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Bound-state calculations of Coulomb three-body systems

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Various geometrical and energetical properties in the symmetric muonic molecular ions $pp\mu, dd\mu, tt\mu$, molecular ions ppe, dde, tte, and exotic system $\mu\mu e$ $(\mu^+\mu^+e^-)$ are determined with high accuracy by using the two-stage strategy proposed by Frolov [Phys. Rev. A **57**, 2436 (1998)]. The significant difference between bound-state spectra in muonic molecular ions $pp\mu, dd\mu, tt\mu$ and molecular ions ppe, dde, tte ions is explained by using the general theory of bound-state spectra in Coulomb three-body systems, which is closely related with the general theory of compact operators. In particular, the principal classification of the bound-state spectra in such systems can be made in the same manner as for compact operators. For instance, the discrete spectrum of a Coulomb three-body system may have the Hilbert-Schmidt, nuclear or finite-dimensional structure. Moreover, this structure can be changed by varying some of the physical parameters (e.g., masses or charges) of the system. The developed theory is applied to the case of symmetric Coulomb three-body systems with unit charges. [S1050-2947(99)02706-7]

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I. INTRODUCTION

The two-stage strategy proposed previously [1] was found to be a very effective and quite simple approach for the construction of extremely accurate wave functions for various three-body systems. In the present study we consider this strategy for the symmetric muonic molecular ions $pp\mu, dd\mu, tt\mu$, ''adiabatic'' molecular ions ppe, dde, tte, and the exotic system $\mu\mu e$ $(\mu^+\mu^+e^-)$. Our main goal is to perform highly accurate calculations for a number of properties of such systems. It should be mentioned that some of the properties of the muonic molecular ions and ppe have been computed previously (see, e.g., [1–6]). The properties of the dde ion can be found in [1, 6] and energies for all adiabatic molecular ions in [7] (see, also, [8] and [9]). In general, all muonic properties found in various calculations for $pp\mu, dd\mu, tt\mu$ agree quite well, but for the internuclear distances and other internuclear properties, e.g., $\langle \delta_{++} \rangle$ and nuclear cusp ν_{++} such an agreement is not so good. Unfortunately, these properties determine the appropriate fusion probabilities and other important characteristics which are of interest for thermonuclear applications. In the case of adiabatic systems such as ppe, dde, tte the situation with nuclear properties is even worse. Presently, we attempt to compute such properties more accurately than in a number of previous studies (see, e.g., [2], and references therein). The basic idea of this study is to apply the two-stage strategy in order to chose the optimal values for the nonlinear parameters. Finally, the convergence rate of the variational expansion used in computations increases significantly. The two-stage strategy is discussed in detail in Sec. II. The results of high-precision calculations for both muonic molecular and molecular ions can be found in Sec. III.

Note that all highly accurate calculations for molecular ions have been performed by using the universal variational expansion in the relative coordinates r_{32}, r_{31}, and r_{21}. In particular, no assumption was made that the internuclear variable r_{21} is slow in the adiabatic systems. This means that from the computational point of view no difference can be found between muonic and molecular ions. However, it should be mentioned that there is a principle difference between the bound-state spectra in muonic and molecular ions. Indeed, the total number of bound states in such systems increases rapidly when the two masses of positively charged particles (i.e., m_1 and m_2) grow to infinity. For instance, there are only two bound states in the $pp\mu$ ion, six bound states in the $tt\mu$ ion, and many dozens of bound states in any of the the molecular ions, e.g., in the tte ion. This problem is discussed in Sec. IV. Here, we consider the general structure of the bound-state spectra in Coulomb three-body systems (and furthermore, in quantum systems). It is shown that the principal classification of bound-state spectra in such systems can be made as for compact operators. In particular, the discrete spectrum of a quantum system may have the Hilbert-Schmidt, nuclear or finite-dimensional structure. This problem is of interest not only from a theoretical point of view, but also in order to develop new, advanced procedures for performing highly accurate calculations in such systems. For instance, the structure of the bound-state spectra in the $pp\mu$ and tte ions and in the He atom differ significantly from each other, but in actual calculations this fact is simply ignored and essentially the same numerical methods are used to determine the bound states in all these systems. The next generation of highly accurate numerical methods should take into account the principal structure of the bound-state spectra in the considered system. Conclusive remarks can be found in the Conclusion.

II. THE TWO-STAGE STRATEGY FOR HIGH-PRECISION, BOUND-STATE CALCULATIONS

In 1968, Delves and Kalotas published a paper [10] on variational calculations of the muonic molecular ion $pp\mu$ [the ground $S(L=0)$ state]. This work contained a few brilliant ideas which have been transformed latterly into a quite simple, but very effective procedure to perform highly accurate, three-body calculations of various systems. In particular, in [10] it was shown that the following variational expansion:

$$\Psi = \frac{1}{2}(1+\kappa\hat{P}_{21})\sum_{i=1}^{N} C_i \exp(-\alpha_i r_{32} - \beta_i r_{31} - \gamma_i \cdot r_{21}) \tag{1}$$

can be used successfully in ground-state ($L=0$) calculations for various Coulomb three-body systems. Here C_i are linear (or variational) parameters and α_i, β_i, and γ_i are nonlinear parameters. The operator P_{21} is the permutation of the two identical (1 and 2) particles in the symmetric systems, where $\kappa=+1$ (or -1), otherwise $\kappa=0$. In the present study only the case $\kappa=+1$ is discussed.

It should be mentioned that the variational expansion Eq. (1) has been used extensively in nuclear physics calculations previously [10]. The main advantage of [10] follows from the observation made in this work: the variational energy E_N depends significantly upon the number of basis functions N (when N is quite large), rather than the concrete values of the nonlinear parameters α_i, β_i, and γ_i. In other words, at large N the dependence E_N can be expressed in the quite simple form which contains (with good accuracy) only the parameter N. In [10] it was represented in the form:

$$E_N = E_\infty + \frac{A}{N^\gamma}, \tag{2}$$

where $E_\infty(<0)$, $A(>0)$ and $\gamma(>0)$ are the three constants. Obviously, E_∞ is the asymptotic (i.e., exact) value of the energy, which formally corresponds to the infinite basis function limit, i.e., $N=\infty$. The numerical value of γ is critically important, since if γ is not large enough (e.g., $\gamma \leqslant 3$), then the procedure will not work successfully. In [10] it was found that $\gamma=8$ for the ground $S(L=0)$ state of the $pp\mu$ ion. This indicates the very fast convergence of Eq. (1) in the considered case.

It follows from Eq. (2) that the variational calculations for the ground state of the $pp\mu$ ion and other similar systems can be made, in principle, with arbitrarily high accuracy, since $E_N \rightarrow E_\infty$, when $N \rightarrow \infty$. However, in reality, a number of various restrictions can be found and performance of such calculations is quite difficult. The first restriction follows from the fact that the parameter γ depends significantly on the particle masses [11]. For instance, for the $pp\mu$, $dd\mu$, and $tt\mu$ ions γ decreases consequently from ≈ 8–8.5 to ≈ 5.5–6. The accuracy of the energy determination decreases correspondingly. This phenomena is called adiabatic divergence of Eq. (2). The detail analysis of adiabatic divergence can be found in [7] or [11] (see, also, the Appendix).

The second restriction follows from the fact that in actual calculations the maximal number of basis functions $N_{\max}$ can not be increased to infinity. Furthermore, such a number $N_{\max}$ is determined almost uniformly if all neccessary quantum numbers and permutation symmetry are given for the considered system. For instance, for the ground $S(L=0)$ state in the $pp\mu$, $dd\mu$, and $tt\mu$ ions the appropriate $N_{\max}$ values equal ≈ 800. For larger dimensions the overlap matrix $\hat{S}$ becomes extremely ill-conditioned, since the corresponding condition number $A(\hat{S}) = \ln(\lambda_{\max}/\lambda_{\min})$ exceeds 65–70 [12]. Here, $\lambda_{\max}$ and $\lambda_{\min}$ designate the maximal and minimal eigenvalues of the overlap ($\hat{S}$) matrix. As a result, the solution of the eigenvalue problem $(\hat{H} - E \cdot \hat{S})\vec{C} = 0$ complicates significantly [12]. Briefly, this means that the approach based on Eq. (2) is quite restricted in real applications.

In order to avoid the second restriction in high precision, variational, three-body calculations we propose to use the two-stage procedure [1]. In this approach the trial wave function Ψ is represented by the sum of the very well optimized, short-term function Ψ_1 and roughly optimized (or even nonoptimized), long-term function Ψ_2. If the total number of terms equals N, then we may write: $\Psi(N) = \Psi_1(N_0) + \Psi_2(N-N_0)$, where $N_0 \ll N$ (and also $N_0 \gg 1$). Let us consider in detail the exponential variational expansion Eq. (1). Since in this case each of the basis functions contains three nonlinear parameters, the short $\Psi_1(N_0)$ function includes three N_0 nonlinear parameters, while the second $\Psi_2(N-N_0)$ function contains three $(N-N_0)$ such parameters. Correspondingly, the first stage of the procedure is to optimize quite well only the three N_0 nonlinear parameters, which is significantly smaller than the total number of these parameters ($3N$) in the trial wave function Ψ. In the second stage the total number of nonlinear parameters grows extensively, but they can be chosen by approximate optimization or even without optimization, e.g., in a regular [10] or quasirandom manner (see, e.g., [2], and references therein). The detail discussion of the regular choice of the nonlinear parameters can be found in [10], while the quasirandom choice is described, e.g., in [2].

Now, for the two-stage procedure one easily finds from Eq. (2):

$$E_N = E_\infty + (E_{N_0} - E_\infty)\left(\frac{N_0}{N}\right)^\gamma, \tag{3}$$

where N_0 is the number of basis functions in the short-term function Ψ_1 and N is the total number of basis functions used. In actual calculations for the ground $S(L=0)$ state in the symmetrical systems $N \approx 700$–800, while $N_0 \approx 200$. Since $\gamma \approx 7-8$, the factor $(N_0/N)^\gamma$ is really small. Since the short-term function Ψ_1 is assumed to be well optimized, the absolute value of the first factor $(E_{N_0} - E_\infty)$ is also very small. Thus, the deviation E_N from E_∞ is represented in the factorized form of the two small terms, and in general, the difference $|E_N - E_\infty|$ is significantly smaller than in the case of Eq. (2) [if all nonlinear parameters in Eq. (1) are chosen without any optimization]. It should be pointed out that the N_0 value has to be large enough, i.e., $N_0 \gg 1$, or in other words, $E_{N_0} \approx E_\infty$. The computational advantage of the proposed two-stage strategy and Eq. (3) is obvious. Indeed, if in actual calculations N does not exceed the $N_{\max}$ value, then even in these cases E_N can be approached (very closely) to the exact E_∞ value, by using a more careful optimization of the short-term energy E_{N_0} obtained with N_0 basis functions. Note also, that if (1) the N_0 value has been chosen, and (2) optimization of the short-term function Ψ_1 has been performed, then the results of the second stage (energy) calcu-

TABLE I. The total energies (E) in muon atomic units ($m_\mu=1,\hbar=1,e=1$) for the ground and first excited states ($*$) of symmetric muonic molecular ions. N designates the number of basis functions used.

N	$E(pp\mu)$	$E(dd\mu)$	$E(tt\mu)$
200	−0.494 386 820 231 708	−0.531 111 135 140 824	−0.546 374 218 843 03
400	−0.494 386 820 247 662	−0.531 111 135 374 284	−0.546 374 225 424 60
500	−0.494 386 820 248 520	−0.531 111 135 400 115	−0.546 374 225 582 94
600	−0.494 386 820 248 739	−0.531 111 135 401 532	−0.546 374 225 606 61
700	−0.494 386 820 248 818	−0.531 111 135 402 154	−0.546 374 225 612 58
750	−0.494 386 820 248 837	−0.531 111 135 402 251	−0.546 374 225 613 09
800	−0.494 386 820 248 853	−0.531 111 135 402 300	−0.546 374 225 613 37
900	−0.494 386 820 248 875	−0.531 111 135 402 340	−0.546 374 225 613 60
1000	−0.494 386 820 248 885	−0.531 111 135 402 353	−0.546 374 225 613 73
1200	−0.494 386 820 248 895	−0.531 111 135 402 366	−0.546 374 225 613 80
N		$E((dd\mu)^*)$	$E((tt\mu)^*)$
600		−0.479 706 380 367 595	−0.496 762 894 221 51
700		−0.479 706 380 368 626	−0.496 762 894 244 93
800		−0.479 706 380 368 825	−0.496 762 894 248 02
900		−0.479 706 380 368 861	−0.496 762 894 248 88
1000		−0.479 706 380 368 878	−0.496 762 894 249 32
1200		−0.479 706 380 368 890	−0.496 762 894 249 78

lations can be represented by Eq. (2). In this case one easily finds that in Eq. (2) $A=(E_{N_0}-E_\infty)N_0^\gamma$.

III. RESULTS

In the present study we consider the ground states in symmetric muonic molecular ions $pp\mu, dd\mu, tt\mu$, molecular ions ppe, dde, tte, and exotic system $\mu\mu e$ (or $\mu^+\mu^+e^-$). All constants, conversion factors and particle masses used in calculations have been taken from [13]. In particular, the particle masses are

$$m_p=1836.152\,701 m_e, \quad m_d=3670.483\,014 m_e,$$

$$m_t=5496.921\,58 m_e, \quad m_\mu=206.768\,262 m_e,$$

Also, in the present study we assume that the masses of the positive and negative muons exactly equal each other.

A. Muonic molecular ions

As is mentioned above, for the muonic molecular ions $pp\mu, dd\mu$, and $tt\mu$ the first stage produces a very compact and highly accurate wave function Ψ_1. The appropriate energy contains approximately 8–10 correct decimal figures (in muon atomic units). The second stage of the procedure gives as a rule 2–3 additional correct decimal figures to the total energy, and generates extremely accurate wave functions, which can be used to compute various properties of these systems. The nonlinear parameters for the second stage of the procedure were chosen quasirandomly from three real intervals (this step is discussed in detail in our work [2]). The variational energies obtained are presented in Table I, while the numerical values for some of the properties (i.e., expectation values) are presented in Table II. In both Tables I and II only muon atomic units are used: $m_\mu=1, e=1$, and $\hbar=1$. The results for $N=200(=N_0)$ (Table I) correspond to the highly accurate short-term wave function Ψ_1. As follows from Table I the accuracy achieved for the total energies E by using the proposed two-stage approach is significantly higher than known from the previous works. But, in principle, such an accuracy can be increased drastically by performing better optimization for the short-term Ψ_1 function. For the excited states in the muonic molecular ions $dd\mu$ and $tt\mu$ we report in Table I only the total energies. The corresponding binding energies are $-35.844\,246\,814\,755\,4$ eV ($N=1200$) and $-83.770\,726\,685\,475$ eV ($N=1200$) for the $dd\mu$ and $tt\mu$ ions, respectively. These figures are significantly more accurate than the values known for those states from previous calculations. But the bound-state properties for the excited states have not been computed, since the first $3N_0$ nonlinear parameters were optimized for the ground states only.

The numerical values for some of the properties (i.e., expectation values) in muon atomic units can be found in Table II. In this table only stable figures from calculations with the higher N are presented for most of the properties. For the two-particle cusps only the best results are given in Table II. The physical meaning for all of the expectation values in Table II is quite clear from the notations used (for more detail, see also [1]). So, here we wish to make only a few following remarks. In all the formulas given below and also in Table II the notations 1 and 2 mean positively charged heavy nuclei, while the notation 3 designates the muon. The notations δ_{31}, δ_{21}, and δ_{321} stand for the two- and three-particle Dirac delta functions, respectively. The two-body cusp ratios are determined in a traditional manner:

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

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

TABLE II. The expectation values $\langle X_{ij}\rangle$ in muon atomic units ($m_\mu=1,\hbar=1,e=1$) of some properties for the ground states in some muonic molecular ions. The notations 1 and 2 designate the two identical particles, while 3 stands for the muon (μ^-).

$\langle X_{ij}\rangle$	$pp\mu$	$dd\mu$	$tt\mu$
$\langle r_{21}^{-2}\rangle$	0.148 722 055 49	0.177 667 878 85	0.191 091 359 2
$\langle r_{31}^{-2}\rangle$	0.995 871 453 79	1.145 319 646 2	1.209 447 757
$\langle r_{21}^{-1}\rangle$	0.351 831 516 25	0.394 750 585 09	0.414 278 473 3
$\langle r_{31}^{-1}\rangle$	0.670 302 578 37	0.728 486 427 95	0.753 513 462 2
$\langle r_{21}\rangle$	3.299 486 184 4	2.834 451 765 8	2.652 824 758
$\langle r_{31}\rangle$	2.385 666 585 6	2.119 931 647 6	2.017 373 311
$\langle r_{21}^2\rangle$	12.390 408 464	8.876 754 641 9	7.662 138 315
$\langle r_{31}^2\rangle$	7.769 503 814 4	5.946 223 219 7	5.312 898 697
$\langle r_{21}^3\rangle$	52.273 664 421 7	30.436 930 50	23.924 390 7
$\langle r_{31}^3\rangle$	31.549 086 335	20.296 958 1	16.858 099 2
$\langle r_{21}^4\rangle$	245.523 499 7	113.481 402	80.308 859 2
$\langle r_{31}^4\rangle$	151.443 715 7	80.396 436 9	61.627 018 7
$\langle (r_{31}\cdot r_{32})^{-1}\rangle$	0.375 475 599 99	0.448 344 486 61	0.481 643 492 2
$\langle (r_{31}\cdot r_{21})^{-1}\rangle$	0.254 910 661 39	0.305 175 663 44	0.328 224 381 8
τ_{31}	0.544 146 849 14	0.534 079 203 14	0.529 392 114 3
τ_{21}	0.151 678 044 55	0.181 105 291 67	0.194 852 825 7
$\langle f\rangle$	0.059 992 935 708	0.062 315 924 485	0.063 409 263 60
$\langle \mathbf{r}_{31}\cdot \mathbf{r}_{32}\rangle$	1.574 299 582 4	1.507 845 898 8	1.481 829 540
$\langle \mathbf{r}_{31}\cdot \mathbf{r}_{21}\rangle$	6.195 204 232 1	4.438 377 320 9	3.831 069 157
$\langle -\frac{1}{2}\nabla_1^2\rangle$	0.286 758 809 20	0.379 017 603 93	0.442 086 315 6
$\langle -\frac{1}{2}\nabla_3^2\rangle$	0.429 803 280 37	0.488 408 956 46	0.513 115 821 7
$\langle \boldsymbol{\nabla}_1\cdot \boldsymbol{\nabla}_2\rangle$	$-0.143\,714\,338\,02$	$-0.269\,626\,251\,40$	$-0.371\,056\,809\,6$
$\langle \boldsymbol{\nabla}_1\cdot \boldsymbol{\nabla}_3\rangle$	$-0.178\,973\,055\,68$	$-0.176\,797\,915\,38$	$-0.163\,793\,708\,5$
$\langle \delta_{31}\rangle$	0.131 500 88	0.158 739 00	0.170 362 2
$\langle \delta_{21}\rangle$	$0.393\,701\times10^{-4}$	$0.243\,841\times10^{-5}$	$0.216\,73\times10^{-6}$
$\langle \delta_{321}\rangle$	$0.555\,167\times10^{-4}$	$0.426\,731\times10^{-5}$	$0.223\,68\times10^{-6}$
ν_{31}	$-0.898\,790\,296$	$-0.946\,674\,495$	$-0.963\,756\,03$
ν_{31} [a]	$-0.898\,787\,928\,788$	$-0.946\,671\,431\,05$	$-0.963\,748\,333\,50$
ν_{21}	4.440 147 68	8.879 636 62	13.128 088
ν_{21} [a]	4.440 122 200 669 27	8.875 837 564 471 09	13.292 469 373 273 5
η	1.044×10^{-12}	2.783×10^{-12}	9.447×10^{-12}
ε	$-253.150\,192\,338\,374$	$-325.070\,689\,006\,490$	$-362.906\,554\,751\,70$

[a] The exact two-particle cusp value [Eq. (5)].

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

where q_i and q_j are the charges and m_i and m_j the masses of the particles.

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 these $\tau_{21},\tau_{32},\tau_{31}$, and $\langle f\rangle$ 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 considered symmetric systems we have $\tau_{32}=\tau_{31}$.

The virial factor η is determined as follows:

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

where $\langle T\rangle$ and $\langle V\rangle$ are the expectation values of the kinetic and potential energy, 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 factors are 1 m.a.u. = 206.768 262 a.u. and 1 a.u. = 27.211 396 1 eV). Note however, that even exact coincidence of the factor η with 0 does not indicate the high quality of the wave function. Indeed, by using the so-called scaling transformation ($\vec{r}_i=\alpha\cdot\vec{r}_i$) one can make the factor η very close to zero, in principle, for an arbitrary wave function. Analogously, an excellent coincidence between computed and expected cusp values can be found in some cases (or easily made) for wave functions which *a priori* have a very poor quality. In particular, for any of the considered muonic molecular ion one can easily construct a few term trial function Eq. (1) which reproduces quite well the bound-state energy and also the exact values for both the ν_{21} and ν_{31} cusps. But for other properties the quality of such a function will be very poor. In general, the wave function has a high quality if (and only if) it reproduces very accurately a large number of the bound-state properties.

The numerical values for the properties in Table II agree quite well with the values known from previous calculations (see, e.g., [2]). Note only that some expectation values in Table II can be expressed as the linear combinations of other properties. For instance, for the three relative vectors $\vec{r}_{32},\vec{r}_{31}$, and $\vec{r}_{21}$ we have

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

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

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

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

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

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

$$\vec{p}_i\cdot\vec{p}_j=\frac{1}{2}(p^2_k-p^2_i-p^2_j) \tag{13}$$

and

$$\langle\vec{p}_i\cdot\vec{p}_j\rangle=\frac{1}{2}(\langle p^2_k\rangle-\langle p^2_j\rangle-\langle p^2_i\rangle), \tag{14}$$

respectively, $[(i,j,k)=(1,2,3)]$. Moreover, if the three $\vec{p}_i$ are determined by the relations $\vec{p}_i=(-\imath)\vec{\nabla}_i$ in Cartesian coordinates, then one finds

$$\langle\vec{\nabla}_i\cdot\vec{\nabla}_j\rangle=\left\langle-\frac{1}{2}\nabla^2_k\right\rangle-\left\langle-\frac{1}{2}\nabla^2_i\right\rangle-\left\langle-\frac{1}{2}\nabla^2_j\right\rangle, \tag{15}$$

where $(i,j,k)=(1,2,3)$. The expectation values form both sides of this equality can be found in Table II. Note, however, that the last three equalities are obeyed only in Cartesian coordinates and only if $\vec{p}_i=(-\imath)\vec{\nabla}_i$. In the present study such a choice is used, and therefore, $\langle\vec{\nabla}_i\cdot\vec{\nabla}_j\rangle$ can be expressed through $\langle-\frac{1}{2}\nabla^2_i\rangle$ and vice versa. Moreover, in the symmetric systems we have $\langle p^2_1\rangle=\langle p^2_2\rangle$ and $\langle\vec{r}_{31}\cdot\vec{r}_{21}\rangle=\langle\vec{r}_{32}\cdot\vec{r}_{21}\rangle$, respectively. This simplifies some of the equations presented above. For the symmetric systems one easily finds that $\langle\vec{\nabla}_1\cdot\vec{\nabla}_2\rangle$ is always negative, since $\langle\vec{\nabla}_1\cdot\vec{\nabla}_2\rangle=-\langle-\frac{1}{2}\nabla^2_3\rangle<0$.

B. Molecular ions

The procedure described above can not be applied directly to the adiabatic molecular ions ppe,dde,tte, and the exotic system $\mu\mu e$ $(\mu^+\mu^+e^-)$. For these systems the parameter γ in Eq. (2) is really small $(\gamma\approx1.25\text{–}1.80)$. This is the adiabatic divergence of Eq. (1) mentioned above (for more detail see Appendix). The source of the problem is quite clear: the relative motion of the two heavy particles (i.e., nuclei or quasinuclei) differs significantly from the electron motion. For the vibrationally ground states in such systems the nuclei are localized. The appropriate wave function $[\simeq\delta(r_{21}-R)$, where R is the nuclear-nuclear distance$]$ cannot be easily and accurately constructed from the exponential basis functions Eq. (1). In order to avoid this problem in [7] it was proposed to use the so-called universal variational three-body expansion. This expansion has the following form:

$$\begin{aligned}\Psi=\frac{1}{2}(1+\kappa\hat{P}_{21})\sum_{i=1}^{N}C_i\\ \times\exp(-\alpha_i r_{32}-\beta_i r_{31}-\gamma_i r_{21})\\ \times\exp(\imath\delta_i r_{32}+\imath e_i r_{31}+\imath f_i r_{21}),\end{aligned} \tag{16}$$

where all other notations are exactly the same as in Eq. (1). Here $\imath$ is the imaginary unit and δ_i,e_i and f_i are the three additional nonlinear parameters. This variational expansion can be successfully applied to computation of the bound states in an arbitrary Coulomb three-body system, including the pure adiabatic ${}^{\infty}\mathrm{H}_2^+$ ion. Note also, that the two nonlinear parameters δ_i and e_i in each of the basis function can be chosen equal to zero identically. In other words, the only internuclear coordinate r_{21} requires the complex nonlinear parameters (for more detail see [1]). The energy convergence is represented well by the formula Eq. (2) when $N\geqslant50\text{–}75$ [in Eq. (16)]. If $N\geqslant75$, then for the ${}^{\infty}\mathrm{H}_2^+$ ion the parameter γ in Eq. (2) $\geqslant6$. For the adiabatic molecular ions tte,dde,ppe this parameter γ is larger than 6.5–7 (when $N\geqslant75$). This means that the two-stage strategy described above can be applied also for adiabatic systems, if $N_0\geqslant75$. In the results of numerous calculations we have found that for adiabatic systems the value of N_0 can be equal to 100 [in Eq. (16)]. In other words, the first stage is the high-quality optimization of the nonlinear parameters in the trial function Eq. (16) with $N_0=100$ basis functions. The maximal number of basis functions used in our present calculations is 500.

TABLE III. The total energies (E) in atomic units ($m_e = 1, \hbar = 1, e = 1$) for the ground states of symmetric molecular ions. N designates the number of basis functions used.

N	$E(tte)$	$E(dde)$	$E(ppe)$	$E(\mu\mu e)$
100	−0.599 503 668 24	−0.598 788 191 453	−0.597 139 054 948 8	−0.585 113 695 960
200	−0.599 506 834 89	−0.598 788 745 520	−0.597 139 058 261 3	−0.585 125 852 260
300	−0.599 506 901 69	−0.598 788 779 015	−0.597 139 062 110 4	−0.585 126 081 539
400	−0.599 506 909 38	−0.598 788 783 185	−0.597 139 063 047 9	−0.585 126 096 363
450	−0.599 506 909 66	−0.598 788 783 703	−0.597 139 063 094 3	−0.585 126 097 079
500	−0.599 506 909 80	−0.598 788 783 890	−0.597 139 063 107 6	−0.585 126 097 176

The choice of the nonlinear parameters for the second stage of the procedure follows in detail [7].

The results of high precision calculations for energies and other properties in adiabatic molecular ions ppe, dde, tte, and exotic system $\mu\mu e$ can be found in Tables III and IV, respectively. In both of these tables only atomic units ($m_e = 1, \hbar = 1$, and $e = 1$) are used. As it follows from Table III, the two-stage approach produces variational energies which are lower than those known previously ([1,3–9]). But note again, that the final accuracy can be increased significantly by performing better optimization for the nonlinear parameters in the short-term wave function Ψ_1 ($N_0 = 100$). The properties from Tables III and IV for ppe and dde ions agree very well with the results of the previous calculations [1], [3], and [6]. Analogous properties for the tte and $\mu\mu e$ ($\mu^+\mu^+e^-$) ions were never reported. Note, however, that for the nuclear two-body cusp ν_{21} and delta function $\langle \delta_{21} \rangle$ even an approximate agreement is not observed (see Table

TABLE IV. The expectation values $\langle X_{ij} \rangle$ in atomic units ($m_e = 1, \hbar = 1, e = 1$) of some properties for the ground states in some molecular ions. The notations 1 and 2 designate the two identical particles, while 3 stands for the electron (e^-).

$\langle X_{ij} \rangle$	tte	dde	ppe	$\mu\mu e$
$\langle r_{21}^{-2} \rangle$	0.246 808 952	0.245 928 351	0.243 923 499	0.230 000 890
$\langle r_{31}^{-2} \rangle$	1.435 633 97	1.432 640 79	1.425 744 87	1.374 907 93
$\langle r_{21}^{-1} \rangle$	0.494 949 538 6	0.493 653 239 5	0.490 707 798 5	0.470 427 325 5
$\langle r_{31}^{-1} \rangle$	0.846 981 677 2	0.845 615 399 5	0.842 492 962 3	0.820 339 760 9
$\langle r_{21} \rangle$	2.035 386 064	2.044 070 089	2.063 913 868	2.205 215 237
$\langle r_{31} \rangle$	1.677 707 696	1.682 346 570	1.692 966 209	1.769 302 444
$\langle r_{21}^{2} \rangle$	4.173 214 590	4.215 643 294	4.313 285 946	5.036 585 56
$\langle r_{31}^{2} \rangle$	3.485 248 982	3.507 528 085	3.558 797 931	3.938 458 00
$\langle r_{21}^{3} \rangle$	8.618 702 31	8.771 220 44	9.125 657 56	11.896 594 0
$\langle r_{31}^{3} \rangle$	8.414 752 32	8.503 741 65	8.709 881 59	10.294 593 0
$\langle r_{21}^{4} \rangle$	17.927 969 1	18.409 472 2	19.542 349 4	29.022 942 1
$\langle r_{31}^{4} \rangle$	22.885 379 5	23.230 194 1	24.034 835 3	30.486 492 2
$\langle (r_{31}r_{32})^{-1} \rangle$	0.614 265 769 80	0.612 265 279 95	0.607 695 916 81	0.575 446 694 24
$\langle (r_{31}r_{21})^{-1} \rangle$	0.420 871 612 67	0.419 458 836 83	0.416 234 396 52	0.393 564 038 61
τ_{31}	0.508 819 323 445	0.508 819 323 445	0.509 171 32 046 3	0.515 336 167 535
τ_{21}	0.255 371 799 452	0.254 335 121 993	0.251 989 49 272 1	0.236 181 640 584
$\langle f \rangle$	0.068 252 611 586	0.068 169 440 730	0.067 981 259 120	0.066 713 493 913
$\langle \mathbf{r}_{31} \cdot \mathbf{r}_{32} \rangle$	1.398 641 687 3	1.399 706 437 9	1.402 154 958 8	1.420 165 222 2
$\langle \mathbf{r}_{31} \cdot \mathbf{r}_{21} \rangle$	2.086 607 295 1	2.107 821 647 0	2.156 642 973 2	2.518 292 778 3
$\langle -\frac{1}{2}\nabla_1^2 \rangle$	4.389 948 286 7	3.620 451 191 8	2.613 370 341 0	0.990 366 383 04
$\langle -\frac{1}{2}\nabla_3^2 \rangle$	0.597 909 667 1	0.596 816 037 4	0.594 292 491 1	0.575 546 617 43
$\langle \delta_{31} \rangle$	0.208 151 732	0.207 727 169	0.206 736 288	0.198 930 331
$\langle \delta_{21} \rangle$	0.126×10^{-7}	0.205×10^{-7}	0.6241×10^{-9}	0.2706×10^{-9}
$\langle \delta_{321} \rangle$	0.604×10^{-7}	0.187×10^{-6}	0.1169×10^{-8}	0.2657×10^{-9}
ν_{31}	−0.999 829 427 0	−0.999 713 191 5	−0.999 449 164 8	−0.995 181 763 7
ν_{31} [a]	−0.999 818 113 1	−0.999 727 630 5	−0.999 455 679 4	−0.995 186 945 4
ν_{21}	−111.8368	−107.1541	−108.7270	−63.0451
ν_{21} [a]	2748.460 790 0	1835.241 507 0	918.076 350 50	103.384 131 00
η	3.228×10^{-9}	6.885×10^{-9}	9.614×10^{-11}	1.6090×10^{-9}
ε	−2.710 196 635 590	−2.691 886 505 863	−2.650 695 384 281	−2.381 884 916 999

[a] The exact two-particle cusp value [Eq. (5)].

IV). The same is true for the three-particle delta function $\langle\delta_{321}\rangle$. Furthermore, we assume that the real $\langle\delta_{21}\rangle$ and $\langle\delta_{321}\rangle$ values for all presented molecular ions are $10^{-9}-10^{-31}$ times smaller than the values given in Table IV. The largest deviations can be found for the dde and tte ions. Indeed, the mass dependence for the $\langle\delta_{21}\rangle$ expectation values in the Coulomb three-body systems was studied in detail in our work [14]. As it follows from Table I in this work, the general dependence between the logarithms of the mass ratio and $\langle\delta_{21}\rangle$ takes the form:

$$\log_{10}\langle\delta_{21}\rangle=\sum_{k\geqslant 0} D_k\left[\log_{10}\left(\frac{m_Z}{m_X}\right)\right]^k, \tag{17}$$

where m_X and m_Z are the particle masses for the $X^+X^+Z^-$ (or $X^-X^-Z^+$) system. In the adiabatic region (where $m_X \geqslant 5m_Z$) we can restrict ourselves (with quite good accuracy) by the first three terms in the last equation, i.e.,

$$\log_{10}\langle\delta_{21}\rangle=D_0+D_1\left[\log_{10}\left(\frac{m_Z}{m_X}\right)\right]+D_2\left[\log_{10}\left(\frac{m_Z}{m_X}\right)\right]^2. \tag{18}$$

By using the results from Table I in [14] we have found the following numerical values for the coefficients in the last equation: $D_0=-4.636\,344\,170\,938$, $D_1=-3.568\,167\,272\,272$ and $D_2=-3.497\,573\,648\,938$. Now, for the $\langle\delta_{21}\rangle$ expectation values in the considered ions one finds from the last equation:

$$\langle\delta_{21}\rangle(tte)=6.071\times10^{-41},\quad \langle\delta_{21}\rangle(dde)=4.352\times10^{-37},$$

$$\langle\delta_{21}\rangle(ppe)=5.621\times10^{-31},\quad \langle\delta_{21}\rangle(\mu\mu e)=7.474\times10^{-16}.$$

These values for the $\langle\delta_{21}\rangle$ delta function are significantly closer to reality, than values presented in Table IV. In particular, the $\langle\delta_{21}\rangle$ expectation values from Table IV gives an extremely large fusion rates for dense deuterium and tritium. Actually, the energy gain from nuclear fusion reactions would be so large in this case, that these gases could not be liquified ever. Furthermore, any experimental work with those substances would be impossible, because of the outcoming intense neutron fluxes.

In principle, such a huge difference between predicted and computed values for $\langle\delta_{21}\rangle,\nu_{21}$, and $\langle\delta_{321}\rangle$ must be explained in the course of the further investigations. Briefly, this indicates that the adiabatic divergence for Coulomb three-body systems is not a completely solved problem. An alternative explanation suggests that such wrong cusps correspond to some effective (i.e., non-Coulomb) potential between two nuclei in the ppe and relative ions. In particular, this explains why the observed deviation between computed and predicted cusps increases in the series $\mu^+\mu^+e^-$, $p^+p^+e^-$, $d^+d^+e^-$, $t^+t^+e^-$, etc.

IV. THE BOUND-STATE SPECTRA IN COULOMB THREE-BODY SYSTEMS

In the previous sections we considered the bound-state properties of the muonic molecular ions ($pp\mu,dd\mu,tt\mu$) and molecular ions (ppe,dde,tte). Note, however, that our present analysis is restricted to the ground states only. Actually, there is no technical problem to compute any of the excited states, since the same variational expansion can be used in such calculations, but the total numbers of bound states differ significantly for muonic and molecular ions. In principle, these two group of ions have completely different structures of bound-state spectra. Such a difference is discussed below in this section, where we consider the classification of the bound-state spectra in Coulomb three-body systems. The proposed classification is based on the fact that the general theory of bound-state spectra in such systems is closely related with the general theory of compact operators. This means that the principal classification of the bound-state spectra in the Coulomb three-body systems can be made in the same manner as for compact operators. In particular, it is shown below that the discrete spectrum of a Coulomb three-body system may have the Hilbert-Schmidt, nuclear or finite-dimensional structure. It should be mentioned that initially this theory was developed only for the Coulomb three-body systems with unit charges. However, later, it was found that the same arguments may be used for an arbitrary quantum system, and finally, the theory can be represented in a more general form.

As is well known the discrete (or bound state) spectra can be found in a large number of quantum systems. Moreover, many different types of discrete spectra have been observed in various experiments and theoretical considerations of quantum systems. Now, the classification of bound-state spectra in quantum systems is of increasing interest for many theoretical problems as well as applications. A few decades ago only atomic, molecular, and nuclear spectra were known. Recently, such spectra for a number of other systems have been observed and studied, e.g., muonic and mesonic atoms and molecules. In terms of this the general classification of the bound-state spectra in quantum systems becomes an actual problem. For these purposes we propose to use the so-called natural classification which is based on the ''nature'' of the Hamiltonian for the discrete spectra $\hat{H}_-$ in quantum systems, and it does not use any ''obvious'' approximations.

Thus, in this section we shall consider the bound-state spectra in quantum systems. Without loss of generality we shall assume that (1) such states are stationary, and (2) they can be found as the solutions of the respective Schrödinger equation [15]:

$$\hat{H}\psi(x)=E\psi(x),$$

where

$$\int \psi^*(x)\psi(x)dx\leqslant K<+\infty, \tag{19}$$

and integration is over the whole domain of x. Here, for simplicity, we may assume that all functions $\psi(x)$ form a complete Hilbert space $\mathcal{H}$. The Hamiltonian operator $\hat{H}$ is a symmetric operator, i.e., $\langle\phi|\hat{H}\psi\rangle=\langle\hat{H}\phi|\psi\rangle$. In general, $\hat{H}$ contains some operators (e.g., differential operators), which are not determined on the whole Hilbert space $\mathcal{H}$. This means that, in general, $\hat{H}$ is not a self-adjoint operator on $\mathcal{H}$.

However, as a rule it can be extended uniformly into a self-adjoint operator by using the following approach.

Let us designate the domain of the $\hat{H}$ operator by $D(\hat{H})$ which is a subset in $\mathcal{H}$, but it is dense in $\mathcal{H}$, i.e., $D(\hat{H})\subset\mathcal{H}$ and $\overline{D(\hat{H})}=\mathcal{H}$ [16]. Also, the range of the operator $\hat{H}$ can be defined by $R(\hat{H})=\hat{H}(D(\hat{H}))$. Obviously, $R(\hat{H})$ is a subset in $\mathcal{H}$. Then, the routine procedure [17] can be applied in order to transform both $D(\hat{H})$ and $R(\hat{H})$ into the closed subspaces $\overline{D(\hat{H})}$ and $\overline{R(\hat{H})}$. The appropriate orthogonal complements of the $\overline{D(\hat{H})}$ and $\overline{R(\hat{H})}$ are called the deficiency subspaces, and the dimensions of $(\overline{D(\hat{H})})^{\perp}$ and $(\overline{R(\hat{H})})^{\perp}$ are the so-called deficiency indices (m_1,m_2) of the operator $\hat{H}$. When (and only when) $m_1=m_2$ the operator $\hat{H}$ can be extended into a self-adjoint operator. This statement is the well-known von Neumann theorem [19].

Usually, in actual physical applications the respective deficiency indices for the Hamiltonian operator $\hat{H}$ are equal. This means that the Hamiltonian operator $\hat{H}$ of an arbitrary quantum system may be extended into a self-adjoint (or hypermaximal [19]) operator. Note that for an arbitrary symmetric operator with real coefficients such an extension can be made directly (i.e., without the von Neumann theorem). Below, we shall designate the self-adjoint extension for the operator $\hat{H}$ by using the same letter $\hat{H}$.

Now, let us apply the spectral theorem to the self-adjoint operator $\hat{H}$. This theorem states that any self-adjoint operator $\hat{H}$ determines a generalized spectral function $\hat{E}(\lambda)$ and may be represented by means of the following spectral integral, i.e.,

$$\hat{H}=\int_{-\infty}^{+\infty}\lambda d\hat{E}(\lambda)=\sum_{i=1}^{N}\lambda_i\hat{E}_i+\int_{\lambda_{tr}-\varepsilon}^{+\infty}\lambda d\hat{E}(\lambda), \qquad (20)$$

where N may be equal either to zero (in this case the sum equals zero), or a finite integer, or an infinite integer number. The appropriate lower limit λ_{tr} in the integral corresponds to the lowest (on the energy) dissociation threshold for the considered quantum system. Without loss of generality we shall suppose below that $\lambda_{\text{tr}}=0$. Note, also that the similar spectral expansion for an operator $\hat{H}$ may be written in the space G which is more general than $\mathcal{H}$ $(\mathcal{H}\subset G)$. However, since our present consideration is restricted to the discrete spectra only, it is not necessary to introduce such a superspace G.

In terms of the last formula we can write the so-called Hamiltonian of the discrete spectrum $\hat{H}_-$ (or the $\hat{H}_-$ operator for short):

$$\hat{H}_-=\sum_{i=1}^{N}\lambda_i\hat{E}_i+\int_{-\varepsilon}^{0}\lambda d\hat{E}(\lambda), \qquad (21)$$

where ε is any small, positive and real number. Obviously, the operator $\hat{H}_-$ is a self-adjoint operator, i.e., all λ_i are real. Moreover, it follows from spectral properties of actual quantum systems that the threshold point $\lambda_{\text{tr}}=0$ is the only limit point for the subset $\{\lambda_i\}$. In other words, if $\lambda_i\neq 0$ then the appropriate eigenspace $\hat{E}_i$ is finite dimensional. This means that the operator $\hat{H}_-$ is a compact self-adjoint operator. One finds this directly from the well-known Hilbert-Schmidt theorem [17], which is of great value in various applications.

Thus, as it follows from the consideration above, the theory of bound state (or discrete) spectra in quantum systems is very closely related with the general theory of compact operators, which is a well developed branch of modern functional analysis [18]. In our present study such a connection is used mainly for the two following purposes: (1) in order to produce the so-called natural classification of the bound-state spectra in quantum systems, and (2) to consider the properties of the so-called Rellich Hamiltonians which have only discrete spectra.

Let us show now that the so-called natural classification of the bound-state spectra in quantum systems can be made in terms of the respective classification scheme for compact operators. Indeed, it is well known (see, e.g., [17]) that compact operators form a closed two-sided ideal I in the ring of bounded operators B. This means that both $\hat{x}\cdot\hat{y}$ and $\hat{y}\cdot\hat{x}$ are compact operators, if $\hat{x}$ is a compact operator and $\hat{y}$ is a bounded operator. Moreover, it can be shown also that I is a maximal two-sided ideal in B. On the other hand, this ideal I contains a number of subideals I_K such that $\hat{x}\cdot\hat{y}\in I_K$ and $\hat{y}\cdot\hat{x}\in I_K$, if $\hat{x}\in I_K$ and $\hat{y}\in I$. The four following subideals have a specific importance for our present consideration. I_{HS} is the class of the Hilbert-Schmidt compact operators, I_N is the class of the so-called nuclear compact operators, I_F is the class of compact operators with the finite range and I_0 is the class of compact operators with zero range. It can be shown that if $\mathcal{H}$ is an infinite-dimensional space, then one finds $I_0\subset I_F\subset I_N\subset I_{HS}\subset I\subset B$.

However, it is not necessary to show explicitly that the $\hat{H}_-$ operator is, e.g., the Hilbert-Schmidt compact operator. Actually, such a classification of the bound-state spectra in quantum systems can be made in terms of the following sum:

$$S_p=\sum_{i=1}^{N}|\lambda_i|^p\dim\{\phi(\lambda_i)\}=\sum_{i=1}^{N}|\lambda_i|^p\dim\{\mathcal{H}_{\lambda_i}\}, \qquad (22)$$

where p is non-negative integer number and $\dim\{\phi(\lambda_i)\}$ is the total (or algebraic) dimension of the appropriate eigenspace $(\mathcal{H}_{\lambda_i})$ corresponding to the eigenvalue λ_i. Note, that the infinite-dimensional space which corresponds to the threshold $\lambda=\lambda_{\text{tr}}=0$ is not included in the last equation. Now, to classify the compact operator we need to determine: (1) the minimal non-negative integer $\overline{p}$ for which S_p^- converges (and S_{p-1}^- diverges, respectively), and (2) the numerical value of this sum is S_p^-. For instance, by following [17] one can show that (1) if $S_p=0$ at $p=0$, then $\hat{H}_-$ has an empty discrete spectrum, i.e., $\hat{H}_-\in I_0$; (2) if S_p converges at $p=0$ and $S_0>0$, then $\hat{H}_-\in I_F$; (3) if S_p converges at $p=1$, but diverges at $p=0$, then $\hat{H}_-\in I_N$; (3) if S_p converges at $p=2$, but diverges at $p=1$, then $\hat{H}_-\in I_{\text{HS}}$, etc.

Let us apply this classification scheme to real physical (quantum) systems. First, consider the Coulomb three-body systems with unit charges $X^+Y^+Z^-$ (or $X^-Y^-Z^+$). They are of interest in various applications, and the general theory for bound-state spectra in these systems can be found in [20]. In particular, it was shown that the total number of bound states in such systems, their energies and other properties depend upon two dimensionless mass ratios, e.g.,

$$v_X = \frac{m_X}{m_X + m_Y + m_Z}, \quad v_Z = \frac{m_Z}{m_X + m_Y + m_Z}, \qquad (23)$$

where $m_i (i = X, Y, Z)$ are the three particle masses (for more details, see [2]).

Now, note that the $\mu^+\mu^-e^-$ ion has an empty bound-state spectrum, i.e., $\hat{H}_-(\mu^+\mu^-e^-) \in I_0$. The $\mu^+e^-e^-$ (Mu^-) and $e^+e^-e^-$ (Ps^-) ions have only one bound (ground) state. That means that in both of these cases $\hat{H}_- \in I_F$. In the muonic molecular ion $p^+p^+\mu^-$ there are two bound states, while in the similar $d^+d^+\mu^-$ and $t^+t^+\mu^-$ ions the bound-state spectra contain five and six such states, respectively. Actually, in all such cases $\hat{H}_- \in I_F$. The difference between them can be detected from the comparison of numerical values for the appropriate S_0 and S_1 sums [Eq. (16)].

It can be shown [20] that when $m_X \rightarrow +\infty$ the total number of bound states in the symmetrical $X^+X^+Y^-$ (i.e., the $\mathrm{H}_2{}^+$ ion) grows to infinity. It follows from [17] that $\hat{H}_-(\mathrm{H}_2{}^+)$ is a nuclear compact operator, i.e., $\hat{H}_-(\mathrm{H}_2{}^+) \in I_N$. However, in the united atom limit (i.e., in the case of the He^+ ion) the $\hat{H}_-$ operator changes its type again and we have $\hat{H}_-(\mathrm{He}^+) \in I_{\mathrm{HS}}$, i.e., the $\hat{H}_-(\mathrm{He}^+)$ operator is the Hilbert-Schmidt compact operator. This explains the principal difference between the bound-state spectra in atoms and in molecular ions. Indeed, for instance, both the H atom and ${}^\infty H_2^+$ ion have an infinite number of bound states, but for the first system $\hat{H}_- \in I_{\mathrm{HS}}$, while for the second $\hat{H}_- \in I_N$. Briefly, we can say that such an infinity of states for the H atom is ''larger'' than that for the ${}^\infty\mathrm{H}_2{}^+$ ion.

The classification of bound-state spectra for other quantum systems (molecular, atomic, nuclear, exotic, etc.) can be made in an analogous manner. In general, the type of the $\hat{H}_-$ operator depends on the asymptotic form (at large distances) of the potential in the lowest-energy decay channel for the system. Note, that in all actual cases such a channel is the two-body channel, i.e., the dissociation problem can be considered as a two-body problem with the interaction potential $V(r)$. The final conclusion depends essentially upon the asymptotic form of $V(r)$. If this asymptotic form has a Coulomb attractive structure [i.e., $V(r) \rightarrow -a/r$, where a is a positive parameter], then the $\hat{H}_-$ operator is a Hilbert-Schmidt operator. If this potential vanishes at $r \rightarrow \infty$ faster than r^{-2}, then the $\hat{H}_-$ operator is a finite compact operator. For the exact r^{-2} asymptotic form (and for definite values of a) one finds $\hat{H}_- \in I_N$.

Let us discuss now the closely related problem on the completeness of the discrete spectrum of eigenfunctions. This question is of interest for some physical applications. However, since the $\hat{H}_-$ operators are compact operators the answer is trivial and follows from the so-called Rellich spectral theorem [21, 22]. This theorem states that if $\lambda = 0$ is not an eigenvalue of $\hat{H}_-$, then $\mathcal{H} = \Sigma_i \oplus \mathcal{H}_{\lambda_i}$, where $\mathcal{H}_{\lambda_i}$ is the eigenspace corresponding to the eigenvalue λ_i. Note that, since $\lambda = 0$ is not an eigenvalue of $\hat{H}_-$, this operator is invertible, i.e., the corresponding $\hat{H}_-^{-1}$ operator exists. Below, we shall call such $\hat{H}_-$ operators as Rellich or invertible compact operators, and designate them as $\hat{H}_R$. In the so-called ''physical form'' the Rellich theorem means that if the threshold state is not an actual physical state in the considered system, then the discrete spectrum eigenfunctions form a complete set in the Hilbert space $\mathcal{H}$. This corresponds, for instance, to the well-known harmonic oscillator. In this case the Hamiltonian H_h is unbounded, but the inverse operator H_h^{-1} is the Rellich compact operator.

In some cases the appropriate substitution of variables can be found which transforms the initial Hamiltonian H (in general, H has the both discrete and continuous spectra) to the Rellich compact operator. For instance, Fock (see, e.g., [23]) used a coordinate transformation for Coulomb systems ($x = 2r/\sqrt{-2E}$) to exclude the continuous spectrum and dissociation threshold. Sometimes this procedure is called the completeness of the discrete spectrum. Note that as a rule, for actual quantum systems the dissociation threshold state is a real physical state (e.g., for the hydrogen atom), i.e., the eigenfunctions of the discrete spectrum do not form a complete set in $\mathcal{H}$. Now, we can determine the Rellich Hamiltonian as an operator (Hamiltonian) which is a Rellich compact operator or its inverse is a Rellich compact operator. The Rellich Hamiltonians are of specific interest in applications, since they have the complete systems of basis functions.

V. CONCLUSION

Thus, in the present study we have performed high-precision, bound-state calculations for a number of Coulomb three-body systems, including adiabatic molecular ions: ppe, dde, tte and one exotic system $\mu^+\mu^+e^-$. The variational energies obtained in the present calculations are lower than the appropriate values known from previous works. Various geometrical and dynamical properties are found to be in good agreement with the results known from earlier computations. Our study indicates that the two-stage strategy [1] works quite well for the energies and many other properties in various adiabatic Coulomb three-body systems, i.e., for molecular ions ppe, dde, tte, and similar systems. However, some problems related with the nuclear cusp and δ function expectation values (between the two positive particles) remain unsolved.

In order to explain the principal difference between the bound-state spectra in nonadiabatic and adiabatic systems, we apply the general theory of the bound-state spectra in Coulomb three-body systems. It is shown that this theory is closely related with the theory of compact operators. Therefore, the principal classification of the bound-state spectra in such systems can be made as for compact operators. In particular, one easily finds three-body systems with (1) finite (and empty) spectrum, e.g., $\mathrm{Ps}^-, pp\mu, dd\mu$ (and $\mu^+\mu^-e^-$) ions; (2) with nuclear spectrum, e.g., the ${}^\infty\mathrm{H}_2^+$ ion; and (3) with Hilbert-Schmidt spectrum, e.g., the He atom or Li^+ ion. Each of these systems has a completely different structure of the bound-state spectrum. The next generations of the highly accurate methods for bound-state calculations should be quite flexible and take into account the principal information about the structure of the bound-state spectrum.

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APPENDIX

Now, let us discuss very briefly the adiabatic divergence of Eq. (1) (for more detail see [7]). The main source of this problem is well known: the Hamiltonian of an arbitrary many-body system changes its type when any two particle masses increase to the infinity and all other masses do not change. Indeed, let us consider, e.g., the three-particle case. In this case, the Hamiltonian takes the following form (in the relative coordinates):

$$\begin{aligned}H=&-\frac{1}{2}\left(\frac{1}{m_3}+\frac{1}{m_2}\right)\left(\frac{\partial^2}{\partial r_{32}^2}+\frac{2}{r_{32}}\frac{\partial}{\partial r_{32}}\right)-\frac{1}{2}\left(\frac{1}{m_3}+\frac{1}{m_1}\right)\left(\frac{\partial^2}{\partial r_{31}^2}+\frac{2}{r_{31}}\frac{\partial}{\partial r_{31}}\right)-\frac{1}{2}\left(\frac{1}{m_2}+\frac{1}{m_1}\right)\left(\frac{\partial^2}{\partial r_{21}^2}+\frac{2}{r_{21}}\frac{\partial}{\partial r_{21}}\right)\\&-\frac{1}{m_3}\frac{r_{32}^2+r_{31}^2-r_{21}^2}{2r_{32}r_{31}}\frac{\partial^2}{\partial r_{32}\partial r_{31}}-\frac{1}{m_2}\frac{r_{32}^2+r_{21}^2-r_{31}^2}{2r_{32}r_{21}}\frac{\partial^2}{\partial r_{32}\partial r_{21}}-\frac{1}{m_1}\frac{r_{31}^2+r_{21}^2-r_{32}^2}{2r_{31}r_{21}}\frac{\partial^2}{\partial r_{31}\partial r_{21}}\\&+V_{32}(r_{32})+V_{31}(r_{31})+V_{21}(r_{21}),\end{aligned}\tag{A1}$$

where for simplicity atomic units are used ($\hbar=1,e^2=1$, and $m_e=1$). This operator is a differential operator of the second order on the relative coordinates r_{32},r_{31}, and r_{21}. However, its structure depends on the ratios of the three particle masses, e.g., m_1/m_3 and m_2/m_3. At certain values of the mass ratios, the Hamiltonian can change its structure. Such mass ratios can be called the singular points for the Hamiltonian Eq. (A1). From Eq. (A1) it is easy to understand that the case when all three masses m_1,m_2, and m_3 are finite (i.e., finite mass ratios) corresponds to the regular (i.e., nonsingular) points. Furthermore, it is easy to see that the situation when only one of the three masses is infinite and the other two are comparable with each other is not a singular point for the Hamiltonian Eq. (A1), since the operator, Eq. (A1), does not change its structure in this case. Such a situation can be found, e.g., for the He atom and He-like ions.

In the case when two masses are significantly greater than the third mass, i.e., when m_1 and m_2 become infinite, one easily finds that the Hamiltonian formally becomes

$$\begin{aligned}H=&-\frac{1}{2\cdot m_3}\left(\frac{\partial^2}{\partial r_{32}^2}+\frac{2}{r_{32}}\frac{\partial}{\partial r_{32}}\right)-\frac{1}{2m_3}\left(\frac{\partial^2}{\partial r_{31}^2}+\frac{2}{r_{31}}\frac{\partial}{\partial r_{31}}\right)\\&-\frac{1}{m_3}\frac{r_{32}^2+r_{31}^2-r_{21}^2}{2r_{32}r_{31}}\frac{\partial^2}{\partial r_{32}\partial r_{31}}+V_{32}(r_{32})\\&+V_{31}(r_{31})+V_{21}(r_{21}).\end{aligned}\tag{A2}$$

This operator does not contain any differential operator on the r_{21} relative coordinate. Actually, here the interparticle distance r_{21} can be considered as an external parameter of the problem. This means that the point ($m_1/m_3=+\infty$, $m_2/m_3=+\infty$) is a singular point in the two-dimensional mass ratio plane (such a point corresponds, e.g., to the $H_2{}^+$ ion). It should be mentioned that in mathematics there are a few methods to consider operators with such singularities in front of the higher-order derivatives (see, e.g., [24]). The so-called small parameter method corresponds to the Born-Oppenheimer approximation in physics [25]. Actually, all terms containing the $r_{21}(=R)$ variable can be separated from the remaining part of the Hamiltonian Eq. (A1). Finally, one will find the two following, completely different problems to solve: (1) one (or light) particle motion, and (2) the motion of two (heavy) particles.

Note, however, that the reduction of the initial Hamiltonian Eq. (A1) to the adiabatic one-particle Hamiltonian Eq. (A2) is based on the assumption that all $\langle\partial^2/\partial r_{21}^2\rangle,\langle\partial/\partial r_{21}\rangle$ and $\langle 1/r_{21}\partial/\partial r_{21}\rangle$ expectation values do not increase together with the masses m_1 and m_2. But this depends essentially upon the properties of the variational expansion used in calculations as well as upon the $V(r_{21})$ potential. In real applications the only Coulomb case is very important, i.e., $V(r_{21})=q_1q_2/r_{21}$. Now, let us consider the variational expansion Eq. (1) for the two following cases $q_1q_2>0$ (repulsion) and $q_1q_2<0$ (attraction). The attraction case corresponds, e.g., to the muonic atoms and ions such as $\mathrm{He}^{2+}\mu^-e^-$. In this case by choosing very large values for the γ_i ($i=1,\ldots,N$) parameters in Eq. (1), one may increase the $\langle\partial^2/\partial r_{21}^2\rangle,\langle\partial/\partial r_{21}\rangle$ and $\langle 1/r_{21}\partial/\partial r_{21}\rangle$ expectation values as many times as needed to keep all terms in the Hamiltonian Eq. (A1), in principle, for arbitrary large masses m_1 and m_2. Finally, in this case ($q_1q_2<0$) we can predict that the variational expansion Eq. (1) will provide highly accurate results for arbitrarily large masses m_1 and m_2.

The situation changes drastically when $q_1q_2>0$ (i.e., repulsion). In this case any possible choice of the nonlinear parameters in Eq. (1) does not increase the $\langle\partial^2/\partial r_{21}^2\rangle,\langle\partial/\partial r_{21}\rangle$ and $\langle(1/r_{21})(\partial/\partial r_{21})\rangle$ expectation values. Finally, at very large m_1 and m_2 masses, appropriate terms in the Hamiltonian Eq. (A1) become negligible. The operator Eq. (A1) is reduced to the form of Eq. (A1), which means that the variational expansion Eq. (1) cannot represent accurately the nuclear motion in adiabatic systems. The final accuracy of the method drops rapidly. This is called the adiabatic divergence of Eq. (1). In contrast with this the variational expansion Eq. (16) is significantly more flexible, since by choosing quite large values for the nonlinear parameters f_i $(i=1,\dots,N)$ one can easily increase the $\langle \partial^2/\partial r_{21}^2\rangle$,$\langle \partial/\partial r_{21}\rangle$, and $\langle (1/r_{21})(\partial/\partial r_{21})\rangle$ expectation values. This means that for arbitrary large masses m_1 and m_2 we cannot lose the nuclear motion. In other words, the variational expansion Eq. (16) allows us to avoid the adiabatic divergence, which is typical for any expansion in the relative coordinates [see, e.g., Eq. (1)].

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