Finite-element calculations for the three-body Coulomb problem with two equal masses

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An accurate numerical finite-element method (FEM) solution of the three-body Coulomb problem with two equal masses is presented. The application of the FEM to systems with mass ratios ranging from 1836 to 1/1836 yields upper bounds for energy eigenvalues to a precision in the range of 10^{-11}–10^{-9} a.u. Expectation values for different operators are computed and discussed. [S1050-2947(96)03507-X]

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I. INTRODUCTION

The dynamical problem of three interacting bodies is one of the oldest challenges in physics. The scientific work in this field can be traced back to the work of Euler in the 18th century. In the beginning of the 20th century, the failure of theory to describe correctly stable three-body Coulomb systems like the hydrogen molecular ion $H_2{}^+$ and the helium atom stimulated the development of modern quantum mechanics beyond the Bohr-Sommerfeld quantization. Three-body problems continue to be of interest in many fields, such as exotic systems in atomic (Ps^-) and molecular ($td\mu$) physics, two-neutron halo structures in nuclear physics, and three quark baryons in high-energy physics.

Traditionally, three-body Coulomb systems are divided into two ''obvious'' physical models: the atomic system in which one mass is much heavier than the other two and the molecular system in which one mass is much lighter than the other two. These models give rise, respectively, to the infinite nuclear mass approximation for two-electron atoms and the Born-Oppenheimer approximation for diatoms.

This partition is somewhat arbitrary, depending on the mass ratios, and a system with three identical masses like $Ps^-(e^+e^-e^-)$ falls into neither category. Many different methods and global basis functions have been used to treat three-body Coulomb systems; the precision of any particular method is strongly dependent on the mass ratios. For atomic systems like the helium atom, the most accurate and widely used is the variational method with a Hylleraas-type global basis set [1]. For molecular systems like $H_2{}^+$, a global basis-set expansion in elliptic coordinates is more suitable [2]. We also mention the hyperspherical coordinate method, which has a rich history in this field; for a complete review of the literature see Ref. [3].

In this work we present a different approach to Coulombic three-body problems. The wave function is not expanded in terms of global basis functions; rather, the domain of the wave function is segmented into tedrahedra, each serving as the domain of a local polynomial basis set. The approximation of the wave function as a linear combination of these local polynomials is called a finite-element-method (FEM) description. FEM treatments for the helium atom in the infinite nuclear mass approximation [4–8] and the hydrogen molecular ion $H_2{}^+$ in the Born-Oppenheimer approximation [9–14] have been presented by several groups. For the three-body problem with arbitrary masses, the FEM has yielded a precision of one part in 10^6 for the energies *and* the expectation values of certain systems [15,16]. Recently it was shown that an adaptive FEM treatment of correlated two-electron wave functions yields energy values to a precision on the order of 10^{-11} with moderate computational effort [8]. In the adaptive FEM the segmentation of the domain is refined automatically; higher-order polynomials are used to reach high precision.

There are several other desirable features of the adaptive FEM that justify its application to Coulombic three-body problems. First, comparing a FEM and a global basis-set wave function approximation with energy values of the same accuracy, the FEM often will yield much better expectation values. This is a consequence of the local approximation behavior of the FEM. Let $\delta\Psi$ be the deviation from the exact wave function. Then, the error in the energy δE is given by

$$\delta E = \langle \delta\Psi | T | \delta\Psi \rangle + \langle \delta\Psi | V | \delta\Psi \rangle \geqslant 0, \tag{1}$$

where T and V are the kinetic and the potential part of the Hamiltonian. Now, an optimization according to the energy minimum principle may exploit the cancellation of the kinetic and potential part in the above expression. This unsatisfactory situation, which can lead to a large deviation from the virial theorem, may occur for global as well as for local approximations. The main difference is that the adaptive FEM tries to minimize δE locally on each tetrahedron, whereas a global scheme tries to minimize δE on the whole domain. Thus the adaptive FEM cannot exploit the cancellation of errors on different tetrahedra (or space regimes). This leads to a better description of the wave function in the FEM case.

Another attractive feature of the adaptive FEM is its flexibility. Since the grid is adapted automatically to the wave function, high-precision results are obtainable independent of the particular structure of the wave function. Finally, the adaptive FEM is a variational method in the sense that the FEM energy values are true upper bounds to the exact energy. But the grid adaptation is not restricted to the energy

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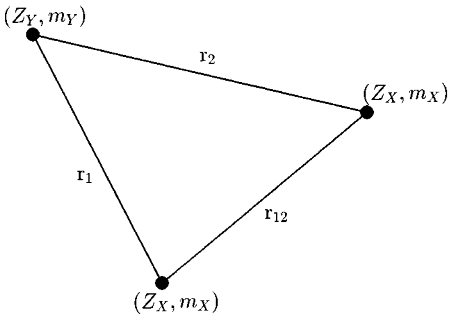

FIG. 1. Two of the three point particles have identical charges Z_X and masses m_X. The remaining particle has the charge Z_Y and the mass m_Y. The distance between the two identical particles is denoted by r_{12}, whereas the distances to the third particle are r_1 and r_2.

criteria. The grid can be optimized with respect to any arbitrary physical property of the wave function.

This work is organized as follows. Section II is devoted to a short description of the variational problem for the three-body Coulomb system with two identical masses. In Sec. III we give numerical details of the computations and present our results. Our goal here is the systematic study of the three-body system with the adaptive FEM, beginning with the atomic problem and ending with the molecular problem. If high-precision results are obtainable for all mass ratios, the adaptive FEM will provide a unifying approach to the study of the three-body problem. We present results for the helium atom ^{4}He, the hydrogen atomic ion ^{1}H$^-$, the Mu$^-$ system ($\mu^+e^-e^-$), the Ps$^-$-system ($e^+e^-e^-$), the Mu$^+$-system ($\mu^+\mu^+e^-$), and the hydrogen molecular ion $H_2{}^+$. The corresponding charge-conjugated systems are identical at this level of description. A short conclusion can be found in Sec. IV.

II. THEORY

We consider the problem of three charged point particles, two having identical masses m_X and identical charges Z_X, and a third with the mass m_Y and the charge Z_Y (see Fig. 1). The Hamiltonian in nine space dimensions is given by (all quantities in the following are given in atomic units)

$$\mathcal{H}=-\frac{1}{2m_X}(\nabla_1^2+\nabla_2^2)-\frac{1}{2m_Y}\nabla_3^2+\frac{Z_XZ_Y}{|\mathbf{r}_1-\mathbf{r}_3|}+\frac{Z_XZ_Y}{|\mathbf{r}_2-\mathbf{r}_3|}+\frac{Z_XZ_X}{|\mathbf{r}_1-\mathbf{r}_2|}. \tag{2}$$

Subtracting the center-of-mass motion and applying an angular-momentum decomposition of the Schrödinger equation result in a system of coupled partial differential equations in the three coordinates $r_1=|\mathbf{r}_1-\mathbf{r}_3|$, $r_2=|\mathbf{r}_2-\mathbf{r}_3|$, and $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$ [17]. For S states (angular momentum $L=0$) we get the Schrödinger equation

$$(T+V(r_1,r_2,r_{12})-E)\Psi(r_1,r_2,r_{12})=0 \tag{3}$$

on $\Psi\in L^2(\Omega\subset\mathcal{R}^3,d\Omega)$. Here the domain Ω and the volume element $d\Omega$ are given by

$$\Omega\equiv\{(r_1,r_2,r_{12})|0\leqslant r_1<\infty,\ 0\leqslant r_2<\infty,\ |r_1-r_2|\leqslant r_{12}\leqslant r_1+r_2\} \tag{4}$$

and

$$d\Omega\equiv 8\pi^2 r_1r_2r_{12}dr_1dr_2dr_{12}. \tag{5}$$

The potential energy has the usual form

$$V(r_1,r_2,r_{12})=\frac{Z_XZ_Y}{r_1}+\frac{Z_XZ_Y}{r_2}+\frac{Z_XZ_X}{r_{12}}, \tag{6}$$

whereas the kinetic-energy operator is the expression:

$$T=\frac{1}{2\mu}\left[\frac{1}{r_1}\frac{\partial^2}{\partial r_1^2}r_1+\frac{1}{r_2}\frac{\partial^2}{\partial r_2^2}r_2\right]+\frac{1}{m_X}\frac{1}{r_{12}}\frac{\partial^2}{\partial r_{12}^2}r_{12}+\frac{1}{2m_Y}\frac{r_1^2+r_2^2-r_{12}^2}{r_1r_2}\frac{\partial^2}{\partial r_1\partial r_2}+\frac{1}{2m_X}\times\left[\frac{r_1^2+r_{12}^2-r_2^2}{r_1r_{12}}\frac{\partial^2}{\partial r_1\partial r_{12}}+\frac{r_2^2+r_{12}^2-r_1^2}{r_2r_{12}}\frac{\partial^2}{\partial r_2\partial r_{12}}\right] \tag{7}$$

with $\mu\equiv m_Xm_Y/(m_X+m_Y)$.

Before proceeding we first want to clarify the connection to the atomic case. In the infinite nuclear mass approximation ($m_Y\rightarrow\infty$, $m_X=m_e$) for two-electron atoms, the kinetic-energy operator is given by [8]

$$T_0=\frac{1}{2m_X}\left[\frac{1}{r_1}\frac{\partial^2}{\partial r_1^2}r_1+\frac{1}{r_2}\frac{\partial^2}{\partial r_2^2}r_2+\frac{2}{r_{12}}\frac{\partial^2}{\partial r_{12}^2}r_{12}+\frac{r_1^2+r_{12}^2-r_2^2}{r_1r_{12}}\frac{\partial^2}{\partial r_1\partial r_{12}}+\frac{r_2^2+r_{12}^2-r_1^2}{r_2r_{12}}\frac{\partial^2}{\partial r_2\partial r_{12}}\right]. \tag{8}$$

Thus we can rewrite T in the form

$$T=\frac{m_X}{\mu}T_0+T_{\mathrm{MP}}, \tag{9}$$

with the mass polarization term given by

$$T_{\mathrm{MP}}=\frac{1}{2m_Y}\left[\frac{r_1^2+r_2^2-r_{12}^2}{r_1r_2}\frac{\partial^2}{\partial r_1\partial r_2}-\frac{r_1^2+r_{12}^2-r_2^2}{r_1r_{12}}\frac{\partial^2}{\partial r_1\partial r_{12}}-\frac{r_2^2+r_{12}^2-r_1^2}{r_2r_{12}}\frac{\partial^2}{\partial r_2\partial r_{12}}-\frac{2}{r_{12}}\frac{\partial^2}{\partial r_{12}^2}r_{12}\right]. \tag{10}$$

Here we used the relation $1/m_X=1/\mu-1/m_Y$. In the limit $m_Y\rightarrow\infty$ the mass polarization term vanishes, whereas m_X/μ goes to 1. Applying the scaling transformation,

$$r_1'=(\mu/m_X)r_1,\quad r_2'=(\mu/m_X)r_2,\quad r_{12}'=(\mu/m_X)r_{12}, \tag{11}$$

allows us to reexpress Eq. (3) as

$$[T_0+(\mu/m_X)T_{\mathrm{MP}}+V(r_1,r_2,r_{12})-(m_X/\mu)E]\Psi(r_1,r_2,r_{12})=0, \tag{12}$$

where we have suppressed all primes. Neglecting the mass polarization term and setting $\epsilon_0=(m_X/\mu)E$ yield the Schrödinger equation for the atomic infinite nuclear mass approximation:

$$[T_0+V(r_1,r_2,r_{12})-\epsilon_0]\Psi_0(r_1,r_2,r_{12})=0. \tag{13}$$

TABLE I. Cutoff values r_c used for the different systems to truncate the infinite domain to a finite tetrahedron and mass parameters (from Ref. [31]) used in the numerical calculations.

System	Cutoff r_c	Mass parameter (in a.u.)	
^{4}He	$120a_0$		
^{1}H$^-$	$600a_0$	m_α	$10^4/1.370\ 933\ 54$
Mu$^-$	$600a_0$	m_p	1836.152 701
Ps$^-$	$1200a_0$	m_μ	206.768 262
Mu$^+$	$600a_0$	m_e	1
H$_2{}^+$	$600a_0$		

In the case of a sufficiently small parameter $\kappa \equiv \mu/m_Y$ the neglected mass polarization term can be accounted for by perturbation theory. Then the energy E for the three-body problem assumes the form

$$E=\frac{\mu}{m_X}\left[\epsilon_0+\frac{\mu}{m_Y}\epsilon_1+\left(\frac{\mu}{m_Y}\right)^2\epsilon_2+\cdots\right], \qquad (14)$$

with $\epsilon_1=\langle\Psi_0|(m_Y/m_X)T_{\mathrm{MP}}|\Psi_0\rangle$ and the ϵ_i for $i>1$ being the corresponding higher-order energy coefficients.

The molecular Born-Oppenheimer limit of Eq. (3) is discussed in Ref. [17]. The $L=0$ case corresponds to electronic Σ states. Adiabatic corrections to the Born-Oppenheimer energy can also be treated with perturbation theory.

In our FEM we treat the Coulomb three-particle problem in the unscaled variational form

$$\begin{aligned}\int_\Omega d\Omega\Bigg\{&\frac{1}{2\mu}\left[\left(\frac{\partial\Psi}{\partial r_1}\right)^2+\left(\frac{\partial\Psi}{\partial r_2}\right)^2\right]+\frac{1}{m_X}\left(\frac{\partial\Psi}{\partial r_{12}}\right)^2\\&+\frac{1}{2m_Y}\frac{r_1^2-r_2^2+r_{12}^2}{r_1r_2}\frac{\partial\Psi}{\partial r_1}\frac{\partial\Psi}{\partial r_2}+\frac{1}{2m_X}\\&+\left(\frac{r_1^2+r_{12}^2-r_2^2}{r_1r_{12}}\frac{\partial\Psi}{\partial r_1}\frac{\partial\Psi}{\partial r_{12}}+\frac{r_2^2+r_{12}^2-r_1^2}{r_2r_{12}}\frac{\partial\Psi}{\partial r_2}\frac{\partial\Psi}{\partial r_{12}}\right)\\&+V(r_1,r_2,r_{12})\Psi^2\Bigg\}=I_{\min}=E. \qquad (15)\end{aligned}$$

Depending on the parameters m_X, m_Y, Z_X, and Z_Y the solution of the above variational problem describes the zero-angular-momentum states of different atomic or molecular systems, see Table I. Solutions for fixed Z_X, Z_Y and mass ratio m_X/m_Y are identical except for a trivial scale transformation (11), as we can see from the Schrödinger equation (12).

III. NUMERICAL PROCEDURE AND RESULTS

In order to obtain an initial triangulation we must first truncate the infinite domain to a sufficiently large but finite domain. Outside the finite domain the wave function is assumed to be zero. Therefore we introduce a cutoff value r_c and take advantage of the permutation symmetry in r_1 and r_2 by considering the domain

$$\begin{aligned}\Omega(r_c)=\{(r_1,r_2,r_{12})|0\leqslant r_1\leqslant r_c,\\0\leqslant r_2\leqslant r_1,r_1-r_2\leqslant r_{12}\leqslant r_1+r_2\}. \qquad (16)\end{aligned}$$

$\Omega(r_c)$ is given in the positive half plane in (r_1,r_2,r_{12}) by a tetrahedron with vertices at the points $P_0=(0,0,0)$, $P_1=(r_c/2,r_c/2,0)$, $P_2=(r_c/2,r_c/2,r_c)$, and $P_3=(r_c,0,r_c)$. In our calculations we use cutoff values between $r_c=120a_0$ and $r_c=1200a_0$ (see Table I). These values are sufficiently large not to affect the numerical results presented here.

Starting with the single tetrahedron describing the domain $\Omega(r_c)$ we split successively (six times) only the tetrahedron containing P_0. The refinement of each tetrahedron results in eight smaller tetrahedra (see Ref. [8]). In this way a grading in the grid is produced that locates smaller tetrahedra near the point P_0. Local Lagrange polynomials [18] of order p are defined on each of the tetrahedra. These Lagrange polynomials $\phi_i^{(p)}$ are continuous on Ω and form a basis $\{\phi_i^{(p)},i=1,2,\ldots,M\}$ for the FEM approximation of Ψ in the domain:

$$\Psi\approx\tilde{\Psi}^{(p)}_{\mathrm{FEM}}=\sum_{i=0}^{M}C_i\phi_i^{(p)}. \qquad (17)$$

Inserting this ansatz into the variational problem (15), computing the integrals via a numerical Gaussian integration, and carrying out a variation with respect to the expansion coefficients C_i leads to a general matrix eigenvalue problem that can be solved by standard methods.

In general, the resulting FEM approximation will be very crude. To improve this first FEM approximation we look for tedrahedra on which the error of the FEM wave function is larger than the average local approximation error. The local FEM approximation error can be measured by a local error estimator based on the energy norm of the difference $\tilde{\Psi}^{(p)}_{i,\mathrm{FEM}}-\tilde{\Psi}^{(p+1)}_{i,\mathrm{FEM}}$, where $\tilde{\Psi}^{(p)}_{i,\mathrm{FEM}}$ and $\tilde{\Psi}^{(p+1)}_{i,\mathrm{FEM}}$ are the continuous local FEM approximations of order p and $p+1$, respectively, on the ith tedrahedron. For a detailed description and discussion of the local error estimator we refer to Ref. [14]. Only the tetrahedra collected by the local error estimator are refined. The resulting new grid is used to compute an improved FEM approximation. The grid can be successively refined level by level until the desired precision is reached and is only restricted by the available computer power. The dimensions of the sparse matrices in these calculations are between 3×10^5 and 4×10^5. The CPU times range from a few hours up to several days on a Silicon Graphics PowerChallenge workstation.

First we apply the adaptive FEM to the atomic system helium ^{4}He and to the hydrogen atomic ion system ^{1}H$^-$. In Table II we list the final FEM results: energy eigenvalues, expectation values for powers of the interparticle distances, and the deviations from the virial theorem. These results are compared with the high-precision results (10^{-16} a.u. in the energy) of Drake [1].

For helium, the grid contains 2037 grid points after nine refinement steps according to the local error estimator; quintic Lagrange polynomials were used. The FEM energy eigenvalue lies 4×10^{-12} a.u. above the value of Drake. This is consistent with the error ($<10^{-11}$ a.u.) we would expect from the convergence behavior and from the error estimator implemented. The deviation from the virial theorem given by $\Delta_{T,V}$ is an indicator of the precision of the expectation values for $\langle 1/r\rangle$ and $\langle 1/r_{12}\rangle$. Let us write $\Delta_{T,V}$ in the form [8]

TABLE II. FEM expectation values for atomic three-particle Coulomb problems including the mass polarization term explicitly in the Hamiltonian. Included are benchmark values of Drake [1]. Drake uses slightly different mass values, which account for the relativistic mass effect due to the atomic binding energy. The difference in the reduced mass is 1.1×10^{-14} a.u. for helium and 2.7×10^{-13} a.u. for the hydrogen atomic ion, which is at least two orders of magnitude smaller than the accuracy reached here by the FEM calculations. The energy values listed here are corrected to our mass parameters, whereas Drake's expectation values for various operators are computed with his original mass values, see Drake [1].

Quantity	^{4}He	^{1}H$^-$
Number of gridpoints	2037	2333
E (a.u.)	$-2.903\,304\,557\,734\,390$	$-0.527\,445\,881\,114\,178$
E_{FEM} (a.u.)	$-2.903\,304\,557\,730$	$-0.527\,445\,881\,110$
Estimated error (a.u.)	$<10^{-11}$	$<10^{-11}$
$\Delta_{T,V}$ (a.u.)	1.5×10^{-10}	1.8×10^{-11}
$\langle 1/r\rangle$ (a_0^{-1})	1.688 076 584 672	0.682 853 384 851
$\langle 1/r\rangle_{\text{FEM}}$ (a_0^{-1})	1.688 076 584 77	0.682 853 384 96
$\langle 1/r_{12}\rangle$ (a_0^{-1})	0.945 697 223 221	0.310 815 007 474
$\langle 1/r_{12}\rangle_{\text{FEM}}$ (a_0^{-1})	0.945 697 223 30	0.310 815 007 66
$\langle r\rangle$ (a_0)	0.929 607 915 011	2.712 095 626 603(1)
$\langle r\rangle_{\text{FEM}}$ (a_0)	0.929 607 914 91	2.712 095 621 4
$\langle r_{12}\rangle$(a_0)	1.422 247 512 605	4.415 692 603 503(2)
$\langle r_{12}\rangle_{\text{FEM}}$ (a_0)	1.422 247 512 43	4.415 692 593 4
$\langle r^2\rangle$ (a_0^2)	1.193 834 894 419	11.931 747 756 25(5)
$\langle r^2\rangle_{\text{FEM}}$ (a_0^2)	1.193 834 894 05	11.931 747 62
$\langle r_{12}^2\rangle$ (a_0^2)	2.517 061 842 475	25.237 175 606 7(1)
$\langle r_{12}^2\rangle_{\text{FEM}}$ (a_0^2)	2.517 061 841 70	25.237 175 34

$$\Delta_{T,V}\equiv\langle T\rangle+\frac{\langle V\rangle}{2}=\delta\langle T\rangle+\frac{\delta\langle V\rangle}{2}=\delta E-\frac{\delta\langle V\rangle}{2}$$

$$=\delta E+Z\delta\langle 1/r\rangle-\frac{\delta\langle 1/r_{12}\rangle}{2}, \qquad (18)$$

where δE is the error in the energy and $\delta\langle\ \rangle$ denotes the deviation from the exact expectation value. Since in our FEM calculations the error in the energy is minimized, the value for $\Delta_{T,V}$ is dominated by the errors in the expectation values for the operators $1/r$ and $1/r_{12}$. For helium, $\Delta_{T,V}$ is on the order of 1.5×10^{-10} a.u. Indeed, the difference between the FEM expectation values and Drake's benchmark results are on the order of $10^{-10}a_0^{-1}$. For the other non-Hamiltonian expectation values we would expect an increase in error. But, comparing the FEM expectation values with the benchmark values of Drake, the error in $\langle r\rangle$ and $\langle r_{12}\rangle$ is still on the order of $10^{-10}a_0$, whereas the error in $\langle r^2\rangle$ and $\langle r_{12}^2\rangle$ increases to $4\times10^{-10}a_0^2$ and $8\times10^{-10}a_0^2$, respectively.

The final grid for the hydrogen atomic ion contains 2333 grid points after 11 refinement steps. The precision of the energy eigenvalue for the hydrogen atomic ion reaches the same level as in the helium case. The main difference is that $\Delta_{T,V}$ is lowered by one order of magnitude; however, this is *not* indicative of a more precise FEM wave function. Since $\delta\langle 1/r\rangle=1.1\times10^{-10}a_0^{-1}$ and $\delta\langle 1/r_{12}\rangle=1.9\times10^{-10}a_0^{-1}$, the two contributions in (18) nearly cancel for $Z=1$, resulting in a value for $\Delta_{T,V}$ that is on the order of 1.8×10^{-11} a.u. The precision of the expectation values $\langle 1/r\rangle$ and $\langle 1/r_{12}\rangle$ is comparable to that of the helium results. We note that the non-Hamiltonian expectation values $\langle r^2\rangle$ and $\langle r_{12}^2\rangle$ for the hydrogen atomic ion are significantly less accurate than the helium results. One explanation is the difference in the screening effect for $Z=1$ and $Z=2$. The hydrogen ion wave function decays asymptotically with a preexponential factor $(1+r_1)^{-1}$, [19] which is harder to describe by polynomials than the asymptotic wave function for the helium atom.

Having established the precision of the FEM in the atomic case, we now address the more difficult problem of applying the method to systems that are neither atomic nor molecular in character. Here we study the negative muonium ion ($\mu^+e^-e^-$), the negative positronium ion ($e^+e^-e^-$), and the muonic molecular ion ($\mu^+\mu^+e^-$). These exotic systems have been the subject of many theoretical treatments that predict them to be (meta)stable. To our knowledge only the negative muonium ion [20,21] and the positronium negative ion [22] have been observed experimentally.

Although $m_Y\approx207m_X$ for the negative muonium ion Mu$^-$, the mass polarization term is sufficiently large that the

TABLE III. FEM energy values for the negative muonium ion ($\mu^+e^-e^-$), the negative positronium ion ($e^+e^-e^-$), the muonic molecular ion ($\mu^+\mu^+e^-$), and hydrogen molecular ion ($p^+p^+e^-$). We assume the extrapolated exact FEM values to be exact to all figures given (further digits are put in parentheses). Included are energy values computed by several other groups. Since often different muon masses are used, high-precision results for the muonic ion have been corrected with Eq. (14) to the muon mass in Table I. For the energy values obtained for the muonic molecular ion in the literature the muon mass shift plays no role. The binding energy is computed by the difference between the FEM energy and the threshold energy $\epsilon_{\text{th}} = -0.5 m_X m_Y/(m_X + m_Y)$ (in a.u.; conversion factor 1 a.u. = 27.211 396 181 eV).

	$\mu^+e^-e^-$	$e^+e^-e^-$	$\mu^+\mu^+e^-$	$p^+p^+e^-$
Number of gridpoints	2388	2267	3325	3612
Estimated error (a.u.)	$<10^{-11}$	$<10^{-11}$	$\sim10^{-11}$	$<10^{-9}$
Energy (a.u.)	0.525 054 806 239	0.262 005 070 231	0.585 126 097 208	0.597 139 062 3
extrapolated exact	0.525 054 806 24(1)	0.262 005 070 23(2)	0.585 126 097 2(16)	0.597 139 06(2 6)
	0.525 054 815 7326[a]	0.262 005 070 232 2[a]	0.585 126[h]	0.597 139 063 2[i]
	0.525 054 811 0646[b]	0.262 005 070 232[d]	0.585 123[g]	0.597 139 063 1[j]
	0.525 054 806 163[a,b,k]	0.262 005 069[c]	0.584 928 65[d]	
	0.525 054 807 4[c]	0.262 004 89[e]		
	0.525 054 803 3[c,k]	0.262 004 857[f]		
		0.262 000 7[g]		
Binding energy (eV)	0.747 261 227 3	0.326 674 722 2	2.381 884 925	2.650 695 370

[a] Frolov and Yeremin [23] ($m_\mu = 206.769$).

[b] Frolov and Yeremin [23] ($m_\mu = 206.768\,64$).

[c] Petelenz and Smith [24] ($m_\mu = 206.768\,6$).

[d] Frolov and Bishop [25] ($m_\mu = 206.768\,64$).

[e] Ho [26].

[f] Haftel and Mandelzweig [28].

[g] Mohallem [27] ($m_\mu = 206.7686$).

[h] McKenna and Webster [29] ($m_\mu = 206.768\,65$).

[i] Wolniewicz and Poll [2] ($m_p = 1836.1528$).

[j] Moss [32] ($m_p = 1836.152\,701$).

[k] Corrected to $m_\mu = 206.768\,262$.

system cannot be treated as purely atomic. Variational calculations with Hylleraas-type functions converge more slowly than in the case of helium. The FEM result for Mu$^-$ energy is lower than any values found in the literature (see Table III). A direct comparison to the energy values of other groups is complicated by the use of different mass values. The mass dependence of the energy can be seen by comparing the high-precision energy values for two different values for m_μ of Frolov and Yeremin [23]. Using this ''isotope shift'' for an extrapolation of their energy to our mass value (Table I) according to expansion (14) reduces the difference between their result and the FEM result to less than 10^{-10} a.u. FEM results for the expectation values are also the most accurate to date. In Table IV we compare them with the results of Petelenz and Smith [24], who applied the integral transform method with a trial wave function containing 150 exponential basis functions.

The negative positronium ion Ps$^-$ is the only three-body Coulomb system with equal masses that has been observed experimentally. The challenge to calculate the binding energy of this system has been the subject of many theoretical studies, including the variational method [24–26], the molecular approach [27], and the hyperspherical method [28]. The most accurate result for the energy has been obtained by Frolov and Bishop [25], who used 900 basis functions in an exponential variational expansion in the interparticle distances. The FEM eigenvalue is identical with their result to 12 significant digits (see Table III). The FEM results for the expectation values are the most accurate in the literature and are compared with the variational results of Petelenz and Smith [24] in Table IV.

The positive muonium ion Mu$^+$ is the first system we study with $m_X > m_Y$; however, the mass ratio is such that the adiabatic terms cannot be treated by low-order perturbation theory as in a truly molecular system. The 600-term exponential variational expansion of Frolov and Bishop [25] has only a precision of one part in 10^4. Here the molecular approach of Mohallem [27] yields a precision of 3×10^{-6} a.u. McKenna and Webster [29] used a nonadiabatic wave function expansion in prolate spheroidal elliptic coordinates and their result given, unfortunately only up to six digits, agrees with the FEM result. The FEM energy for Mu$^+$ is by far the most accurate in the literature; with a slight increase in numerical effort, a precision of one part in 10^{11} was reached (see Table III). The FEM expectation values for Mu$^+$ are the first to appear in the literature (see Table IV).

Finally, we apply the FEM to the hydrogen molecular ion. As the masses of the two identical particles increase the amount of numerical work to reach a certain precision increases. (This is a direct consequence of the use of interparticle distances for all systems studied.) The FEM reaches the (relatively low) precision of 10^{-9} a.u. on a grid with 3612 grid points. Since the nonadiabatic ground-state energy of this system has been computed by many groups to a high precision, we include in Table III only the results of Wolniewicz and Poll [2] and Moss [30]. The FEM expectation values for $H_2{}^+$, like those of the other nonatomic systems studied, are the most accurate in the literature.

IV. CONCLUSION

The adaptive finite-element method offers an alternate approach to studying three-body Coulomb systems. In terms of accuracy, it is competitive over the entire range of masses; in

TABLE IV. FEM expectation values of various operators for the negative muonium ion ($\mu^+e^-e^-$), the negative positronium ion ($e^+e^-e^-$), the muonic molecular ion ($\mu^+\mu^+e^-$), and hydrogen molecular ion ($p^+p^+e^-$). The deviation from the virial theorem is given by $\Delta_{T,V} \equiv \langle T\rangle + \langle V\rangle/2$. We assume the FEM values to be exact to all figures given (further digits are put in parentheses). Included are expectation values obtained by several other groups. For the number of digits given for the expectation values in the literature the use of different muon masses plays no role. All values are given in atomic units.

Property	$\mu^+e^-e^-$	$e^+e^-e^-$	$\mu^+\mu^+e^-$	$p^+p^+e^-$
Number of grid points	2388	2267	3325	3612
$\Delta_{V,T}$ (a.u.)	1.7×10^{-11}	1.1×10^{-11}	-1.8×10^{-10}	2.4×10^{-9}
$\langle 1/r\rangle$ (a_0^{-1})	0.679 654 500 (84)	0.339 821 023 (12)	0.820 339 75(9)	0.842 492 9(63)
	0.679 654 66[a]	0.339 821 02[a]		0.842 492[i]
		0.339 831 3[e]		0.842 494[j]
		0.339 8[f]		0.842 49[c]
$\langle 1/r_{12}\rangle$ (a_0^{-1})	0.309 199 389 (17)	0.155 631 905 (76)	0.470 427 32(4)	0.490 707 (798)
	0.309 199 50[a]	0.155 631 90[a]		
		0.155 654 3[e]		
		0.155 6[f]		
$\langle r\rangle$ (a_0)	2.727 182 9 (77)	5.489 633 2(38)	1.769 302 45 (2)	1.692 966 (20)
	2.727 182 2[a]	5.489 633 3[a]		1.692 97[i]
		5.489 1[f]		1.692 96[j]
		5.488 352[e]		1.693 0[c]
		5.506[g]		
$\langle r_{12}\rangle$ (a_0)	4.439 280 0 (81)	8.548 580 6(26)	2.205 215 24(7)	2.063 913 (88)
	4.439 278 5[a]	8.548 580 8[a]	2.205 214[b]	2.063 913[b]
		8.547 6[f]		2.063 91[j]
		8.546 111 29[e]		2.063 92[i]
		8.580[g]		
$\langle r^2\rangle$ (a_0^2)	12.074 193 (85)	48.418 936 (25)	3.938 458 0 (59)	3.558 797 (87)
	12.074 159[a]	48.418 936[a]		
		48.415 2[h]		
		48.393 6[f]		
		48.379 317[e]		
		48.75[g]		
$\langle r_{12}^2\rangle$ (a_0^2)	25.514 53 (6 1)	93.178 631 (90)	5.036 585 6 (10)	4.313 286 (038)
	25.514 462[a]	93.178 633[a]		4.313 277 9[d]
		93.171 4[h]		4.313 29[j]
		93.128 3[f]		4.313 31[i]
		93.100 697 0[e]		
		93.94[g]		

[a] Petelenz and Smith [24] ($m_\mu = 206.768\,6$).

[b] McKenna and Webster [29] ($m_\mu = 206.768\,65$).

[c] Bishop and Cheung [35] ($m_p = 1836.152\,75$).

[d] Bishop [36] ($m_p = 1836.152\,75$).

[e] Haftel and Mandelzweig [28].

[f] Ho [26].

[g] Kolos *et al.* [33].

[h] Bhatia and Drachman [34].

[i] Babb and Shertzer [16] (PT).

[j] Babb and Shertzer [16] (FEM).

some cases, the FEM values for the energy and expectation values are the most accurate in the literature. The adaptive FEM also has the advantage of allowing one to solve the Schrödinger equation in identical coordinates for atomic and molecular systems, and everything in between, with exactly the same basis functions. The local polynomials are flexible enough to provide an accurate approximation to the cusps in the wave function at the singularities; they are equally efficient in the asymptotic region, where relatively few basis functions can be used over a large region of coordinate space. Finally, the ability to optimize the grid with respect to physical parameters other than the energy suggests that the FEM will be a valuable tool for future studies in atomic and molecular physics.

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