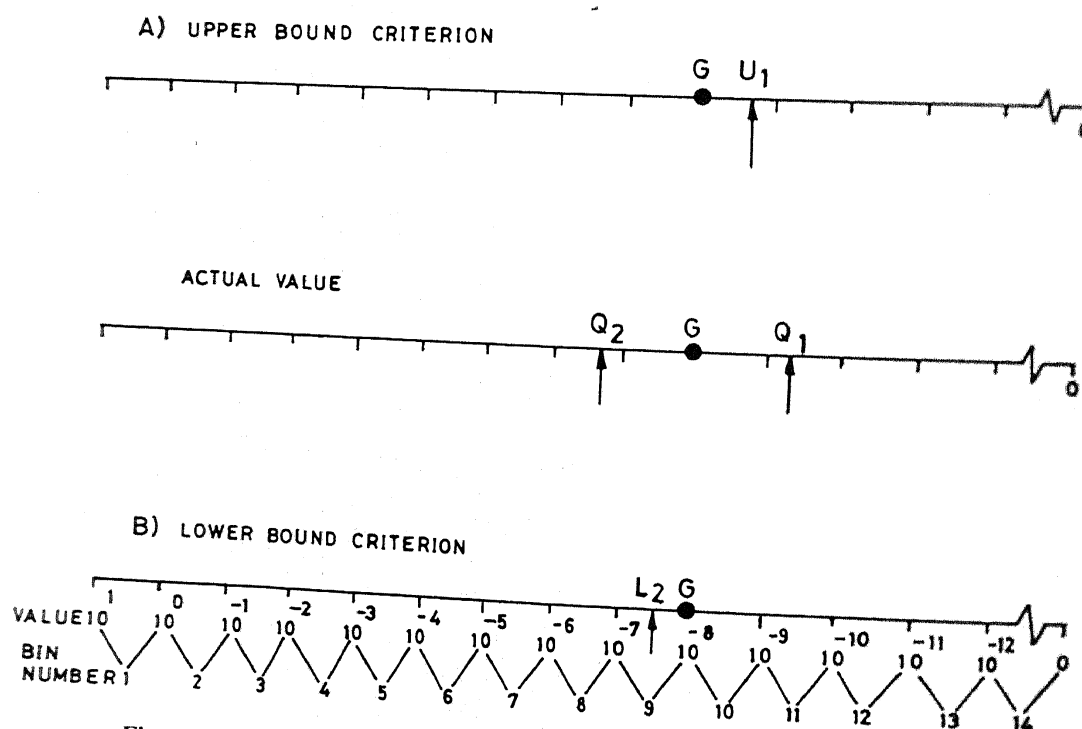

Figure 1. A schematic diagram demonstrating the criteria used in the implementation of §§ 5 and 6 for details.) the upper (A) as well as lower (B) bounds. The cut-off value, G, is chosen to be 10^{-8}. (See
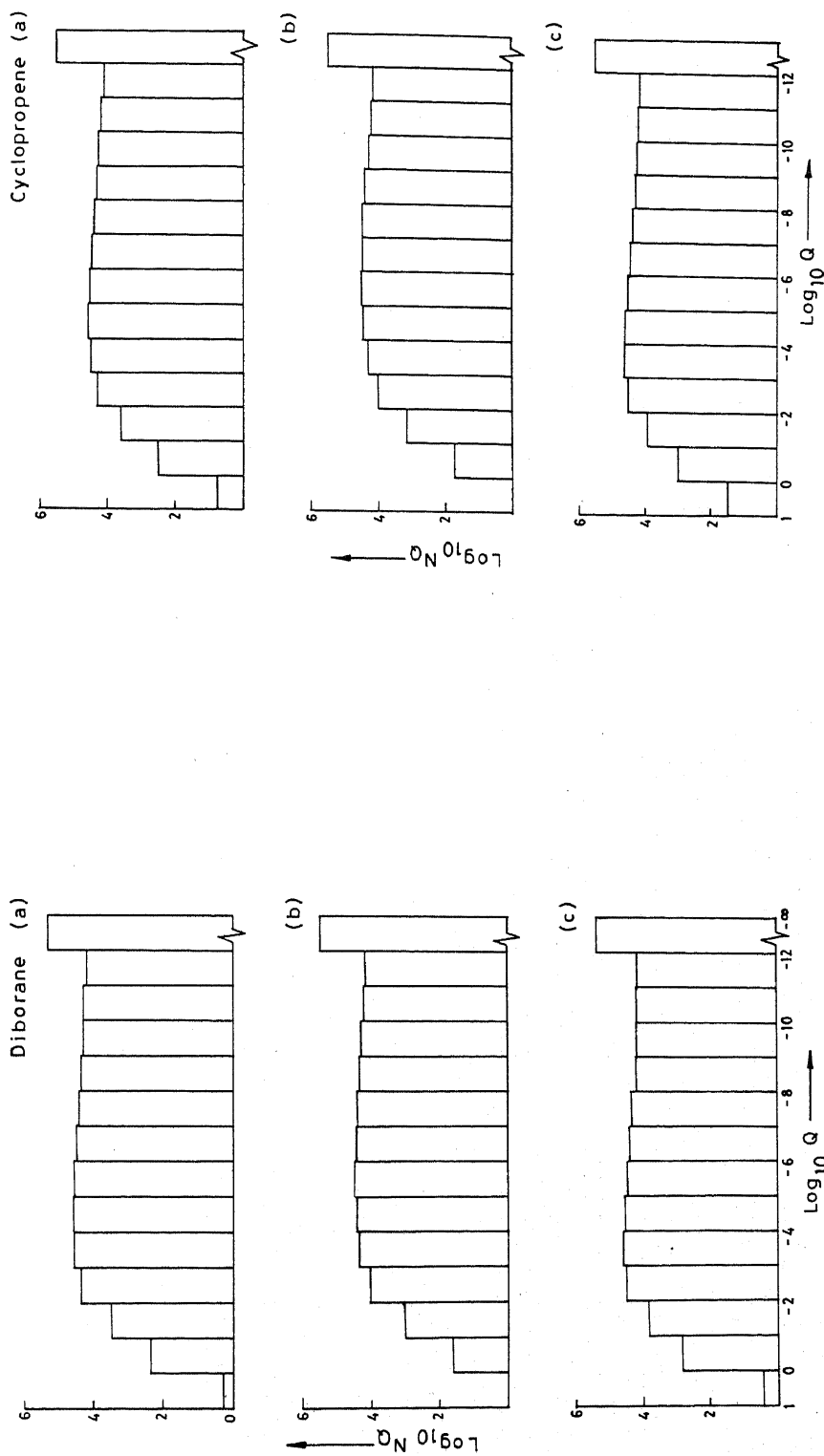
Figure 2. A histogram depicting the logarithm (to the base 10) of the number of Q-integrals, $\log_{10} N_Q$ in the respective bins shown in figure 1, versus logarithm (to the base 10) of the actual value of the Q-integrals, $\log_{10} Q$, for the diborane molecule. **(a)** Similar histograms for the lower **(b)** and the upper **(c)** bounds, respectively (see text, §5, for details).

Figure 3. A histogram for $\log_{10} N_Q$ versus $\log_{10} Q$ in the respective bins shown in figure 1, for the cyclopropene molecule **(a)** and analogous histograms for the lower **(b)** and upper **(c)** bounds.
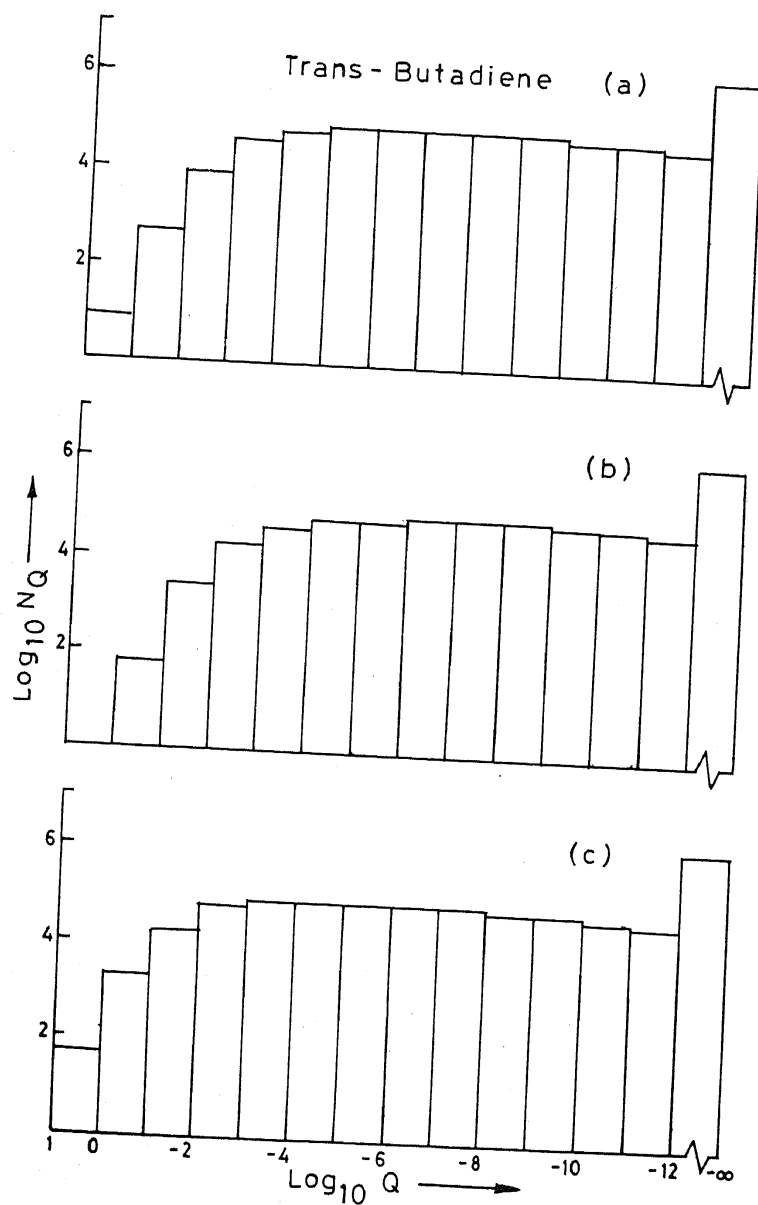
Figure 4. A histogram for $\log_{10} N_Q$ versus $\log_{10} Q$ in the respective bins shown in figure 1, for the *trans*-butadiene molecule (a) and analogous histograms for the lower (b) and upper (c) bounds, respectively.

histograms are drawn for the cases of cyclopropene, *trans*-butadiene and naphthalene molecules. The visual impact created by the plots is in fact a very mitigated one: the scale of ordinates being logarithmic, enhancement by one unit implies, in reality, multiplication by a factor of 10. The plots also reveal the breathtaking similarity among the histograms for the actual integrals Q and the corresponding lower and upper bounds. It must be emphasized that for an upper-bound histogram, the integrals to the *right* of the cut-off value are negligible, while a lower-bound histogram gives exactly a complementary criterion, viz. the integrals to the *left* of the cut-off value have to be evaluated. Once a Q-evaluation becomes imperative, one may enhance the efficiency by adopting the strategy of "differential accuracy" depending on the actual values of the bounds: the farther an integral estimate lies to the *left* of the cut-off, the more accurate the evaluation of the actual
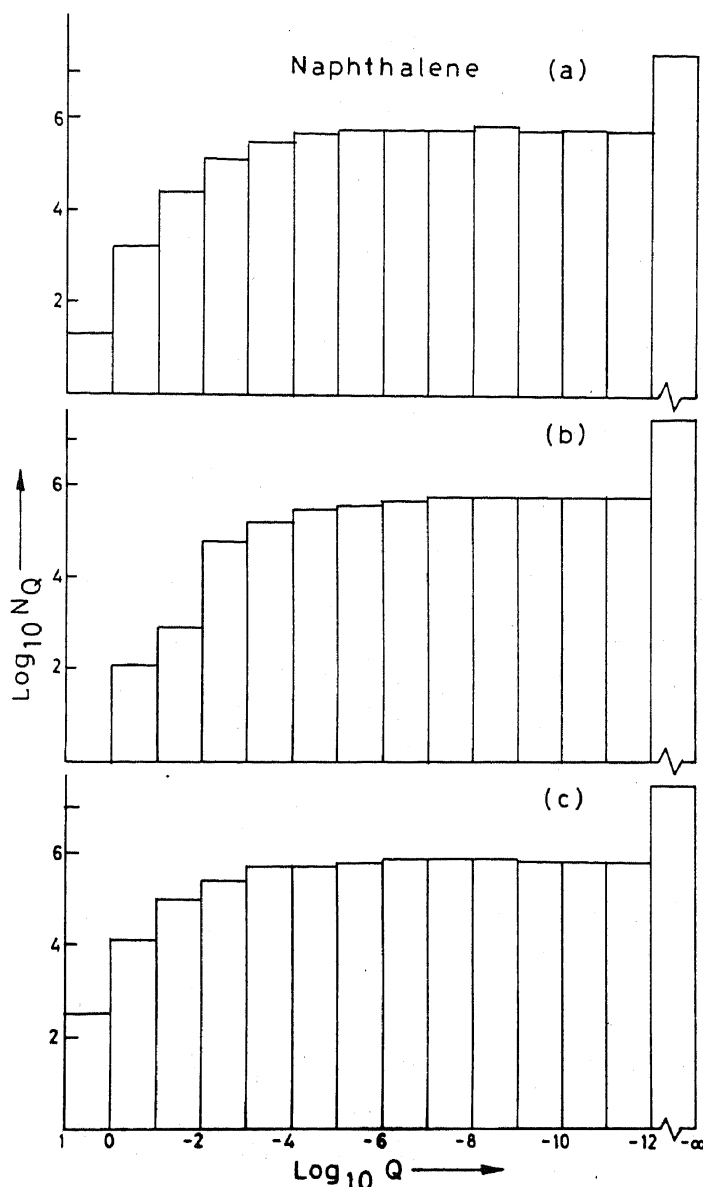
Figure 5. A histogram for $\log_{10}N_Q$ versus $\log_{10}Q$ in the respective bins shown in figure 1, for the naphthalene molecule (a) and analogous histograms for the lower (b) and upper (c) bounds, respectively.

value demanded (cf. Clementi 1972, and §4 of the present work). It may be inferred from the above test-cases that with a cut-off value of $G = 10^{-8}$, a significant fraction ($\sim 70\%$ to 95%) of the s-type Gaussian electron-repulsion integrals are in fact negligible, even for small molecules. Thus, the evaluation of these integrals may be completely avoided right at the primitive Gaussian level, leading to an enhancement in the efficiency of the program by an order of magnitude in terms of the CPU time and disk-space requirements. For larger molecules, one expects even more dramatic results. Extension to the p- and d-type Gaussians is straightforward vide the bounds provided in §5.

In conclusion, it may be stated that in this study, an attempt has been made to provide a comprehensive integrated view of rigorous studies on the inequalities

involving the two-electron repulsion integrals in general. Novel lower bounds to these repulsion integrals at a practical level, directly implementable in any *ab initio* Gaussian package have been derived, in addition to some new upper bounds. In essence, this work endows rigour to the criteria earlier used by Clementi and others (Clementi *et al* 1973; Clementi and Mehl 1974; Clementi and Roetti 1974). It is envisaged that these bounds can be harnessed in more general *ab initio* level programs.

Further bounds to the electron-repulsion integrals within Gaussian bases can be extracted via the Dirichlet principle (Schrader and Prager 1962) and Lieb's (1979) elegant results discussed in §§ 2 and 3, respectively. This work is already in progress in our laboratory.

Acknowledgements

Appendix

Expressions for electron repulsion integrals over Gaussian basis-sets involve (Boys 1950; Shavitt 1965) the special functions $F_m(t)$.

$$F_m(t) = \int_0^1 u^{2m} e^{-tu^2} \, du.$$

A variety of upper and lower bounds to F_0, F_1 and F_2 will be derived here.
(1)   Bounds to $F_0(t)$.
Note that $F_0(t)$ is a monotone decreasing function, since $F_0'(t) \leq 0$ for finite $t \geq 0$. The maximum value attained by F_0 is 1, viz. $F_0(0) = 1$.
Hence, a trivial bound is $F_0(t) \leq 1$.   (A1)
Also note the following: For $0 \leq u \leq 1$,

$$F_0(t) = \int_0^1 e^{-tu^2} \, du \geq \int_0^1 e^{-tu} \, du = (1 - e^{-t})/t.$$ (A2)

Another bound is obtained by the following considerations:

$$F_0(t) \geq \int_0^1 e^{-t} \, du = e^{-t}.$$ (A3)

For $t \leq 5$, the following bounds are obtained by series expansion.

$$F_0(t) \leq 1 - (t/3) + (t^2/10),$$

and

$$F_0(t) \geq 1 - (t/3) + (t^2/10) - (t^3/42).$$ (A4)

2. Bounds to $F_1(t)$

$$F_1(t) = \int_0^1 u^2 e^{-tu^2} du$$

$$\leqslant \int_0^1 u e^{-tu^2} du$$

$$= (-1/2t) e^{-tu^2} \Big|_0^1$$

$$= (1 - e^{-t})/(2t). \tag{A5}$$

Yet another upper bound to $F_1(t)$ may also be derived readily.

$$F_1(t) = \int_0^1 u^2 e^{-tu^2} du \leqslant \int_0^1 u^2 e^{-tu} du$$

$$= (2/t^3) - (2 + 2t + t^2) \exp(-t)/t^3. \tag{A6}$$

Some simpler upper bounds to F_1 and F_2 are given by:

$F_1 \leqslant 1/3$, and $F_2 \leqslant 1/5$, and in general,

$$F_m \leqslant 1/(2m+1) \tag{A7}$$

3. For some further inequalities, note that $x \leqslant e^{x-1}$.

Substitute $x = tu^2$ to obtain $tu^2 \leqslant e^{tu^2 - 1} = e^{tu^2}/e$.

Hence, $etu^2 \leqslant \exp(tu^2)$ yielding $\exp(-tu^2) \leqslant (etu^2)^{-1}$.

This leads to the result

$$F_1(t) = \int_0^1 u^2 e^{-tu^2} du \leqslant (1/et). \tag{A8}$$

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