Properties of some exotic five-particle systems

J. Zs. Mezei,[1] J. Mitroy,[2] R. G. Lovas,[1] and K. Varga[1,3]
[1]*Institute for Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), P.O. Box 51, 4000 Debrecen, Hungary*
[2]*Faculty of Science, Northern Territory University, Casuarina, North Territory 0909, Australia*
[3] *Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830*
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The stability of a number of exotic systems consisting of $N=5$ unit charge particles is investigated using the stochastic variational method. Several interesting exotic molecules are found to be stable. The properties of the most intriguing systems consisting of two electrons and two positrons (e.g., e^+PsH or Li^+Ps_2) are investigated in great detail.

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I. INTRODUCTION

The chemical binding of systems of charged particles is known to depend crucially on the mass of the particles. The structures of (p,e^-,e^-), (p,p,e^-), and (e^+,e^+,e^-) are very different and some other combination of these particles, e.g., (p,e^+,e^-) are unbound. The bound states of small molecules formed by heavy multiply charged nuclear centers and a small number of electrons are well known. Much less is known about the possible stability/existence of systems formed by particles of unit charge (e.g., e^-,e^+,μ^-,p,d,t, etc.) although the stability of three- and four-particle systems for different mass ratios of the constituents has been investigated [1–3].

The simplest examples of these exotic systems are the positronium ion (e^+,e^-,e^-) (predicted by Wheeler [4], experimentally observed by Mills [5]), the Ps_2 molecule (e^+,e^+,e^-,e^-) (predicted by Hylleraas and Ore [6], not observed yet in nature), or the PsH system (predicted in Ref. [6] and indirectly observed in Ref. [7]). These systems have been extensively studied by various theoretical methods in the last few years [8].

Most recently, the e^+PsH system formed by attaching a positron to PsH has been shown to be electronically stable [9]. The existence of these small systems raises the question as to whether (similarly to molecules) larger stable systems containing positrons can also be formed. One can ask whether a system of *m* electrons *n* positrons [for example, an $(3e^-,3e^+)$ system] is bound or whether a positron, a positronium, a Ps^- ion or a Ps_2 molecule can attach itself to an atom or molecule.

Other examples of Coulombic systems where the binding mechanism is very different from that of atoms or molecules are the positronic atoms (atoms forming a bound state with a positron, e.g., Lie^+; or positronium LiPs) and the excitonic complexes (systems of electrons and holes in semiconductors). The positronic atoms have been subject of intensive theoretical studies in the last few years [10–18]. These atoms have not been experimentally observed yet, although possible experimental protocols have been discussed [19]. However, there is experimental evidence for the existence of excitonic complexes [20–23].

The prediction of the stability of Coulombic few-body systems requires very sophisticated calculations. The difficulty can largely be attributed to the fact that the correlations between like and opposite charges are quite different due to the attractive and repulsive interaction. Another factor which plays a crucial role in the binding mechanism is the Pauli principle. For systems with identical particles the antisymmetry requirement seriously restricts phase space accessible to the the particles by not allowing the energetically most favorable configurations. The small binding energies of these loosely bound systems require very accurate calculations.

The present study is based on the stochastic variational method [24,25]. Correlated Gaussian functions are used for the basis because their matrix elements are readily available for *N*-particle systems. This variational approach gives a fairly accurate variational upper bound for the energies of the few-particle systems studied here.

In Sec. II the stochastic variational method is introduced and the basis functions used in the different calculations are described. A number of different five-particle systems are investigated in the Sec. III. The last section summarizes the results and discusses possibilities for further research.

II. THE STOCHASTIC VARIATIONAL METHOD

All calculations reported in this work used the stochastic variational method (SVM) or a variant of this method. In the SVM, the wave function is approximated by a linear combination of correlated Gaussians

$$\Psi=\sum_{i=1}^{K} c_i\phi(A_i,\mathbf{x}), \tag{1}$$

$$\phi(A,\mathbf{x})=\mathcal{A}\{e^{-(1/2)\mathbf{x}^\dagger A\mathbf{x}}\chi_{SM_S}\}, \tag{2}$$

where $\mathbf{x}=(\mathbf{x}_1,\ldots,\mathbf{x}_{N-1})$ is a set of relative coordinates, χ_{SM_S} is the spin function, and A is a matrix of nonlinear variational parameters with

$$\mathbf{x}^\dagger A\mathbf{x}=\sum_{i,j=1}^{(N-1)} A_{ij}\mathbf{x}_i\cdot\mathbf{x}_j. \tag{3}$$

and $\mathcal{A}$ is an antisymmetrizer. The wave function is antisymmetrized for each group of identical particles. If a five particle system, for example, consists of two pairs of identical

particles and a third kind of particle (e.g., a $p^+p^+e^-e^-\mu^+$ system), then the wave function is antisymmetrized for the indentical pairs (for the two protons and for the two electrons). Sometimes we want to elucidate the role of the Pauli principle in the binding mechanism by introducing a fictitious particle "x" which has the same mass and charge as an electron, for example, but is a "distinguishable form of it." In such case there is no antisymmetrization between x and the electrons. The energy difference between the two cases (i.e., when the particle x is distinguishable and when it is identical) shows the effect of the antisymmetrization.

The above ansatz leads to a generalized eigenvalue problem. The upper bound of the ground state energy and the linear coefficients are obtained by matrix diagonalization. The correlated Gaussians offer computational advantages: fast analytical evaluation of the matrix elements and good approximation to various wave functions. They also have well-known drawbacks such as their slow convergence (compared to exponential functions) and the fact that they do not satisfy the cusp condition.

The Hamiltonian of this Coulombic system is written as

$$H=-\sum_{i=1}^{N}\frac{\hbar^2}{2m_i}\nabla_i^2+\sum_{i<j}^{N}\frac{q_iq_j}{|\mathbf{r}_i-\mathbf{r}_j|}. \tag{4}$$

The particles are assumed to have unit charges, that is $|q_i|=1$. We use atomic units so the energy is measured in Hartree H $(=m_e e^4/\hbar^2)$ and the length is measured in units of the Bohr radius $(a=\hbar^2/m_e e^2)$ (m_e is the mass of the electron).

The accuracy of these variational calculations strongly depends on the optimization of the nonlinear parameters. The number of parameters to be optimized is usually very large even for a relatively small system. Conventional deterministic optimization methods require many repeated diagonalizations and recalculation of matrix elements and may not find the global energy minimum due to the presence of local minima.

Our procedure is a stochastic parameter search which does not get trapped in local minima. To avoid rediagonalization of large nonsparse matrices, only one basis function is changed at a time. That also restricts the number of nonlinear parameters optimized at the same time to those in $\phi(A_i,\mathbf{x})$. The quadratic form in the exponent of the correlated Gaussian can be written in an equivalent form

$$\mathbf{x}^{\dagger}A\mathbf{x}=\sum_{k<l}^{N}\alpha_{kl}(\mathbf{r}_k-\mathbf{r}_l)^2, \tag{5}$$

where $\mathbf{r}_i$ are the positions of the particles and α_{ij} can be expressed by A_{ij} and vice versa. The advantage of this notation is that it explicitly connects the nonlinear parameters α_{ij} to the pair correlation between particle i and j. The $\mathbf{r}_k-\mathbf{r}_l$ relative distances do not form a linearly independent set of coordinates and therefore one can choose some of the α_{ij} to be negative (provided that A remains positive definite and hence the wave function square integrable). We did not find any obvious advantage in allowing negative values of α_{ij} and restricted the calculations for positive α_{ij}.

TABLE I. Energy of Coulombic few-body systems (in atomic units). The mass of the proton is assumed to be infinite in PsH and it is taken as $1836.1527m_e$ in H_2.

System	SVM	Basis size	Other method
PsH	−0.789196553	1200	−0.7891967147 [29]
H_2	−1.164023731	100	−1.164025023 [27]
Ps_2	−0.516003778	1200	−0.516001 [30]
H_3^+	−1.3185	500	

The stochastic variational method systematically improves the correlation functions between the particles by testing different random α_{ij} sets and choosing the one which gives the lowest energy. In the first stage a basis is constructed by adding one randomly selected new basis states to the basis. In the next stage these basis states are cyclically reoptimized by replacing the previous parameters by a new better random set. This process is repeated until the energy and wave function are deemed to be sufficiently accurate.

The method has been tested on a number of many-body problems of different areas of physics and it has been proved to be highly accurate and reliable [25]. A comprehensive description can be found in Ref. [25].

This variational trial function works very well for various systems. In some systems such as in molecules, the particle densities are very tightly localized at large distances. Gaussian trial functions are not sufficiently flexible to describe these systems compactly. The functions $e^{(-1/2)\alpha_{ij}(\mathbf{r}_i-\mathbf{r}_j)^2}$ peak at $\mathbf{r}_i=\mathbf{r}_j$ and a huge basis is needed to approximate very tightly localized density distributions of the nuclear centers, dramatically slowing down the convergence of the wave function. To avoid that problem the following trial function may be used, viz

$$\phi(A,\mathbf{x})=\mathcal{A}\{|\mathbf{v}|^{2k}e^{-(1/2)\mathbf{x}^{\dagger}A\mathbf{x}}\chi_{SM_S}\}, \tag{6}$$

with

$$\mathbf{v}=\sum_{i=1}^{N-1}u_i\mathbf{x}_i\,. \tag{7}$$

This function is a special case of the "global vector representation" [26] for zero angular momentum. The linear combination coefficients u_i and the power of $\mathbf{v}$ are new variational parameters. The ability of the SVM to obtain very accurate binding energies can be seen from Table I where SVM energies are compared with state of the art calculations for a number of few body systems. The difficulties of using simple correlated Gaussians in nonadiabatic molecular calculations has been noted elsewhere and remedies similar to that adopted here have been proposed [27]. The above formulation works well for two-center molecules such as H_2 or LiH, but it is considerable less efficient for three-center system such as H_3^+. We have included the nonadiabatic energy of H_3^+ obtained by this basis in Table I. To our best knowledge there is no other nonadiabatic calculation reported in the literature. The convergence for that system is very slow and

our result may not be very accurate. The mass ratio in this case is 1/1836 and the Born-Oppenheimer approach is certainly the method of choice for such systems. The correlated Gaussians provide very accurate solution up to about 1/20 mass ratio and the systems considered in this work are within this limit.

For systems with more than 5 or 6 particles, the SVM becomes very time consuming and it becomes desirable to approximate the Hamiltonian by assuming a inert core for larger atoms. For example, the Li^+Ps_2 system consists of four electrons, two positrons, and the nucleus. While a fully *ab initio* calculation was able to establish the electronic stability of this system [9], the time consuming nature of the calculation prevented the continuation of the calculation to get an accurate estimate of the binding energy. The fixed core variant of the SVM was introduced to permit calculations on complex atomic systems by treating the core and valence electrons differently [14,15]. The tightly bound core electron orbitals are obtained from a Hartree-Fock calculation and are only used to compute the effective potential for the valence electrons.

III. RESULTS OF CALCULATIONS

In this section we denote a heavy charged particle of arbitrary mass by the symbol M^+ or M^-. Light particles are denoted by m^+ or m^-. When the particle corresponds to a known particle (e.g., protons, electrons, muons, and their antiparticles) the symbol for the particle is used.

A. (m^+,m^+,m^+,m^-,m^-)

The first set of calculations investigated the system consisting of five equal mass particles. No evidence of binding could be found for systems consisting of four positive (negative) charges and one negative (positive) charge.

For the system consisting of three positive charges and two negative charges the ability to bind depended on whether the systems consisted of bosons or fermions. For a system consisting of three positively charged fermions and two negatively charged fermions, no evidence of binding was seen. The constraints imposed by the Pauli principle act to prevent the system from binding. For example, the five-particle system consisting of three electrons and two positrons does not have a bound state.

However, if the third positive particle is distinguishable from the other two, then the system can form a bound state. We refer to such a system as ''bosonic'' since all the particles are effectively distinguishable once the spin projections are taken into consideration. An example of a five-particle system of distinguishable particles is the (e^-,e^-,e^+,e^+,x) system, where x is a fictitious particle which has the same mass as the electron but is distinguishable from both the electron and the positron. The energies of a number of equal mass boson and fermion system (with mass equal to m_e) are listed in Table II. The Ps^- ion and Ps_2 are well known examples of such systems.

In Table II the energies of the bosonic and fermionic systems are equal up to $N=4$. In the bosonic case the particles

TABLE II. Energies of N-particle systems of unit charges and equal masses. The total charge is 0 and 1 for N even and odd, respectively. Atomic units are used.

N	Fermion	Boson
2	−0.250000	−0.250000
3	−0.26200	−0.26200
4	−0.516004	−0.516004
5	no bound state	−0.556489

are considered to be spinless and the spatial part of the wave function is asymmetric in the coordinates of the identical particles. In the fermionic case we have considered particles with half spin. The lowest energy state turns out to be the state where the spin of the pairs of identical particles are coupled to zero. In this state the spin part of the wave function is antisymmetric and the space part has to be symmetric. Therefore both the bosonic and fermionic system have symmetric spatial part and their ground state energies are equal.

The bound systems consisting of five distinguishable particles of equal mass may not seem to be of any practical importance because there are no such system in the real world. This stability, however, often survives when masses of the constituents are changed. For example, when the distinguishable particle in the (e^-,e^-,e^+,e^+,x) system is a proton the system still is stable. This system (which is discussed later) is an example of a physical system predicted by the presented calculations that can be formed (although it would obviously be a very difficult experiment to prove its existence).

B. (M^+,M^+,M^+,m^-,m^-)

The most well-known stable Coulombic five particle system is the H_3^+ molecule. The three protons form an equilateral triangle and share the two electrons, the system is stable for $\sigma=m/M\approx 0$. The previous section has shown that the equal mass $(m^+,m^+,m^+,m^-,m^-)(\sigma=1)$ system with three identical particles is not bound. In an earlier study [28] an attempt was made to find the mass ratio where the stability is lost. It has been found that the system is bound provided that the positively charged particles are at least five times heavier than the negative one $(0<\sigma=m/M<0.2)$. Beyond this mass ratio, the system dissociates into a (M^+,M^+,m^-,m^-) system plus M^+. Another possible dissociation channel is (M^+,M^+,m^-) plus (M^+,m^-). The energy of this channel $3+2$ is always higher than that of the $4+1$.

This shows that the H_3^+ molecule would remain stable even if the protons were be much lighter. A system of three holes and two electrons in semiconductors might be a realistic example of this case. The system consisting of three protons and two negatively charged muons, i.e., $(p^+,p^+,p^+,\mu^-,\mu^-)$ can be mentioned as an exotic example where $\sigma<0.2$ (see Table III). The mass ratio between the muon and the proton is about $\sigma=0.11$ which is much larger than that in the hydrogen atom $(\sigma=0.0005)$. The energy of the proton-muon atom is −92.92 a.u. and the average

TABLE III. Energies and other properties of selected exotic five particle systems (in atomic units). The notation r^2_{ab} stands for the expectation value of the square distance between particle "a" and "b." The energies of the relevant thresholds are also included. ($m_p = 1836.1527 m_e$, $m_d = 3670.4827 m_e$, $m_t = 5496.92158 m_e$, $m_{\mu^-} = 206.76826 m_e$), $\eta = \langle T \rangle / \langle 2V \rangle$.

Category	System	Threshold
B	$(p^+,p^+,p^+,\mu^-,\mu^-)$	(p^+,p^+,μ^-,μ^-)
E	−203.10453	−199.63069
η	0.999984	0.999998
$r^2_{p^+p^+}$	4.28×10^{-4}	1.47×10^{-4}
$r^2_{\mu^-\mu^-}$	2.93×10^{-4}	2.35×10^{-4}
$r^2_{p^+\mu^-}$	3.32×10^{-4}	1.35×10^{-4}
C	(p^+,p^+,e^-,e^-,μ^+)	(p^+,p^+,e^-,e^-)
E	−1.296583	−1.164023
η	0.999741	0.999989
$r^2_{p^+p^+}$	3.86	2.26
$r^2_{e^-e^-}$	5.63	5.92
$r^2_{p^+\mu^+}$	4.15	
$r^2_{e^-\mu^+}$	4.48	
$r^2_{p^+e^-}$	3.77	3.22
D	$(p^+,\mu^+,\mu^+,e^-,e^-)$	(p^+,μ^+,e^-,e^-)
E	−1.271788	−1.149679
η	0.999833	0.999614
$r^2_{\mu^+\mu^+}$	4.62	
$r^2_{e^-e^-}$	5.73	6.04
$r^2_{p^+\mu^+}$	4.05	2.36
$r^2_{e^-\mu^+}$	3.95	3.28
$r^2_{p^+e^-}$	3.76	3.89
D	(p^+,e^+,e^+,e^-,e^-)	(p,e^+,e^-,e^-)
E	−0.8099127	−0.788865
η	1.0000029	0.999991
$r^2_{p^+e^+}$	31.917	16.2709
$r^2_{p^+e^-}$	7.493	7.8242
$r^2_{e^-e^-}$	15.166	15.8941
$r^2_{e^+e^+}$	65.682	
$r^2_{e^+e^-}$	33.808	15.5927
D	(d^+,e^+,e^+,e^-,e^-)	(d,e^+,e^-,e^-)
E	−0.81007844	−0.7890280
η	1.0000017	0.9999915
$r^2_{p^+e^+}$	31.906	16.2621
$r^2_{p^+e^-}$	7.487	7.8183
$r^2_{e^-e^-}$	15.157	15.8839
$r^2_{e^+e^+}$	65.674	
$r^2_{e^+e^-}$	33.800	15.5881
E	(p^+,p^+,e^-,e^-,μ^-)	(p^+,p^+,μ^-,e^-)
E	−102.750286	−102.723336
η	0.99999887	1.000000012
$r^2_{p^+\mu^-}$	1.81×10^{-4}	1.81×10^{-4}
$r^2_{e^-e^-}$	23.4847	
$r^2_{p^+e^-}$	11.0676	3.0011
$r^2_{p^+p^+}$	2.89×10^{-4}	2.89×10^{-4}
$r^2_{e^-\mu^-}$	11.0676	3.0011
E	(d^+,t^+,μ^-,e^-,e^-)	(d^+,t^+,μ^-,e^-)
E	−111.889612	−111.864106
η	1.0000135	1.00000034
$r^2_{t^+\mu^-}$	1.26×10^{-4}	1.26×10^{-4}
$r^2_{d^+\mu^-}$	1.37×10^{-4}	1.37×10^{-4}
$r^2_{t^+e^-}$	9.8831	2.9965
$r^2_{d^+e^-}$	9.8831	2.9965
$r^2_{e^-\mu^-}$	9.8831	2.9965
$r^2_{e^-e^-}$	21.1378	
$r^2_{t^+d^+}$	1.93×10^{-4}	1.93×10^{-4}
G	(p^+,p^+,p^-,e^-,e^-)	(p^+,p^+,p^-,e^-)
E	−481.605173	−481.580324
η	1.0000016	1.00000029
$r^2_{p^+p^+}$	2.76×10^{-5}	2.76×10^{-5}
$r^2_{e^-e^-}$	21.382	
$r^2_{p^+e^-}$	9.9285	2.995
$r^2_{p^+p^-}$	1.43×10^{-5}	1.43×10^{-5}
$r^2_{p^-e^-}$	9.9285	2.995

square distance between the proton and muon $r^2_{p^+\mu^-}$ is 8.6 $\times10^{-5}$ atomic unit. The molecule formed by two proton-muon atoms is deeply bound just like the hydrogen molecule [any (M^+,M'^+,m^-,m^-) system is bound irrespective of the M/M' ratio if $m<M,M'$]. The binding energy divided by the reduced mass of the proton-muon atom is 0.07 in (p^+,p^+,μ^-,μ^-) and 0.02 in $(p^+,p^+,p^+,\mu^-,\mu^-)$. The corresponding ratios of H_2 and H_3^+ are 0.16 and 0.18, that is the $(p^+,p^+,p^+\mu^-,\mu^-)$ much more loosely bound than the H_3^+. That is also clear by comparing the average square distances between the protons in Table III. In $(p^+,p^+,p^+\mu^-,\mu^-)$ the protons are further away from each other so the system is more loosely bound and by increasing σ it will dissociate. The energy of the (p^+,p^+,μ^-) ion is −102.22 a.u., corroborating the fact that the energy of the 3+2 dissociation channel is higher than that of the 4+1.

C. $(p^+,p^+,e^-,e^-,m_{x^+})$

In this example the properties of the system are investigated as mass of one of heavy particle in H_3^+ is changed.

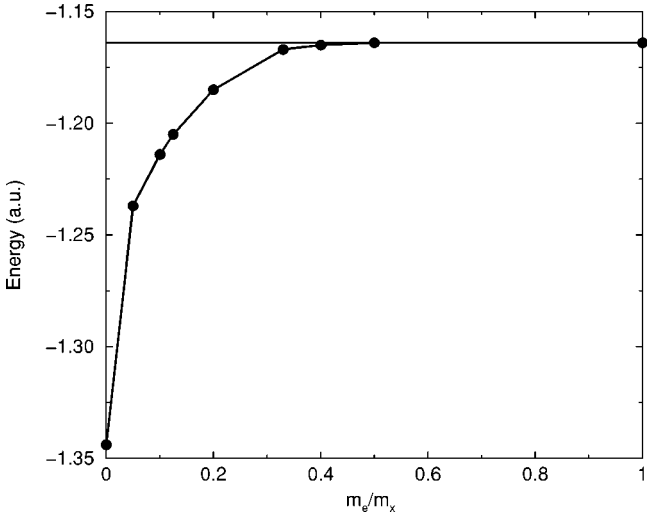

FIG. 1. Energy of $(p^+,p^+,e^-,e^-,m_{x^+})$ as a function of m_e/m_x. The dots shows the mass ratios where the energies were calculated. The horizontal line marks the H_2 threshold. Atomic units are used.

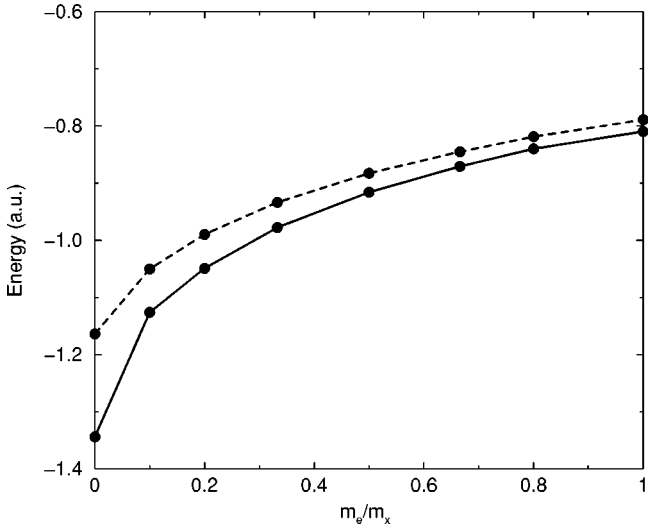

FIG. 2. Energy of $(M^+,m_{x^+},m_{x^+},e^-,e^-)$ as a function of m_e/m_x (solid line). The dashed line shows the energy of the (M^+,m_{x^+},e^-,e^-) threshold. Atomic units are used.

Figure 1 shows how the total energy varies with $\sigma = m_e/m_x$. The total energy rapidly decreases toward the energy of the H_2 threshold. The system becomes unbound around $m_x/m_e = 2.5$. This result shows that a H_2 molecule can bind a positively charged particle provided that it is at least 2.5 times heavier than an electron. So while the H_2 cannot bind a positron it forms a bound system with a positive muon μ^+ (see Table III). The properties of this system is fairly similar to that of H_3^+. In H_3^+ the three protons form an equilateral triangle, here the two protons and the muon form an isosceles triangle where the two protons are somewhat closer to each other than to the muon. Correspondingly, the electrons are slightly closer to the protons that to the muon. By decreasing mass of the x^+ the distance between the protons and x^+ increases and the electrons remain localized around the protons. Eventually beyond $m_{x^+}/m_{e^-} = 2.5$ the system dissociates into H_2 plus x^+.

The investigation of the general (M^+,M^+,m^-,m^-,m'^+) case would be too tedious but one can expect similar results. The system is bound for $m' \approx M$ but the stability is lost somewhere when the mass of m' approaches to m.

D. $(M^+,m_{x^+},m_{x^+},e^-,e^-)$

Starting again from H_3^+ changing the mass of two heavy particles at the same time (or alternatively, by adding two positive charges to H^-), yet an other stable system the $(M^+,m_{x^+},m_{x^+},e^-,e^-)$ can be created. This system can dissociate into 4+1 $[(M^+,m_{x^+},e^-,e^-)+m_{x^+}$ and $(m_{x^+},m_{x^+},e^-,e^-)+M^+]$ and 3+2 $[(M^+,m_{x^+},e^-)+(m_{x^+},e^-)$ and $(M^+,e^-)+(m_{x^+},m_{x^+},e^-)]$ subsystems. Figure 2 shows the binding energies as a function of $m_e/m_x<1$. Fixing the mass of the heavy particle (M) to be equal to the mass of the proton $M^+ = 1836.1527 m_e$ and assuming that $m_e<m_x$ the 4+1 threshold is the lowest (relevant). Examples for bound systems $(p^+,\mu^+,\mu^+,e^-,e^-)$ (Table III) or (p^+,e^+,e^+,e^-,e^-). This latter system will be investigated in detail later. Table III shows that the energy of $(p^+,\mu^+,\mu^+,e^-,e^-)$, just like that of (p^+,p^+,μ^+,e^-,e^-) is the previous example, is close to that of H_3^+. The proton and the muon are likely to form an isosceles triangle but now the like particles are further away from each other so the base of the triangle is longer than the sides in this case. The most important difference is that by changing the m_e/m_x ratio between 0 and 1 this system remains bound.

E. $(M^+,M^+,e^-,e^-,m_{x^-})$

Another Coulombic five-body system which has attracted attention is the H_2^- ion. This ion is not bound, but the $H\text{-}H^-$ potential energy curve has an attractive part beyond 3.5 a.u. This leads to speculation about the possibility of resonant states of this system. The fact that the H_2^- is not bound is a consequence of the Pauli principle. Adding a negatively charged particle x^- which has the same mass as the electron (but is distinguishable from it) to the hydrogen molecule gives a bound system. Its binding energy is about 0.096 a.u. The x^- particle can cling to the H_2 molecule because the Pauli principle does not constrain its motion.

Figure 3 shows the dependence of the binding energy on the mass ratio m_e/m_x. The threshold in this case is the energy of the (M^+,M^+,e^-,m_{x^-}) four-body system. The calculation is not trivial because the energy and structure very strongly depends on the m_x/M mass ratio. For $m_x/M \approx 0$ we practically have a hydrogen molecule. In the case of $m_x/M \approx 1$, the (M^+,M^+,m_{x^-}) system forms a Ps^+-ion-like system. Due to the heavy masses the size of this system will be very small compared to that of Ps^+ and this small (M^+,M^+,m_{x^-}) system will act as a positive charge and binds the electron. The distances between the particles in (M^+,M^+,m_{x^-}) will be very small compared to the distance between the center of mass of (M^+,M^+,m_{x^-}) and the electron. This system can bind one more electron forming $(M^+,M^+,m_{x^-},e^-,e^-)$, which is akin to H^-. One can take

μ^- in place of x^-. The (p^+,p^+,μ^-) system is bound, and as the present calculation shows the (p^+,p^+,e^+,μ^-) and the (p^+,p^+,e^-,e^-,μ^-) systems are also bound. These systems remain bound even if the masses of the heavy particles are slightly differ, that is the $(M_1^+,M_2^+,e^-,e^-,m_{x^-})$ system also bound roughly for $1/3<M_1/M_2<1$.

The accurate calculation of the stability domain for four different masses would be very difficult. This last example shows that a (t,d,μ^-) molecule can bind one or two electrons (Table III). The average distances in Table III show that both the (p^+,p^+,μ^-,e^-,e^-) and the (t^+,d^+,μ^-,e^-,e^-) system can be considered as a $[(p^+,p^+,\mu^-),e^-,e^-]$ and a $[(t^+,d^+,\mu^-),e^-,e^-]$ three body system. The (p^+,p^+,μ^-) and ions form a tiny center and act as a positive charge. Let us take the example of (p^+,p^+,μ^-). Its energy is -102.2202 a.u. The square distance between the two proton is 2.89×10^{-4} a.u. the square distance between the proton and muon is 1.81×10^{-4}. By adding one or two electrons these distances do not change so the (p^+,p^+,μ^-) subsystem remains unchanged. The binding energies of the (p^+,p^+,μ^-,e^-) and the (p^+,p^+,μ^-,e^-,e^-) systems are 0.50 a.u. and 0.027 a.u. just like that of the H atom and H^- ion.

F. $(M^+,M^-,m^+,m^-,m_{x^+})$

The next system considered is $(M^+,M^-,m^+,m^-,m_{x^+})$. The four-body system (M^+,M^-,m^+,m^-) is akin to the hydrogen-antihydrogen system and it is known to be unbound if the mass ratio m/M is smaller than 0.45. If the mass ratio m/M is small, the two heavy particle of opposite charges form a small neutral particle and the ion formed by the m^+, m^-, and m_{x^+} particle will not be able to form a bound five-body system with it.

G. (M^+,M^+,M^-,m^-,m^-)

This system can be characterized by a single mass ratio $\sigma=m/M$. If $m<M$ then the dissociation threshold is the energy of the (M^+,M^+,M^-,m^-) system. The energy of (M^+,M^+,M^-,m^-) as a function of sigma is shown in Fig. 4. The (M^+,M^+,M^-,m^-,m^-) system is bound with respect to this threshold (see Fig. 5). The (p^+,p^+,p^-,e^-,e^-) system would be an example for this case (see Table III). This example shows that a hydrogen molecule is capable to bind an antiproton forming a system similar to H^-. If $m>M$ then the relevant dissociation threshold is given by the energy of (M^+,M^+,m^-,m^-). The (M^+,M^+,M^-,m^-,m^-) system is bound in the $1<m/M<2$ interval (see Fig. 6).

There is a very interesting difference between these two cases. In the first case σ is between 0 and 1. For small σ values the three heavy M particles form a small positive charge c^+ and that composite particle binds the two ligther charges forming (c^+,m^-,m^-). The size of the composite particle is small and it behaves as a single structureless positive charge. The mechanism and the system is very similar to H^-. In the second case $1/\sigma$ varies between 0 and 1. Here in the limiting case where $1/\sigma=0$ one has two heavy m^- particles and a composite positive charge C^+ formed by (M^+,M^+,M^-). This composite particle, however, cannot be viewed as structureless in the presence of the heavier m^- particles. Energetically it is more favorable to form a $(M^+,m^-)+(M^+,m^-)$ molecule than a (C^+,m^-,m^-) system so the binding is lost somewhere between $1/\sigma=1$ and $1/\sigma=0$.

H. $(e^+,e^+,e^-,e^-,m_{x^+})$

The previous examples started from systems with two heavy positive and two light negative charges. The other end of the mass spectrum where one has two light positive and two light negative charges was also investigated. In this case the two negative particles were electrons and the two positive particles were positrons. The sign of the charge of m_x is not important in this case. For the calculations reported in this section the extra charged particle m_{x^+} is assumed to be distinguishable from the electron and the positron.

The five-body binding energy versus the m_e/m_x ratio is shown in Fig. 7. When the system has a mass ratio satisfying $m_x>m_e$, the lowest energy threshold is the energy of the $(m_{x^+},e^-,e^-,e^+)+e^+$ dissociation channel. This system is bound for all mass ratios such that $m_x>m_e$ and the binding energy of the five-particle system is seen to increase with increasing m_x.

When the mass of the distinguishable particle is lighter than that of the electron, i.e., $m_x<m_e$, the threshold energy is the energy of $Ps_2+m_{x^+}$. The binding energy decreases steadily as m_x is decreased. The system is no longer capable of forming a five-particle bound state when $m_x=0.56\times m_e$. The structure of the $(e^+,e^+,e^-,e^-,m_{x^+})$ system increasingly resembles the structure of a system best described as $m_{x^+}Ps_2$ as the $m_x\rightarrow0.56m_e$ dissociation limit is approached.

These systems are electronically stable but annihilation between electron-positron pairs is possible. The most likely annihilation process is the 2γ process which results in two γ rays being emitted. The matrix element for this process is proportional to the probability of finding an electron and a positron at the same position in a spin singlet state [see Eq. (21) in Ref. [15]]. The annihilation rate for the 2γ decay summed over all possible final states [31–33] is

$$\Gamma=4\pi c\alpha^4a_0^2N_e\langle\Psi|\hat{O}^s\delta(\mathbf{r}_e-\mathbf{r}_p)|\Psi\rangle. \tag{8}$$

The symbols in front of the integral sign represent the usual quantities in atomic physics, c is the speed of light, α is the fine structure constant. The operator $\hat{O}^s$ is a projection operator that selects spin-0 combinations of the electron and the positron. The $\mathbf{r}_e$ and $\mathbf{r}_p$ vectors are the positions of an electron and a positron.

I. The e^+PsH system.

The e^+PsH system (p,e^-,e^-,e^+,e^+) corresponds to a model with $m_x=m_p$ and it is clear from Fig. 7 that this system is bound. The system is stable against dissociation into the $H+Ps^+$, $p+Ps_2$, or the $PsH+e^+$ channels. The lowest threshold is the energy of the $PsH+e^+$ channel (-0.789197 a.u.) and e^+PsH is bound by 0.021050 Hartree

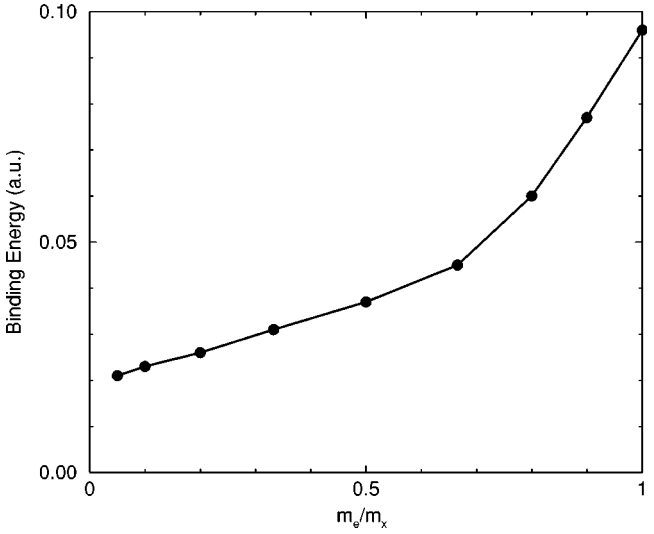

FIG. 3. Binding energy of $(p^+,p^+,e^-,e^-,m_{x^-})$ as a function of m_e/m_x. Atomic units are used.

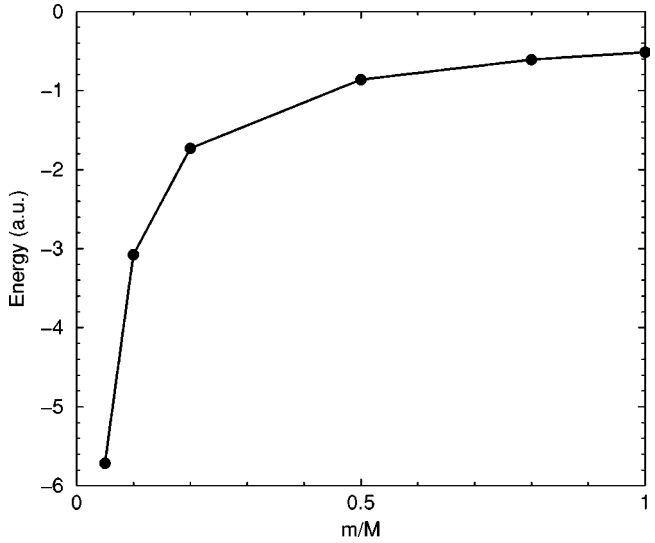

FIG. 4. Energy of (M^+,M^+,M^-,m^-) as a function of m/M for $m<M$. Atomic units are used. The figure corresponds to $m=m_e$, the energy unit should be multiplied by m/m_e for other choice of m.

with respect to this threshold. The e^+PsH system has been investigated more carefully since it represents the simplest stable coulombic system that can be formed with two positrons (apart from Ps_2 and the antimatter analogues of PsH).

Some of the properties of e^+PsH are listed in Table IV. It is intriguing to compare the relative distances between the particles in PsH and e^+PsH. The electron-nucleus or electron-electron relative distances are almost the same in the two systems and indicates that the electron charge distribution is not altered by the addition of the second positron. This would suggest that the second positron is likely to be found at comparatively large distances from the nucleus since an additional positron located outside the electronic charge cloud could not have much effect on the electron charge distributions. This is confirmed by the fact that the average nucleus-positron distance of e^+PsH is larger than that of PsH. Furthermore, the annihilation rate of e^+PsH, 2.74×10^9 s^{-1} is only 10% larger than the PsH annihilation rate. This is also consistent with a model consisting of the additional positron orbiting the PsH subsystem at a relatively large distance from the nucleus.

J. The Li^+Ps_2 and Na^+Ps_2 systems

The stability of the $(e^+,e^+,e^-,e^-,m_{x^+})$ system for such a wide variety of m_x suggests that other singly charged objects could also bind two electrons and two positrons. The lithium cation, Li^+ can substitute for m_x and it has been previously shown that this system can form an electronically stable complex [9,13]. This system is denoted as Li^+Ps_2 since this seems to give the best intuitive description of the structure [13].

Although the Li^+Ps_2 system consists of seven particles, a triply charged nucleus, four electrons and two positrons, for all practical purposes the system is best described as a five particle system. Two of the electrons are tightly bound to the Li^{3+} nucleus (with binding energies of about 100 eV) and therefore to a good approximation the Li^+ core can be regarded as a single entity.

Calculations for the Li^+Ps_2 system have been performed within the fixed core SVM. Although a fully *ab initio* seven particle calculation has been carried out upon the Li^+Ps_2 system, the calculation was extremely tedious and the wave function was far from converged [9,13]. The fixed core SVM model with only five active particles was able to generate a model energy that was much closer to convergence. The present results represent a continuation of the calculation reported in Ref. [13] and the details of the model Hamiltonian were unchanged. The basis dimension has been enlarged and further optimization of the energy was carried out. The results of this improved calculation are presented in Table IV. The binding energy only changed by 2% and other expecta-

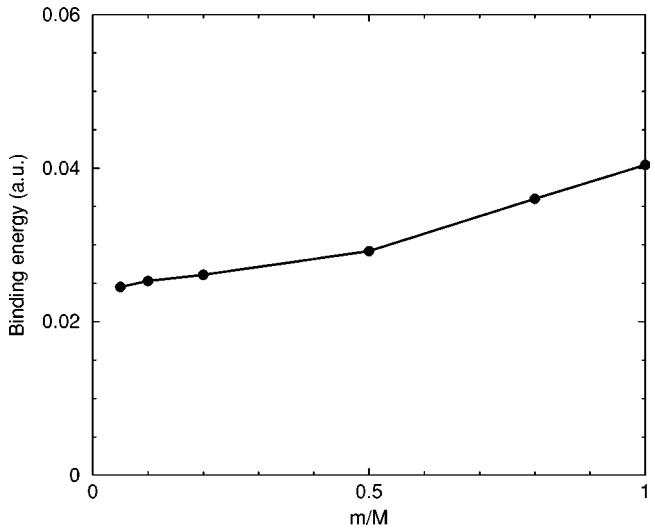

FIG. 5. Binding energy of (M^+,M^+,M^-,m^-,m^-) as a function of m/M for $m<M$. Atomic units are used and $m=m_e$ is assumed. See the caption of Fig. 4 as well.

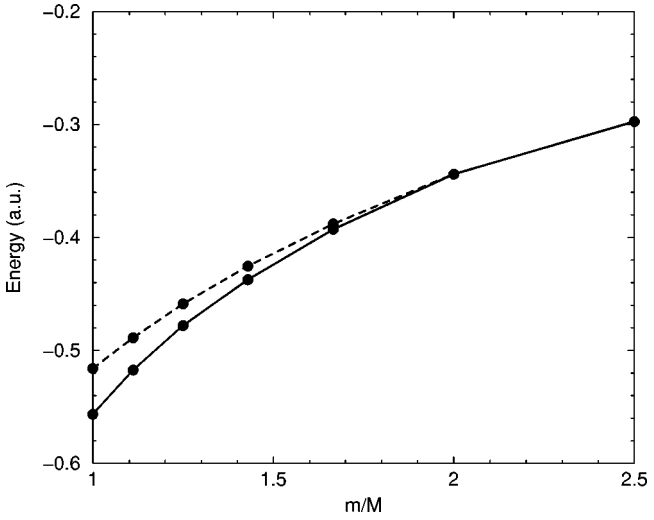

FIG. 6. Energy of (M^+,M^+,M^-,m^-,m^-) as a function of m/M for $m>M$ (solid line). The dashed line shows the energy of the (M^+,M^+,m^-,m^-) threshold. Atomic units are used and $m=m_e$ is assumed. See the caption of Fig. 4 as well.

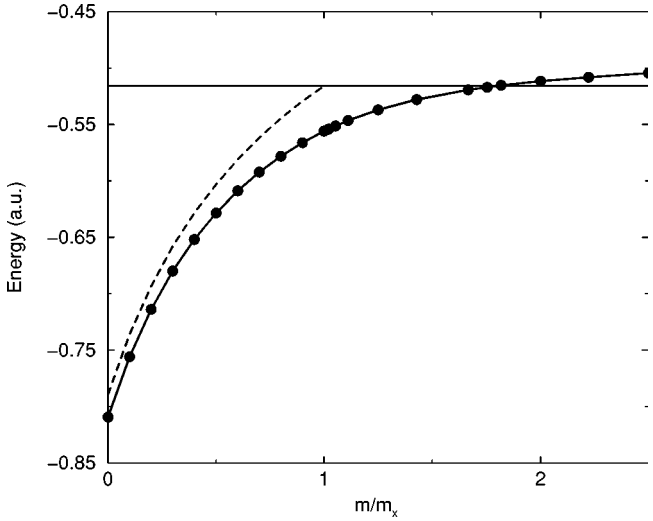

FIG. 7. Energy of $(m_{x^+},m^+,m^+,m^-,m^-)$ (solid line). The horizontal line shows the energy of the Ps_2 atom, the dashed line is the energy of the (m_{x^+},m^+,m^-,m^-) threshold. Atomic units are used and $m=m_e$ is assumed.

tion values were similarly unaffected. The present results should be regarded as superseding earlier values.

The interparticle expectation values listed in Table IV justify the usage of Li^+Ps_2 to denote this system. All of the expectation values are within 5% of the expectation values of the Ps_2 ground state.

The lithium atom is not the only alkali atom that can bind two positrons and an additional electrons. The next obvious candidate is sodium and it has previously been shown that the system best described as Na^+Ps_2 is electronically stable [13] with a binding energy of about 0.0057 Hartree. While this binding energy was sufficiently large to clearly indicate binding, the wave function was far from converged. Once again, the results reported in Table IV for Na^+Ps_2 represent a continuation of the calculations reported in Ref. [13]. Although the binding energy of Na^+Ps_2 has increased by almost 10% to 0.0063 Hartree, most of the expectation values have hardly changed from the values reported in Ref. [13]. The interparticle radial expectation values listed in Table IV agree with those of Ps_2 to within 2% and confirm that the best intuitive description is as a Ps_2 molecule bound to the Na^+ core.

The electronic and positronic structure of Li^+Ps_2 and Na^+Ps_2 and the existence of what appears to be a Ps_2 subsystem can explained in terms of energetics and the structure of the $(e^+,e^+,e^-,e^-,m_{x^+})$ system. When the mass of m_{x^+} is changed, one effectively changes the binding energy of the (m_{x^+},e^-) subsystem. Systems with small m_{x^+} are characterized by a well defined Ps_2 subsystem since the mass scaled interaction potential between the m_{x^+} and the e^- is not strong enough to disrupt the Ps_2 subsystem. In Table IV, results are presented for $m_{x^+}=0.7m_e$. The $(0.7m_{e^+},e^-)$ subsystem has a binding energy of 0.20588 Hartree. Since the binding energy of the $(0.7m_{e^+},e^-)$ subsystem is roughly similar to the binding energies of the (Li^+,e^-) (0.198 Hartree) and (Na^+,e^-) (0.188 Hartree) alkali atoms it can be regarded as an analogue of an alkali atom. An earlier work on the simpler (m_{x^+},e^-,e^+) system was able to explain positron binding to group I and IB atoms by using the energy of the (m_{x^+},e^-) subsystem as the characteristic variable [34]. The structure of the $(0.7m_{e^+},e^+,e^+,e^-,e^-)$ system shows obvious similarities to Na^+Ps_2 and Li^+Ps_2 and the binding energy and annihilation rate of the $(0.7m_{e^+},e^+,e^+,e^-,e^-)$ system are close to that of Li^+Ps_2. Also the interparticle expectation values generally lie within 5% of Li^+Ps_2 and Na^+Ps_2.

However, when m_{x^+} increases, the Ps_2 cluster undergoes obvious distortions. The $(1.0m_{e^+},e^+,e^+,e^-,e^-)$ system has an annihilation rate that is 25% smaller than that of Ps_2. In addition, $\langle r_{e^-e^-}\rangle$ has gotten smaller as the the electrons have started to approach m_{x^+}. There has been an increase in $\langle r_{e^+e^+}\rangle$ and $\langle r_{e^+e^-}\rangle$ for the larger value of m_{x^+}. In the limiting case, $m_{x^+}=\infty$, the system collapses to a positron orbiting PsH.

The crucial mass ratio of $(e^+,e^+,e^-,e^-,m_{x^+})$ occurs when $m_x=0.56\times m_e$. This corresponds to an energy for the (m_{x^+},e^-) subsystem of 0.1795 Hartree. Since the heavier alkali atoms (K, Rb, Cs) all have binding energies smaller than this, one is lead to the conclusion that Ps_2 binding to the heavier alkali ions cannot be guaranteed.

K. Miscellaneous systems

Systems of unit charge particles have been considered so far. One can extend this study for atoms or molecules consisting multiple charged heavy centers. Other examples of a five-body Coulomb systems consist of the lithium hydride cation, LiH^+ and positronic lithium e^+Li [10]. The stability of these systems with the two different mass extremes (i.e., e^+ to p) suggests stability for all possible masses in between; therefore the system μ^+Li is probably stable.

TABLE IV. Properties of the family of systems consisting of (e^+,e^+,e^-,e^-) and another positive singly charged object (x^+). The basis size is denoted by K. All quantities are given in atomic units. Properties of PsH and Ps_2 are shown for the sake of comparison. The masses of the proton, and Li and Na nucleii are assumed to be infinite.

Property	e^+PsH^∞	Li^+Ps_2	Na^+Ps_2	$m_x=m_e$	$m_x=0.7m_e$	PsH^∞	Ps_2
K	850	660	780	600	400	1000	1000
$\langle V\rangle/\langle T\rangle$	1.999980			1.999938	1.999999	1.999999	
E	−0.810247	−0.529408	−0.522319	−0.556489	−0.528733	−0.789197	−0.516004
ε	0.021050	0.013404	0.006315	0.040485	0.012129		
$\langle r_{x^+e^-}\rangle$	2.281	6.458	7.772	4.987	7.344	2.312	
$\langle r_{x^+e^+}\rangle$	4.944	7.397	8.486	6.598	8.371	3.662	
$\langle r_{e^-e^-}\rangle$	3.507	5.871	5.977	5.482	5.767	3.575	6.033
$\langle r_{e^+e^+}\rangle$	7.382	6.261	6.158	6.599	6.295		6.033
$\langle r_{e^+e^-}\rangle$	4.966	4.706	4.648	4.965	4.765	3.480	4.487
Γ	2.744	3.881	4.044	3.247	3.717	2.470	4.470

IV. SUMMARY

Several intriguing few-particle systems have been studied in this paper. Some of these calculations may help to test other techniques, since the calculation of the binding energies of these exotic systems is a stringent test of the efficiency and accuracy of any few-body approach.

There are a large variety of systems that can be formed by five unit charge particles. To calculate the stability domain as a function of the masses of particles would be quite complicated task. We have tried to highlight a few different possibilities in this paper. The first, rather trivial observation is that the total charge of a bound five particle system must be ± 1, that is, we did not find any bound system with $(+,-,-,-,-)$ charges. Another simple rule is that if the particles are distinguishable and their masses are equal or nearly equal then they form a bound system. The main forces to determine the stability domains are the Pauli principle and the mass ratios. The Pauli principle severely restricts the available configuration space so for example a five particle system formed by (m^+,m^+,m^+,m^-,m^-)-like indistinguishable particles is unbound and the stability domain of the (M^+,M^+,M^+,m^-,m^-)-type systems is very limited. This latter system is only stable if the mass difference is so large that the three slowly moving positive charges can be adiabatically treated, that is they are practically distinguishable.

Another group of stable combinations can be defined when three charges, e.g., $(+,+,-)$, form a charged composite particle, and the two remaining particles does not polarize or disturb this subsystem. In this case we have a quasi three-particle system and the stability of this system follows from the stability of the corresponding well studied three-particle systems. Examples are the (p^+,p^+,p^-), (p^+,p^+,μ^-), or (t^+,d^+,μ^-) plus two lighter particle (e.g., electron) systems. These systems are all behave as the H^- ion and although we treated them as five particle systems one can equivalently and accurately solve these cases as three-body problems. The region where the $(+,+,-)$ system can be considered as a structureless single charge very much depends on the mass ratios of the constituents and the two ''valence'' particle in the five-body system. For example, one cannot simplify the five-body system to a H_2^+ or $Ps^+=(e^+,e^+,e^-)$-like three-body system because the $(+,+,-)$ subsystem will not behave as a point charge in the presence of heavier particles.

A group of stable systems can be generated by changing the mass of some of the constituent of the H_3^+ ion. This system remains stable, for example, if the mass of two protons is continuously decreased till their mass is equal or even a little lighter then the electron mass. So just like the H_2 and Ps_2, the H_3^+ and (p^+e^+,e^+,e^-,e^-) can also be connected by a changing the mass of two positive charges.

The present results for the systems with two positrons represent an improvement on those calculated previously. The fact that the $(e^+,e^+,e^-,e^-,m_{x^+})$ system is not stable for $m_x<0.56\times m_e$ has implications for the binding of Ps_2 to the alkali cations. The ability of the heavier alkali cations (i.e., K^+, Rb^+, and Cs^+) to bind Ps_2 is by no means certain.

There is a very strong interest in excitonic complexes (systems of electrons and holes) in semiconductors. The main motivation of this research is that light emitted by the electron-hole recombinations in these systems can be used to make better lasers, photodiodes, etc. Some of the system studied in this paper may have direct relevance to that research. The predicted bound state of $(PsHe^+)$ and $(M^+,m_{x^+},m_{x^+},e^-,e^-)$, for example, suggests that a biexciton (bound state of two electrons and two holes) can form a bound state with a donor (a single fixed positive charge present in some semiconductors). Similar example is a system of two electrons and three holes (e,e,h,h,h) or possible a (e,e,h,h,h') system where one of the hole is different from the other two.

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