Atomic and molecular three-body ions with positively charged muons

Alexei M. Frolov
Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6
(Received 25 August 2003; published 17 February 2004)

The properties of some atomic and molecular three-body ions which contain positively charged muons μ^+ are considered. In particular, the ground states in the muonium ion Mu^- (or $\mu^+e^-e^-$) and muon-hydrogen molecular $p^+\mu^+e^-$,$d^+\mu^+e^-$,$t^+\mu^+e^-$ ions are studied in details. The energies of these systems have been determined to high accuracy: $E(Mu^-)=-0.525\,054\,806\,243\,526\,329\,29$ a.u., $E(p^+\mu^+e^-)=-0.589\,903\,785\,389\,587\,726\,1$ a.u., $E(d^+\mu^+e^-)=-0.590\,255\,352\,152\,246\,417\,7$ a.u., and $E(t^+\mu^+e^-)=-0.590\,374\,098\,892\,682\,888\,0$ a.u. The interparticle distances, δ functions, two-particle cusps, and some other bound-state properties are also presented for all considered systems. The photodetachment of the Mu^- ion is briefly discussed.

DOI: 10.1103/PhysRevA.69.022505 PACS number(s): 36.10.Dr, 31.15.Ar

The ability of positively charged muons μ^+ to form various atomic and molecular structures with electrons and hydrogen nuclei has been well known since the middle of the 1950s (see, e.g., [1] and references therein). In this study we want to consider a number of atomic and molecular three-body ions which contain positively charged muons μ^+. The muon μ^+ is considered below as a point particle with charge $q_{\mu^+}=+e$ and mass $m_{\mu^+}=206.768\,262m_e$, where e is the proton charge and m_e is the electron mass. In particular, the main goal of this study is to determine the energies and bound-state properties of the muonium ion Mu^- (or $\mu^+e^-e^-$) and $p^+\mu^+e^-$, $d^+\mu^+e^-$, and $t^+\mu^+e^-$ muon-molecular ions. Here and below, p^+, d^+, and t^+ are the nuclei of hydrogen (protium), deuterium, and tritium, respectively. Also, everywhere in this study e^- designates the electron—i.e., $q_{e^-}=-e$.

Note that the molecular $p^+\mu^+e^-$, $d^+\mu^+e^-$, and $t^+\mu^+e^-$ ions can be considered as the muon-substituted H_2^+ family of molecular ions. These ions have been studied in a number of earlier works [2–4]. In general, these muon-molecular ions are of great interest for theoretical studies, since they can be considered as semiadiabatic (or soft-adiabatic) three-body systems. In fact, it has already been shown in [2–4] that the $p^+\mu^+e^-$, $d^+\mu^+e^-$, and $t^+\mu^+e^-$ molecular ions are less adiabatic systems than the hydrogen molecular ions HD^+, HT^+, and DT^+. This directly related to the fact that the muon mass $m_\mu=206.768\,262m_e$ is ≈ 9 times smaller than the corresponding proton mass $m_p=1836.152\,701m_e$ [5]. Therefore, one can also expect that the isotope effects in the muon-hydrogen molecular ions are significantly larger than it can be found in the hydrogen molecular ions HD^+, HT^+, and DT^+.

To study the bound-state spectra and isotope effects in the $p^+\mu^+e^-$, $d^+\mu^+e^-$, and $t^+\mu^+e^-$ molecular ions both the nonadiabatic and adiabatic methods can be applied. However, in [2,3] it was found that the fully adiabatic (or Born-Oppenheimer [6]) methods developed for the hydrogen molecular $^\infty H_2^+$ ion cannot provide even sufficient accuracy for the muon-hydrogen molecular ions. The same problem can be found for the muonium ion Mu^- (or $\mu^+e^-e^-$), which was considered earlier in [7–11]. The adiabatic methods which can very accurately reproduce the total energy of the $^\infty H^-$ ion are not sufficiently accurate in applications to the Mu^- ion. The reason is obvious, since the motion of the "nucleus" in the Mu^- ion cannot be neglected even in the first approximation. Finally, the perturbation methods produce significant numerical errors in applications to the Mu^- ion.

To determine the ground bound states in the Mu^- and $p^+\mu^+e^-$, $d^+\mu^+e^-$, and $t^+\mu^+e^-$ ions to very high accuracy in this study we used the approach developed in [12]. The approach developed in [12] is a highly accurate, nonadiabatic, variational method which can be applied to various three-body systems, including all known adiabatic three-body ions. Note that the muonium ion Mu^- is the two-electron three-body system with unit charges and heavy central particle μ^+. As is well known (see, e.g., [7]) such ions have only one bound (ground) $^1S(L=0)$ state. In contrast with this, the energy spectrum of each of the muon-hydrogen molecular ions $p^+\mu^+e^-$, $d^+\mu^+e^-$, and $t^+\mu^+e^-$ contains a number of bound states. However, in this study we shall restrict ourselves to consideration of the ground $S(L=0)$ states only.

Below all considered ions are assumed to be the nonrelativistic Coulomb three-body systems which contain the three-point particles with charges q_1,q_2,q_3 and masses m_1,m_2,m_3. The nonrelativistic approximation means that $|\mathbf{p}_i|\ll m_ic$, where $i=1,2,3$. In general, the nonrelativistic consideration is accurate only if all electron-muon and electron-nucleus distances r_{ij} exceed the corresponding Compton length $\Lambda=\hbar/m_ec=\alpha a_0\approx 3.861\,593\,228\times 10^{-11}$ cm [5]. Here and below $r_{ij}=r_{ji}=|\mathbf{r}_i-\mathbf{r}_j|$ and $(ij)=(ji)=(32)$, (31), and (21).

In atomic units $\hbar=1$, $m_e=1$, and $e=1$, the nonrelativistic Hamiltonian H for an arbitrary Coulomb three-body system can be written in the form

$$H=-\frac{1}{2m_1}\nabla_1^2-\frac{1}{2m_2}\nabla_2^2-\frac{1}{2m_3}\nabla_3^2+\frac{q_3q_2}{r_{32}}+\frac{q_3q_1}{r_{31}}+\frac{q_2q_1}{r_{21}}, \tag{1}$$

where m_1,m_2,m_3 and q_1,q_2,q_3 are the particle masses and charges. In the present case, for the Mu^- ion the subscripts 1 and 2 mean electrons, while the subscript 3 designates the

positively charged muon μ^+. In the muon-hydrogen ions $p^+\mu^+e^-$, $d^+\mu^+e^-$, and $t^+\mu^+e^-$ the subscript 2 always stands for the hydrogen nucleus p^+,d^+,t^+, while the subscripts 1 and 3 mean the muon μ^+ and electron e^-, respectively. Our present goal is to determine the solutions of the corresponding Schrödinger equation for the bound-state spectra $H\Psi=E\Psi$, where $E<0$. In this study we apply the approach [12] which allows one to obtain such solutions to arbitrarily high, in principle, accuracy.

The approach developed in [12] is based on the use of exponential variational expansion in perimetric coordinates u_1, u_2, and u_3 which can be written in the form [12]

$$\Psi=\frac{1}{\sqrt{2}}(1+\kappa\hat{P}_{21})\sum_{i=1}^{N} C_i\exp(-\alpha_i u_1-\beta_i u_2 - \gamma_i u_3)\exp(\imath\cdot\delta_i u_1+\imath\cdot e_i u_2+\imath\cdot f_i u_3), \quad (2)$$

where C_i $(i=1,\ldots,N)$ are the linear (or variational) parameters, while α_i, β_i, γ_i, δ_i, e_i, and f_i are the nonlinear parameters $(i=1,\ldots,N)$. The choice of these nonlinear parameters is discussed below. The three perimetric coordinates u_1, u_2, and u_3 are truly independent and always positive—i.e., $0\leqslant u_i<+\infty$ for $i=1,2,3$. These three perimetric coordinates are simply related to the three scalar relative (or interparticle) coordinates $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$:

$$u_i=\frac{1}{2}(r_{ik}+r_{ij}-r_{jk}),\quad r_{ij}=u_i+u_j, \quad (3)$$

where $r_{ij}=r_{ji}$ and $i\neq j\neq k=(1,2,3)$ [12]. In Eq. (2) the operator $\hat{P}_{21}$ is the permutation of the two identical (1 and 2) particles (electrons) in the symmetric Mu^- ion. For all nonsymmetric muon-hydrogen ions the factor κ equals zero, while for the ground $S(L=0)$ state in the Mu^- ion we have $\kappa=+1$. In fact, the variational expansion, Eq. (2), corresponds to the case $L=0$, where L is the total angular momentum of the considered system. The generalization of Eq. (2) to the case of arbitrary L can be found, e.g, in [12].

In fact, in actual computations, the highly accurate trial functions Ψ can be produced only by using a complete optimization of the nonlinear parameters α_i, β_i, γ_i, δ_i, e_i, and f_i $(i=1,\ldots,N)$ in Eq. (2). Below, the choice of the nonlinear parameters in Eq. (2) proceeds as follows [12]. Let i be the number (or index) of the basis function in Eq. (2) $(1\leqslant i\leqslant N)$ and $k=\mathrm{mod}(i,3)+1$, where $\mathrm{mod}(i,3)$ designates modular division (i.e., an integer remainder after division of i by 3). The number 3 corresponds to the three-box version which is used in our present calculations. The same version was used successfully in variational calculations of various three-body systems [12]. In this version the parameters α_i, β_i, γ_i, δ_i, e_i, and f_i are chosen quasirandomly from the six intervals $[A_1^{(k)},A_2^{(k)}]$, $[B_1^{(k)},B_2^{(k)}]$, $[G_1^{(k)},G_2^{(k)}]$, $[D_1^{(k)},D_2^{(k)}]$, $[E_1^{(k)},E_2^{(k)}]$, and $[F_1^{(k)},F_2^{(k)}]$:

$$\alpha_i=\langle\langle \tfrac{1}{2}\, i(i+1)\sqrt{2}\rangle\rangle(A_2^{(k)}-A_1^{(k)})+A_1^{(k)},$$

$$\beta_i\langle\langle \tfrac{1}{2}\, i(i+1)\sqrt{3}\rangle\rangle(B_2^{(k)}-B_1^{(k)})+B_1^{(k)},$$

$$\gamma_i=\langle\langle \tfrac{1}{2}\, i(i+1)\sqrt{5}\rangle\rangle(G_2^{(k)}-G_1^{(k)})+G_1^{(k)},$$

$$\delta_i=\langle\langle \tfrac{1}{2}\, i(i+1)\sqrt{7}\rangle\rangle(D_2^{(k)}-D_1^{(k)})+D_1^{(k)},$$

$$e_i=\langle\langle \tfrac{1}{2}\, i(i+1)\sqrt{11}\rangle\rangle(E_2^{(k)}-E_1^{(k)})+E_1^{(k)},$$

$$f_i=\langle\langle \tfrac{1}{2}\, i(i+1)\sqrt{13}\rangle\rangle(F_2^{(k)}-F_1^{(k)})+F_1^{(k)},$$

where $k=1,2,3$ and the symbol $\langle\langle\cdots\rangle\rangle$ designates the fractional part of a real number. As easy to understand the boundaries of six mentioned intervals—i.e., $A_1^{(k)},A_2^{(k)},\ldots,F_1^{(k)},F_2^{(k)}$—are the actual nonlinear parameters of the method. The parameters in the exponents in Eq. (2) (i.e., $\alpha_i,\beta_i,\gamma_i,\delta_i,e_i,f_i$, $i=1,\ldots,N$) are chosen quasirandomly and not varied in calculations; i.e., they are not actual (i.e., varied) nonlinear parameters of the method. In fact, these parameters are usually called the lattice points of the variational expansion, Eq. (2), rather than the nonlinear parameters. Note that the total number of actual nonlinear parameters used in this stage of the procedure equals 36 $(2\times6\times3$ for the considered three-box version).

The second stage of our procedure [12] is essentially a scaling of the lattice points chosen in the first step. The scaling itself is performed as follows. The families of the parameters α_i, β_i, γ_i, δ_i, e_i, and f_i (which correspond to the same k) are multiplied by the positive factor λ_k $(k=1,2,3)$. Then, this parameter λ_k is also varied. The total number of such additional parameters equals 3 (3×1). Also, one additional variational parameter is used to perform a scaling for all lattice points in Eq. (2). Finally, this method produces a properly balanced wave function which represents the considered bound state very accurately. Note that the total number of actual nonlinear parameters in this version of the procedure equals 40. These 40 actual nonlinear parameters were optimized in calculations with a relatively small number $(N\leqslant1000)$ of basis functions used in Eq. (2). In fact, this procedure has been used for the $p^+\mu^+e^-$, $d^+\mu^+e^-$, and $t^+\mu^+e^-$ ions. For the Mu^- ion it was found that the use of complex parameters decreases the overall efficiency of our method. Therefore, for the Mu^- ion we assumed that $\delta_i=e_i=f_i=0$ for $i=1,\ldots,N$. In this case another version of the procedure [12] has been used. This version contains only 28 actual nonlinear parameters [12].

The total ground-state energies of the considered ions (computed in atomic units) are presented in Tables I and II. Table I contains the total energies determined for the muon-hydrogen $p^+\mu^+e^-$, $d^+\mu^+e^-$, and $t^+\mu^+e^-$ ions. Table II contains the total energies obtained for the Mu^- ion. For the Mu^- ion the results from two different series of calculations (with two different sets of nonlinear parameters) are shown. The masses of muon μ^+ and proton p^+ are presented above, while for the tritium and deuterium masses we used the values $m_t=5496.921\,58m_e$ and $m_d=3670.483\,014m_e$ [5]. As follows from Tables I and II our results for the Mu^-, $p^+\mu^+e^-$, $d^+\mu^+e^-$, and $t^+\mu^+e^-$ ions are significantly more accurate than the results obtained for the systems considered in earlier studies, including our works [4,11]. As we mentioned above in computations of the Mu^-

TABLE I. The total energies E (in atomic units $m_e=1$, $\hbar=1$, $e=1$) for the ground states of the muon-hydrogen $p^+\mu^+e^-$, $d^+\mu^+e^-$, and $t^+\mu^+e^-$ ions. N designates the total number of basis functions used in Eq. (2). $E_p^{(a)}$ are the best variational energies known from earlier calculations.

N	$p^+\mu^+e^-$	$d^+\mu^+e^-$	$t^+\mu^+e^-$
2000	−0.5899037853895875798	−0.5902553521522462749	−0.5903740988926827463
2600	−0.5899037853895877109	−0.5902553521522464031	−0.5903740988926828736
3000	−0.5899037853895877230	−0.5902553521522464146	−0.5903740988926828850
3500	−0.5899037853895877261	−0.5902553521522464177	−0.5903740988926828880
$E_p^{(a)}$ [4]	−0.589903728	−0.590255253	−0.59037390
$E_p^{(a)}$ [3]	−0.589904	−0.590225	−0.590374

ion all δ_i, e_i, and f_i parameters ($i=1,\ldots,N$) in Eq. (2) were chosen to be equal to zero identically. For the muon-hydrogen $p^+\mu^+e^-$, $d^+\mu^+e^-$, and $t^+\mu^+e^-$ ions all $6\times N$ nonlinear parameters in Eq. (2) were used. Note that all our present calculations were performed by using MPFUN, a multiprecision FORTRAN-90 computation package developed by Bailey [13,14].

Table III contains some bound-state properties (in atomic units) for the Mu^- and $p^+\mu^+e^-$, $d^+\mu^+e^-$, and $t^+\mu^+e^-$ ions. The properties shown include the expectation values of linear distances r_{ij} and its various powers $r_{ij}^{-1}, r_{ij}^2, r_{ij}^3, r_{ij}^4$ [$(ij)=(ji)=(32),(31),(21)$]. Also, the two- and three-particle δ functions and two-particle cusps are presented on Table III. The notation δ_{31}, δ_{21}, and δ_{321} stands for the two- and three-particle Dirac delta functions, respectively. The two-body cusp ratios are determined in a traditional manner [15,16]:

$$\nu_{ij}=\frac{\left\langle \delta(\mathbf{r}_{ij})\dfrac{\partial}{\partial r_{ij}}\right\rangle}{\langle\delta(\mathbf{r}_{ij})\rangle}, \tag{4}$$

where $\delta_{ij}=\delta(\mathbf{r}_{ij})$ is the appropriate Dirac delta function and $(ij)=(32)$, (31), and (21). The exact value of ν_{ij} equals

$$\nu_{ij}=q_iq_j\frac{m_im_j}{m_i+m_j}, \tag{5}$$

where q_i and q_j are the charges and m_i and m_j the masses of the particles. For the two- and three-particle cusps only the best results are given in Table III. For all other bound-state properties only stable figures from calculations with the higher N are presented in this table.

The expectation values of the two interparticle cosine functions are determined traditionally:

$$\tau_{ij}=\langle\cos(\mathbf{r}_{ik}\wedge\mathbf{r}_{jk})\rangle=\left\langle\frac{\mathbf{r}_{ik}\cdot\mathbf{r}_{jk}}{r_{ik}r_{jk}}\right\rangle, \tag{6}$$

where $(i,j,k)=(1,2,3)$. The quantity $\langle f\rangle$ is expressed in terms of the relative coordinates (r_{31},r_{32},r_{21}) or perimetric coordinates (u_1,u_2,u_3) [where $u_i=\frac{1}{2}(r_{ij}+r_{ik}-r_{jk})$ and $(i,j,k)=(1,2,3)$] as follows:

$$\langle f\rangle=\left\langle\psi\left|\frac{u_1}{r_{32}}\frac{u_2}{r_{31}}\frac{u_3}{r_{21}}\right|\psi\right\rangle$$
$$=\int\int\int|\psi(u_1,u_2,u_3)|^2u_1u_2u_3du_1du_2du_3. \tag{7}$$

The value $\langle f\rangle$ can be calculated directly or by applying τ_{ij}. Their coincidence indicates that the $\tau_{21},\tau_{32},\tau_{31}$ and $\langle f\rangle$ expectation values have been computed correctly. The equalities

$$\tau_{21}+\tau_{32}+\tau_{31}=1+4\langle f\rangle \tag{8}$$

hold for an arbitrary three-body system. For the symmetric Mu^- ion we have $\tau_{32}=\tau_{31}$.

The virial factor η is determined as follows:

TABLE II. The total energies E (in atomic units $m_e=1$, $\hbar=1$, $e=1$) for the ground state of the Mu^- ion ($\mu^+e^-e^-$) computed for two different sets of nonlinear parameters. N designates the total number of basis functions used in Eq. (2). $E_p^{(a)}$ are the best variational energies known from earlier calculations.

N	E	E
2000	−0.525 054 806 243 526 328 74	−0.525 054 806 243 526 328 53
2500	−0.525 054 806 243 526 329 04	−0.525 054 806 243 526 328 90
3000	−0.525 054 806 243 526 329 19	−0.525 054 806 243 526 329 09
3500	−0.525 054 806 243 526 329 26	−0.525 054 806 243 526 329 19
3800	−0.525 054 806 243 526 329 29	−0.525 054 806 243 526 329 25
$E_p^{(a)}$	−0.525 054 806 243 451 [11]	

TABLE III. The expectation values $\langle X_{ij}\rangle$ in atomic units ($m_e=1$, $\hbar=1$, $e=1$) of some properties for the ground states of the Mu^- ion. The notation 1 and 2 designates the two electrons, while 3 stands for the muon (μ^+).

$\langle X_{ij}\rangle$	Value	$\langle X_{ij}\rangle$	Value
$\langle r_{21}^{-1}\rangle$	0.30919938897549610	$\langle r_{31}^{-1}\rangle$	0.67965450073127438
$\langle r_{21}\rangle$	4.43928009200701804	$\langle r_{21}^2\rangle$	25.5145363622570757
$\langle r_{31}\rangle$	2.7271829824915462	$\langle r_{31}^2\rangle$	12.074193983236396
$\langle r_{21}^3\rangle$	184.0773129096977	$\langle r_{31}^3\rangle$	77.63368972657732
$\langle r_{21}^4\rangle$	1632.23450788031	$\langle r_{31}^4\rangle$	663.917823028855
$\langle (r_{31}r_{32})^{-1}\rangle$	0.3782270843836621	$\langle \mathbf{r}_{31}\cdot\mathbf{r}_{32}\rangle$	−0.6830741978921419
$\langle (r_{31}r_{21})^{-1}\rangle$	0.250177168395846	$\langle \mathbf{r}_{31}\cdot\mathbf{r}_{21}\rangle$	12.7572681811285379
$\langle (r_{32}r_{31}r_{21})^{-1}\rangle$	0.19728255714621		
$\langle -\frac{1}{2}\nabla_1^2\rangle$	0.261186844278620267	$\langle \nabla_1\cdot\nabla_2\rangle$	0.0319963556535331443
$\langle -\frac{1}{2}\nabla_3^2\rangle$	0.554370044210773683	$\langle \nabla 1\cdot\nabla_3\rangle$	−0.554370044210773683
τ_{31}	0.649201369272202025	$\langle \delta_{31}\rangle$	0.1621506815
τ_{21}	−0.103813878094673723	$\langle \delta_{21}\rangle$	2.6816805×10^{-3}
$\langle f\rangle$	0.048647215112432582	$\langle \delta_{321}\rangle$	4.8441×10^{-3}
ν_{31}	−0.99518694698	ν_{21}	5.00000090121
ν_{31} [a]	−0.99518694534779330252	ν_{21} [a]	0.5
η	5.3114×10^{-19}	ε [b] (eV)	−0.7472612251974200943

[a]The expected cusp value ν_{ij} determined from Eq. (5).

[b]The corresponding conversion factor is assumed to be equal 27.211 3961 (eV/a.u.) exactly.

$$\eta=\left|1+\frac{\langle V\rangle}{2\langle T\rangle}\right|, \tag{9}$$

where $\langle T\rangle$ and $\langle V\rangle$ are the expectation values of the kinetic and potential energies, respectively. The deviation of the factor η from zero indicates, in principle, the quality of the wave function used. The appropriate binding energies ε are given in eV (the conversion factor is 1 a.u. $=27.211\,396\,1$ eV).

The numerical values for the properties of the Mu^- ion presented in Table III agree quite well with the values known from previous highly accurate calculations [11]. For the $p^+\mu^+e^-$, $d^+\mu^+e^-$, and $t^+\mu^+e^-$ ions the properties presented in Table IV were never determined before. Approximately, however, all computed properties for these ions coincide quite well with the bound-state properties obtained for the HD^+, HT^+, and DT^+ and other similar ions computed in [17,18]. Note also that some expectation values in Tables III and IV can be expressed as linear combinations of other properties. For instance, for the three relative vectors $\mathbf{r}_{32}$, $\mathbf{r}_{31}$, and $\mathbf{r}_{21}$ we have

$$\mathbf{r}_{32}-\mathbf{r}_{31}+\mathbf{r}_{21}=0. \tag{10}$$

Therefore, the three equalities $[(i,j,k)=(1,2,3)]$

$$\mathbf{r}_{ik}\cdot\mathbf{r}_{jk}=\frac{1}{2}(r_{ik}^2+r_{jk}^2-r_{ij}^2) \tag{11}$$

hold in any case. For the appropriate expectation values one finds (see Table III)

$$\langle \mathbf{r}_{ik}\cdot\mathbf{r}_{jk}\rangle=\frac{1}{2}(\langle r_{ik}^2\rangle+\langle r_{jk}^2\rangle-\langle r_{ij}^2\rangle). \tag{12}$$

Analogously, since $\mathbf{p}_1+\mathbf{p}_2+\mathbf{p}_3=0$, then we write

$$\mathbf{p}_i\cdot\mathbf{p}_j=\frac{1}{2}(p_k^2-p_i^2-p_j^2) \tag{13}$$

and

$$\langle \mathbf{p}_i\cdot\mathbf{p}_j\rangle=\frac{1}{2}(\langle p_k^2\rangle-\langle p_j^2\rangle-\langle p_i^2\rangle), \tag{14}$$

respectively $[(i,j,k)=(1,2,3)]$. Moreover, since in atomic units the momenta $\mathbf{p}_i=(-\imath)\nabla_i$, one finds

$$\langle \nabla_i\cdot\nabla_j\rangle=-\langle -\tfrac{1}{2}\nabla_k^2\rangle+\langle -\tfrac{1}{2}\nabla_i^2\rangle+\langle -\tfrac{1}{2}\nabla_j^2\rangle, \tag{15}$$

where $(i,j,k)=(1,2,3)$. The expectation values form both sides of this equality can be found in Table III. In the symmetric Mu^- ion one easily finds that $\langle \nabla_1\cdot\nabla_3\rangle$ is always

TABLE IV. The expectation values (in atomic units) of some properties $\langle X \rangle$ for the ground states in the $\mu^+ p^+ e^-$, $\mu^+ d^+ e^-$, and $\mu^+ t^+ e^-$ ions. Below, the subscript 3 designates the electron e^- and 2 stands for the tritium nucleus, while 1 means the positively charged muon μ^+.

$\langle X \rangle$	$\mu^+ p^+ e^-$	$\mu^+ d^+ e^-$	$\mu^+ t^+ e^-$
$\langle r_{32}^{-2} \rangle$	1.38332194784	1.38406696683	1.38432262287
$\langle r_{21}^{-2} \rangle$	0.235393174082	0.235795882291	0.235932101935
$\langle r_{31}^{-1} \rangle$	1.40714678328	1.40938499014	1.41013666166
$\langle r_{32}^{-1} \rangle$	0.832504177058	0.833363252051	0.833652289885
$\langle r_{31}^{-1} \rangle$	0.825557229434	0.825987226271	0.826133929221
$\langle r_{21}^{-1} \rangle$	0.478253835879	0.478839774488	0.479038021799
$\langle (r_{32} r_{21})^{-1} \rangle$	0.403857276839	0.404607338234	0.404860449311
$\langle (r_{31} r_{21})^{-1} \rangle$	0.400950460207	0.401516032474	0.401707784198
$\langle (r_{31} r_{32})^{-1} \rangle$	0.588047623894	0.588984310799	0.589301003123
$\langle (r_{32} r_{31} r_{21})^{-1} \rangle$	0.292109652184	0.292650204842	0.292832860753
$\langle r_{32} \rangle$	1.73294284709	1.73035612531	1.72948502899
$\langle r_{31} \rangle$	1.74533389087	1.74347585046	1.74284532381
$\langle r_{21} \rangle$	2.14964905895	2.14554247881	2.14415469516
$\langle r_{32}^2 \rangle$	3.76133939760	3.74882857311	3.74461804494
$\langle r_{31}^2 \rangle$	3.81085696015	3.80116394256	3.79788068759
$\langle r_{21}^2 \rangle$	4.74623777621	4.72508380133	4.71794443387
$\langle r_{32}^3 \rangle$	9.55863681256	9.50723369267	9.48995122332
$\langle r_{31}^3 \rangle$	9.73421804773	9.69244532255	9.67832039520
$\langle r_{21}^3 \rangle$	10.7539564303	10.6722728207	10.6447534610
$\langle r_{32}^4 \rangle$	27.4754408819	27.2680167923	27.1983640343
$\langle r_{31}^4 \rangle$	28.1087048740	27.9346664434	27.8759163656
$\langle r_{21}^4 \rangle$	24.9848269401	24.7028465179	24.6080527942
$\langle \tau_{31} \rangle$	0.516872352652	0.516938604988	0.516959506009
$\langle \tau_{32} \rangle$	0.509692554936	0.509316132642	0.509190209532
$\langle \tau_{21} \rangle$	0.242221311233	0.242677080065	0.242831397092
$\langle f \rangle$	0.0671965547342	0.0672329545237	0.0672452782596
$\langle \mathbf{r}_{32} \cdot \mathbf{r}_{21} \rangle$	2.34836010683	2.33637421594	2.33234089561
$\langle \mathbf{r}_{31} \cdot \mathbf{r}_{21} \rangle$	2.39787766938	2.38870958539	2.38560353826
$\langle \mathbf{r}_{31} \cdot \mathbf{r}_{32} \rangle$	1.41297929077	1.41245435717	1.41227714933
$\langle -\frac{1}{2} \nabla_1^2 \rangle$	1.27714953992	1.30663336903	1.31696266243
$\langle -\frac{1}{2} \nabla_2^2 \rangle$	1.26666136753	1.29535220954	1.30541199577
$\langle -\frac{1}{2} \nabla_3^2 \rangle$	0.583082232791	0.583634614301	0.583821110754
$\langle \boldsymbol{\nabla}_2 \cdot \boldsymbol{\nabla}_1 \rangle$	1.96072867465	2.01835096427	2.03855354744
$\langle \boldsymbol{\nabla}_3 \cdot \boldsymbol{\nabla}_1 \rangle$	0.59357040518	0.59491577379	0.595371777406
$\langle \boldsymbol{\nabla}_3 \cdot \boldsymbol{\nabla}_2 \rangle$	0.57259406040	0.57235345481	0.572270444102
$\langle \delta(\mathbf{r}_{32}) \rangle$	0.2045743	0.2049599	0.2050891
$\langle \delta(\mathbf{r}_{31}) \rangle$	0.1997232	0.1998020	0.1998292
$\langle \delta(\mathbf{r}_{21}) \rangle$	0.11927×10^{-10}	0.12713×10^{-10}	0.12971×10^{-10}
$\langle \delta(\mathbf{r}_{321}) \rangle$	0.8664×10^{-10}	1.0106×10^{-10}	1.0469×10^{-10}
ν_{32}	-0.99947434	-0.99974636	-0.99983689
ν_{32} [a]	-0.9994556794329	-0.9997276304980	-0.9998181130841
ν_{31}	-0.99519759	-0.99519757	-0.99519759
ν_{31} [a]	-0.9951869453478	-0.9951869453478	-0.9951869453478
ν_{21}	65.886	67.724	68.448
ν_{21} [a]	185.8408179408	195.7416064837	199.2725679222

[a]The expected cusp value ν_{ij} determined from Eq. (5).

positive, since $\langle \nabla_1 \cdot \nabla_3 \rangle = \langle -\frac{1}{2}\nabla_3^2 \rangle = T_3 > 0$. In this study we assume that the $\nabla_i \cdot \nabla_j$ operator acts on its right. A different expression can be found for the scalar product of two gradients, since $\langle \nabla_i \psi \cdot \nabla_j \psi \rangle = -\langle \psi \nabla_i \cdot \nabla_j \psi \rangle$.

In conclusion, we want to discuss briefly the photodetachment of the Mu^- ion. This problem is closely related to the asymptotic form of the three-body wave function obtained above for the Mu^- ion. In general, the photodetachment of the Mu^- ion can be represented in the form $Mu^- + \hbar\omega = Mu + e^-$, where $\hbar\omega$ designates the incident photon and Mu is the muonium two-body system $(\mu^+ e^-)$. A detail study of the photodetachment of the Mu^- and other similar ions will be published elsewhere. Here we restrict ourselves to the approximate description which is based on Bethe's method [19,20]. Bethe's method was originally developed to describe the photodetachment of the weakly bound deuterium nucleus [19,21]. Later, it was found that the same approach can be used to describe the photodetachment of an arbitrary weakly bound system, including Coulomb three-body ions such as $^\infty H^-$ and Ps^- ions [22,23].

In application to the Mu^- ion, Bethe's method allows one to obtain the following formula for the photodetachment cross section $\sigma(p)$ (for more details, see [24]):

$$\sigma(p) = \frac{64\pi^2 \alpha a_0^2}{3(1+m_\mu^{-1})^5} \frac{C^2 p^3}{(p^2+\gamma^2)^3} = \frac{4.302\,552 \times 10^{-17}}{(1+m_\mu^{-1})^5} \frac{C^2 p^3}{(p^2+\gamma^2)^3} \ \text{cm}^2, \qquad (16)$$

where $p = |\mathbf{p}|$ is the momentum of the outgoing electron (i.e., photoelectron), $\alpha = 7.297\,353\,08 \times 10^{-3}$ is the dimensionless fine-structure constant, and $a_0 = 5.291\,772\,49 \times 10^{-9}$ cm is the Bohr radius. Also, in this formula $m_\mu = 206.768\,262 m_e$ is the muon mass and C is a constant which is determined from the asymptotic form of the three-body wave function

$$\psi(r) = \frac{C}{r^\beta} \exp(-\gamma r) = \Psi(r, 0, r), \qquad (17)$$

where C is a numerical constant, $\Psi(r_{32}, r_{31}, r_{21})$ is the highly accurate three-body wave function, Eq. (2), β is some positive constant, and γ is another positive constant, which is uniformly related to the ionization potential $I[I = (\gamma^2/2)(1 + m_\mu^{-1})]$. By using our highly accurate wave functions we have found that for the Mu^- ion $\beta = 1$. In fact, the expression for the photodetachment cross section presented above, Eq. (16), has been produced by assuming that $\beta = 1$ in Eq. (17) for the Mu^- ion. Also, from our highly accurate wave functions constructed for the Mu^- ion we have found that $C = 0.318\,022$ [24]. Now, the photodetachment cross section of the Mu^- ion in cm^2 takes the form

$$\sigma(p) = 4.247\,798 \times 10^{-18} \frac{p^3}{(p^2+\gamma^2)^3} \ \text{cm}^2. \qquad (18)$$

Since for the Mu^- ion $\gamma = 0.233\,791\,2$, one finds from the last expression that the maximal photodetachment cross section $\sigma(p=\gamma) = 4.155\,03 \times 10^{-17}$ cm^2. The maximal photodetachment cross section for the $^\infty H^-$ ion is $\approx 4.104\,03 \times 10^{-17}$ cm^2. This value was obtained by using our extremely accurate variational wave function recently produced for the $^\infty H^-$ ion [$E(^\infty H^-) = -0.527\,751\,016\,544\,377\,196\,586\,5$ a.u.].

Thus, in this study the problem of the ground bound states in the Mu^- $(\mu^+ e^- e^-)$ and $p^+\mu^+e^-$, $d^+\mu^+e^-$, and $t^+\mu^+e^-$ ions has been considered. The ground-state energies and other bound-state properties of these systems have been determined to high accuracy. In fact, the numerical accuracy achieved in the present study is sufficient for all present and future experimental needs. The obtained variational energies for all considered systems [$E(Mu^-) = -0.525\,054\,806\,243\,526\,329\,29$ a.u., $E(p^+\mu^+e^-) = -0.589\,903\,785\,389\,587\,726\,1$ a.u., $E(d^+\mu^+e^-) = -0.590\,255\,352\,152\,246\,417\,7$ a.u., and $E(t^+\mu^+e^-) = -0.590\,374\,098\,892\,682\,888\,0$ a.u.] are significantly more accurate than the total energies known for these systems from earlier calculations. The lowest order relativistic $(\sim\alpha^2)$ and QED $(\sim\alpha^3)$ corrections to the total energies of the considered ground states are expected to be small $(\approx 1 \times 10^{-5}$ and $\approx 5 \times 10^{-7}$ a.u., respectively). In fact, an accurate evaluation of these correction for all considered ions is the goal of our next study.

The electron-''nuclear'' cusps in all considered systems have been determined very accurately. The electron-electron cusp in the Mu^- ion has also been determined quite accurately. However, the muon-nuclear cusps computed in the $p^+\mu^+e^-$, $d^+\mu^+e^-$, and $t^+\mu^+e^-$ ions are not even approximately correct. This problem is well known (see, e.g., [18] and references therein) for the adiabatic three-body systems $X^+Y^+e^-$, where $\min(m_X, m_Y) \gg m_e = 1$. In fact, in such systems the two heavy nuclei X^+ and Y^+ move in the field of some effective (or averaged) potential $V(r_{XY})$. Here $r_{XY} = |\mathbf{r}_X - \mathbf{r}_Y|$ is the corresponding internuclear distance. For the adiabatic systems the potential $V(r_{XY})$ differs significantly from the original Coulomb potential $q_X q_Y / r_{XY}$. Therefore, the cusp computed for the $V(r_{XY})$ potential can also be different from the known Coulomb cusp, Eq. (5). Note, however, that for the considered soft-adiabatic systems $p^+\mu^+e^-$, $d^+\mu^+e^-$, and $t^+\mu^+e^-$ the agreement between predicted and computed muon-nuclear cusps is significantly better than such an agreement observed for actual adiabatic ions $p^+d^+e^-$, $p^+t^+e^-$, and $d^+t^+e^-$ considered in [18]. In general, the cusp problem for the Coulomb adiabatic systems warrants further theoretical and numerical studies.

It is a pleasure to thank David H. Bailey (Lawrence Berkeley National Laboratory, Berkeley, California) and Anand K. Bhatia (NASA, Goddard Space Flight Center, Greenbelt, Maryland) for valuable help and stimulating discussions and the Natural Sciences and Engineering Research Council of Canada for financial support.

[1] W. Heitler, *The Quantum Theory of Radiation*, 3rd ed. (Oxford University Press, London, 1954).
[2] D. McKenna and B. Webster, J. Chem. Soc., Faraday Trans. 1 **80**, 589 (1984).
[3] D. McKenna and B. Webster, J. Chem. Soc., Faraday Trans. 1 **81**, 225 (1985).
[4] A.M. Frolov and V.H. Smith, Jr., J. Phys. B **28**, L449 (1995).
[5] E.R. Cohen and B.N. Taylor, Phys. Today **53**(8), 9 (2000).
[6] M. Born and J.R. Oppenheimer, Ann. Phys. (Leipzig) **84**, 457 (1927).
[7] A.M. Frolov and A.Yu. Yeremin, J. Phys. B **22**, 1263 (1989).
[8] A.M. Frolov, Z. Phys. D: At., Mol. Clusters **2**, 61 (1986).
[9] A.K. Bhatia and R.J. Drachman, Phys. Rev. A **58**, 2787 (1987).
[10] P. Petelenz and V.H. Smith, Jr., Phys. Rev. A **36**, 5125 (1987).
[11] A.M. Frolov, Phys. Rev. A **58**, 4479 (1998).
[12] A.M. Frolov, Phys. Rev. E **64**, 036704 (2001).
[13] D.H. Bailey, ACM Trans. Math. Softw. **21**, 379 (1995).
[14] D.H. Bailey, Comput. Sci. Eng. **2**, 24 (2000).
[15] T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).
[16] R.T Pack and W. Byers Brown, J. Chem. Phys. **45**, 556 (1966).
[17] A.K. Bhatia, Phys. Rev. A **58**, 2787 (1998).
[18] A.M. Frolov, J. Phys. B **35**, L331 (2002).
[19] H.A. Bethe and R. Peierls, Proc. R. Soc. London, Ser. A **148**, 146 (1935).
[20] H.A. Bethe and C. Longmire, Phys. Rev. **77**, 647 (1950).
[21] A.I. Akhiezer and V.B. Berestetskii, *Quantum Electrodynamics* (Interscience, New York, 1965).
[22] T. Ohmura and H. Ohmura, Phys. Rev. **118**, 154 (1960).
[23] A.K. Bhatia and R.J. Drachman, Phys. Rev. A **32**, 3745 (1985).
[24] A.M. Frolov, J. Phys. B (to be published).