

# Precise variational calculation of some S-states of Coulomb three-body systems with two identical particles

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Received: 3 October 1997 / Revised: 16 February 1998 / Accepted: 13 March 1998

**Abstract.** A generalized Hylleraas basis set with two nonlinear parameters is used to study three-body systems with two equal masses interacting *via* coulomb forces within the framework of non-relativistic quantum mechanics. Accurate variational bounds for the ground state of some of these systems are obtained improving the rate of convergence of the calculation with respect to an usual Hylleraas basis set. A study of the interparticle densities is also carried out.

**PACS.** 36.10.Dr Positronium, muonium, muonic atoms and molecules – 31.10.+z Theory of electronic structure, electronic transitions, and chemical binding

## 1 Introduction

The quantum mechanics problem of three bodies with two equal masses interacting *via* Coulomb forces is currently the focus of much research [1–12]. As is widely commented in reference [10], these systems have been traditionally divided into two *classes* or physical models, the atomic one in which one mass is much heavier than the other two so an infinite nuclear mass approximation is used, and the molecular one in which one mass is much lighter than the other two and the Born-Oppenheimer approximation is applied. As is discussed in *e.g.* references [10,11] this division is rather arbitrary and it is necessary to use a unified approach.

If  $\lambda$  is the ratio between the mass of the two equal masses and the mass of the other particle, this parameter  $\lambda$  goes from  $10^{-3}$  (the atoms He and H<sup>-</sup>), to  $10^3$  (the molecules H<sub>2</sub><sup>+</sup> and  $\mu^+\mu^+e^-$  (the muonic molecular ion)). There also are *hybrid systems* with respect to these two extreme physical pictures such as  $e^-e^-e^+$  (Ps<sup>-</sup>),  $\pi^+\pi^+\mu^-$ ,  $\mu^+\mu^+\pi^-$ ,  $p^+p^+\mu^-$ ,  $d^+d^+\mu^-$  or  $t^+t^+\mu^-$ , where  $\pi$  stands for pion,  $d$  for deuterium and  $t$  for tritium.

Several techniques have been applied in the literature to treat some of these systems. Non variational techniques, such as the hyperspherical-harmonic method, have been widely applied to many systems as for example the ground state of the positronium negative ion, Ps<sup>-</sup> [7]; in reference [10] one can find a complete review of the application of this method to Coulomb three body systems. In the field of variational methods we also have two kinds

of techniques; the first one is based on the finite-element method [11] which for some systems provides the most accurate eigenvalues known in the literature and the second one is the more traditional method of expanding the solution in terms of an auxiliary basis set that was initially developed to study bound states of atomic helium in the infinite nuclear mass approach and then applied to the problem of three body Coulomb systems including the polarization mass term in the hamiltonian. Several global basis functions have been used to treat three-body Coulomb systems. One of these basis is the one built from explicitly correlated Slater-type geminals which has been applied to several bound states of helium-like ions [13], and to some other different three-body Coulomb systems [3,4,6,9]. Other basis functions are based on the Hylleraas type basis set and have been developed and applied to study, mainly, the first states of the helium-like ions [14–24] although they have been also applied to the study of the doubly excited states of Helium [25–27] and some other systems [1,2,5,8,12]. The main aim of all these works is the determination of very accurate eigenvalues, giving also some of them the expectation values of some operators which are powers of interparticle distances or Dirac delta functions.

On the other hand, although it is known the central role of the interparticle distribution function to understand the dynamic of fermionic systems [28], this quantity is only well known for some bound states of the atomic helium and its isoelectronic series [29–32] and for the first S-states of Lithium and its isoelectronic series [33]

The purpose of this work is double. First we use a generalization of the Hylleraas expansion which is specially adequate to describe those systems of molecular nature, improving the rate of convergence with respect to

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previous calculations. In particular we shall work in the scheme introduced by Pekeris [14], in which the wave function is built in isoperimetric coordinates in terms of linear combinations of Laguerre polynomials multiplied by an exponential. Once obtained the best wave function for the different systems here studied we shall perform a systematic study of the interparticle distributions, mainly to the corresponding to the one of the two identical particles. This function reveals some interesting features about the atomic or molecular dynamic behavior of these systems, which is related to the parameter  $\lambda$ , *i.e.* the ratio between the masses of their components. This ratio is the parameter that determines the rate of convergence of any calculation.

The scheme of the work is the following. In the next section we shall introduce the basis set used in this work. In Section 3 a systematic analysis of the convergence is performed. In Section 4 we shall present the best results provided by this basis set as compared with the most accurate values known in the literature for the systems above mentioned. In particular we have made a systematic study of the interparticle densities of these systems and its properties. Finally some conclusions can be found in Section 5.

## 2 Basis set

For  $S$  states of three particles Coulomb systems the Hamiltonian can be written, once subtracted the center of mass motion, in terms of the so called isoperimetric coordinates defined as  $u = -r_1 + r_2 + r_{12}$ ,  $v = r_1 - r_2 + r_{12}$  and  $w = r_1 + r_2 - r_{12}$ , introduced by Coolidge and James [34], being the range of each one of them from zero to infinity. Here  $r_{12}$  is the distance between the two identical particles and  $r_i$ ,  $i = 1, 2$  is the distance between the different particle and each one of the other two. In units  $\hbar = e = 1$  the hamiltonian is

*See equation (1) below*

where  $m$  is the mass of any of the two equal particles and  $M$  is the mass of the different one. The range of the isoperimetric coordinates suggests us to build bases in terms of

$$\phi_{klm}(u, v, w) = L_k(\alpha u)L_l(\gamma v)L_m(\beta w) e^{-(\alpha u + \gamma v + \beta w)/2} \quad (2)$$

where  $L_k(x)$  is the Laguerre polynomial of degree  $k$  and  $\alpha$ ,  $\gamma$  and  $\beta$  are non-linear variational parameters. Since the singlet (triplet) states must be symmetric (antisymmetric) under the exchange of the two identical particles, it is convenient that the elements of the basis have the form

$$\phi_{klm}(u, v, w) \pm \phi_{lkm}(v, u, w). \quad (3)$$

In the case  $\alpha = \gamma$ , the orthogonality property of Laguerre polynomials makes that the number of elements in the basis that are not orthogonal to one given is small. This number becomes much greater when  $\alpha \neq \gamma$  as a consequence of the loss of orthogonality between  $L_n(\alpha x)$  and  $L_m(\gamma x)$  ( $x = u, v$ ) [27].

This basis generalizes the ones proposed by Pekeris and co-workers [14, 24] that fulfill the condition  $\alpha + \gamma = \beta$  leading to an exponential dependence in the form  $\exp[-(\gamma r_1 + \alpha r_2)]$  without any dependence on  $r_{12}$ . In his study of the ground state of two-electron atoms, Pekeris also imposed  $\alpha = \gamma$  [14] and fixed  $\alpha$  as the square root of minus the binding energy of the corresponding eigenstate. Later  $\alpha$  was taken as a variational parameter [21, 22], increasing the rate of convergence. In order to study the  $P$ -states of Helium [24], the restriction is eliminated as the screening of the charge felt by the two electrons is different. As a matter of fact, due to the loss of the orthogonality, powers of  $u$ ,  $v$  and  $w$  were used in [24] instead of the Laguerre polynomials. Both basis have been also used in the last years to study the doubly excited states of Helium [25–27] (in this case, Laguerre polynomials have been used in the basis even when  $\alpha \neq \gamma$ ). From all these facts, we can conclude that the basis with  $\alpha + \gamma = \beta$  has proved to be

$$\begin{aligned} H = & -\frac{2}{m(u+v)(u+w)(v+w)} \left[ \left( v(u+v) + 2w(u+v+w) \right) u \frac{\partial^2}{\partial u^2} + \left( v^2 - u^2 + 2uv + 2w(u+v+w) \right) \frac{\partial}{\partial u} \right. \\ & + \left( u(u+v) + 2w(u+v+w) \right) v \frac{\partial^2}{\partial v^2} + \left( u^2 - v^2 + 2uv + 2w(u+v+w) \right) \frac{\partial}{\partial v} + \left( u(u+w) + v(v+w) \right) w \frac{\partial^2}{\partial w^2} \\ & + (u^2 + v^2 - 2w^2) \frac{\partial}{\partial w} - 2uw(u+w) \frac{\partial^2}{\partial u \partial w} - 2vw(v+w) \frac{\partial^2}{\partial v \partial w} \left. \right] - \frac{2}{M(u+w)(v+w)} \left[ uv \left( \frac{\partial^2}{\partial u^2} + \frac{\partial^2}{\partial v^2} - 2 \frac{\partial^2}{\partial u \partial v} \right) \right. \\ & \left. + w(u+v+w) \frac{\partial^2}{\partial w^2} + (v-u) \frac{\partial}{\partial u} + (u-v) \frac{\partial}{\partial v} + (u+v+2w) \frac{\partial}{\partial w} \right] - \frac{2(u+v+2w)}{(u+w)(v+w)} + \frac{2}{u+v} \quad (1) \end{aligned}$$

**Table 1.** Study of the rate of convergence for the basis with one and two non-linear variational parameters for the systems  $p^+e^-e^-$ ,  $p^+p^+\mu^-$  and  $p^+p^+e^-$ . For each value of the parameter  $N$  there are two entries corresponding to the basis with one (1) and two (2) non linear parameters. In the last row we show the best ground state eigenvalues of the systems from reference [23] ( $p^+e^-e^-$ ) and the present work.

$N$	Basis	$p^+e^-e^-$	$p^+p^+\mu^-$	$p^+p^+e^-$
5	1	-0.527 401 963	-0.494 286 091	-0.583 234 64
	2	-0.527 402 591	-0.494 372 447	-0.591 836 06
12	1	-0.527 445 850	-0.494 386 816 9	-0.594 672 48
	2	-0.527 445 851	-0.494 386 820 1	-0.596 993 55
15	1	-0.527 445 876 636	-0.494 386 820 195	-0.596 006 26
	2	-0.527 445 876 647	-0.494 386 820 243	-0.597 124 43
“Exact”		-0.527 445 881 114	-0.494 386 820 248 9	-0.597 139 063 123

very effective in the description of the atomic systems but, as we will show below, does not work properly to describe molecular systems.

A way of improving the basis is not to impose  $\alpha + \gamma = \beta$ . Moreover, as we shall study the ground state, and for simplicity, we shall take  $\alpha = \gamma$ . The main advantage of this choice is to take into account the correlation between the two identical particles in the exponential that will become

$$e^{-\beta(r_1+r_2)/2}e^{-(\alpha-\beta/2)r_{12}}. \quad (4)$$

For any calculation we shall only include  $k + l + m \leq N$ , so  $N$  will limit the dimension of the basis. This dimension is 34, 252, 444, 715, 1078, 1729 and 2856 for  $N = 5, 12, 15, 18, 21, 25$  and 30 respectively, which are the values of  $N$  we have worked with. The diagonalization is performed by using a Sturmian sequence from the Householder tri-diagonalization method to the hamiltonian matrix once we have applied the Choleski method to the norm matrix [35]. This may be carried out in double precision for any of the dimensions used and will generate a variational wave function in the form

$$\begin{aligned} \Psi(r_1, r_2, r_{12}) &= e^{-[\alpha(u+v)+\beta w]/2} \\ &\times \sum_{k,l,m} C_{klm} [L_k(\alpha u)L_l(\alpha v) + L_l(\alpha u)L_k(\alpha v)]L_m(\beta w). \end{aligned} \quad (5)$$

The two non-linear variational parameters are varied using the simplex iterative method [35] in order to minimize the expectation value of the hamiltonian.

### 3 Convergence

With the basis discussed in the previous section we have studied the following systems: i) Both the muonic ( $\mu^+\mu^+e^-$ ) and the hydrogen ( $p^+p^+e^-$ ) molecular ions, ii) the muonic molecular ions  $p^+p^+\mu^-$ ,  $d^+d^+\mu^-$  and  $t^+t^+\mu^-$  where  $d$  and  $t$  stand for deuterium and tritium, respectively (for these two last systems we have also studied their excited state of  $S$ -type, denoted by  $d^+d^+\mu^{-*}$  and  $t^+t^+\mu^{-*}$ ) and iii) some exotic systems such as  $\mu^+\mu^+\pi^-$ ,  $\pi^+\pi^+\mu^-$ ,  $d^+d^+p^-$  and  $t^+t^+p^-$ . All these systems have

been the object of a lot of works (see for example Refs. [9, 11] for a review on these systems where have been obtained for most of them the best ground state eigenvalues and different expectation values to date). To compare our results with those of references [9, 11] we have used the following particle masses in atomic units:  $m_\mu = 206.768262$ ,  $m_p = 1836.152701$ ,  $m_d = 3670.483014$ ,  $m_t = 5496.92158$  and  $m_\pi = 273.12695$ . Here we shall present the results for both the hydrogen and the muonic molecular ions in atomic units, for the exotic systems  $d^+d^+p^-$  and  $t^+t^+p^-$  in proton atomic units ( $m_p = 1$ ,  $\hbar = 1$  and  $e = 1$ ) and for all the other systems we have used the muon atomic units ( $m_\mu = 1$ ,  $\hbar = 1$  and  $e = 1$ ).

First we will study the improvement that the basis with two non-linear parameters represents with respect to the one with only one non-linear parameter. To do that we have selected three systems with very different values of  $\lambda$ . We show in Table 1 the ground state eigenvalues of the  $p^+e^-e^-$ ,  $p^+p^+\mu^-$  and  $p^+p^+e^-$  systems in terms of the parameter  $N$ , *i.e.* in term of the dimension of the basis used. As we can see the rate of convergence is much better for the basis introduced in this work than for the one with only one non-linear parameter ( $\alpha = \gamma = \beta/2$ ) except for the atomic system where the improvement is very small. From this behavior we have concluded that the basis does not provide an important improvement for atomic systems and so we have not included them in this work.

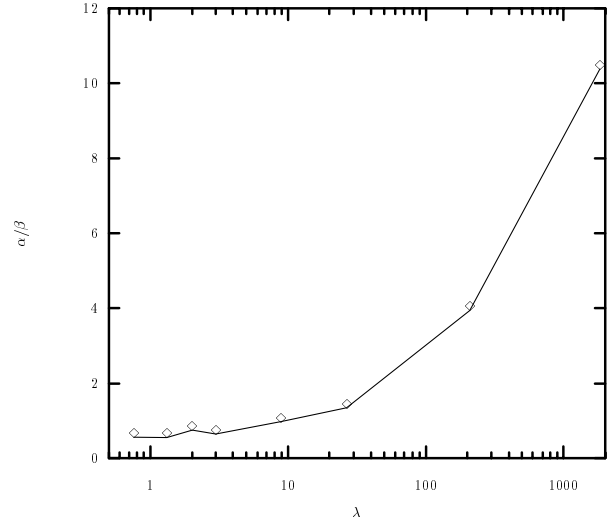
Once compared the basis with one and two non-linear parameters we shall study the rate of convergence of the new basis for some of the systems before mentioned. We have selected in Table 2 the systems  $\mu^+\mu^+\pi^-$ ,  $t^+t^+\mu^-$ ,  $\mu^+\mu^+e^-$  and  $p^+p^+e^-$ . A general result is that the smaller is the value of the parameter  $\lambda$ , the slower is the rate of convergence, except for the hydrogen molecular ion. Thus for the molecule  $\mu^+\mu^+\pi^-$  it is necessary to work with a basis of 2856 terms ( $N = 30$ ) to reproduce the best previous results of reference [9] and this same occurs with the  $\pi^+\pi^+\mu^-$  and  $d^+d^+p^-$  systems. For increasing values of  $\lambda$  the rate of convergence improves and there are several systems which do not need a very large expansion to be described with our choice of the basis set with a good precision. This is the case of the muonic molecular ions as for example the  $t^+t^+\mu^-$  one. Finally we also study in Table 2 the rate of convergence for the molecules  $\mu^+\mu^+e^-$

**Table 2.** Total energies for the ground state of the systems  $\mu^+\mu^+\pi^-$ ,  $t^+t^+\mu^-$ ,  $\mu^+\mu^+e^-$  and  $p^+p^+e^-$  in terms of the parameter  $N$  which governs the dimension of the basis. The results are given in muon atomic units ( $m_\mu = 1$ ,  $\hbar = 1$  and  $e = 1$ ) for the first system, in proton atomic units ( $m_p = 1$ ,  $\hbar = 1$  and  $e = 1$ ) for the second one and in atomic units for the last two.

		$\mu^+-\mu^+-\pi^-$	$\lambda = 0.757041$
$N$	$\alpha$	$\beta$	$E$
12	0.437355	0.886903	-0.297 689 246 868 5
15	0.473365	0.974718	-0.297 689 261 805 6
18	0.521250	0.978750	-0.297 689 263 662 9
21	0.548743	1.062651	-0.297 689 263 939 6
25	0.594115	1.114015	-0.297 689 264 006 7
30	0.66	1.175	-0.297 689 264 018 2
Ref. [9]	-	-	-0.297 689 264 018 2
		$t^+-t^+-\mu^-$	$\lambda = 26.584939$
$N$	$\alpha$	$\beta$	$E$
12	2.496670	1.434181	-0.546 374 225 556 4
15	2.382438	1.773875	-0.546 374 225 613 42
18	2.38	1.77	-0.546 374 225 613 79
21	2.37125	1.784375	-0.546 374 225 613 813
25	2.38	1.77	-0.546 374 225 613 816
Ref. [9]	-	-	-0.546 374 225 598
		$\mu^+-\mu^+-e^-$	$\lambda = 206.768262$
$N$	$\alpha$	$\beta$	$E$
12	5.740231	1.299277	-0.585 126 052 379 13
15	6.23	1.3674	-0.585 126 097 102 08
18	6.2	1.511	-0.585 126 097 218 89
21	6.4	1.68	-0.585 126 097 219 191
25	6.3	1.6	-0.585 126 097 219 193
Ref. [11]	-	-	-0.585 126 097 216
		$p^+-p^+-e^-$	$\lambda = 1836.152701$
$N$	$\alpha$	$\beta$	$E$
12	7.929196	1.172106	-0.596 993 545 606
15	8.692250	1.231895	-0.597 124 428 960
18	9.461878	1.293713	-0.597 138 076 827
21	11.38867	1.284445	-0.597 139 018 757
25	12.625	1.29125	-0.597 139 062 820
30	13.5	1.3	-0.597 139 063 123
Ref. [11]	-	-	-0.597 139 062 6
Ref. [38]	-	-	-0.597 139 063 1

and  $p^+p^+e^-$ . The most unfavorable case is that of the hydrogen molecular ion, that is common with other methods of calculation [11]. We can notice how the energy of the  $\mu^+\mu^+e^-$  molecule is better than those previously reported and the ground state eigenvalue of the  $p^+p^+e^-$  is equal to the most accurate in the literature.

We have used the simplex algorithm to determine the values of  $\alpha$  and  $\beta$  and these are the values of the parameters shown in the different tables. However, the parameters can spread over a given interval providing similar results. For example, in the molecular ion  $\mu^+\mu^+e^-$  with  $N = 15$  we obtain the first nine digits in the energy ( $-0.585126097$  a.u.) for any of the values  $\alpha$  and  $\beta$  in the intervals (6.2,6.4) and (1.3,1.5), respectively. When  $N = 21$  the intervals for the parameters to obtain the energy with twelve exact digits ( $-0.585126097219$  a.u.) increase to (5.2,7.1) and (1.2,2.0), respectively, that reflects



**Fig. 1.** The ratio of the two non-linear parameters,  $\alpha/\beta$ , in terms of the ratio of the masses,  $\lambda = m/M$ , for the results shown in Table 3.

the fact that for  $N \rightarrow \infty$  the results must be independent of the values of both parameters. The behavior for the other systems is similar to the one described for the muon molecular system.

## 4 Energies and densities

The best results for the energies of all the systems here studied are shown in Table 3 where they are compared with the best ones in the literature. The energies here reported are, in general, the best to date. We also show in this table the parameters  $N$ ,  $\alpha$  and  $\beta$ . Let us note that while  $\beta$  is nearly constant for all the systems studied,  $\alpha$  increases with  $\lambda$ . A plot of the ratio  $\alpha/\beta$  in terms of  $\lambda$  is shown in Figure 1. As it can be seen, this ratio is nearly constant and approximately 1/2, which it is the value used for atomic systems, when  $\lambda \leq 2$ . For greater values of  $\lambda$ , this value increases rapidly. This is showing us the transition from the atomic behavior to the molecular one. For those systems for which  $\lambda$  is close to the unity (*i.e.* the masses of all the particles are similar), the basis introduced in this work should not appreciatively improve the results which could be obtained with the basis of references [21, 22].

All the systems studied in the present work have two equal masses and so we can consider two different interparticle distributions. The first one,  $\rho(\mathbf{r})$ , defined by

$$\rho(\mathbf{r}) = \frac{1}{2} \sum_{i=1,2} \int d\mathbf{r}_1 d\mathbf{r}_2 \delta(\mathbf{r} - \mathbf{r}_i) |\Psi(r_1, r_2, r_{12})|^2 \quad (6)$$

provides the probability density of finding one of the two identical particles separated by the vector  $\mathbf{r}$  from the unlike one.

The second interparticle density,  $h(\mathbf{s})$ , is the probability distribution for the interparticle distance between

**Table 3.** Total energies for the bound states of  $S$ -type of the systems here studied as compared with the best results in the literature. Atomic units are used for the two last systems, proton atomic units ( $m_p = 1$ ,  $\hbar = 1$  and  $e = 1$ ) for the third and fourth ones and muon atomic units ( $m_\mu = 1$ ,  $\hbar = 1$  and  $e = 1$ ) for all the other systems.

System( $\lambda$ )	$N$	$\alpha$	$\beta$	$E$
$\mu^+-\mu^+-\pi^-$ (0.757041) Ref. [9]	30	0.66	1.175	-0.297 689 264 018 2 -0.297 689 264 018 2
$\pi^+-\pi^+-\mu^-$ (1.320933) Ref. [9]	30	0.71	1.28	-0.299 116 691 535 0 -0.299 116 691 534 2
$d^+-d^+-p^-$ (1.999007) Ref. [9]	30	0.95	1.27	-0.352 625 679 560 7 -0.352 625 679 560 3
$t^+-t^+-p^-$ (2.993717) Ref. [9]	25	1.086752	1.679110	-0.400 036 945 672 8 -0.400 036 945 672 1
$p^+-p^+-\mu^-$ (8.880244) Ref. [9]	25	1.80625	1.8575	-0.494 386 820 248 96 -0.494 386 820 248 58
$d^+-d^+-\mu^-$ (17.751675) Ref. [9]	25	2.75	1.6	-0.531 111 135 402 45 -0.531 111 135 402
$d^+-d^+-\mu^{-*}$ Ref. [9]	25	1.2052	1.127238	-0.479 706 380 368 5 -0.479 706 380 368
$t^+-t^+-\mu^-$ (26.584939) Ref. [9]	25	2.38	1.77	-0.546 374 225 613 816 -0.546 374 225 598
$t^+-t^+-\mu^{-*}$ Ref. [9]	25	1.747142	1.274507	-0.496 762 894 249 5 -0.496 762 894 248
$\mu^+-\mu^+-e^-$ (206.768262) Ref. [11]	25	6.3	1.6	-0.585 126 097 219 193 -0.585 126 097 216
$p^+-p^+-e^-$ (1836.152701) Ref. [11] Ref. [38]	30	13.5	1.3	-0.597 139 063 123 -0.597 139 062 6 -0.597 139 063 1

those two identical particles and is given by

$$h(\mathbf{s}) = \int d\mathbf{r}_1 d\mathbf{r}_2 \delta(\mathbf{s} - \mathbf{r}_{12}) |\Psi(r_1, r_2, r_{12})|^2. \quad (7)$$

These two densities are the so called single-particle density ( $\rho(\mathbf{r})$ ) and two-body or intracule density ( $h(\mathbf{s})$ ) in the case of atomic systems [28]. Both functions are spherically symmetric for all the states and systems here studied, so they will be hereafter denoted by  $\rho(r)$  and  $h(s)$ , respectively.

For the wave function used in this work equation (5), it is possible to perform analytically all the integrals required to calculate both  $\rho(r)$  and  $h(s)$  densities, obtaining

$$\rho(r) = e^{-2\alpha r} \sum_{k=-1}^{2N} a_k r^k + e^{-2\beta r} \sum_{k=-1}^{2N-1} b_k r^k \quad (8)$$

with  $a_{-1} = -b_{-1}$ , and

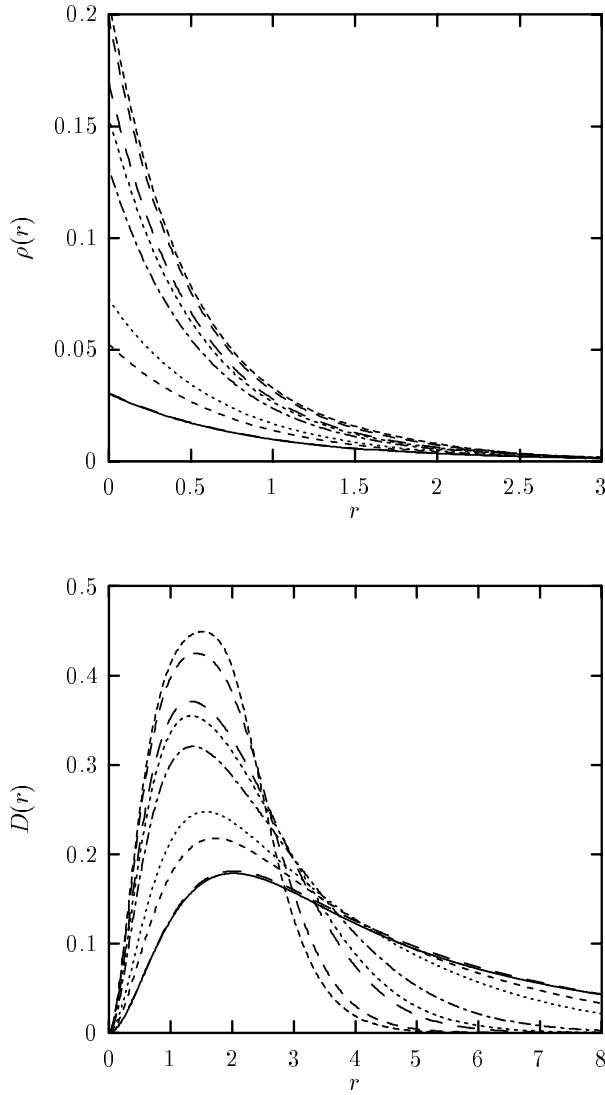
$$h(s) = e^{-2\alpha s} \sum_{k=0}^{2N+2} d_k s^k \quad (9)$$

where all the coefficients  $a_k$ ,  $b_k$  and  $d_k$  can be analytically evaluated once the linear coefficients  $C_{klm}$  which determine the variational wave function of equation (5) have been obtained. As it can be seen, the parameter  $\alpha$  determines the shape of  $h(s)$ .

We have calculated both functions for the ground states of the different systems here studied. In Figure 2

we show the density  $\rho(r)$  and the radial probability function  $D(r) = 4\pi r^2 \rho(r)$ . As we can see  $\rho(r)$  has a similar behavior to the single-particle density of atomic systems in their ground state, *i.e.* it decreases monotonically for all the cases studied. We can notice that the  $D(r)$  function is more peaked around its maximum when  $\lambda$  increases what means that the particles are more localized in the space as the ratio between their masses increases. For small values of  $\lambda$ ,  $\alpha$  is approximately half of  $\beta$  and thus is the more important parameter to describe  $\rho(r)$  at large distances as we can see in equation (8). When  $\lambda$  increases,  $\alpha$  and the ratio  $\alpha/\beta$  also do and then the role of  $\beta$  becomes more important in the description of the density.

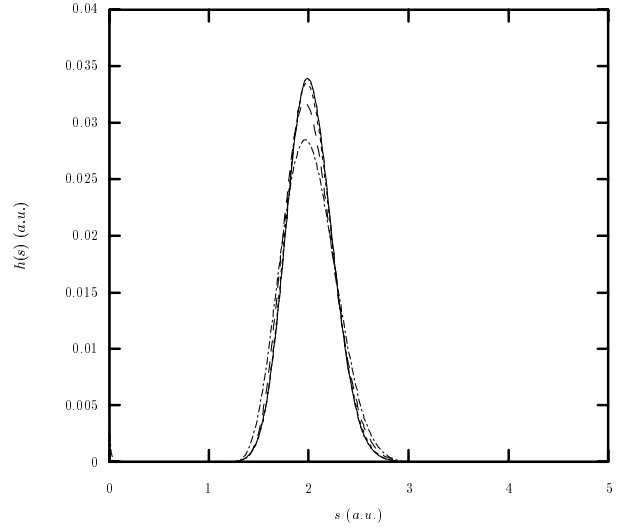
In general it is not easy to get a good description for the density distribution  $h(s)$  for any of the systems studied. Maybe the most significant case is that of the hydrogen molecular ion. To illustrate this we present in Figure 3 the  $h$ -function obtained with four different levels of accuracy. We have taken  $N = 12, 15, 18$  and  $21$ , which correspond to a basis of dimension 252, 444, 715 and 1078, respectively. The energies obtained with these wave functions are  $-0.596993$ ,  $-0.597124$ ,  $-0.597138076$  and  $-0.597139018$  atomic units respectively. It is apparent that it is necessary to work with  $N = 18$  in order to have a good description of the  $h$ -distribution. In this same figure we have plotted the density distribution  $h(s)$  obtained for the best  $N = 18$   $\beta = 2\alpha$  basis which provides an energy of  $-0.596641$ . We can see that the description is the worst of all the cases shown, what informs us about the enormous



**Fig. 2.** Upper plot: interparticle density  $\rho(r)$  of the ground state of the different systems here studied. The bigger is the value of the density at the origin, the bigger is the value of  $\lambda$ . Lower plot: radial density distribution  $D(r)$  for the same cases than in the upper plot. The same convention of lines is used in both plots. Atomic units are used for the  $p^+p^+e^-$  and  $\mu^+\mu^+e^-$  systems, proton atomic units for the  $d^+d^+p^-$  and  $t^+t^+p^-$  ones, and muon atomic units for the rest.

sensitiveness of this quantity to a good parameterization of the basis used.

As the function  $h(s)$  is related to the dynamical behavior of the two equal particles, it must reflect the transition from atomic to molecular systems. We have shown it in Figures 4 and 5 for the ground state of all the systems ordered with increasing  $\lambda$ . In Figure 4 we have plotted the  $h(s)$  distribution corresponding to the systems  $\mu^+\mu^+\pi^-$ ,  $\pi^+\pi^+\mu^-$  (upper plot) in muon atomic units, and  $d^+d^+p^-$  and  $t^+t^+p^-$  (lower plot) in proton atomic units. In Figure 5 we show the  $h(s)$  function of the systems  $p^+p^+\mu^-$ ,  $d^+d^+\mu^-$  and  $t^+t^+\mu^-$  (upper plot) in muon atomic units,



**Fig. 3.** Plot of the interparticle density  $h(s)$  of the ground state of the hydrogen molecular ion  $p^+p^+e^-$  for various values of the parameter  $N$ . (Long dashed, short dashed, dotted and solid line for  $N = 12, 15, 18$  and  $21$ , respectively). The density corresponding to  $N = 21$  superimposes to the one of  $N = 18$ . The dot-dashed line corresponds to the  $h(s)$  distribution for the optimum  $N = 18, \beta = 2\alpha$  basis.

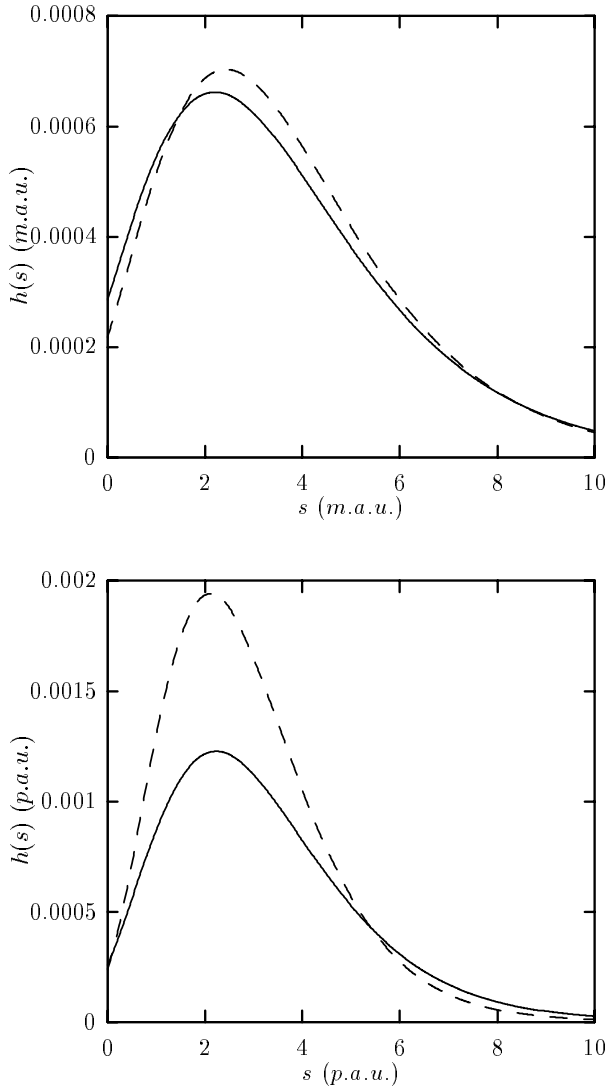
and of the molecular ions  $\mu^+\mu^+e^-$  and  $p^+p^+e^-$  (lower plot) in atomic units. As we can see the  $h(s)$  distribution has a similar behavior for all the systems, *i.e.* it increases from a given value at the coalescence point ( $s = 0$ ) to a maximum value at a finite interparticle distance  $s_0$ , which is approximately two units for all the plotted systems. From  $s_0$ ,  $h(s)$  decreases monotonically to zero. However the shape of  $h(s)$  is different from one to other system. For small values of  $\lambda$ , the parameter  $\alpha$  is also small and this function looks like the one of atomic systems [30], *i.e.* it is spread along a great distance. When  $\lambda$  increases,  $\alpha$  also does and so  $h(s)$  is more localized around its maximum as it is expected in a molecular system.

Different values obtained from the best wave functions reported in the previous section are showed in Tables 4-7. These quantities are the energy,  $E$ , of the system, the binding energy  $\epsilon$  defined as the difference between  $E$  and the threshold energy ( $E_{th} = -0.5mM/(m+M)$ ); we have used the conversion factor 27.211 366 181 to present the results in eV. Another quantity is the virial factor  $\eta$  defined by

$$\eta = \frac{\langle V \rangle}{\langle T \rangle} + 2 \quad (10)$$

where  $\langle V \rangle$  and  $\langle T \rangle$  are the expectation values of the potential and kinetic energy, respectively. The difference with respect to zero (*i.e.* the exact value of  $\eta$ ), is a measure of the quality of the solution found [36]. Some other quantities are the expectation value of the kinetic energy,  $\langle T \rangle$ , the expected values

$$\langle r^n \rangle = \int r^n \rho(r) dr; \quad n = -2, -1, 1, 2, 3 \quad (11)$$



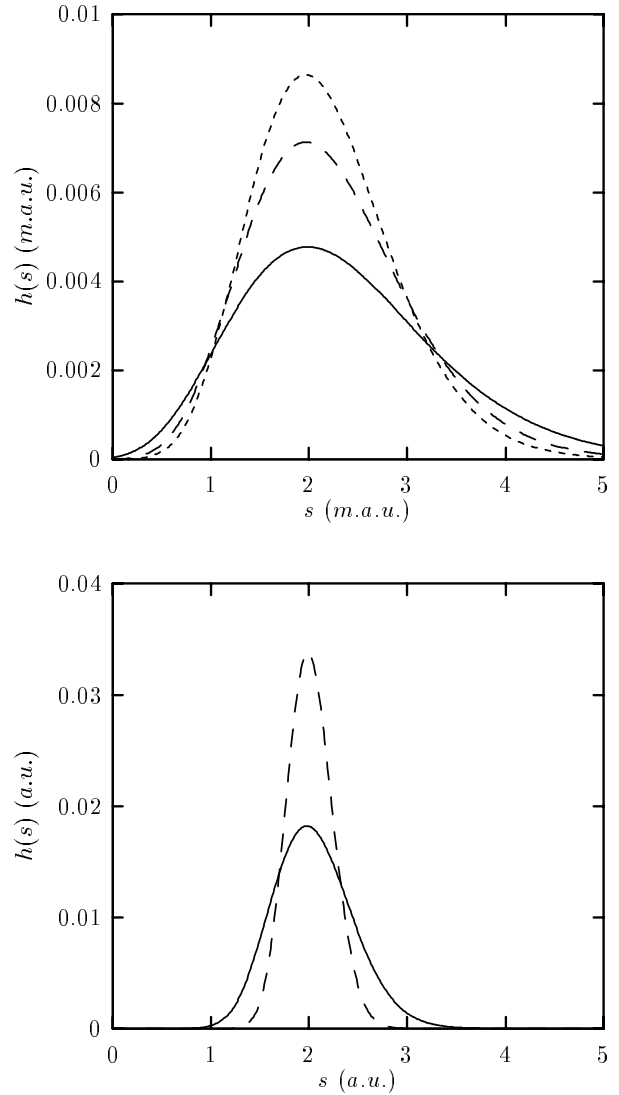
**Fig. 4.** Plot of the interparticle density  $h(s)$  of the ground state of different systems for small values of  $\lambda$ . Upper plot:  $\mu^+\mu^+\pi^-$  (dashed line) and  $\pi^+\pi^+\mu^-$  (solid line). Muon atomic units are used. Lower plot:  $d^+d^+p^-$  (solid line) and  $t^+t^+p^-$  (dashed line) systems. Proton atomic units are used.

and

$$\langle s^n \rangle = \int s^n h(s) ds; \quad n = -2, -1, 1, 2, 3 \quad (12)$$

and the values  $\rho(0)$ ,  $h(0)$ ,  $\nu = \rho'(0)/2\rho(0)$  and  $\nu_{12} = h'(0)/2h(0)$ . These two last quantities are the two body cusp ratio for  $\rho(r)$  and  $h(s)$ , respectively. For a general three body Coulomb system of masses  $m_i$  and charges  $q_i$ ,  $i = 1, 2, 3$  the exact value of the two body cusp ratio for particles  $j$  and  $k$  is given by [37]

$$q_j q_k \frac{m_j m_k}{m_j + m_k}. \quad (13)$$



**Fig. 5.** The interparticle density  $h(s)$  of the ground state of different systems for bigger values of  $\lambda$ . Upper plot:  $p^+p^+\mu^-$  (solid line),  $d^+d^+\mu^-$  (long dashed line) and  $t^+t^+\mu^-$  (short dashed lines). Muon atomic units are used. Lower plot:  $\mu^+\mu^+e^-$  (solid line) and  $p^+p^+e^-$  (dashed line) molecules. Atomic units are used.

So, an additional test for evaluating the quality of the solutions can be performed by studying how well the two body cusp ratios  $\nu$  and  $\nu_{12}$  are satisfied.

To avoid round errors in the last figures of the eigenvalues and of the coefficients of the wave functions which can modify the values of some of the quantities studied we have made a last calculation of the wave function in quadruple precision (32 digits).

In Table 4 we show all these quantities for the muonic molecular ions  $p^+p^+\mu^-$ ,  $d^+d^+\mu^-$  and  $t^+t^+\mu^-$ . The values of the eigenvalue, the virial and of the cusp conditions improve those previously reported in the literature (see Ref. [9] and references therein); therefore the description of the different properties is expected to be also the best.

**Table 4.** Different properties of the ground state of the  $p^+p^+\mu^-$ ,  $d^+d^+\mu^-$  and  $t^+t^+\mu^-$  molecules. Muon atomic unit are used. The notation [x] means  $10^x$ .

	$p^+p^+\mu^-$	$d^+d^+\mu^-$	$t^+t^+\mu^-$
$E$	-0.494 386 820 248 90	-0.531 111 135 402 45	-0.546 374 225 613 816
$\epsilon$	253.15019309	325.070689974	362.90655583
$\langle T \rangle$	0.494 386 820 248 68	0.531 111 135 402 34	0.546 374 225 613 809
$\eta$	4.49 [-13]	7.10 [-14]	1.24 [-14]
$\langle r^{-2} \rangle$	0.995871450344	1.145319640544	1.209447746650
$\langle r^{-1} \rangle$	0.670302578373	0.728486427949	0.753513462251
$\langle r \rangle$	2.385666585620	2.119931647555	2.017373310755
$\langle r^2 \rangle$	7.769503814378	5.946223219653	5.312898696639
$\langle r^3 \rangle$	31.54908633414	20.29695806223	16.85809914695
$\langle s^{-2} \rangle$	0.148722055479	0.177667878712	0.191091359122
$\langle s^{-1} \rangle$	0.351831516249	0.394750585093	0.414278473274
$\langle s \rangle$	3.299486184358	2.834451765779	2.652824757574
$\langle s^2 \rangle$	12.39040846406	8.876754641773	7.662138314320
$\langle s^3 \rangle$	52.27366441986	30.43693049989	23.92439065402
$\rho(0)$	0.131500861	0.1587389692	0.170362122
$\nu$	-0.8987879806	-0.9466714843	-0.9637483466
$\nu(\text{exact})$	-0.8987879287820	-0.9466714310522	-0.9637483334950
$h(0)$	3.937035 [-5]	2.438687 [-6]	2.158931 [-7]
$\nu_{12}$	4.4399512	8.876045	13.2925904
$\nu_{12}(\text{exact})$	4.440122200669	8.875837564471	13.29246937327

**Table 5.** Different properties of the  $d^+d^+\mu^{-*}$ ,  $t^+t^+\mu^{-*}$  and  $d^+d^+p^-$  systems. Muon atomic unit are used for the two first and proton atomic units for the last. The notation [x] means  $10^x$ .

	$d^+d^+\mu^{-*}$	$t^+t^+\mu^{-*}$	$d^+d^+p^-$
$E$	-0.479 706 380 368 5	-0.496 762 894 249 5	-0.352 625 679 560 7
$\epsilon$	35.84424692	83.77072693	966.68405796
$\langle T \rangle$	0.479 706 380 364 8	0.496 762 894 249 2	0.352 625 679 560 3
$\eta$	7.62 [-12]	7.31 [-13]	9.67 [-13]
$\langle r^{-2} \rangle$	0.947919764567	1.019685967763	0.507401334288
$\langle r^{-1} \rangle$	0.591325294979	0.635216112698	0.462968991583
$\langle r \rangle$	3.616306080007	2.965847587998	3.848088932637
$\langle r^2 \rangle$	20.54097545278	12.88610525812	22.57053339520
$\langle r^3 \rangle$	147.1073784931	69.01366536064	180.5752799456
$\langle s^{-2} \rangle$	0.073267410869	0.104340453756	0.068009477070
$\langle s^{-1} \rangle$	0.223237829224	0.276906436897	0.220686624046
$\langle s \rangle$	5.694739215564	4.453656633527	5.797779744039
$\langle s^2 \rangle$	37.41878612299	22.47682795653	41.45949441119
$\langle s^3 \rangle$	273.6005734629	123.1480143469	358.4356038605
$\rho(0)$	0.1371458494	0.1481589635	0.05010598
$\nu$	-0.94667206	-0.963748506	-0.66655701
$\nu(\text{exact})$	-0.9466714310522	-0.9637483334950	-0.6665563520030
$h(0)$	1.6742238 [-6]	2.42666148 [-7]	2.5779519 [-4]
$\nu_{12}$	8.88011	13.292987	0.99947950
$\nu_{12}(\text{exact})$	8.875837564471	13.29246937327	0.9995037482452

The same is made in Table 5 for the excited states  $d^+d^+\mu^{-*}$  and  $t^+t^+\mu^{-*}$  and for the  $d^+d^+p^-$  system and in Table 6 for the systems  $t^+t^+p^-$ ,  $\pi^+\pi^+\mu^-$  and  $\mu^+\mu^+\pi^-$ . For these systems we also have a slight improvement in the values  $\eta$ ,  $\nu$  and  $\nu_{12}$  with respect to previous calculations.

Finally, in Table 7 we show the results for the  $\mu^+\mu^+e^-$  and  $p^+p^+e^-$  systems for which we have showed neither the  $h(0)$  nor the cusp ratio for the density  $h(s)$  because the values obtained for  $\nu_{12}$  are far from the exact ones. This

is due to the fact that  $h(s)$  is nearly zero for small values of  $s$  and so this part of the density is not important in the minimization process because the variational method tries to minimize the energy on the whole domain. We have not found any calculated values of these quantities in the literature. The results found for some expectation values reproduce those of Ackermann and Shertzer [11] and others such as  $\langle r^{-2} \rangle$ ,  $\langle r^3 \rangle$ ,  $\langle s^{-2} \rangle$  and  $\langle s^3 \rangle$  are the first time to appear in the literature.



**Table 6.** Different properties of the  $\mu^+\mu^+\pi^-$ ,  $\pi^+\pi^+\mu^-$  and  $t^+t^+p^-$  systems. Muon atomic unit are used for the two first and proton atomic units for the last. The notation  $[x]$  means  $10^x$ .

	$t^+t^+p^-$	$\pi^+\pi^+\mu^-$	$\mu^+\mu^+\pi^-$
$E$	-0.400 036 945 672 852	-0.299 116 691 535 0	-0.297 689 264 018 2
$\epsilon$	1260.77851535	81.84985914	73.81850518
$\langle T \rangle$	0.400 036 945 673 049	0.299 116 691 533	0.297 689 264 02
$\eta$	-4.93 [-13]	5.22 [-12]	-8.27 [-12]
$\langle r^{-2} \rangle$	0.653536135421	0.364655208086	0.359752442908
$\langle r^{-1} \rangle$	0.529919891696	0.389596825348	0.384901003865
$\langle r \rangle$	3.256460570962	4.711332016209	4.904732674436
$\langle r^2 \rangle$	15.61694422211	34.98997089800	39.22537827812
$\langle r^3 \rangle$	99.33973619727	364.0541039242	451.3535852296
$\langle s^{-2} \rangle$	0.090444169517	0.047458309242	0.045985078909
$\langle s^{-1} \rangle$	0.259765892046	0.180960267628	0.174423479691
$\langle s \rangle$	4.794813695979	7.249287114260	7.714412161008
$\langle s^2 \rangle$	27.71624137288	66.21558475182	76.58564183407
$\langle s^3 \rangle$	189.6346976635	745.6912170983	955.0386115382
$\rho(0)$	0.07242508	0.030783333	0.030425736
$\nu$	-0.74960503	-0.56913957	-0.56913992
$\nu(\text{exact})$	-0.7496066955496	-0.5691387268936	-0.5691387268936
$h(0)$	2.37982134 [-4]	2.1715150 [-4]	2.8456898 [-4]
$\nu_{12}$	1.4966954	0.6603971	0.4999175
$\nu_{12}(\text{exact})$	1.496858506650	0.6604663292087	0.5

**Table 7.** Different properties of the  $\mu^+\mu^+e^-$  and  $p^+p^+e^-$  molecular ions. Atomic unit are used. The notation  $[x]$  means  $10^x$ .

	$\mu^+\mu^+e^-$	$p^+p^+e^-$
$E$	-0.585 126 097 219 193	-0.597 139 063 123
$\epsilon$	2.3818849253	2.6506953926
$\langle T \rangle$	0.585 126 097 219 193	0.597 139 063 132
$\eta$	1.1 [-16]	-1.62 [-11]
$\langle r^{-2} \rangle$	1.3749080127	1.4180673806
$\langle r^{-1} \rangle$	0.8203397594	0.8424929624
$\langle r \rangle$	1.7693024514	1.6929662082
$\langle r^2 \rangle$	3.9384580545	3.5587979297
$\langle r^3 \rangle$	10.294593431	8.7098303735
$\langle s^{-2} \rangle$	0.2300008891	0.2166562614
$\langle s^{-1} \rangle$	0.4704273243	0.4907077986
$\langle s \rangle$	2.2052152449	2.0639138669
$\langle s^2 \rangle$	5.0365855992	4.3132859413
$\langle s^3 \rangle$	11.896594181	9.1255668897
$\rho(0)$	0.198930501	0.206736480
$\nu$	0.9951869565	0.999455911
$\nu(\text{exact})$	0.99518694534779	0.9994556794329

An analysis of the Tables 3-7 shows that the parameter  $\lambda$  governs the behavior of most of quantities which characterize the shape of the systems. For instance the expected value  $\langle r \rangle$  decreases when  $\lambda$  increases and this same occurs with the expected value  $\langle s \rangle$  what means that the molecules become more compact. In fact when the parameter  $\lambda$  tends to infinity the expected value  $\langle s \rangle$  approaches 2 (in units

of the smaller mass) that is the Born–Oppenheimer result [9]. Something similar happens for the values of both densities,  $\rho(r)$  and  $h(s)$ , at the origin:  $\rho(0)$  increases when  $\lambda$  does while  $h(0)$  decreases in such a way that the values of  $h(0)$  become negligible for high  $\lambda$ . Let also note that the value of the parameter  $\alpha$  increases, in general, with  $\lambda$  which is related to the fact that the probability distribution  $h(s)$  is more peaked around its equilibrium distance as can be seen from equation (9).

## 5 Conclusions

We have utilized a Hylleraas two-parameter basis set to study  $S$  bound states of three-body Coulomb systems with unit charges and two equal masses. This basis allows us to obtain analytical expressions for the interparticle distribution functions,  $\rho(r)$  and  $h(s)$ , and to perform calculations for any number of states of the basis. The results obtained for the eigenvalues are the most accurate in the literature for the systems here studied. This basis also provides accurate values for the cusps of the densities improving previous results, except for both the hydrogen ( $p^+p^+e^-$ ) and the muonic ( $\mu^+\mu^+e^-$ ) molecular ions for which the cusp ratio  $\nu_{12}$  is not well reproduced.

This work has been partially supported by the Spanish Dirección General de Investigación Científica y Técnica (DG-ICYT) under contract PB95–1211–A and by the Junta de Andalucía.

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