Maximum-entropy analysis of the electron-pair density in many-electron systems

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The maximum-entropy formalism is used to obtain approximations to the spherically averaged electron-pair density $h(u)$ in terms of the first few interelectronic moments. This method leads to the least biased results by the information not used. In particular, tight analytical and numerical approximations to the electron-electron repulsion energy E_{ee} and to the central electron-pair density $h(0)$ are obtained. Chebyshev inequalities are also applied to obtain bounds on $h(u)$, showing the complementarity of both methods. For illustration, the accuracy of the bounds and approximations obtained are studied by means of Hylleraas-type wave functions.

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I. INTRODUCTION

The intracule or electron-pair density $I(\mathbf{u})$, i.e., the probability density associated with the interelectronic vector $\mathbf{u} \equiv \mathbf{r}_1 - \mathbf{r}_2$, is a fundamental ingredient in the study of the electron-electron correlation problem [1,2]. Moreover, it is a quantity of great utility for constructing energy functionals within a density-functional theory framework [2] and it is related to several experimentally measurable quantities, such as x-ray scattering cross sections [3].

For central field atoms, it is sufficient [1] to deal with the spherically averaged electron-pair density, namely,

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

Some interesting physical and chemical properties of atomic and molecular N-electron systems can be described by means of the radial expectation values of $h(u)$:

$$\langle u^\alpha \rangle = \int u^\alpha I(\mathbf{u}) d\mathbf{u} = 4\pi \int_0^\infty u^{\alpha+2} h(u) du \equiv 4\pi \mu_{\alpha+2}$$

$$(\alpha > -3) \tag{2}$$

where the normalization is $\langle u^0 \rangle = \frac{N(N-1)}{2}$ (the number of electron pairs). It is worthwhile to point out here that the radial expectation value $\langle u^{-1} \rangle$ is equal to the electron-electron repulsion energy E_{ee}.

The major problem in studying physical properties of many-electron systems in terms of the electron-pair density $h(u)$ is that, even for very simple systems such as two-electron ions, it is really difficult not only to obtain rigorous structural properties of $h(u)$ but also to perform a numerical treatment based on realistic models.

The main rigorous property known about $h(u)$, apart from the quantum-mechanical non-negativity, is probably the so-called *electron-electron cusp condition* [4], i.e., the equality between the electron-pair density and its first derivative at the origin, $h'(0) = h(0)$, which has been derived from the Schrödinger equation in the infinite nuclear mass approximation.

Other rigorous known results [5] are the variational lower bounds to the maximum value $h_{\max}$ of the electron-pair density $h(u)$. These bounds are expressed in terms of two or three low-order radial expectation values $\langle u^\alpha \rangle$.

Recently [6], the so-called *extended cusp condition* has been observed for two-electron light ions, by means of Hylleraas-type wave functions [7]. This property is expressed in the form

$$h'(u) \leq h(u) \ , \tag{3}$$

which becomes an equality (the usual cusp condition) for $u = 0$. The above mentioned expression has been essential in obtaining bounds to the central electron-pair density $h(0)$ [8] (which is a measure of the probability of the electron-electron coalescence) as well as to the electron-electron repulsion energy E_{ee} [6], in terms of the first few radial expectation values $\langle u^\alpha \rangle$.

Within the Hylleraas framework, it has also been shown that the electron-pair density is unimodal [6,9] (i.e., it has a single maximum, located not necessarily

at $u = 0$) for some two-electron atomic systems. This fact has allowed [6,9] the determination of a bound from above for location $u_{\max}$ of the absolute maximum of $h(u)$, in terms of radial ($\langle u^{\alpha} \rangle$) and logarithmic ($\langle \ln u \rangle$) expectation values.

In summary, only a few rigorous or approximate properties of $h(u)$ are known up to now. In this work we obtain tight approximations to the electron-pair density by using very limited information: the first few moments of the pair density. In doing so we apply the maximum-entropy (ME) method, based on information theory [10], which chooses, among all admissible densities, the least biased function compatible with the information we actually have. The choice is made by maximizing the information entropy functional, defined by

$$S_h \equiv -\int_0^{\infty} h(u) \ln h(u) du \tag{4}$$

for the whole set of densities which satisfy the constraints imposed by the knowledge of some of their moments.

The calculated moments of these ME densities can be used as approximations to the unknown moments of the density. In particular, the method provides very simple approximations to $h(0)$ and E_{ee} in terms of the moments used as constraints. This ME analysis is complemented with the construction of lower and upper bounds on $h(u)$ by using moment theory and Chebyshev inequalities [11].

In Sec. II we briefly review the way of obtaining the solution of an underdetermined moment problem by means of the ME technique. In Sec. III this technique is applied to the electron-pair density and the main results are obtained.

II. THE ELECTRON-PAIR DENSITY AND THE MAXIMUM-ENTROPY APPROACH

The ME approach to the solution of underdetermined inverse problems was introduced some time ago in the literature [12,13]. Since then, diverse techniques based on this general formalism or on related concepts of information theory have been successfully applied in a great variety of fields including radioastronomy [14], parameter spectral estimation [15], particle physics [16,17], signal theory [18], atomic physics [19], or density-functional theory [20]. See Ref. [21] for more recent applications.

We are interested in obtaining information on the electron-pair density $h(u)$ in terms of its first $M+1$ moments μ_i, closely related to the radial expectation values $\langle u^{i-2} \rangle$ by Eq. (2) as $\mu_i = \langle u^{i-2} \rangle / 4\pi$. Therefore we are faced with an undetermined inverse moment problem. Clearly there exists an infinite variety of functions whose first $M+1$ moments coincide, and a unique reconstruction of $h(u)$ from this limited information is not possible.

Jaynes studied (in his entropy concentration theorem [13]) in what sense the distribution of ME has a favored status and showed how strongly distributions of lower entropy are ruled out. Given incomplete information, the ME distribution is the one that can be realized in the greatest number of ways and the majority of all possible distributions compatible with our information have entropy very close to the maximum. So entropy maximization protects us against spurious details for which there is no evidence in the data.

The ME technique follows the ME principle [13], i.e., it chooses, among those compatible densities, the most *plausible* in the sense that it is the least biased density for the unmeasured moments. This choice can be performed if $h(u)$ is interpreted as a probability density and the corresponding information entropy [see Eq. (4)] is maximized under the conditions that the first $M+1$ moments be known.

Therefore, we have to solve the following Lagrange multiplier problem:

$$\delta \left[-\int_0^{\infty} h(u) \ln h(u) du + \sum_{i=0}^{M} \lambda_i \left(\mu_i - \int_0^{\infty} h(u) u^i du \right) \right] = 0 \tag{5}$$

with the convention that $\lambda_i = 0$ if the moment μ_i is not considered. This functional variation with respect to the unknown $h(u)$ gives the following expression for the ME solution:

$$h^{\mathrm{ME}}_{1,2,\ldots,M}(u) = \exp \left[-\sum_{i=0}^{M} \left(\lambda_i u^i + \delta_{i,0} \right) \right] , \tag{6}$$

where the subscripts $1, 2, \ldots, M$ give the list of moments included in the constraints for Eq. (5) and the Lagrange parameters $\lambda_0, \ldots, \lambda_M$ must be calculated from the constraints

$$\int_0^{\infty} h^{\mathrm{ME}}_{1,2,\ldots,M}(u) u^i du = \mu_i \quad (i = 0, 1, \ldots, M) \tag{7}$$

so that the considered moments of $h(u)$ and $h^{\mathrm{ME}}_{1,2,\ldots,M}(u)$ are the same.

The ME solution of generalized moment problems, such as this one, leads in general to difficulties which depend on the type of moments we are going to deal with [22], the interval of integration [23], and the eventual inclusion of statistical errors in the moments [24].

The ME solution must be numerically calculated for $M > 1$, solving the extremely nonlinear system of equations (7). This solution always exists in the case of a finite integration range owing to the monotonicity properties of the moment sequence which in turn leads to the convexity of the potential function [25]:

$$U(\lambda_1, \lambda_2, \ldots, \lambda_M) = \sum_{i=1}^{M} \lambda_i \mu_i + \ln V , \tag{8}$$

where we use normalized densities, such that $\mu_0 = 1$ and the partition function is

$$V(\lambda_1, \ldots, \lambda_M) \equiv e^{-(\lambda_0 + 1)} = \int_0^{\infty} \exp \left(-\sum_{i=1}^{M} \lambda_i u^i \right) du , \tag{9}$$

TABLE I. Value of the electron-pair density at the origin $h(0)$ and the radial expectation values $\langle u^n \rangle$ with $n = -2, -1, 0, 1$, and 2, for the two-electron ions with nuclear charge $Z = 1, 2, 3, 5$, and 10. The calculations were performed by means of Hylleraas-type wave functions [7]. Hartree atomic units are used throughout.

Z	$h(0)$	$\langle u^{-2} \rangle$	$E_{ee} = \langle u^{-1} \rangle$	$\langle u^0 \rangle$	$\langle u \rangle$	$\langle u^2 \rangle$
1	0.0028	0.1553	0.3111	1	4.4065	25.0595
2	0.1068	1.4651	0.9458	1	1.4221	2.5165
3	0.5352	4.0829	1.5677	1	0.8623	0.9271
5	3.3162	13.3080	2.8147	1	0.4824	0.2908
10	32.6619	59.6975	5.9372	1	0.2295	0.0659

which unique minimum is the ME solution

$$\mu_i = \mu_i^{(1,2,\ldots,M)} , \tag{10}$$

where

$$\mu_i^{(1,2,\ldots,M)} \equiv \int_0^\infty u^i h_{1,2,\ldots,M}^{\mathrm{ME}}(u) du . \tag{11}$$

The above important result is not valid in our semi-infinite integration range, and the ME solution does not always exist. The non-negativity of $h(u)$ does not guarantee the existence of a ME solution, and extra conditions must be fulfilled. In fact, for several particular number of moments considered, some analytical and numerical conditions are known.

Apart from the elementary case $M = 1$, the following relation has been proved for the case $M = 2$ [26]:

$$\mu_1^2 \leq \mu_0 \mu_2 \leq 2\mu_1^2 , \tag{12}$$

where the first inequality is a consequence of positivity and the second one is an extra condition for the existence of the $h_{1,2}$ density.

There are no proven conditions when the order of moments is changed (i.e., for $h_{1,3}$, $h_{2,3}$, etc.) except for densities such as $h_{2,4}$, for which the moment conditions can be related to those of the density

$$h'_{1,2}(u) \equiv h_{1,2}([3u^2/2]^{1/3}) \tag{13}$$

having normalized moments $\mu'_1 = \mu_2$ and $\mu'_2 = \mu_4$ so that the conditions become

$$\mu_2^2 \leq \mu_0 \mu_4 \leq 2\mu_2^2 . \tag{14}$$

There are no analytical conditions for the first three normalized moments in order to have a ME density. Then, some numerical computations are needed. Kociszewski [27] found the allowed region in the space of moments and in a recent paper this result was also obtained and generalized by Tagliani [28]. This latter work shows that for $M \geq 4$ there exists a distribution of ME which is different from those for the cases $M = 2$ and $M = 3$. The mutual relations between the moments are just those imposed by non-negativity.

We have checked that the radial expectation values for the heliumlike systems with nuclear charge $Z = 1, 2, 3, 5, 10$ fulfill the conditions for $M = 2$ but not the numerical constraints for the case $M = 3$. Therefore the ME density $h_{1,2,3}$ does not exist as well as $h_{2,4}$ since the moments do not verify Eq. (14). As we do not have conditions for the existence of ME densities with no consecutive constraints we have tried to find these solutions seeking a maximum of the entropy functional.

In the following section this technique is applied to the electron-pair density $h(u)$, obtaining model-independent estimations of this function as well as of important quantities such as the central value $h(0)$ and the electron-electron repulsion energy E_{ee}. To have an idea of the accuracy of the bounds and approximations to the electron-pair density $h(u)$ and other related quantities, a numerical study by means of Hylleraas-type wave functions [7] is carried out for some two-electron ions.

III. MAXIMUM-ENTROPY DENSITIES

A. One normalized constraint

ME densities constructed by using only one constraint (besides the normalization imposed by the knowledge of

TABLE II. Value of the one-moment ME approximation $h_1^{\mathrm{ME}}(0)$ to the electron-pair density at the origin $h(0)$ and relative errors of the one-moment ME approximations $h_1^{\mathrm{ME}}(0)$, $\langle u^0 \rangle^{(1)}$, $\langle u \rangle^{(1)}$, and $\langle u^2 \rangle^{(1)}$ for the two-electron ions with nuclear charge $Z = 1, 2, 3, 5$, and 10. The calculations were performed by means of Hylleraas-type wave functions [7]. Hartree atomic units are used throughout.

Z	$h_1^{\mathrm{ME}}(0)$	$100\frac{\lvert h(0) - h_1^{\mathrm{ME}}(0) \rvert}{h(0)}$	$100\frac{\lvert \langle u \rangle - \langle u \rangle^{(1)} \rvert}{\langle u \rangle}$	$100\frac{\lvert \langle u^2 \rangle - \langle u^2 \rangle^{(1)} \rvert}{\langle u^2 \rangle}$
1	0.0065	131.45	69.84	141.02
2	0.1806	69.10	66.90	142.80
3	0.8462	58.10	60.79	125.43
5	5.0070	51.20	56.56	138.31
10	47.7658	46.23	53.52	112.44

TABLE III. Value of the one-moment ME approximation $h_2^{\mathrm{ME}}(0)$ and $\langle u^{-1}\rangle^{(2)}$ to the electron-pair density at the origin $h(0)$ and to the electron-electron repulsion energy $E_{ee} = \langle u^{-1}\rangle$, respectively, and relative errors of the one-moment ME approximations $h_2^{\mathrm{ME}}(0)$, $\langle u^{-1}\rangle^{(2)}$, $\langle u\rangle^{(2)}$, and $\langle u^2\rangle^{(2)}$ for the two-electron ions with nuclear charge $Z = 1, 2, 3, 5$, and 10. The calculations were performed by means of Hylleraas-type wave functions [7]. Hartree atomic units are used throughout.

Z	$h_2^{\mathrm{ME}}(0)$	$100\frac{\lvert h(0)-h_2^{\mathrm{ME}}(0)\rvert}{h(0)}$	$E_{ee}^{(2)} = \langle u^{-1}\rangle^{(2)}$	$100\frac{\lvert\langle u^{-1}\rangle-\langle u^{-1}\rangle^{(2)}\rvert}{\langle u^{-1}\rangle}$	$100\frac{\lvert\langle u\rangle-\langle u\rangle^{(2)}\rvert}{\langle u\rangle}$	$100\frac{\lvert\langle u^2\rangle-\langle u^2\rangle^{(2)}\rvert}{\langle u^2\rangle}$
1	0.0041	46.42	0.3144	1.06	9.32	30.17
2	0.1126	5.43	0.9658	2.11	7.32	18.76
3	0.5238	2.13	1.6122	2.83	8.38	20.72
5	3.0822	7.06	2.9107	3.41	9.41	22.63
10	29.2863	10.02	6.1648	3.83	10.02	23.77

TABLE IV. Value of the one-moment ME approximation $h_3^{\mathrm{ME}}(0)$ and $\langle u^{-1}\rangle^{(3)}$ to the electron-pair density at the origin $h(0)$ and to the electron-electron repulsion energy $E_{ee} = \langle u^{-1}\rangle$, respectively, and relative errors of the one-moment ME approximations $h_3^{\mathrm{ME}}(0)$, $\langle u^{-1}\rangle^{(3)}$, $\langle u\rangle^{(3)}$, and $\langle u^2\rangle^{(3)}$ for the two-electron ions with nuclear charge $Z = 1, 2, 3, 5$, and 10. The calculations were performed by means of Hylleraas-type wave functions [7]. Hartree atomic units are used throughout.

Z	$h_3^{\mathrm{ME}}(0)$	$100\frac{\lvert h(0)-h_3^{\mathrm{ME}}(0)\rvert}{h(0)}$	$E_{ee}^{(3)} = \langle u^{-1}\rangle^{(3)}$	$100\frac{\lvert\langle u^{-1}\rangle-\langle u^{-1}\rangle^{(3)}\rvert}{\langle u^{-1}\rangle}$	$100\frac{\lvert\langle u\rangle-\langle u\rangle^{(3)}\rvert}{\langle u\rangle}$	$100\frac{\lvert\langle u^2\rangle-\langle u^2\rangle^{(3)}\rvert}{\langle u^2\rangle}$
1	0.0031	11.48	0.3447	10.78	12.15	22.07
2	0.0914	14.48	1.0557	11.61	11.04	18.71
3	0.4231	20.97	1.7679	12.77	12.27	19.60
5	2.4834	25.11	3.2056	13.88	13.14	20.22
10	23.5257	27.97	6.8034	14.71	13.65	20.80

TABLE V. Value of the two-moment ME approximation $h_{1,2}^{\mathrm{ME}}(0)$ to the electron-pair density at the origin $h(0)$, optimal values of the parameters λ_1 and λ_2 (see text for further details), and relative errors of the two-moment ME approximations $h_{1,2}^{\mathrm{ME}}(0)$, $\langle u\rangle^{(1,2)}$, and $\langle u^2\rangle^{(1,2)}$ for the two-electron ions with nuclear charge $Z = 1, 2, 3, 5$, and 10. The calculations were performed by means of Hylleraas-type wave functions [7]. Hartree atomic units are used throughout.

Z	$h_{1,2}^{\mathrm{ME}}(0)$	λ_1	λ_2	$100\frac{\lvert h(0)-h_{1,2}^{\mathrm{ME}}(0)\rvert}{h(0)}$	$100\frac{\lvert\langle u\rangle-\langle u\rangle^{(1,2)}\rvert}{\langle u\rangle}$	$100\frac{\lvert\langle u^2\rangle-\langle u^2\rangle^{(1,2)}\rvert}{\langle u^2\rangle}$
1	0.0047	0.1604	0.0549	66.67	4.5	15.5
2	0.1291	0.4139	0.5368	20.79	3.2	10.3
3	0.6262	0.9033	1.3334	16.98	2.9	9.2
5	3.8018	1.9157	3.9580	14.64	2.7	8.7
10	36.9358	4.8748	15.2988	13.07	2.6	8.3

TABLE VI. Value of the two-moment ME approximation $h_{1,3}^{\mathrm{ME}}(0)$ to the electron-pair density at the origin $h(0)$, optimal values of the parameters λ_1 and λ_3 (see text for further details), and relative errors of the two-moment ME approximations $h_{1,3}^{\mathrm{ME}}(0)$, $\langle u\rangle^{(1,3)}$, and $\langle u^2\rangle^{(1,3)}$ for the two-electron ions with nuclear charge $Z = 1, 2, 3, 5$, and 10. The calculations were performed by means of Hylleraas-type wave functions [7]. Hartree atomic units are used throughout.

Z	$h_{1,3}^{\mathrm{ME}}(0)$	λ_1	λ_3	$100\frac{\lvert h(0)-h_{1,3}^{\mathrm{ME}}(0)\rvert}{h(0)}$	$100\frac{\lvert\langle u\rangle-\langle u\rangle^{(1,3)}\rvert}{\langle u\rangle}$	$100\frac{\lvert\langle u^2\rangle-\langle u^2\rangle^{(1,3)}\rvert}{\langle u^2\rangle}$
1	0.0048	0.2980	0.0047	70.21	3.12	11.58
2	0.1442	0.9680	0.1288	34.95	1.90	6.91
3	0.6918	1.7335	0.5266	29.25	1.76	6.50
5	4.1664	3.2958	2.7853	25.64	1.67	6.23
10	40.2568	7.2309	24.3416	23.23	1.62	5.97

TABLE VII. Value of the two-moment ME approximation $h_{1,4}^{\mathrm{ME}}(0)$ to the electron-pair density at the origin $h(0)$, optimal values of the parameters λ_1 and λ_4 (see text for further details), and relative errors of the two-moment ME approximations $h_{1,4}^{\mathrm{ME}}(0)$, $\langle u\rangle^{(1,4)}$, and $\langle u^2\rangle^{(1,4)}$ for the two-electron ions with nuclear charge $Z = 1, 2, 3, 5$, and 10. The calculations were performed by means of Hylleraas-type wave functions [7]. Hartree atomic units are used throughout.

Z	$h_{1,4}^{\mathrm{ME}}(0)$	λ_1	λ_4	$100\frac{\lvert h(0)-h_{1,4}^{\mathrm{ME}}(0)\rvert}{h(0)}$	$100\frac{\lvert\langle u\rangle-\langle u\rangle^{(1,4)}\rvert}{\langle u\rangle}$	$100\frac{\lvert\langle u^2\rangle-\langle u^2\rangle^{(1,4)}\rvert}{\langle u^2\rangle}$
1	0.0053	0.3800	0.0004	87.94	6.84	8.23
2	0.1538	1.1766	0.0350	43.65	4.10	4.96
3	0.7328	2.0471	0.2356	36.91	3.90	4.71
5	4.3927	3.8122	2.2162	32.46	3.73	4.48
10	42.3114	8.2574	40.4389	29.54	3.62	4.35

$\langle u^{-2}\rangle = 4\pi\mu_0$) can be easily obtained in an analytical way. The most interesting cases are the following.

1. $\mu_1 = \langle u^{-1}\rangle/4\pi$ constraint

$$h_1^{\mathrm{ME}}(u) = \frac{\langle u^{-2}\rangle^2}{4\pi\langle u^{-1}\rangle}\exp\left(-\frac{\langle u^{-2}\rangle}{\langle u^{-1}\rangle}u\right), \tag{15}$$

which predicts the expectation values

$$\langle u^k\rangle \sim \langle u^k\rangle^{(1)} = \Gamma(k+3)\frac{\langle u^{-1}\rangle^{k+2}}{\langle u^{-2}\rangle^{k+1}} \quad (k > -3) \tag{16}$$

and the approximation for the central value of the electron-pair density

$$h(0) \sim h_1^{\mathrm{ME}}(0) = \frac{\langle u^{-2}\rangle^2}{4\pi\langle u^{-1}\rangle}. \tag{17}$$

In Table I the Hylleraas values of the electron pair density at the origin, $h(0)$, and the radial expectation values $\langle u^n\rangle$ ($n = -2, -1, 0, 1, 2$) are included for some two electron ions. Table II shows a numerical comparison of the above model-independent results with those obtained by using Hylleraas wave functions. As can be seen, this very simple approximation does not lead to very tight results and the information content of $\langle u^{-1}\rangle$ alone is not large.

2. $\mu_2 = \langle u^0\rangle/4\pi = N(N-1)/8\pi$ constraint

In this case the ME solution is

$$h_2^{\mathrm{ME}}(u) = \left(\frac{2}{N(N-1)}\right)^{1/2}\left(\frac{\langle u^{-2}\rangle}{2\pi}\right)^{3/2} \times \exp\left(-\frac{\langle u^{-2}\rangle}{N(N-1)}u^2\right) \tag{18}$$

and we call its corresponding expectation values $\langle u^k\rangle^{(2)}$. This ME density produces the following analytical approximations to $h(0)$:

$$h(0) \sim h_2^{\mathrm{ME}}(0) = \left(\frac{2}{N(N-1)}\right)^{1/2}\left(\frac{\langle u^{-2}\rangle}{2\pi}\right)^{3/2} \tag{19}$$

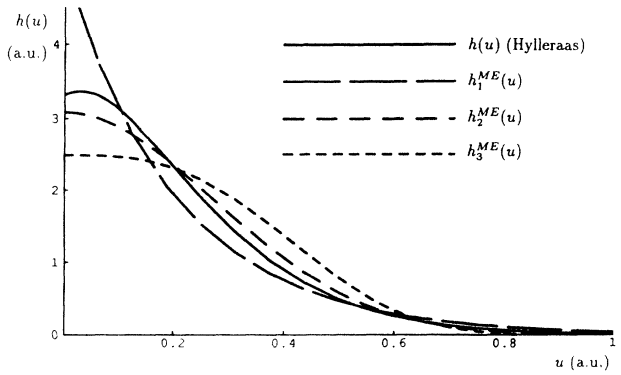

FIG. 1. ME approximations to the B^{3+} electron-pair density in terms of one normalized constraint (see text for further details). Hartree atomic units (a.u.) are used.

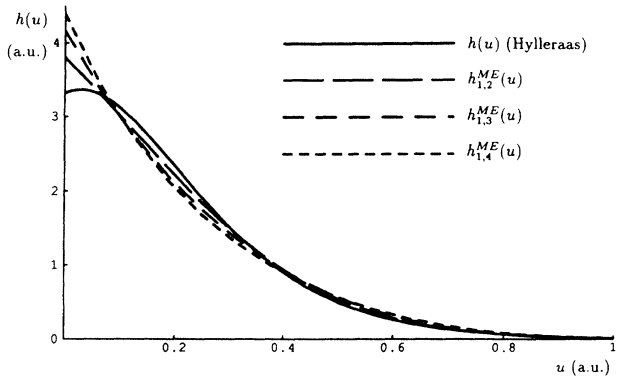

FIG. 2. ME approximations to the B^{3+} electron-pair density in terms of two normalized constraints (see text for further details). Hartree atomic units (a.u.) are used.

as well as to the electron-electron repulsion energy E_{ee}

$$E_{ee} = \langle u^{-1}\rangle \sim \langle u^{-1}\rangle^{(2)} = \left(\frac{N(N-1)\langle u^{-2}\rangle}{\pi}\right)^{1/2} \tag{20}$$

Table III shows how the above predictions have an average relative error with respect to the Hylleraas parameters of 6% (except $Z = 1$) and 3%, respectively. The predictions for the following moments are also good: relative errors of 9% and 23%, respectively:

$$\langle u\rangle \sim \langle u\rangle^{(2)} = \left(\frac{[N(N-1)]^3}{\pi\langle u^{-2}\rangle}\right)^{1/2}, \tag{21}$$

$$\langle u^2\rangle \sim \langle u^2\rangle^{(2)} = \frac{12}{N^2(N-1)^2\langle u^{-2}\rangle}. \tag{22}$$

The quality of the preceding results can also be compared to the rigorous bounds on $h(0)$ obtained in [8] by using much more numerical information on the mono-

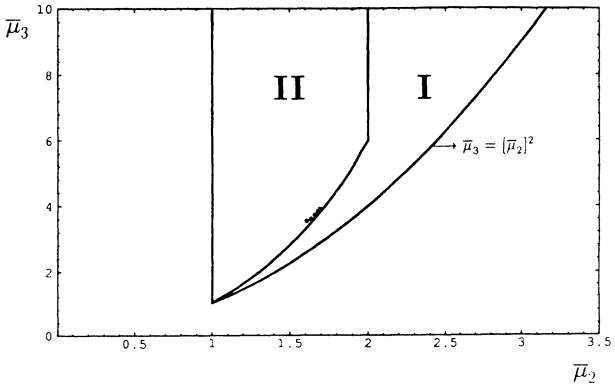

FIG. 3. Existence conditions for ME distributions having prescribed the first three moments in terms of relative moments $\overline{\mu}_2 = \mu_2/\mu_1^2$ and $\overline{\mu}_3 = \mu_3/\mu_1^3$. Regions I and II represent the positivity inequalities for these relative moments. Moreover, region I is allowed and region II is forbidden for the existence of a ME distribution in accordance with the Kociszewski [27] conditions. Hartree atomic units (a.u.) are used.

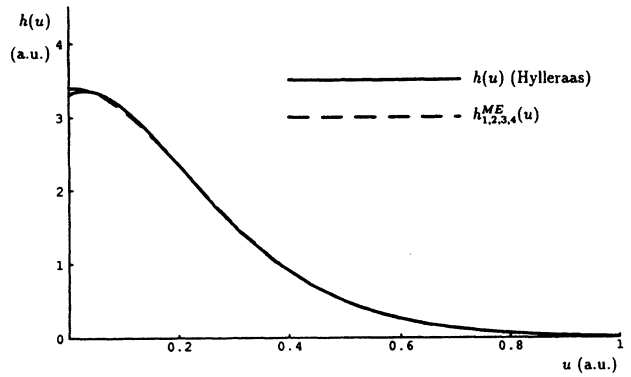

FIG. 4. ME approximations to the B^{3+} electron-pair density in terms of four normalized constraints (see text for further details). Hartree atomic units (a.u.) are used.

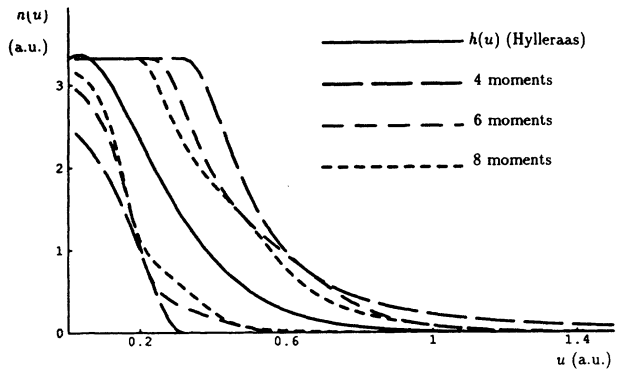

FIG. 5. Test of the Chebyshev bounds accuracy for the B^{3+} electron pair density by using four, six, and eight moments obtained by means of Hylleraas-type wave functions. Hartree atomic units (a.u.) are used.

tonicity properties of $h(u)$. It is worthwhile to remark on the simplicity of the preceding results as well as their general validity [based only on the non-negativity of $h(u)$].

3. $\mu_3 = \langle u \rangle / 4\pi$ constraint

The form of the ME density in this case is

$$h_3^{\mathrm{ME}}(u) = A \exp(-Bu^3) \ , \tag{23}$$

where

$$A = \frac{3\langle u \rangle}{4\pi\Gamma(4/3)} \left(\frac{\langle u^{-2} \rangle}{3\langle u \rangle} \right)^{4/3} \ , \quad B = \frac{\langle u^{-2} \rangle}{3\langle u \rangle} \ . \tag{24}$$

Table IV collects the numerical approximations obtained for $h(0)$ and for some expectation values of the electron-pair density. These results show that the information content of this constraint is lower than that of μ_2. We have also checked that the information content of the μ_4 constraint is clearly lower than that of the previous cases.

Figure 1 shows these three ME densities and the pair density constructed using Hylleraas wave functions. It is observed that $h_2(u)$ is a better approximation to $h(u)$ compared to $h_1(u)$ and $h_3(u)$.

B. Two moment constraints

In this subsection we construct the numerical ME approximations by using two constraints besides the normalization. The ME approximations have the following expression:

$$h_{i,j}^{\mathrm{ME}}(u) = A_{ij} \exp(-\lambda_i u^i - \lambda_j u^j) \ , \tag{25}$$

where the information used is $\langle u^{-2} \rangle$, $\langle u^{i-2} \rangle$, and $\langle u^{j-2} \rangle$.

In Table V the results for $h_{1,2}^{\mathrm{ME}}(u)$ are quoted and average relative errors of 16% (except for $Z = 1$), 3%, and 10% are obtained for $h(0)$, $\langle u \rangle$, and $\langle u^2 \rangle$, respectively.

Table VI shows the results obtained by $h_{1,3}^{\mathrm{ME}}(u)$, which are of an average error of 37%, 4.4%, and 5.3% for $h(0)$, $\langle u^0 \rangle$, and $\langle u^2 \rangle$, respectively.

Similarly, Table VII shows the results for $h_{1,4}^{\mathrm{ME}}(u)$, which leads to less accurate approximations of 46%, 4.4%, and 5.3% for $h(0)$, $\langle u^0 \rangle$, and $\langle u \rangle$, respectively. One can see how the approximation $h_{1,2}^{\mathrm{ME}}(u)$ has a larger information content than that of its companions.

The ME density $h_{2,4}^{\mathrm{ME}}$ does not exist for $Z = 1, 2, 3, 5, 10$ as we have remarked in Sec. II.

For illustration, in Fig. 2 we show the ME approximations for $Z = 5$ obtained in this subsection, i.e., $h_{1,2}^{\mathrm{ME}}$, $h_{1,3}^{\mathrm{ME}}$, and $h_{1,4}^{\mathrm{ME}}$. Clearly, our ME solutions do not verify the cusp condition because the information we use is very limited.

C. More than two constraints: ME densities and Chebyshev bounds

The values $\langle u^{-2} \rangle$, $\langle u^{-1} \rangle$, $\langle u^0 \rangle$, and $\langle u \rangle$ do not verify the Kociscewski [27] or Tagliani [28] constraints as shown in Fig. 3, where the points close to the edge of region II correspond to the relative moments obtained from the aforementioned expectation values of the electron-pair density for the five ions we are considering here ($Z = 1, 2, 3, 5, 10$). So, the $h_{1,2,3}^{\mathrm{ME}}(u)$ density does not exist for them.

For the sake of completeness, we have constructed the $h_{1,2,3,4}^{\mathrm{ME}}(u)$ density in order to have a more accurate approximation of $h(u)$ but at the price of using more information. This ME approximation has been plotted together with the Hylleraas electron-pair density in Fig. 4, where its accuracy is apparent. It is also observed that the value of $h(0)$ given by this approximation does improve the results of $h_2^{\mathrm{ME}}(u)$ or $h_{1,2}^{\mathrm{ME}}(u)$, which were the most predictive ME densities for this parameter by using less information.

On the other hand, it is interesting to point out that the knowledge of some moments of the electron-pair density allows one to obtain complementary information to that given by the ME method. In this sense, the well-known Chebyshev inequalities [11] provide upper and lower bounds on $h(u)$ on the assumption of decreas-

ing monotonicity of this function. Figure 5 shows these bounds when four, six, and eight moments are used. It is observed that the upper bound goes below $h(u)$ around the nucleus. The reason is that the electron-pair density is not a monotonically decreasing function everywhere.

Finally, let us remark that the results obtained in this section show the powerfulness of the ME method when inferences from very limited information has to be made.

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