

Bounds for the atomic Hartree–Fock electronic density

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Abstract. Some upper bound estimates for the atomic Hartree–Fock electronic density are presented. The bounds are derived in terms of the total kinetic energy, and some results also depend on one of the expectation values of r^{-1} or r^{-2} . The bounds have been numerically evaluated for He, Ne and Ar. The upper bound estimates obtained are found to be satisfactory for small to moderate values of the radial distance, but not very close to the nucleus.

1. Introduction

Although reasonably accurate Hartree–Fock atomic electronic densities are available, it is of interest to know how the Hartree–Fock electronic density is bounded in various regions of configuration space. It is also of particular interest to know in terms of what quantities the Hartree–Fock electronic density can be bounded.

In the current literature, there are very few rigorous bounds available for the atomic electronic density. Most known results have been derived only in the last few years (Ahlrichs *et al* 1978, 1981, Hoffmann-Ostenhof *et al* 1978a,b, Hoffmann-Ostenhof 1979, Hoffmann-Ostenhof and Morgan 1981, King 1983, Tal 1978, Tal and Levy 1980, Rédei 1963). Much of the recent interest has centred on deriving rigorous results for the asymptotic behaviour of the electronic density, with the principal focus being atomic systems. Molecular systems have received far less attention. Unfortunately, many of the results derived are not useful for numerical computations; the work of Hoffmann-Ostenhof *et al* (1978a) being an exception.

The bounds presented herein connect the electronic density with the kinetic energy of the atom. Some of the results also involve expectation values of the operators r^{-1} or r^{-2} . One important application offered by a knowledge of sharp inequalities for the electronic density is a direct means to obtain bounds for expectation values of different operators.

One limitation of almost all the bounds available in the literature, and of the results presented in this work, is that the region in the immediate vicinity of the nucleus is poorly described. This is not a difficulty for calculating bounds for most expectation values; the exception being those expectation values that are based on operators that are very sensitive to the region of configuration space close to the nucleus. One bound has been given previously which applies specifically to the case $r = 0$ for atomic systems (Hoffmann-Ostenhof *et al* 1978a), but this result is not useful for finding bounds on expectation values, although it is important for understanding how the electronic density is bounded at the nucleus.

2. Theory

King (1983) has recently derived a number of bounds for the exact atomic electronic density starting from Block's inequality (Block 1957) which takes the form (prime denotes differentiation)

$$|y(r)|^2 \leq \mathcal{M}(r) \int_a^b [f(x)(y(x)')^2 + g(x)y(x)^2] dx. \quad (1)$$

The function $\mathcal{M}(r)$, which is independent of $y(r)$, is obtained in terms of the solutions of the following Sturm–Liouville equation

$$(fw')' - gw = 0 \quad (2)$$

which is the Euler–Lagrange equation for the functional

$$F(w(x)) = \int_a^b [f(x)(w(x)')^2 + g(x)w(x)^2] dx. \quad (3)$$

f and g are arbitrary positive functions in equation (1).

With the appropriate choice of the functions f and g , and by expressing y in terms of a suitable function of the electronic density, various upper bounds can be determined for the electronic density from equation (1). For four different cases employing fairly simple choices for the functions f and g , the upper bound estimates obtained from equation (1) are summarised in table 1. The symbols appearing in each bound are defined in the table footnote. c_1 and c_2 are positive constants. The positive constant α appearing in each bound is arbitrary.

The bounds listed under cases C and F in the table have been obtained from cases B and E respectively by employing the well known inequalities

$$\langle \Psi | r_1^{-1} | \Psi \rangle^2 \leq 2T/N \quad (4)$$

Table 1. Bounds for the Hartree–Fock atomic electronic density.

Case	Function f	Function g	Bound for ρ_{HF}
A	c_1	c_2	$\rho_{\text{HF}}(r) \leq \frac{1}{8\pi r^2} [1 - \exp(-2\alpha r)] (\alpha N + 2T/\alpha)$
B	c_1	$c_2 r^{-1}$	$\rho_{\text{HF}}(r) \leq \frac{I_1(\beta) K_1(\beta) (2T + \alpha^2 N \langle \Psi r_1^{-1} \Psi \rangle)}{2\pi r}$
C	c_1	$c_2 r^{-1}$	$\rho_{\text{HF}}(r) \leq \frac{(2T)^{1/2} [(2T)^{1/2} + \alpha^2 N^{1/2}] I_1(\beta) K_1(\beta)}{2\pi r}$
D	$c_1 r^2$	c_2	$\rho_{\text{HF}}(r) \leq \frac{T}{2\pi r} [(2 - \delta)\delta]^{1/2}$
E	c_1	$c_2 + c_1 p(p+1)r^{-2}$	$\rho_{\text{HF}}(r) \leq \frac{I_{p+1/2}(\gamma) K_{p+1/2}(\gamma) \{2T + N[\alpha^2 + p(p+1)\langle \Psi r_1^{-2} \Psi \rangle]\}}{4\pi r}$
F	c_1	$c_2 + c_1 p(p+1)r^{-2}$	$\rho_{\text{HF}}(r) \leq \frac{I_{p+1/2}(\gamma) K_{p+1/2}(\gamma) [\alpha^2 N + 2T(2p+1)^2]}{4\pi r}$

N is the number of electrons, T the Hartree–Fock kinetic energy, $\alpha = (c_2/c_1)^{1/2}$, $\beta = 2\alpha r^{1/2}$, $\gamma = \alpha r$ and $\delta = \frac{1}{2} N \langle \Psi | r_1^{-2} | \Psi \rangle / T$. I_n and K_n are modified Bessel functions of the first and second kind respectively.

$$\langle \Psi | r_1^{-2} | \Psi \rangle \leq 8T/N \quad (5)$$

where T is the kinetic energy and N is the number of electrons. This leads to bounds involving the kinetic energy alone. Ψ represents the Hartree-Fock wavefunction.

One constraint that must be satisfied for case D is that

$$\delta < 1 \quad (6)$$

where

$$\delta = \frac{N \langle \Psi | r_1^{-2} | \Psi \rangle}{4T}. \quad (7)$$

If equation (6) is not satisfied, it can be shown that

$$\rho_{\text{HF}}(r) \leq T/2\pi r. \quad (8)$$

The expression given in equation (8) assumes the optimum choice for the parameter α , which in this case corresponds to the limit $\alpha \rightarrow 0$. The analogue of case A for the exact electronic density was obtained by Hoffmann-Ostenhof and Hoffmann-Ostenhof (1978).

3. Numerical applications

Because some of the bound estimates have non-simple analytic forms, it is not immediately obvious which inequality is most sharp at any given r value. The exception to this statement occurs in the limits of small r and large r values. In these limits, the bounds become sufficiently simple so that the optimum value of the parameter α can be determined analytically. For other values of r , simple analytic expression for α cannot be obtained. In this case the optimum value of α has been determined iteratively.

The bounds have been evaluated for He, Ne and Ar. The results are shown in figures 1–6. The Hartree-Fock wavefunctions employed are those from the Clementi-Roetti tables (Clementi and Roetti 1974). For case E, only the situation $p = 1$ is shown. Preliminary calculations for $p = 2$ gave bounds which were somewhat less sharp than the case $p = 1$. All results are reported in atomic units.

For He, $\delta = 1.048$, so equation (6) is not satisfied and the appropriate bound for case D is given by equation (8). From figure 1 it is observed that cases A, B and D all converge at small r . It can be shown that the limit $r \rightarrow 0$ for cases A, B and C allows the bounds presented in the table to be simplified to equation (8). That is, all these bounds are equivalent in the small r limit.

For both Ne ($\delta = 0.8069$) and Ar ($\delta = 0.6952$), equation (6) is satisfied. Therefore, at small r , case D represents the best bound. This can be observed from figures 4 and 6 for $r = 0.03$ – 0.04 . At slightly larger values of r (i.e. $r \approx 0.1$) case B represents the best bound estimate for Ne and Ar.

For middle range to larger r values, case A represents the best approximation, as can be observed from figures 1, 3 and 5. Case D is the worst bound for large r (see figures 1, 3 and 5), which is due to its fall-off as r^{-1} , compared to the fall-off of case A, which is r^{-2} .

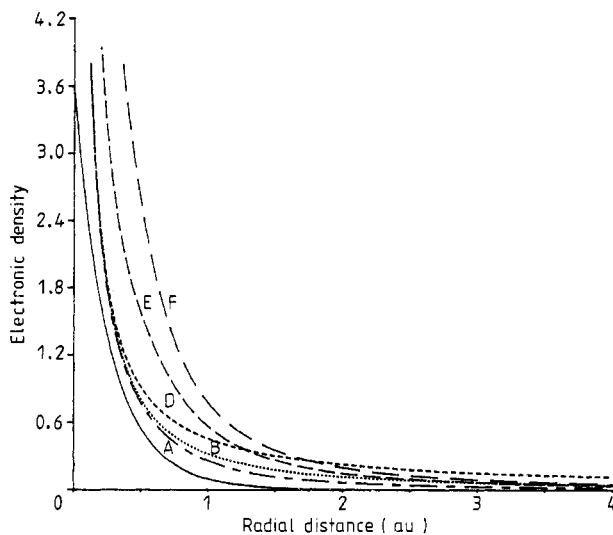


Figure 1. Bounds for the atomic Hartree-Fock electronic density for helium. The full curve is the Hartree-Fock density computed from the Clementi-Roetti wavefunction. Each of the assigned letters refers to a bound formula presented in table 1. Bound C is not presented since it coincides very closely with bound B.

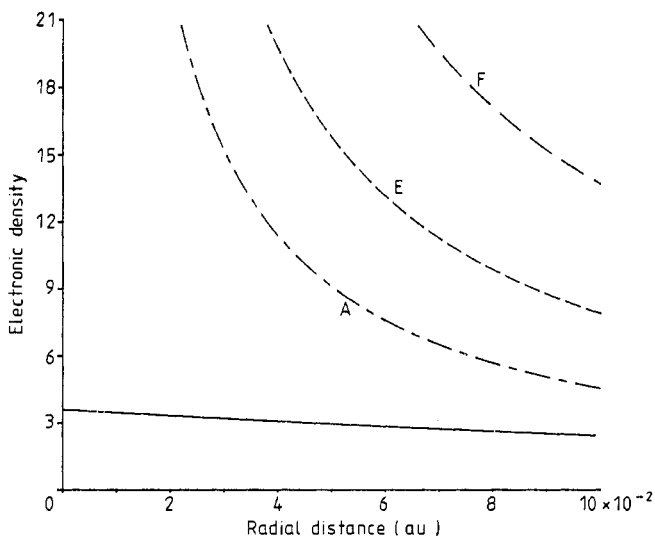


Figure 2. Bounds for the electronic density for helium for the region close to the nucleus. Bounds B, C and D are not presented in the figure because they coincide very closely with bound A. The full curve is the known Hartree-Fock density.

4. Discussion

From the numerical results presented, it is clear that no bound presented in the table is the best for all values of r . Cases A, B and D represent the best approximation for $\rho_{\text{HF}}(r)$; the latter two typically being better at small r and case A generally better at medium to larger values of r .

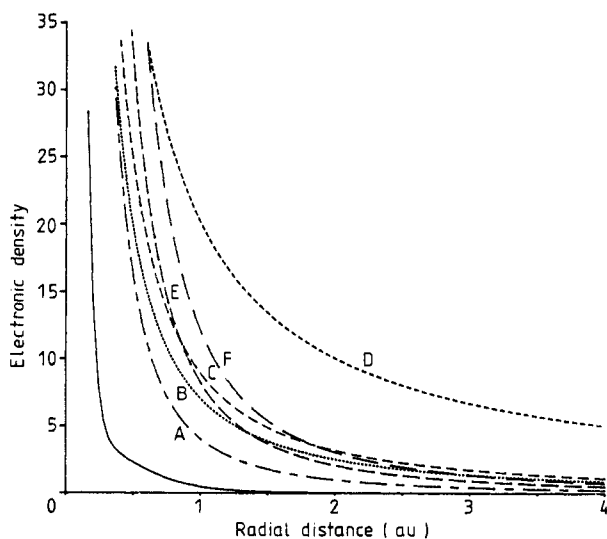


Figure 3. Bounds for the electronic density for the neon atom. The full curve is the known Hartree-Fock density.

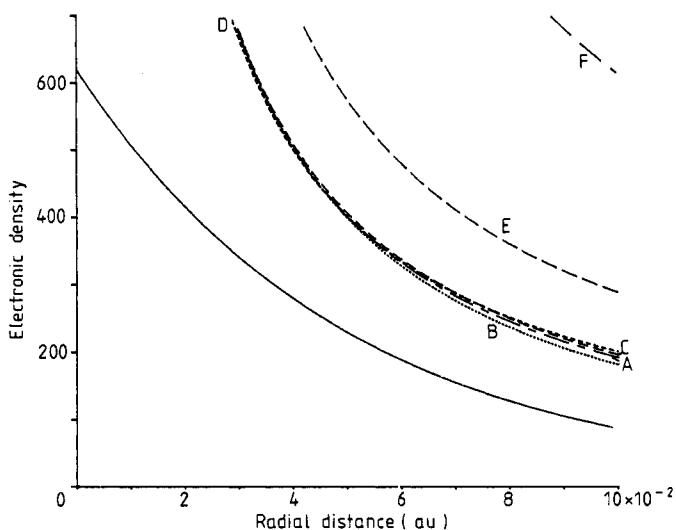


Figure 4. Bounds for the electronic density for the neon atom for the region near the nucleus. The full curve is the known Hartree-Fock density.

All the bounds exhibit divergent behaviour at $r = 0$, and hence these inequalities must be restricted to the case $r > 0$ (and preferably for values of r not too close to the nucleus). In addition, the long-range asymptotic behaviour predicted by these bounds is not the exponential fall-off expected for the true Hartree-Fock electronic density. The difficulties associated with bounding the electronic density at both short and long range considerably complicates the problem of finding bounds for expectation

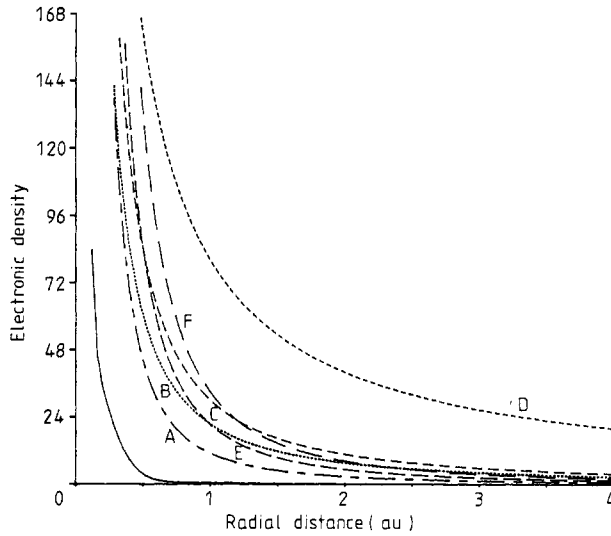


Figure 5. Bounds for the electronic density for the argon atom. The full curve is the known Hartree-Fock density.

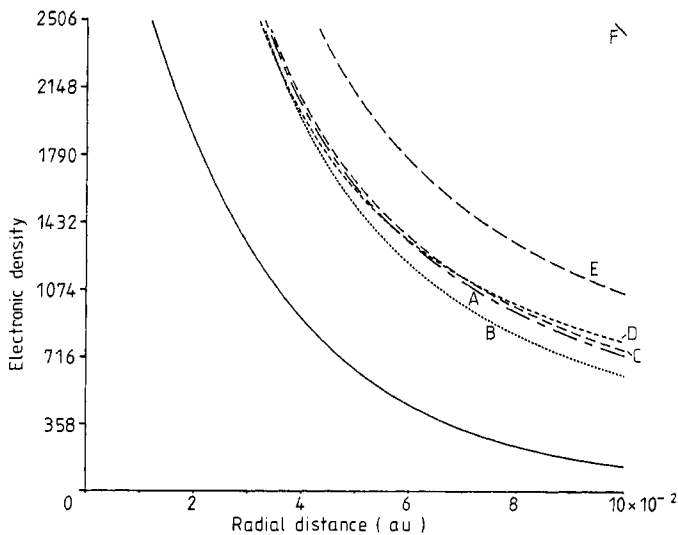


Figure 6. Bounds for the electronic density for the argon atom for the region near the nucleus. The full curve is the known Hartree-Fock density.

values. Work is under way to obtain bounds which are satisfactory at both short and long range.

In order to use bounds as a criterion for differentiating between basis sets, particularly those of high quality, very sharp bounds would be required. The present results would not be satisfactory for this purpose. Determination of tight bounds on $\rho(r)$, which would be useful for selecting one basis set over another, is an important open question.

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