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Variational calculation of the energy levels for the $td\mu$ ion

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We present variational calculations of the energy levels of the $td\mu$ ion relevant for muon-catalyzed fusion. We used very large generalized Hylleraas basis sets. For all the levels the results are better than literature data. For the most important, weakly bound state of $td\mu$ we obtained a binding energy of 660.01 meV which we estimate to be accurate to about 0.1 meV. For the remaining states the energies converge much faster and we were able to achieve accuracy of about 1 μeV or better.

I. INTRODUCTION

The $td\mu$ molecular ion—consisting of triton and deuteron nuclei and of a muon—has been the subject of several papers in the last few years. The reason for this interest is the importance of this ion for the muon-catalyzed fusion process.[1] The latest experiments[2] have shown that as many as 150 fusions can be produced by a single muon in its lifetime. These results have greatly increased hopes for muon-catalyzed fusion to become an efficient energy source.

Due to the mass of the muon (207 times greater than the mass of the electron) the $td\mu$ ion is basically a nonadiabatic system. A very high accuracy of calculations for the bound states of this ion is required[3] to guide the experiments. Variational calculations for muonic molecular ions date back to the early 1960s[4-6] but the accuracy of these calculations did not allow any conclusions to be drawn about the existence of weakly bound states of these ions. Such states play a critical role in the formation of these ions. The complete set of the bound-energy levels for the $td\mu$ ion was reliably computed for the first time in 1980 by Vinitsky *et al.*[7] using an expansion in adiabatic states. A few years later variational calculations by Bhatia and Drachman[8] and by Frolov and Efros[9] confirmed the correctness of the results of Vinitsky *et al.* for most of the states. However, the variational calculations gave quite different results for the highest bound state of $td\mu$, i.e., the second level in P symmetry (rotational quantum number $J=1$). This state is probably the most important one since its energy controls the formation rate of $td\mu$ ions. Later calculations by Hu,[10,11] Frolov and Efros,[12] and most recently by Korobov, Puzynin, and Vinitsky[13] brought the variational results close to those of Ref. 7. Also, the calculations with the adiabatic expansion method have been recently improved.[14] However, although some of the latest papers claim to reach accuracy of about 1 meV, for all states the final energies in different papers are much more than 1 meV apart.

II. METHOD

We are solving a complete three-body Coulomb problem defined by the Hamiltonian[8]

$$H=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\left(\frac{\mu_1}{\mu_2}\right)\nabla_2^2-\left(\frac{\mu_1}{m}\right)\nabla_1\cdot\nabla_2-\frac{1}{r_1}-\frac{1}{r_2}+\frac{1}{r_{12}}\ , \tag{1}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the vectors from the muon to the triton and deuteron, respectively, r_{12} denotes the distance between the nucleons, and $\mu_i=mM_i/(m+M_i)$, $i=1,2,\ldots$ are the reduced masses of the muon-triton and muon-deuteron systems, respectively. We assumed units such that $\hbar=e=\mu_1=1$. The values of M_1, M_2, and m are (in units of the electron mass) 5496.899, 3670.481, and 206.7686, respectively. These masses are the same as in most of the recent papers on the subject. Later on we will discuss the effect of variation of the masses. We used a value of 13.6058041 eV for the infinite-mass Rydberg constant. All our calculations with large basis set were performed in 29–32 decimal digits arithmetic. The $td\mu$ wave functions have been expanded in the following generalized[4] Hylleraas basis sets:

$$\psi=\sum_{i=1}^{N}c_i r_1^{k_i}r_2^{l_i}r_{12}^{m_i}e^{-\alpha r_1-\beta r_2-\gamma r_{12}}\ \text{for } S \text{ states}\ , \tag{2}$$

$$\psi=\sum_{i=1}^{N_1}c_i r_1^{k_i}r_2^{l_i}r_{12}^{m_i}e^{-\alpha r_1-\beta r_2-\gamma r_{12}}\cos\theta_1+\sum_{i=1}^{N_2}\bar{c}_i r_1^{k_i}r_2^{l_i}r_{12}^{m_i}e^{-\bar{\alpha} r_1-\bar{\beta} r_2-\bar{\gamma} r_{12}}\cos\theta_2\ \text{for } P \text{ states}\ . \tag{3}$$

Our basis set has the angular component defined in the same way as in the work of Frolov and Efros.[9,12] This component differs by transformations from the basis sets used by Bhatia and Drachman[8] and by Hu.[10,11] The isotropic part is more general than that used by Bhatia and Drachman since it contains $\exp(-\gamma r_{12})$. The basis set of Hu contains a combination of two exponential terms for each set of powers of coordinates. This choice makes the basis more flexible but also increases substantially the time of calculation of the matrix elements. We have tried this approach and decided that the use of uncontracted functions should be more efficient, though it may need

longer expansions. In addition, in all of Hu's calculations, except for those of Ref. 10, cusp conditions are imposed on the basis functions. As it is shown in Ref. 15, cusp conditions in our basis set lead in general to a slower convergence of energies. No cusp conditions have been imposed in the present work. The basis set used by Frolov and Efros did not employ any powers of the distances for the S states and only the first powers (necessary due to the symmetry requirement) for the P states. Instead the authors used different exponents for each function obtained in some random manner.

III. RESULTS

Our results for all the states considered—except for the excited P state—are displayed in Table I. The notation here is (k,l,m,ω), where k, l, m are maximum powers defined by Eqs. (2) and (3) and ω is the maximum of $k_i+l_i+m_i$. The data given in Table I fully specify our basis sets, so that our results can be reproduced. Unfortunately, most of the literature papers do not contain enough information to enable such a reproduction. For all states we have obtained energies better than the literature data. We were quite surprised by the obtained improvement since the literature data seemed to be well converged. The convergence patterns shown in Table I are quite convincing and we believe that an accuracy of at least 1 μeV has been achieved for all three states.

For the 00 state (the notation here is Jv where v denotes consecutive levels with a given J) we made a rather simple choice of basis functions. Comparison of the results in the 157 and 164 basis sets clearly shows that a better basis set is obtained if one takes higher powers for r_{12} than for the other two coordinates. We employed this principle for all the larger basis sets. It is quite likely that a more careful choice of the basis functions could further improve the convergence. We have not attempted to do so since the convergence was already extremely fast. We have used various sets of exponents for this state. Results with two such sets are reported in Table I. These sets were obtained by optimizing the exponents in a smaller and a larger basis set. We see that the better exponents improve the energy for smaller basis sets ($N=200$ and 246) but

TABLE I. Binding energies (in eV) for 00, 01, and 10 states of the $td\mu$ ion with various expansions. Exponents α, β, and γ are listed for each basis set. We assumed that 1 muonic atom unit of energy is exactly equal to 5422.5347 eV.

state 00						state 01						state 10					
number of terms	k	l	m	ω	energy	number of terms	k	l	m	ω	energy	number of terms	k	l	m	ω	energy
exponents: 0.757 0.721 0.982						exponents: 0.627 0.500 0.841						exponents: 0.678 0.642 1.098					
84	6	6	6	6	319.0357	84	6	6	6	6	33.605	166	6	6	6	7	232.4613
120	7	7	7	7	319.1205	120	7	7	7	7	34.463	240	8	8	8	8	232.4674
164	8	8	7	8	319.1293	164	8	8	7	8	34.6771	330	9	9	9	9	232.47056
157	6	6	8	8	319.1378	157	6	6	8	8	34.7153	555	9	9	9	12	232.47149
200	6	6	9	9	319.1389	200	6	6	9	9	34.7973						
246	6	6	10	10	319.1395	246	6	6	10	10	34.8245						
266	7	7	10	10	319.1395	266	7	7	10	10	34.8249						
294	6	6	11	11	319.1397	294	6	6	11	11	34.8314						
						343	6	6	12	12	34.8332						
exponents: 0.749 0.694 1.383						385	7	7	12	12	34.8335	exponents: 0.770 0.772 1.199					
						638	8	8	12	15	34.834434						
200	6	6	9	9	319.13968							302	6	6	8	9	232.47089
246	6	6	11	11	319.13972	exponents: 0.727 0.483 0.803						430	8	8	10	10	232.471490
294	6	6	11	11	319.13973							544	8	8	10	11	232.471524
343	6	6	12	12	319.139742	385	7	7	12	12	34.8337						
385	7	7	12	12	319.1397512	638	8	8	12	15	34.834438	exponents: 0.662 0.617 1.352					
415	8	8	12	12	319.1397515	1027	11	11	16	17	34.834463						
490	8	8	13	13	319.1397520	1995	11	11	16	25	34.834465	302	6	6	8	9	232.471213
968	10	10	15	17	319.139752159							430	8	8	10	10	232.471492
1158	11	11	16	18	319.139752161							544	8	8	10	11	232.471529
												820	7	7	10	14	232.471536
literature												1072	9	9	12	15	232.471537
Ref. 7			-		319.15	Ref. 7			-		34.87	Ref. 7			-		232.44
Ref. 8			440		319.062	Ref. 8			440		34.573	Ref. 8			440		232.416
			extr.		319.25	Ref. 9			250		34.82381				extr.		232.416
Ref. 9			250		319.13805				extr.		34.84	Ref. 9			250		232.4205
			extr.		319.140	Ref. 10			230		34.689				extr.		232.48
Ref. 10			230		319.086				280		34.733	Ref. 12			250		232.2906
			280		319.094				330		34.772				350		232.4471
			330		319.115				380		34.776				extr.		232.4940
			380		319.117							Ref. 10			150		232.417
Ref. 11			450		319.13382										250		232.434
			500		319.13419										300		232.436
												Ref 11			692		232.46859
															740		232.46867

for larger basis set ($N \geq 294$) the reoptimization did not give any significant improvement. This is, of course, a manifestation of the well-known fact that in an infinite-size basis the precise values of the exponents are irrelevant. We checked that a reoptimization of the exponents in the basis set of 490 functions led to an improvement smaller than 0.1 μeV. We also optimized a large basis set with six nonlinear parameters (different exponents for functions with small and large $k_i+l_i+m_i$) with a similar effect. We conclude that our best energy is convergent up to at least 1 μeV. We were pushing for such a high accuracy since it was necessary to obtain convergent sticking fractions for this state.[15]

The literature values cited in Table I show that some workers have obtained a false convergence, i.e., their results suggest that the basis set became saturated while the energy value was in fact quite far from the true limit. Our final energy for the 00 state is 78, 5.6, and 1.7 meV better than the best values of Refs. 8, 11, and 9, respectively. One should notice the correct value of the Frolov and Efros[9] extrapolated energy. In contrast, the extrapolated value of Bhatia and Drachman[8] gives a larger error than their best calculated result. This observation shows that the extrapolations do not necessarily lead to improved values. The nonvariational result of Vinitsky *et al.*[7] differs from our convergent value by 1 in the last digit given in Ref. 7. Thus, the accuracy of such calculations was about 10 meV compared to the present accuracy of 1 μeV.

Although our 00 state energy is converged to at least 1 μeV, only the value up to about 1 meV has physical meaning due to uncertainties in the nuclear and muon masses and even due to roundings of the conversion factor from muon atomic units to electronvolts (our value of this factor was 5422.5347). In a recent paper[16] Hu reports a 695-term calculation giving energy of 319.140098 eV. This result was obtained, however, with different masses: $M_1=5496.918$ and $m=206.769$ electron masses. We recalculated our energy with these masses in the basis set of 490 functions obtaining 319.1401224 eV (with the conversion factor equal to 5422.5456). We estimate the convergent energy with these masses to be 319.140123 eV.

For the 01 state the energy seems to be converged to about 1 μeV although the convergence is slower than for the 00 state. Our best energy is 261, 58, and 10.6 meV better than the best energies of Refs. 8, 10, and 9, respectively. The nonvariational result of Ref. 7 differs by 40 meV from our value. The extrapolation of Frolov and Efros[9] is again quite reasonable; it overshoots by only about 6 meV. Our binding energy recomputed with the masses used by Hu[16] is 34.8343 eV and therefore it is 0.7 meV larger than the value obtained by Hu.[16]

For the lowest P state (10) our energy is probably also converged to about 1 μeV. The final energy is 56, 24.4, and 2.9 meV better than the final results of Refs. 8, 12, and 11, respectively. The nonvariational result of Ref. 7 differs by 0.03 eV. The earlier extrapolation of Frolov and Efros[9] is quite good, as it gives the energy too large by about 8 meV. However, their later extrapolation[12] is too large by as much as 22.5 meV. These results show again how unreliable the extrapolations are. Our binding energy with the 544-term basis set recalculated using masses of Ref. 16 is 232.471 698 eV.

The excited P state (11) presented a much greater difficulty. For this state simple choices of the basis functions, i.e., assuming some fixed values for k, l, m, and ω, led to a rather slow convergence. This convergence can be significantly improved if only some terms are selected from a given basis set. Such a selection can be performed by considering the improvement in energy obtained by appending an additional function to a basis set. We have used several techniques of such selection. However, this method requires repeated diagonalizations of the Hamiltonian matrix. Since the time of diagonalization grows as the cubic power of the number of basis functions, this method becomes too time consuming for larger basis sets. We were able to select basis sets with up to 573 functions out of a total of 2016 terms. The energies with these basis sets were very close to those of Refs. 13 and 17 in basis sets of similar size. In the above runs, as well as for the 10 state discussed above, we used the same set of exponents for all the $\cos\theta_1$ and $\cos\theta_2$ terms. This means that with

TABLE II. Binding energies (in meV) for the 11 state of $td\mu$ ion using various basis sets.

	Number of terms	Energy Quadruple exponents	Octuple exponents
	437	641.0	· · ·
	573	656.45	657.51
	1144	658.67	658.94
	1445	659.47	659.62
	1890	659.74	659.82
	2625	659.96	659.98
	3063	660.01	· · ·
Literature			
Ref. 7	· · ·	640	
Ref. 14	· · ·	656	
Ref. 8	440	224	
Ref. 9	375	523.1	
	Extrapolated	600	
Ref. 12	400	607.2	
	Extrapolated	655.4	
Ref. 10	500	628	
Ref. 17	400	604.6	
	500	646.7	
	600	649.6	
Ref. 16	1102	658.0	
Ref. 13	568	647.7	
	844	652.3	
	982	653.7	
	1495	658.9	
	Extrapolated	663 ± 2	
Ref. 18	542	651.14	
	927	656.91	
	1483	658.89	
	1513	659.23	
	2084	659.68	
	Extrapolated	660.4 ± 0.2	

only three nonlinear parameters we were able to match literature results obtained with 12 to 18 such parameters. To further improve our energies we increased the flexibility of our basis set by using different exponents for the $\cos\theta_1$ and $\cos\theta_2$ terms and by using a different set of exponents for terms with $k_i+l_i+m_i \leq 12$ from those for the remaining terms, i.e., using a quadruple set of exponents. To check the convergence of the energies we also optimized an octuple set of exponents with different exponents for the sum of powers within 1–6, 7–12, 13–18, and 19–30 range. Our results with such basis sets are shown in Table II and compared with the literature data. The exponents and values of the powers are available from the authors upon request.

The pattern of convergence of our results, and in particular comparison of energies with quadruple and octuple exponents, suggests that the error of our binding energy for the 11 state may be about 0.1 meV. We have extrapolated our results with the formula of Frolov and Efros[12]: $E(N)=E(\infty)+CN^{-\gamma}$ where $E(\infty)$, C, and γ were optimized to obtain the best least-squares fit to our energies. Using our three largest quadruple exponents calculations leads to the extrapolated value of 660.1 meV. If four such energies are used, we get 660.2 meV. As we have discussed above, the extrapolated result is not necessarily better than the best calculated value. It seems safe, however, to assume that the true value of the energy for this state is 660.1 ± 0.1 meV. Thus, for the first time the energy of the 11 state has been computed with accuracy better than 1 meV necessary to theoretically predict the formation rate of $td\mu$.

As one may see from Table II, our results for the 11 state are better than all the literature values. The literature energy closest to ours is the very recent basis set 2084 result by Korobov, Puzynin, and Vinitsky[18] which is by 0.33 meV worse than our energy with 3063 functions. These authors used a slightly different mass for the triton than used by us. We recalculated our basis set 1890 (octuple exponents) binding energy with their mass obtaining the value of 659.85 meV, i.e., 0.03 meV larger than our result in the same basis. Thus, for this state the uncertainties in the masses are not important. The extrapolated energy of Ref. 18, equal to 660.4 meV, is 0.3 meV larger than ours. However, comparison of this energy with the earlier extrapolated energy (663 meV) by the same authors[13] suggests that their extrapolations tend to overestimate the binding energy.

After adding the relativistic corrections[19] our binding energy for the 11 state can be used to predict formation rate of the $td\mu$ ion. Work in this direction is in progress in our group.

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