

# The electron-pair density of atomic systems. Rigorous bounds and application to helium

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Received: 5 March 1992 / Final version: 31 July 1992

**Abstract.** Firstly, the monotonicity properties of the electron-pair density  $I(\mathbf{u})$  of atomic systems are investigated. Let  $h(u)$  denote the spherically-averaged electron-pair density of an arbitrary  $N$ -electron system, which essentially coincides with  $I(\mathbf{u})$  in the case of atoms. It is found that the interelectronic function  $g_\alpha(u) = h(u)/u^\alpha$ ,  $\alpha \geq 0$ , is not only monotonically decreasing from the origin for  $\alpha \geq \alpha_1 = \max\{uh'(u)/h(u)\}$  but it also has the property of convexity for  $\alpha \geq \alpha_2$ , where the value of  $\alpha_2$  is given in the text. Secondly, the Stieltjes technique is used to obtain rigorous, simple and compact inequalities which involve three interelectronic radial expectation values  $\langle u^k \rangle$ . These inequalities are universal in the sense that they are valid for both ground and excited states in the whole periodic table. Thirdly, for those systems with a unimodal  $h(u)$ , i.e. having a single maximum at  $u = u_{max}$ , are found (i) upper bounds to  $u_{max}$  in terms of any number of moments  $\langle u^k \rangle$  via the above-mentioned technique, and (ii) lower bounds to the maximal value  $h_{max} \equiv h(u_{max})$  by means of two arbitrary moments  $\langle u^k \rangle$  in a variational way. A particular case of the latter bound leads to a rigorous upper bound to the total electron-electron repulsion energy  $E_{ee}$  of the system, namely  $E_{ee} \leq \left[ \frac{9\pi}{8} N^2 (N-1)^2 h_{max} \right]^{1/3}$ . Finally, the electron-pair density of Helium is analysed in detail and the quality of the above mentioned inequalities is studied by means of the  $M$ -term Hylleraas-type wavefunctions, with  $M = 1, 2, 3, 6, 10$  and  $20$ . We observe that in the 20-term case, which is shown to be very close to the exact one,  $\alpha_1$  and  $\alpha_2$  take the values 0.0414 and 0.2067, respectively. Moreover, in such a case we found that some of the above mentioned inequalities are very accurate.

PACS: 31.10.+z; 31.20.Tz; 71.10.+x

## I. Introduction

The study of structural properties of the intracule or electron-pair density  $I(\mathbf{u})$ ,  $\mathbf{u}$  being the interelectronic vector, is basic to understand the chemistry and physics of atomic

and molecular systems. This is not only because  $I(\mathbf{u})$  is the major quantity in the associated electron-electron correlation problem but also because it is of great utility in density-functional models of exchange and correlation energies [1]. As long as we are concerned with atomic systems, it is sufficient [2] to investigate the spherically-averaged electron-pair density  $h(u)$  defined by

$$h(u) = \frac{1}{4\pi} \int I(\mathbf{u}) d\Omega_{\mathbf{u}}.$$

The global behavior of this quantity is of paramount importance to gain physical insight in the internal structure of atomic systems. Indeed, for example, (i) it allows to interpret some general aspects of the atomic periodic table such as the Hund's first rule [1, 3], (ii) a fundamental quantity like the interelectronic repulsion energy  $E_{ee}$  is given by its centroid as

$$\begin{aligned} E_{ee} = \langle u^{-1} \rangle &\equiv \int_0^\infty u^{-1} P(u) du \\ &= 4\pi \int_0^\infty uh(u) du \equiv 4\pi\mu_1 \end{aligned}$$

where  $P(u) = 4\pi u^2 h(u)$  is the so-called radial electron-pair density, and (iii) it reveals aspects of the short-range correlation in the atomic Coulomb hole which is very difficult to grasp otherwise [4–6].

The density  $h(u)$ , like any arbitrary density function defined on the interval  $[0, \infty)$ , may be fully characterized [7] by means of its moments  $\mu_k$  which are, apart from a factor  $4\pi$ , the interelectronic radial expectation values  $\langle u^k \rangle$ :

$$\begin{aligned} \mu_k &\equiv \int_0^\infty u^k h(u) du = \frac{1}{4\pi} \int_0^\infty u^{k-2} P(u) du \\ &= \frac{\langle u^{k-2} \rangle}{4\pi}, \quad k > -1. \end{aligned}$$

In this paper, we study both analytically and numerically the monotonicity properties of  $h(u)$  or, better, of the

**Table 1.** Comparison between the values of various ground-state quantities of the He atom calculated by means of several  $M$ -term Hylleraas-type wavefunctions and the exact ones. The symbols  $E$ ,  $h(0)$  and  $\langle u^k \rangle$  denote the total energy, the electron-pair density at the origin and the  $k$ th-interelectronic radial expectation value. Atomic units are used throughout

	Hylleraas-type wavefunction						Exact
	1-term	2-term	3-term	6-term	10-term	20-term	
$-E$	2.847656	2.891121	2.902432	2.903329	2.903603	2.903718	23.903724
$h(0)$	0.191202	0.119912	0.116122	0.111970	0.109598	0.107053	0.106352
$\langle u^{-2} \rangle$	1.89844	1.55270	1.48305	1.47393	1.46881	1.46531	1.46477
$\langle u^{-1} \rangle$	1.05469	0.974297	0.947174	0.946045	0.946006	0.945832	0.945818
$\langle u^0 \rangle$	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
$\langle u \rangle$	1.29630	1.37243	1.42058	1.42188	1.42174	1.42202	1.42207
$\langle u^2 \rangle$	2.10700	2.32730	2.50449	2.51109	2.51576	2.51607	2.51644
$\langle u^3 \rangle$	4.09694	4.66983	5.24207	5.27141	5.31261	5.30611	5.30800
$\langle u^4 \rangle$	9.24882	10.7844	12.6608	12.7874	13.0385	12.9727	12.9812

density function

$$g_\alpha(u) = \frac{h(u)}{u^\alpha}, \quad \alpha \geq 0 \quad (1)$$

in terms of the associated values  $\langle u^k \rangle$ . In Sect. II the Stieltjes-moment-problem technique [7] is used to obtain new and rigorous universal inequalities which involve three interelectronic radial expectation values. This technique was recently introduced in the study of atomic structure [8–11] and shown to be a very useful tool to gain physical insight. Then, in Sect. III, the same technique is applied to a unimodal electron-pair density  $h(u)$ , i.e. having only a single maximum at  $u = u_{\max}$ . In doing so, rigorous upper bounds to  $u_{\max}$  are shown in terms of an arbitrary number of moments  $\langle u^k \rangle$ . Also, rigorous, simple and compact lower bounds to the maximal value  $h_{\max} \equiv h(u_{\max})$  are variationally found by means of two arbitrary moments  $\langle u^k \rangle$ . Finally, in Sect. IV, the electron-pair density of helium is numerically studied by means of the so-called Hylleraas-type wavefunction of  $M$  terms, with  $M = 1, 2, 3, 6, 10$  and  $20$ . In particular, besides the well-known unimodality [12] of  $h(u)$ , we obtain two additional properties:

1.  $h(u)/u^\alpha$  is monotonically decreasing from the origin for every  $\alpha \geq \alpha_1 \equiv \max\{uh'(u)/h(u)\}$ , where  $\alpha_1$  is given in Table 1.
2.  $h(u)/u^\alpha$  is convex for every  $\alpha \geq \alpha_2$ , where the values of  $\alpha_2$  are also given in Table I for different  $M$ 's.

These properties together with the universal inequalities described in the following sections allow to find numerous interesting relationships for the He atom which involve the interelectronic moments  $\langle u^k \rangle$ ,  $u_{\max}$  and  $h_{\max}$ . Discussion of these relationships follows and then a few sentences are made as concluding remarks.

## II. Universal relationships among interelectronic radial expectation values

Here we study the monotonicity properties of the interelectronic density function  $g_\alpha(u)$  defined by (1). This is

equivalent to studying the following non-negativity condition:

$$H_p(u; \alpha) \equiv (-1)^p \frac{d^p}{du^p} \left[ \frac{h(u)}{u^\alpha} \right] \geq 0 \quad (2)$$

where  $p$  is any, but fixed, non-negative integer number. If (2) is satisfied, one says [11] that  $h(u)/u^\alpha$  is monotone of order  $p$ . Remark that the first few cases  $p = 0, 1$  and  $2$  express the non-negativity, unimodality at the origin (or monotonic decreasing from the origin) and the convexity properties of  $h(u)/u^\alpha$ , respectively.

Working out the differentiation involved in (2), one realizes that, for a fixed  $p$ , the condition

$$\begin{aligned} & (-1)^p \frac{p!}{\Gamma(\alpha)} \sum_{k=0}^p (-1)^k \\ & \times \frac{\Gamma(\alpha+k)}{k!(p-k)!} \frac{1}{u^{\alpha+k}} \frac{d^{p-k} h(u)}{du^{p-k}} \geq 0 \end{aligned} \quad (3)$$

defines a value  $\alpha_p$  such that for  $\alpha \geq \alpha_p$  the interelectronic function  $h(u)/u^\alpha$  is monotone of order  $p$ . Assuming the existence of the value  $\alpha_p$ , one notices that the inequality (3) reduces to

$$\begin{aligned} p=0, & \quad h(u) \geq 0 \\ p=1, & \quad \alpha h(u) - uh'(u) \geq 0 \\ p=2, & \quad u^2 h''(u) - 2\alpha uh'(u) + \alpha(\alpha+1)h(u) \geq 0 \end{aligned}$$

respectively. These expressions show that

$$\begin{aligned} \alpha_0 &= 0, \quad \alpha_1 = \max \left\{ \frac{uh'(u)}{h(u)} \right\}, \\ \alpha_2 &= \max \{ f(u) \} \end{aligned} \quad (4)$$

where

$$\begin{aligned} f(u) &= \frac{1}{2h(u)} \{ 2uh'(u) - h(u) \\ & \quad + [(h(u) - 2uh'(u))^2 - 4u^2 h(u) h''(u)]^{\frac{1}{2}} \}. \end{aligned}$$

Then, apart from the well-known quantum-mechanical non-negativity character of  $h(u)/u^\alpha$ , one obtains two important characteristics of the electron-pair density  $h(u)$ :

1. The function  $h(u)/u^\alpha$  with  $\alpha \geq \alpha_1$  is monotone of first order, i.e. is unimodal with mode at the origin. This tells us that it is monotonically decreasing from the origin.
2. The function  $h(u)/u^\alpha$  with  $\alpha \geq \alpha_2$  is monotone of second order, i.e. it has the property of convexity.

Now, we apply the Stieltjes-moment-problem technique [7] to the function  $u^m H_p(u; \alpha)$  for any  $m \geq 0$ . It states that the moments of that function, i.e. the quantities

$$v_j \equiv v_j(\alpha, p, m) = \int_0^\infty u^{j+m} H_p(u; \alpha) du \quad (5)$$

must satisfy the following inequalities:

$$\Delta_k^{(i)} \geq 0 \quad \text{for } i=0 \text{ and } 1, \quad \text{and } k=0, 1, 2, \dots \quad (6)$$

The  $\Delta$ -symbol denotes the Hadamard determinant

$$\Delta_k^{(i)} = \begin{vmatrix} v_{m+i} & v_{m+i+1} & \cdots & v_{m+i+k} \\ v_{m+i+1} & v_{m+i+2} & \cdots & v_{m+i+k+1} \\ \vdots & \vdots & \ddots & \vdots \\ v_{m+i+k} & v_{m+i+k+1} & \cdots & v_{m+i+2k} \end{vmatrix} \quad (7)$$

The calculation of the integral given in (5) produces

$$v_j = \frac{p! \Gamma(t + \alpha + p + 3)}{4\pi \Gamma(t + \alpha + 3)} \langle u^j \rangle \quad (8)$$

for  $t = m + j - \alpha - p - 2 > -3$ . The combination of (6), (7) and (8) leads to a rich variety of new rigorous relationships which involve interelectronic radial expectation values  $\langle u^k \rangle$  of any order  $k$ . The simplest non-trivial case, i.e. for  $i=0$ ,  $k=1$  and  $m=0$  gives

$$v_0 v_2 \geq v_1^2$$

which leads to the important inequality

$$\langle u^{n-2} \rangle \langle u^n \rangle \geq F(n, \alpha_p, p) \langle u^{n-1} \rangle^2, \quad n > -1 \quad (9)$$

with  $p=0, 1, 2, \dots$ , and

$$F(n, \alpha_p, p) = \frac{(n + \alpha_p + 2)(n + \alpha_p + p + 1)}{(n + \alpha_p + 1)(n + \alpha_p + p + 2)}. \quad (10)$$

Notice that the optimal value  $\alpha_p$  (i.e. the minimal value of  $\alpha$  which verifies the inequality (3) for a given  $p$ ) was taken into account; it makes the inequality to be most accurate. One should realize that  $\alpha_p$  varies not only with  $p$  but it depends also on the specific system that one is dealing with. Let us mention here that  $\alpha_p \leq \alpha_{p+1}$  as one can see by working with (3).

The relationships (3)–(4) and (9)–(10) are universal in the sense that they may be applied to any many-electron system and are valid for both ground and excited states. Let us now consider some particular cases:

1. For  $p=0$ , i.e. assuming only the non-negativity property of  $h(u)$ , one has

$$\langle u^{n-2} \rangle \langle u^n \rangle \geq \langle u^{n-1} \rangle^2, \quad n > -1$$

2. For  $p=1$ , i.e. from the unimodality at the origin of  $h(u)/u^{\alpha_1}$ , one has

$$\langle u^{n-2} \rangle \langle u^n \rangle \geq \frac{(n + \alpha_1 + 2)^2}{(n + \alpha_1 + 2)^2 - 1} \langle u^{n-1} \rangle^2, \quad n > -1 \quad (12)$$

where  $\alpha_1 = \max \left\{ \frac{uh'(u)}{h(u)} \right\}$  as pointed out by (4).

3. For  $p=2$ , i.e. from the convexity of  $h(u)/u^{\alpha_2}$ , one has

$$\langle u^{n-2} \rangle \langle u^n \rangle \geq \frac{(n + \alpha_2 + 2)(n + \alpha_2 + 3)}{(n + \alpha_2 + 2)(n + \alpha_2 + 3) - 2} \times \langle u^{n-1} \rangle^2, \quad n > 1 \quad (13)$$

where  $\alpha_2 = \max \{ f(u) \}$  as given in (4).

For  $p \geq 3$ , one needs to solve an ordinary differential equation of order equal to or higher than three in order to obtain  $\alpha_p$  defined by (3), what is generally complicated. This is the reason for us to consider only the cases  $p=0, 1$  and  $2$  in specific systems, as will be done for helium in Sect. V. In these cases, the evaluation of  $\alpha_p$  is much easier as we have to evaluate a differential equation of, at most, second order.

These inequalities may be used for many purposes. In particular, by making  $n=0$  and  $1$  in (13) one easily obtains rigorous bounds to the interelectronic repulsion energy  $E_{ee}$ . Indeed, with  $n=0$  one has a lower bound which depends on  $\langle u \rangle$ ,  $\alpha_2$  and  $N$ , the number of electrons of the system, and with  $n=1$  one has an upper bound which depends on  $\langle u^{-2} \rangle$ ,  $\alpha_2$  and  $N$ .

To end this section let us point out that the inequalities (6)–(8) may supply an infinity of relationships involving interelectronic radial expectation values  $\langle u^k \rangle$  of either integer order or fractional (in fact real; remember that  $m \geq 0$ ) order  $k$ .

### III. Many-electron systems with a unimodal electron-pair density

Here we consider an arbitrary  $N$ -electron system having a unimodal electron-pair density  $h(u)$ . Specific systems with a unimodal  $h(u)$  at their ground states are e.g. the helium-like atoms [12] from  $\text{H}^-$  through  $\text{Mg}^{10+}$ . Let  $u_{\max}$  and  $h_{\max}$  be the location of the single maximum and the maximal value  $h(u_{\max})$  of the density  $h(u)$ , respectively. We look for rigorous bounds to  $u_{\max}$  and  $h_{\max}$  in terms of the radial interelectronic expectation values  $\langle u^k \rangle$ .

The main results of this section are:

1. Upper bonds to  $u_{\max}$ . It is found that

$$u_{\max} \leq U_0 \quad (14)$$

and

$$u_{\max} \leq U_1 \quad \text{when} \quad U_1 \leq U_0 \quad (15)$$

where  $U_0$  and  $U_1$  are given by

$$U_0 = \frac{2\langle u^{-1} \rangle}{\langle u^{-2} \rangle} \quad (16)$$

$$U_1 = \frac{2\langle u^{-2} \rangle \langle u \rangle - \frac{3}{2}N(N-1)\langle u^{-1} \rangle - A}{\frac{3}{2}N(N-1)\langle u^{-2} \rangle - 4\langle u^{-1} \rangle^2}. \quad (17)$$

In writing (17) we have used the normalization  $\langle u^0 \rangle = 4\pi\mu_2 = \frac{1}{2}N(N-1)$  and the symbol  $A$  which is defined as

$$A = \left[ -\frac{27}{4}N^2(N-1)^2\langle u^{-1} \rangle^2 + 4\langle u^{-2} \rangle^2 \langle u \rangle^2 - 18N(N-1)\langle u^{-2} \rangle \langle u^{-1} \rangle \langle u \rangle + 32\langle u^{-1} \rangle^3 \langle u \rangle + \frac{27}{8}N^3(N-1)^3\langle u^{-2} \rangle \right]^{\frac{1}{2}}.$$

It is worthwhile to point out that the procedure used to find the bounds (15), which will be described below, allows to obtain better but more complicated bounds which include a higher number of interelectronic expectation values.

2. Lower bounds to  $h_{\max}$ . It will be shown below that

$$h_{\max} \geq h(s, t) \equiv C(s, t) \left( \frac{\langle u^t \rangle^{s+3}}{\langle u^s \rangle^{t+3}} \right)^{\frac{1}{s-t}} \quad (18)$$

where  $s$  and  $t$  are real numbers,  $s > t$ , and

$$C(s, t) = \frac{1}{4\pi} \left[ \frac{(t+3)^{s+3}}{(s+3)^{t+3}} \right]^{\frac{1}{s-t}}. \quad (19)$$

Some particular cases are given by

$$h(-1, -2) = \frac{1}{8\pi} \frac{\langle u^{-2} \rangle^2}{\langle u^{-1} \rangle} \quad (20)$$

$$\begin{aligned} h(0, -2) &= \frac{1}{4\sqrt{3}\pi} \left( \frac{\langle u^{-2} \rangle^3}{\langle u^0 \rangle} \right)^{\frac{1}{2}} \\ &= \frac{1}{4\pi} \left( \frac{2\langle u^{-2} \rangle^3}{3N(N-1)} \right)^{\frac{1}{2}} \end{aligned} \quad (21)$$

$$h(0, -1) = \frac{2}{9\pi} \frac{\langle u^{-1} \rangle^3}{\langle u^0 \rangle^2} = \frac{8}{9\pi} \frac{\langle u^{-1} \rangle^3}{[N(N-1)]^2}. \quad (22)$$

The last bound is particularly interesting because it may also be used to obtain a rigorous upper bound to the total electron-electron repulsion energy  $E_{ee} = \langle u^{-1} \rangle$  of an  $N$ -electron system via  $h_{\max}$  as

$$E_{ee} \leq \left[ \frac{9\pi}{8} N^2(N-1)^2 h_{\max} \right]^{\frac{1}{3}} \quad (23)$$

This is the only result which connects the electron-electron repulsion energy  $E_{ee}$  of an  $N$ -electron system with some characteristics of the electron-pair density  $h(u)$  of the system. Here we should mention that Kinoshita [13, 14] was able to get an upper bound to  $E_{ee}$  by means of the kinetic energy for a two-electron system, which may be easily generalized to any  $N$ -electron system.

Following the same reasoning as Gálvez et al. [15] one can easily show that, for a fixed  $s$ , the sharper these lower bounds  $h(s, t)$ , the smaller is  $t$ . A careful analysis of the inequalities (18) as well as other new and old inequalities which involve  $E_{ee}$  will be done elsewhere.

Let us now prove all these results. To find the bounds to  $u_{\max}$  given by (16)–(17), one must apply the Stieltjes technique to the positive-definite function  $\phi(u) = (\beta - u)h'(u)$  with  $\beta \equiv u_{\max}$ . To do that, firstly one calculates the moments of this function which are

$$\begin{aligned} \xi_j &= \int_0^\infty u^j \phi(u) du = (j+1)\mu_j - \beta j \mu_{j-1} \\ &\text{if } j > 0 \end{aligned} \quad (24)$$

Then, according to the Stieltjes moment problem [7], the inequalities

$$\Delta_k^{(1)} = \begin{vmatrix} \xi_1 & \xi_2 & \cdots & \xi_{k+1} \\ \xi_2 & \xi_3 & \cdots & \xi_{k+2} \\ \vdots & \vdots & \ddots & \vdots \\ \xi_{k+1} & \xi_{k+2} & \cdots & \xi_{2k+1} \end{vmatrix} \geq 0 \quad (25)$$

for  $k=0, 1, \dots$  are fulfilled. Inserting the values of  $\xi_j$  given by (24) into (25) and taking into account the properties of determinants, one gets the following general determinantal inequalities:

$$\Delta_k^{(1)} = \begin{vmatrix} 1 & \beta & \beta^2 & \cdots & \beta^{k+1} \\ \mu_0 & 2\mu_1 & 3\mu_2 & \cdots & (k+2)\mu_{k+1} \\ 2\mu_1 & 3\mu_2 & 4\mu_3 & \cdots & (k+3)\mu_{k+2} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ (k+1)\mu_k & (k+2)\mu_{k+1} & (k+3)\mu_{k+2} & \cdots & (2k+2)\mu_{2k+1} \end{vmatrix} \geq 0 \quad (26)$$

valid for any non-negative integer  $k$ . The first two inequalities are

$$\begin{aligned} \Delta_0^{(1)} &= 2\mu_1 - \mu_0\beta \geq 0 \\ \Delta_1^{(1)} &= 8\mu_1\mu_3 - 9\mu_2^2 + (6\mu_1\mu_2 - 4\mu_0\mu_3)\beta \\ &\quad + (3\mu_0\mu_2 - 4\mu_1^2)\beta^2 \geq 0 \end{aligned} \quad (27)$$

which allow to get the searched bounds  $U_0$  and  $U_1$  as given by (15)–(17). Similar bounds depending on a higher number of moments may be easily obtained by means of

the consideration of the cases  $k=2, 3, \dots$  in (26). Finally, let us find the lower bound to  $h_{\max}$  given by (18). We will do that by following a procedure already used by Gálvez et al. [15, 16]. Since, by definition,  $h_{\max} \geq h(u)$  for all  $u$ , one has that for any positive  $q$

$$h_{\max} \geq \left[ \frac{1}{\langle u^0 \rangle} \int [h(u)]^{q+1} d\mathbf{u} \right]^{\frac{1}{q}} \equiv \left( \frac{\omega_{q+1}}{\langle u^0 \rangle} \right)^{\frac{1}{q}} \quad (28)$$

where  $\omega_q$  is the so-called *frequency moment* of order  $q$  of the density function  $h(u)$ . On the other hand, it is known [17] that  $\omega_n$  (with  $n$  not necessarily integer but greater than one) is bounded from below as

$$\omega_n \geq f(\alpha, \beta, n) \langle u^0 \rangle^n \left[ \frac{\langle u^\beta \rangle^{n(\alpha+3)-3}}{\langle u^\alpha \rangle^{n(\beta+3)-3}} \right]^{\frac{1}{\alpha-\beta}} \quad (29)$$

provided  $\alpha > \beta > 3(1-n)/n$  and with

$$\begin{aligned} f(\alpha, \beta, n) &= n^n (\alpha - \beta)^{2n-1} \\ &\times \left[ 4\pi B \left( \frac{n(\beta+3)-3}{(\alpha-\beta)(n-1)}, \frac{2n-1}{n-1} \right) \right]^{-(n-1)} \\ &\times \left( \frac{[n(\beta+3)-3]^{n(\beta+3)-3}}{[n(\alpha+3)-3]^{n(\alpha+3)-3}} \right)^{\frac{1}{\alpha-\beta}}. \end{aligned} \quad (30)$$

The combined use of both inequalities (28)–(29) produces a set of lower bounds to  $h_{\max}$  which have an increasing behavior with  $q$ . So, the best lower bound will occur for  $q \rightarrow \infty$ . The last lower bound turns out to be  $h(s, t)$  as given in the inequality (18), what completes the proof.

#### IV. The electron-pair density of helium

The electron-pair density  $h(u)$  of the ground-state of He has been calculated by many authors [12, 18–22]. Here we have investigated this function by means of the  $M$ -term Hylleraas-type wavefunctions [23] with  $M=1, 2, 3, 6, 10$  and 20. To be as reliable as possible, first we calculate the total ground state energy  $E$  of our system as well as several quantities directly connected with the density  $h(u)$  such as its value at the origin,  $h(0)$ , and several interelectronic radial expectation values  $\langle u^k \rangle$ , with  $-2 \leq k \leq 4$ . The comparison of these values with the corresponding exact ones is shown in Table 1. It illustrates that the 20-term values are very close to the exact ones [24].

We have found that  $h(u)$  is indeed unimodal as other authors [11] have already shown. The location of the single maximum,  $u_{\max}$ , and the maximal value the function,  $h(u_{\max}) \equiv h_{\max}$ , varies with  $M$  as shown in Table 2.

Soon we found that  $h(u)$  has no monotone properties from the origin but two important results came up:

1.  $h(u)$  is unimodal with mode near the origin, but not at the origin, as previously shown by other authors [12]. The location of the single maximum,  $u_{\max}$ , and the maximal value of the density,  $h_{\max}$ , are given in Table 2.

**Table 2.** Values of the coordinates,  $u_{\max}$  and  $h_{\max}$ , of the maximum of the ground-state electron-pair density  $h(u)$  of the He atom. The values of the parameters  $\alpha_1$  and  $\alpha_2$ , as given by (31), are also shown. The calculation was done in the Hylleraas framework described in the text. Atomic units are used throughout

Hylleraas-type wavefunction	Maximum		$\alpha_1$	$\alpha_2$
	$u_{\max}$	$h(u_{\max})$		
1-term	0.000000	0.191202	0.0000000	0.087126
2-term	0.162781	0.127021	0.0283162	0.183845
3-term	0.140105	0.120845	0.0196774	0.163095
6-term	0.163425	0.118766	0.0289043	0.181186
10-term	0.175298	0.117329	0.0333685	0.191409
20-term	0.190546	0.116545	0.0414379	0.206741

**Table 3.** Values of the upper bounds  $U_0$  and  $U_1$  to the location  $u_{\max}$  of the maximum of the electron-pair density  $h(u)$  of He. The ratios  $R(s, t) = H(s, t)/h_{\max}$  are given, in percent, for  $(s, t) = (0, -1)$ ,  $(0, -2)$  and  $(-1, -2)$ .  $H(s, t)$  are the lower bounds to the maximal intensity  $h_{\max}$  of  $h(u)$  as defined in the text. The  $M$ -term Hylleraas-type wavefunctions are used. Atomic units are also used throughout

$M$	$u_{\max}$		$h_{\max}$		
	$U_1$	$U_0$	$R(0, -1)$	$R(0, -2)$	$R(-1, -2)$
1	0.751	1.111	43.4	62.8	71.1
2	0.886	1.255	51.5	70.0	77.5
3	0.893	1.277	49.7	68.7	76.5
6	0.906	1.284	50.4	69.2	76.9
10	0.917	1.288	51.0	69.7	77.3
20	0.924	1.291	51.4	69.9	77.5

2. The interelectronic function  $h(u)/u^\alpha$  is monotonically decreasing from the origin for  $\alpha \geq \alpha_1$  and has the property of convexity for  $\alpha \geq \alpha_2$ , where the parameters  $\alpha_1$  and  $\alpha_2$  have the values shown in Table 2 as calculated in the above mentioned Hylleraas framework. Notice that the 20-term values, which are almost the exact ones, give

$$\alpha_1 = 0.0414 \quad \text{and} \quad \alpha_2 = 0.2067. \quad (31)$$

Then, the sets of inequalities obtained in the two previous sections may be applied to the helium case. The inequalities of Sect. II, which allow to correlate three interelectronic moments  $\langle u^n \rangle$  of successive orders, are highly accurate. For illustration, the accuracy of the inequality (13) is always higher than 85% and slightly depends on both the order  $n$  and the number  $M$  of terms of the wavefunction. The particular cases  $n=0$  and  $n=1$  together with the  $\alpha_2$ -value given by (31) allow to bound in both senses the total electron-electron repulsion energy  $E_{ee}$  of He as

$$1.1741 \langle u \rangle^{-1} \leq E_{ee} \leq 0.8470 \langle u^{-2} \rangle^{\frac{1}{2}}.$$

The interval defined by these two bounds to  $E_{ee}$  may be still narrowed by taking a  $p$ -value  $p_0 > 2$  in the inequality (9); this requires the knowledge of the parameter  $\alpha_{p_0}$ , which is obtained by numerically solving the corresponding inequality (2).

The inequalities of Sect. III are based only on the unimodality of the intracule density  $h(u)$  and they correlate

the coordinates  $(u_{\max}, h_{\max})$  of the single maximum of  $h(u)$  with the interelectronic moments  $\langle u^n \rangle$ . In the helium case, the upper bounds  $U_0$  and  $U_1$  given by (16)–(17), for the location  $u_{\max}$  of the maximum, are numerically shown in Table 3. By comparing these bounds with the appropriate value of  $u_{\max}$  given in Table 2, one observes that its quality is poor. Although the accuracy of these bounds may be improved as more as we want by taking into account the inequalities (26) for values of  $k$  higher than 1 (what means to consider additional moments  $\langle u^n \rangle$  of integer order  $n$  other than  $-2, -1, 0$  and  $1$ ), we think that this is not the right way to operate due to the so complicated expressions for the resulting bounds. We believe that it would be better to obtain bounds similar to (16)–(17) which are based not only on the unimodality property but also on other characteristics of the density  $h(u)$  as it will be shown elsewhere.

The lower bounds  $h(s, t)$  to the maximal value of  $h(u)$  given by (18)–(22) depend only on two interelectronic moments  $\langle u^n \rangle$ . For illustrative purposes, let us consider those given by (20)–(22) which for the He atom are as

$$h(-1, -2) = 0.03979 \frac{\langle u^{-2} \rangle^2}{\langle u^{-1} \rangle} \quad (32)$$

$$h(0, -2) = 0.04594 \langle u^{-2} \rangle^{\frac{3}{2}} \quad (33)$$

$$h(0, -1) = 0.07074 \langle u^{-1} \rangle^3. \quad (34)$$

The quality of these bounds is numerically studied in Table 3 by means of the above mentioned Hylleraas-type wavefunctions. From the ratios  $R(s, t) = h(s, t)/h_{\max}$ , given in percent, one observes that the best bound is  $h(-1, -2)$ , its accuracy being of 77.5% in the 20-terms case. In this calculation the values of the moments  $\langle u^{-1} \rangle$  and  $\langle u^{-2} \rangle$  were taken from Table 1. Regarding Table 3 one realizes that, since  $u_{\max}$  is near the origin and that moments of negative order grasp better such a region of the density, we can further improve this accuracy by considering two moments of higher negativity order; possibly, moments of fractional order between  $-3$  and  $-2$ , but this will be studied elsewhere [25]. Another way to further improve the quality of these bounds is, of course, by including a higher number of moments, but this is much more cumbersome.

Finally, let us concentrate our attention on the total interelectronic repulsion energy  $E_{ee} = \langle u^{-1} \rangle$ . For the He atom, the inequality (23) gives the upper bound

$$E_{ee} \leq 2.41799 h_{\max}^{\frac{1}{3}} \quad (35)$$

and the particular cases  $n=0$  and  $n=1$  of the inequality (13) together with the value of  $\alpha_2$  given by (31) provide the following lower and upper bounds:

$$1.1741 \langle u \rangle^{-1} \leq E_{ee} \leq 0.8470 \langle u^{-2} \rangle^{\frac{1}{3}}. \quad (36)$$

Although the mathematical and physical origin of these two inequalities (35) and (36) is very different, both of them are very accurate. Indeed, from the information given in Tables 1 and 2 one can see that the accuracy of

the inequality (35) is 80% and that of the inequality (36) is about 90%.

## V. Concluding remarks

First of all we have proved that, although the electron-pair density  $h(u)$  is non-monotone, there always exists a value of  $\alpha$  such that the electron-pair function  $h(u)/u^\alpha$  is not only monotonically decreasing from the origin but also convex for any atom in both ground and excited states. Then, this result together with the Stieltjes moment-problem technique have been used to obtain universal relationships which involve three interelectronic radial expectation values  $\langle u^n \rangle$  of successive integer orders.

In addition, for those atoms having a unimodal  $h(u)$ , upper bounds to the location  $u_{\max}$  of the single maximum in terms of an arbitrary number of values  $\langle u^n \rangle$  and lower bounds to the maximal intensity  $h(u_{\max})$  by means of two arbitrary values  $\langle u^n \rangle$  are obtained in a rigorous way.

Finally, the electron-pair density  $h(u)$  of the He atom is investigated and the quality of all the above mentioned bounds is studied by means of the  $M$ -term Hylleraas-type wavefunctions. It is found that the interelectronic function  $h(u)/u^{0.04}$  is monotonically decreasing from the origin and  $h(u)/u^{0.21}$  is convex everywhere. The accuracy of the resulting bounds is, often, bigger than 80% in the 20-term case, which is shown to be very close to the exact one.

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