Global and local properties of the S states of the $dt\mu$ molecular ion: A finite-element study

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An accurate finite-element method (FEM) is applied to solve the three-dimensional Schrödinger equation for the S states of the $dt\mu$ molecular ion. Using an adaptive refinement of the grid and higher-order polynomials the energy eigenvalues are obtained with a relative precision better than 10^{-11}. The deviation from the virial theorem, the two-body cusp ratios, and the expectation values $\langle 1/r\rangle, \langle r\rangle, \langle r^2\rangle, \langle \delta(r)\rangle$ for the three interparticle distances are computed and discussed. The FEM values turn out to be comparable to results obtained with sophisticated global basis sets. Special local refinement techniques are applied to study the expectation values for the Dirac delta functions. New benchmark values for these local properties are presented.
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I. INTRODUCTION

Local properties of the wave function play an important role for many few-body systems. Examples are the hyperfine splitting in muonic systems [1], the annihilation rate in a positronic or antiprotonic system [2,3], or the dt fusion rate in the study of muon catalyzed fusion [4–8]. The quality of a certain local property of a wave function, however, cannot be determined from the quality of the energy eigenvalue and a method to reduce systematically the error of such properties is still lacking. Several attempts have been made to overcome this problem, including the addition of terms that appear in the Fock expansion, using more diffuse operators [9], or the correlation function hyperspherical harmonic method [10]. But the success of each of these is limited to certain applications. It has been suggested that the FEM should yield significantly improved expectation values due to its local interpolation scheme [11]; to our knowledge this has never been shown or studied systematically. In a previous study [12] an adaptive finite-element method (FEM) [13–15] was applied to solve the three-dimensional Schrödinger equation for the ground states of three-body Coulomb systems with two equal masses. The high precision achieved in this direct numerical treatment motivated us to apply the FEM to three-body Coulomb systems with three unequal masses. We chose the prominent $dt\mu$ system for a case study because it has been investigated extensively in connection with muon-catalyzed fusion; see [16–21] and references therein. We restrict ourselves to the lowest two states in the manifold $L=0$, which in the adiabatic limit are labeled by (0,0) and (0,1).

It is the main goal of this work to show that a FEM treatments of a three-body problem with three unequal masses can achieve highly accurate results in terms of energy and expectation values. Focusing on the expectation values for the Dirac delta function, we study how a special local grid refinement can be applied to improve the accuracy of local properties computed usually with global basis sets. When the FEM was applied to the $dt\mu$ system in a previous study [22], a binding energy accurate to 5 significant digits was obtained. High precision values for the binding energies have been presented by several groups; see, for example, [23–27]. A convergence up to 12 and 8 significant digits has been achieved for the energy eigenvalue of the ground state and the (0,1) state, respectively [28,29]. Using a simplified version of the integral transform (generator coordinate) method high precision expectation values for various operators have been published for both S states [30].

II. NUMERICAL PROCEDURE AND RESULTS

For total angular momentum zero ($L=0$) the nonrelativistic Schrödinger equation for three interacting charged point particles depends only on the three interparticle distances r_{12}, r_{13}, and r_{23} [31–34]. We treat the Schrödinger equation in the variational form (if not indicated otherwise, all quantities in this work are given in atomic units)

$$8\pi^2 \int_\Omega r_{12} r_{13} r_{23} \left\{ \frac{1}{2\mu_{12}} \left(\frac{\partial \Psi}{\partial r_{12}}\right)^2 + \frac{1}{2\mu_{13}} \left(\frac{\partial \Psi}{\partial r_{13}}\right)^2 + \frac{1}{2\mu_{23}} \left(\frac{\partial \Psi}{\partial r_{23}}\right)^2 + \frac{1}{2m_1} \frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{r_{12} r_{13}} \frac{\partial \Psi}{\partial r_{12}} \frac{\partial \Psi}{\partial r_{13}} \right.$$

$$\left. + \frac{1}{2m_2} \frac{r_{23}^2 + r_{12}^2 - r_{13}^2}{r_{23} r_{12}} \frac{\partial \Psi}{\partial r_{23}} \frac{\partial \Psi}{\partial r_{12}} + \frac{1}{2m_3} \frac{r_{13}^2 + r_{23}^2 - r_{12}^2}{r_{13} r_{23}} \frac{\partial \Psi}{\partial r_{13}} \frac{\partial \Psi}{\partial r_{23}} + V(r_{12}, r_{13}, r_{23}) \Psi^2 \right\} dr_{12} dr_{13} dr_{23} = I_{\min} = E, \quad (1)$$

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TABLE I. The energy E, the binding energy $E_{\rm bin}$, and the expectation values for various operators for the S states of $dt\mu$. The threshold energy for the dissociation into $t\mu$ and d is given in atomic units by $\epsilon_{\rm thr}=-0.5m_t m_\mu/(m_t+m_\mu)$. The conversion factor 1 a.u.=27.211 3961 eV is applied. The FEM results are converged to all figures given; additional digits are given in parentheses. The mass values $m_\mu=206.768\,262$, $m_d=3670.483\,014$, and $m_t=5496.921\,58$ are used.

Property	(0,0)	(0,1)
Number of grid points	3288	3509
E (a.u.)	−111.364 346 91(4)	−100.916 425 77(3)
	−111.364 346 90[a]	−100.916 425 766[a]
$E_{\rm bin}$ (eV)	319.136 967	34.834 446
	319.136 967[a]	34.834 446[a]
$\Delta_{T,V}$ (a.u.)	3.0e-8	7.0e-8
$\Delta_{T,V}$ (a.u.)	1.4e-8[a]	1.1e-8[a]
$\langle 1/r_{t\mu}\rangle$ (a_0^{-1})	156.795 600(92)	145.849 22(35)
$\langle 1/r_{d\mu}\rangle$ (a_0^{-1})	149.431 424(79)	106.421 30(15)
$\langle 1/r_{dt}\rangle$ (a_0^{-1})	83.498 331(83)	50.437 67(34)
$\langle r_{t\mu}\rangle$ $(10^{-2}a_0)$	0.978 738 45(55)	1.324 550(98)
	0.978 738 456[a]	1.324 550 984[a]
$\langle r_{d\mu}\rangle$ $(10^{-2}a_0)$	1.024 292 71(49)	1.902 243(25)
	1.024 292 716[a]	1.902 243 430[a]
$\langle r_{dt}\rangle$ $(10^{-2}a_0)$	1.328 982 55(34)	2.496 141(59)
	1.328 982 556[a]	2.496 141 767[a]
$\langle r_{t\mu}^2\rangle$ $(10^{-4}a_0^2)$	1.262 377 5(38)	2.750 792(35)
	1.262 377 542[a]	2.750 792 364[a]
$\langle r_{d\mu}^2\rangle$ $(10^{-4}a_0^2)$	1.375 772 0(32)	5.238 725(58)
	1.375 772 038[a]	5.238 727 619[a]
$\langle r_{dt}^2\rangle$ $(10^{-4}a_0^2)$	1.938 414 4(13)	7.164 69(22)
	1.938 414 422[a]	7.164 694 220[a]

[a]Bishop, Frolov, and Smith [30].

where the reduced masses are given by $\mu_{ij}=m_i m_j/(m_i+m_j)$. The potential energy has the usual form

$$V(r_{12},r_{13},r_{23})=\frac{Z_1Z_2}{r_{12}}+\frac{Z_1Z_3}{r_{13}}+\frac{Z_2Z_3}{r_{23}}. \tag{2}$$

A self-adaptive multilevel finite-element method (FEM) [14] is used to treat the variational problem (1). First, we select the set of mass parameters $m_\mu=206.7686$ a.u., $m_d=3670.481$ a.u., and $m_t=5496.899$ a.u. The adaptive FEM obtained a binding energy of $E_{\rm bin}=319.139\,752\,153$ eV after fourteen refinement steps on a grid with 4560 points. This energy value has a relative error of 3×10^{-12} compared to the bench mark value $E_{\rm bin}=319.139\,752\,161$ eV, which were obtained with up to 1400 explicitly correlated Slater type geminals [28,29].

After having verified that accurate energy eigenvalues for $dt\mu$ can be obtained with the adaptive FEM, we turn to expectation values for various operators. Therefore we change the mass parameters to the (more recent and reliable) set of mass values $m_\mu=206.768\,262$, $m_d=3670.483\,014$, and $m_t=5496.921\,58$ [35]. The FEM results obtained for the (0,0) and (0,1) states are listed in Table I. The results are compared with the benchmark values obtained by Bishop, Frolov, and Smith [30]. Improved FEM results may be computed by further refinement steps, however, the number of refinement steps is restricted by the requirements on the computer being used. The FEM and the global approach [30] show excellent agreement, but despite the fact that the FEM energy eigenvalues are one order of magnitude more accurate the expectation values are not improved by the FEM. This is a surprising result since the FEM expectation values are usually of very high accuracy. The reason for this result becomes obvious when inspecting the deviations from the virial theorem $\Delta_{T,V}=\langle T\rangle+\langle V\rangle/2$, where T and V denote the kinetic and potential part of the Hamiltonian, respectively. Since the error in the energy eigenvalue ($<10^{-11}$) is small compared to $\Delta_{T,V}<10^{-7}$ the accuracy of the FEM expectation values is determined by the deviation from the virial theorem; see Ref. [12] for a discussion. The large deviation from the virial theorem indicates that the FEM energy eigenvalue is lowered by the cancellation of errors in different parts of the Hamiltonian. Such a cancelation of errors is well known for energy optimized global basis sets and seems to play a role in FEM calculations on energy optimized grids as well. The situation is different in the global basis set expansion of Bishop *et al.* [30], where the deviations from the virial theorem and the errors in the energies are of the same order of magnitude. This is probably a consequence of the quasirandom choice of the nonlinear parameters in the integral transform method.

An attractive feature of the FEM is the flexibility of the method. Hence, we use the adaptive refinement to improve

TABLE II. The integrated cusp values $\nu(r_{ij})=\langle\delta(r_{ij})\partial/\partial r_{ij}\rangle/\langle\delta(r_{ij})\rangle$ and the expectation values for the Dirac delta functions for the (0,0) state. The exact values for the integrated cusp values are given by $\nu_{ij}=Z_iZ_jm_im_j/(m_i+m_j)$.

Property		Relative precision
$\nu(r_{d\mu})$ (a_0^{-1})	−195.741 42[a]	9×10^{-7}
	−195.741 606 34[b]	1×10^{-9}
	−195.742 14[c]	3×10^{-6}
	−195.741 606 48	exact
$\nu(r_{t\mu})$ (a_0^{-1})	−199.272 37[a]	1×10^{-6}
	−199.272 567 62[b]	2×10^{-9}
	−199.272 09[c]	2×10^{-6}
	−199.272 567 92	exact
$\nu(r_{dt})$ (a_0^{-1})	2203.889[a]	1×10^{-3}
	2200.879 824[b]	1×10^{-7}
	2200.014[c]	4×10^{-4}
	2200.879 985	exact
$\langle\delta(r_{d\mu})\rangle$ $(10^6a_0^{-3})$	1.366 003 73[a]	
	1.366 003 81[b]	
	1.366 003 4[c]	
$\langle\delta(r_{t\mu})\rangle$ $(10^6a_0^{-3})$	1.542 707 30[a]	
	1.542 707 39[b]	
	1.542 706 8[c]	
$\langle\delta(r_{dt})\rangle$ (a_0^{-3})	7.838 43[a]	
	7.841 86[b]	
	7.841 95[c]	

[a]FEM, energy optimized.
[b]FEM, $\langle\delta(r_{ij})\rangle$ optimized.
[c]Bishop, Frolov, and Smith, 1995 [30].

the expectation values for the Dirac delta functions $\delta(r_{ij})$, see [14]. The corresponding FEM results can be compared with the FEM results for energy optimized grids and the benchmark values obtained by Bishop, Frolov, and Smith [30], see Table II. An indication for the relative precision of the expectation values for Dirac delta functions is given by the quality of the two-body cusp ratios $\nu(r_{ij}) = \langle \delta(r_{ij}) \partial/\partial r_{ij} \rangle / \langle \delta(r_{ij}) \rangle$. The special local refinement improves the benchmark values of Bishop *et al.* [30] by several orders of magnitude.

III. CONCLUSION

The adaptive FEM turned out to be a valuable method for the treatment of general three-body Coulomb problems with a total angular momentum of zero. A relative precision better than 10^{-11} is easily achieved for the energy eigenvalues of the *S* states of $dt\mu$. The precision of the expectation values and the deviation from the virial theorem are comparable to sophisticated global basis set expansions. A cancellation of errors in a different part of the Hamiltonian is observable for the FEM, as is well known for expansions in global basis sets that are strictly optimized to minimize the energy eigenvalue. Thus, the local interpolation scheme of the finite element method does *not* lead to a superior overall precision of the wave function if compared to global basis set approaches. This seems to be a direct consequence of the adaption of the FEM grid according to the energy minimum principle. Remarkably, in the adaptive FEM these error cancellations occur only for three-body problems in which a fast electronic (or muonic) motion is coupled with a slow ''vibrational'' nuclear-nuclear motion. A similar error cancellation has been observed for the application of the adaptive FEM to the hydrogen molecular ion H_2^+, but not in such cases as the helium atom or the Ps^- system ($e^+e^-e^-$) [12] in which no slow nuclear-nuclear motion is involved. In global basis set expansions for $dt\mu$, on the other hand, this error cancellation does not occur if the nonlinear parameters are chosen quasirandomly as in the integral transform generator coordinate method [30]. This is strongly indicated by the fact that the deviation from the virial theorem and the error in the energy eigenvalue in the numerical treatment of Bishop *et al.* are of the same order of magnitude. This favorable result is not obtained by the FEM on energy optimized grids, however, the adaptive FEM is not restricted to energy optimized grids; a multilevel local grid refinement according to any physical property is possible. We demonstrated this by the refinement of the grid according to the expectation values for the Dirac delta functions. The resulting expectation values $\langle \delta(r_{ij}) \rangle$ are the most accurate in the literature.

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