Variational expansions for the three-body Coulomb problem

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(Submitted 14 March 1986; resubmitted 15 January 1987)
Zh. Eksp. Teor. Fiz. **92**, 1959–1977 (June 1987)

High-accuracy determinations of the bound states of three-particle Coulomb systems (atoms, ions, and mesic molecules) are considered. An effective method is presented for deriving the matrix elements when the variational exponential expansion with $L \geqslant 2$ is employed. An algorithm for the solution of the eigenvalue problem is described, and the choice of nonlinear parameters in the expansion is discussed. Although the proposed method is capable of yielding high accuracy, it is noted that the rate of convergence may be significantly slower in certain cases.

1. INTRODUCTION

The three-body problem occupies a special position in quantum mechanics. Different special cases of this problem (and their properties) are of interest from both the theoretical point of view and for many applications. The nonformal theoretical interest in the quantum theory of the three-body problem is due to the relatively small number of degrees of freedom that are necessary for the complete description of three-particle systems, which means that their physical parameters can be found from quantum-mechanical first principles without introducing *a priori* ideas about the motion of a particle.[1] An equally important point is that the solutions of the three-body problem exhibit certain qualitative properties that are not present in the two-body case, but appear in problems involving four or more bodies. These properties must be analyzed and taken into account in the solution of the three-body potential problem if a high enough rate of convergence of the variational expansion employed is to be achieved. The use of improved variational procedures and expansions is essential in the solution of more complicated problems, e.g., systems with a larger number of bodies, noncentral potentials containing a strong attraction at short distances, and so on.

In addition to the growing theoretical interest in the analysis of the three-body potential problem, there has been a continuing expansion of the range of practical problems in which high accuracy solution of the corresponding Schrödinger equation and the evaluation of different corrections to it occupy a central position. Here, we must mention, above all, the various problems in atomic spectroscopy and, especially, the explanation of the spectra of multiply-charged helium-like (two-electron) ions, which have recently become accessible.[2] The frequent use of atomic helium as a thermometric material in low-temperature plasmas has led to similar problems. Studies of Rydberg states in helium-like ions and the evaluation of relativistic corrections (primarily for the *S*- and *P*-states) are equally important. Estimates of the practical efficiency of the mesic catalysis of *d,d* and, especially, *d,t* nuclear reactions in mesomolecular physics are also found to reduce to the high-accuracy determination of weakly-bound states of the mesic molecules $dd\mu^*$ ($L = 1$) and $dt\mu^*$ ($L = 1$). The importance of accurate calculations of the weakly-bound state of the $dt\mu$ mesic molecule is clearly demonstrated in Ref. 3. However, apart from mesic catalysis, there are many problems in mesomolecular and mesoatomic physics in which the bound states of systems containing negative muons must be determined with high accuracy.

In this paper, we shall concentrate our attention on three-particle Coulomb systems and their bound states. Considerable advances have been made very recently[4,5] in high-accuracy calculations of the bound states of Coulomb systems. For example, for most bound states of mesic molecules, the uncertainty in the Coulomb binding energy is now less than 10^{-4}–10^{-5} eV (Refs. 4 and 5), whereas not so long ago[6] these energy levels were known only to about 0.1–0.2 eV. This considerable increase in the precision of calculated Coulomb levels of mesic molecules is due to the use of highly effective variational expansions, namely, the exponential[7,8] and the Hylleraas[9,10] expansions. These expansions are also found to ensure high accuracy in the case of the few-nucleon nuclei ^{3}H and ^{3}He and the hypernucleus $^3_\Lambda$H. This means that they, and their analogs in the case of a larger number of constituent particles, are promising techniques for the analysis of the corresponding nuclear and hypernuclear systems. In Section 2, we examine the basic variational principles and techniques used to calculate the bound states of three-body systems. Section 3 presents an account of the variational exponential expansion in terms of relative coordinates, and reports some of the best variational results for a number of systems. The last Section is concerned with the universality of the variational expansion in the three-body Coulomb problem.

2. METHODS OF SOLUTION

Methods based on variational expansions in terms of the relative coordinates r_{31}, r_{32}, r_{21} (or simple combinations of them) have recently assumed particular importance in high-accuracy calculations of the bound states of the three-body Coulomb system. However, for purely adiabatic systems (and only in this case), for which two of the masses are infinite (fixed particles), the Hamiltonian commutes not only with L_z, but also with the additional operator $\hat{\lambda}$. The existence of the latter enables us to separate the variables (ξ, η) in the adiabatic three-body Coulomb problem and to integrate numerically the corresponding one-dimensional equations with any predetermined accuracy (although these equations have an essentially nonhypergeometric form). From the point of view of the theory of group representations, the existence of the additional operator $\hat{\lambda}$ that com-

0038-5646/87/061100-11$04.00

mutes with the Hamiltonian of the adiabatic Coulomb (or two-center) system is not accidental.[11] Even a small departure from the adiabatic situation results in a sharp reduction in the rate of convergence of such methods and of their modifications. Moreover, the adiabatic (or very nearly adiabatic) systems form a narrow and specific subclass of all the three-body Coulomb systems. Systems with intermediate particle masses are encountered much more frequently and, for them, there is no useful additional symmetry. As noted at the beginning of this Section, this is why most methods of solution are based on variational numerical techniques.

All the variational principles used in calculations, and their consequences, are based on the equivalence of the solution of the Schrödinger equation

$$H\psi=E\psi$$

and the problem of finding the stationary points of the energy functional

$$E=\min_{\psi}\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}. \qquad (1)$$

It is readily shown that the smallest eigenvalue of the Hamiltonian H is not simply a stationary point, but the absolute minimum of E as a functional of ψ. Hence, it follows that, for arbitrary ψ, the value of E determined from (1) is an upper bound of the smallest eigenvalue. The fact that the Hamiltonian has only one ground state does not reduce the importance of this theorem because, as a rule, most systems have sets of operators (operator algebras) that commute with the Hamiltonian, and the corresponding states are classified according to the representations of these algebras. All the states of a system are divided into series, each of which corresponds to a particular set of quantum numbers, e.g., in the present paper, we shall use the three-dimensional angular momentum L and total spin S to classify such states, and each $\{LS\}$ series contains a ground state to which the above theorem can be applied. To find the excited states in a particular series, the variational principle is formulated as follows[12]:

$$E_k=\min_{\psi}\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \qquad (2)$$

subject to the condition that $\langle\psi|\psi_i\rangle=0$, where ψ_i ($i=1, 2,\dots, k-1$) are the eigenfunctions corresponding to the lower-lying eigenvalues E_i. Since, in the calculation of the k-th excited state, we must know with high precision $k-1$ eigenfunctions corresponding to lower eigenvalues, the theorem expressed by (2) is often nonconstructive and is replaced by the minimax theorem[12]:

$$E_k=\max_{\omega_i}\min_{\psi}\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \qquad (3)$$

subject to the condition $\langle\psi|\psi_i\rangle=0$, where ω_i ($i=1, 2, 3,\dots, k-1$) are $k-1$ arbitrary functions. We cannot examine here all the consequences of the minimax theorem and merely mention that it was used, as it was in Refs. 4, 5, and 8, to obtain all the results given in the present paper.

The general variational principles outlined above are valid for an arbitrary variational expansion. Usually, calculations of bound states make use of linear variational expansions in terms of the basis functions $\{\varphi_i\}$:

$$\psi=\sum_{i=1}^{N}c_i\varphi_i,$$

where N is the order of the expansion (number of terms).

The energy functional for linear expansions is

$$E=\frac{\langle\mathbf{c}|\hat{H}|\mathbf{c}\rangle}{\langle\mathbf{c}|\hat{S}|\mathbf{c}\rangle},$$

where $\hat{H}$ and $\hat{S}$ are the Hamiltonian ($H_{ij}=\langle\varphi_i|H|\varphi_j\rangle$) and weight ($S_{ij}=\langle\varphi_i|\varphi_j\rangle$) matrices, and $\mathbf{c}$ is a column vector of the linear coefficients. By varying this vector, we can reduce the problem of minimization of $E(\mathbf{c})$ to the equivalent eigenvalue problem:

$$(\hat{H}-E\hat{S})\mathbf{c}=0. \qquad (4)$$

The required eigenvalues are naturally determined from the condition

$$\mathrm{Det}(\hat{H}-E\hat{S})=0. \qquad (5)$$

It is not difficult to prove the variational oscillation theorem[13,14] on the alternation of the roots of the determinants (5) of order N and $N+1$ (the energies determined for the variational expansion of order $N+1$ alternate with the energies determined for the expansion of order N). This theorem is also important in calculations of excited states.

The variational principles mentioned above form a kind of theoretical foundation for variational calculations of bound states. However, variational theorems applied to such problems can also be used to obtain many important relationships such as the virial (and supervirial) theorems, their consequences, the Gell-Mann–Feynman relationships, and so on.

Apart from the basic variational principles, it is also important to consider the correct choice of coordinates in the three-body Coulomb problem because not all coordinates, by far, will guarantee rapid convergence of the expansions. For example, in calculations of the bound states of the helium atom with an infinitely heavy nucleus ($^{\infty}$He), the three necessary scalar coordinates can be chosen in a number of ways: (a) r_1, r_2, r_{21} (here and below, $\mathbf{r}_1$ is the position vector of the first electron in ($^{\infty}$He and $\mathbf{r}_2$ of the second electron, whereas r_{21} is the separation between the electrons); (b) r_1, r_2, $\cos\theta=\mathbf{r}_1\cdot\mathbf{r}_2/r_1r_2$; (c) $r=(r_1^2+r_2^2)^{1/2}$, $\tan\eta=r_1/r_2$, $\cos\theta=\mathbf{r}_1\cdot\mathbf{r}_2/r_1r_2$, etc. If the aim of the solution is to obtain an answer with a predetermined precision, then, of the three possibilities just listed, only (a) is satisfactory[15,4,16] because, for variants (b) and (c), any variational expansion is found converge slowly and, for example, it is practically impossible to obtain the ground state energy in He to six to seven significant figures in a finite time (Ref. 15). This is not the place for a detailed account of the criteria for the correct choice of coordinates in the three-body Coulomb problem. We merely note that the relative coordinates r_{31}, r_{32}, r_{21} (r_1, r_2, r_{21} for $^{\infty}$He) ensure the necessary (sufficiently high) rate of convergence. Relative coordinates were first used by Hylleraas[16] in the problem of the $^{\infty}$He atom (1^1S-state). At present, Hylleraas-type methods have been used to calculate accurately the bound states of simple systems such as H$^-$, He, Li$^+$, and so on,[17] the ion $e^-e^+e^-$ (Ref. 9), and the mesic molecules.[10] The Hylleraas expansion (for $L=0$) is

$$\psi_{L=0}=\sum_{i=1}^{N} c_i r_{31}{}^{i_1} r_{32}{}^{i_2} r_{21}{}^{i_3} \exp(-\gamma_1 r_{31}-\gamma_2 r_{32}-\gamma_3 r_{21}), \tag{6}$$

where $\gamma_1, \gamma_2, \gamma_3$ are positive constants (independent of i). An orthogonal basis similar to the Hylleraas basis is given in Ref. 18. It usefully differs from the latter in that the matrix elements of the Hamiltonian of the $^\infty$He atom can be calculated using integer arithmetic, and the matrix itself is found to be substantially reduced. This approach was subsequently generalized[19] to the case of arbitrary masses (for $L = 0$).

In addition to the Hylleraas expansion used in such problems, there have been many applications (especially recently) of the variational exponential expansion using the relative coordinates, e.g., for $L = 0$. This expansion takes the form

$$\psi_{L=0}=\sum_{i=1}^{N} c_i \exp(-\alpha_1^{(i)} r_{31}-\alpha_2^{(i)} r_{32}-\alpha_3^{(i)} r_{21}). \tag{7}$$

The first generalization of the expansion given by (2) to the case $L = 1$ (for $^\infty$He) was given in Ref. 7. A similar approach was generalized in Ref. 8 to the case of three arbitrary masses and arbitrary values of L, which led to the first successful variational calculation of the weakly-bound excited states of $dd\mu^*$ ($L = 1$) and $dt\mu^*$ ($L = 1$). These are important in connection with the resonance mechanism of formation of the mesic molecules $dd\mu$ (Ref. 20) and $dt\mu$ (Ref. 21). It was subsequently shown[22,23,4,5] that the accuracy of the exponential expansion was no worse than that obtained by Hylleraas-type methods and was often better. It has been shown[4] that the exponential basis can be successfully used for bound states with $L = 2$, which had not been previously done in any of the variational expansions.

Both the Hylleraas and exponential expansions (and other similar expansions) can be obtained by discretizing the corresponding compact integral representations (transforms) of the wave functions[24,7,25]:

$$\psi_{L=0}(r_{31}, r_{32}, r_{21}) = \iiint K(\alpha_1, \alpha_2, \alpha_3; r_{31}, r_{32}, r_{21}) C(\alpha_1, \alpha_2, \alpha_3)\, d\alpha_1\, d\alpha_2\, d\alpha_3, \tag{8}$$

where K is the kernel of the integral transformation (representation). The variational exponential expansion corresponds to the discretization of the three-dimensional Laplace transform, whereas the Hylleraas expansion corresponds to a Mellin transform. They are intimately related to one another and to the Fourier transform. The properties of the two variational expansions (including their rates of convergence in the case of the same system) are therefore very similar but, in specific calculations, the variational exponential expansion (7) usually has many advantages as compared with the Hylleraas expansion (6). This is discussed in detail in Refs. 8 and 25. The main advantage of (7) and of its analogs for $L \geqslant 1$ is undoubtedly its flexibility, which shows itself, for example, in the fact that the $\alpha_j^{(i)}$ can be chosen to be either integers or half-integers [as in the case of (6)], but they can also be reasonably arbitrary rational, irrational, or even negative numbers (provided the conditions for the convergence of integrals in terms of perimetric coordinates are observed[25]). This advantage is particulary important in calculations on weakly-bound states with binding energies approaching zero,[8,26,25] so that the variational exponential expansion is optimal because the number of basis functions required to attain a given precision is usually smaller in this case than that for other variational expansions. We also note that the Laplace transform formulas used to calculate the matrix elements in the three-body Coulomb problem are much simpler than the transformation formulas for the Mellin and other possible integral transforms.[4,25] This leads to much simpler and faster evaluation of the corresponding matrix elements. A particular implementation is presented in the next Section together with the results of high-accuracy calculations performed using the exponential expansion in relative coordinates.

3. THE VARIATIONAL EXPONENTIAL EXPANSION

The variational exponential expansion for arbitrary L, using the relative coordinates (r_{31}, r_{32}, and r_{21}), was given in Ref. 8 in the form

$$\psi_{L0}=\sum_{l=0}^{L}\sum_{i=1}^{N} c_{il} Y_{L0}^{l,L-l}(\mathbf{r}_{31}, \mathbf{r}_{32}) \times \exp(-\alpha_{1l}^{(i)} r_{32}-\alpha_{2l}^{(i)} r_{31}-\alpha_{3l}^{(i)} r_{21}), \tag{9}$$

where the c_{il} are linear parameters and the $\alpha_{jl}^{(i)}$ are the nonlinear parameters. The notation $Y_{LM}^{l,L-l}(x, y)$ is customary[8]:

$$Y_{LM}^{l_1 l_2}(\mathbf{x}, \mathbf{y}) = x^{l_1} y^{l_2} [Y_{l_1 m_1}(\mathbf{n}_x) Y_{l_2 m_2}(\mathbf{n}_y)]_{LM}.$$

The expansion given by (9) can be further symmetrized or antisymmetrized with respect to the first and second particles (indices 1 and 2). The variational calculation based on (9) involves three significant successive stages: the choice of the nonlinear parameters $\alpha_{jl}^{(i)}$, the derivation of the formulas for the matrix elements and their evaluation, and the solution of the eigenvalue problem.

The idea of global chaos or an *a priori* choice of $\alpha_{jl}^{(i)}$, is found to be effective in calculations of the bound states of Coulomb systems. The essence of this approach is to use an *a priori* generation of the parameters $\alpha_{jl}^{(i)}$ from a parallelotope in α-space (space of imaginary momenta). The variational calculation on the three-particle Coulomb system is performed using these $\alpha_{jl}^{(i)}$. In the global chaos approach or the *a priori* generation of the $\alpha_{jl}^{(i)}$, these quantities are called nonlinear parameters merely by convention, which is misleading since they are not varied in the course of the variational calculation and are chosen only once and often without optimizing the parallelotope.[5] The true nonlinear parameters in this method are the six numbers specifying the dimensions of the parallelotope in α-space.[7]

In an earlier paper,[1)] we used a different choice of $\alpha_{jl}^{(i)}$ in (9), known as the method of stepwise optimization.[27] The essence of this method is that the $(N + 1)$st triple of nonlinear parameters $\{\alpha_{1l}^{(N+1)}, \alpha_{2l}^{(N+1)}, \alpha_{3l}^{(N+1)}\}$ is chosen by repeated trials (i.e., repeated solution of the eigenvalue problem). Out of the several tens or even hundreds of trial triples, we eventually select the best eigenvalue solution, i.e., the solution which maximizes the variational reduction in $E^{(N+1)}$ as compared with the preceding $E^{(N)}$. Stepwise optimization of the nonlinear parameters was first suggested in Ref. 28 and was subsequently implemented in specific calculations in Refs. 29 and 30. Note that, in this method, the $\alpha_{jl}^{(i)}$

are the true nonlinear parameters that *are* varied (in contrast to the global chaos method). Moreover, to attain a specific dimension N in the stepwise optimization technique, we have to repeatedly solve the eigenvalue problem. This means that, because of the computational time involved, high values of N are usually difficult to achieve in the stepwise optimization technique. On the other hand, if we use the asymptotic formula[8,25]

$$E(N_i)=E(\infty)+A/N_i^{\gamma}, \tag{10}$$

where $E(\infty)$, A, γ are constants (independent of N_i), we can readily see that it is more convenient to use large values of N_i (especially for large γ). When the number of nonlinear parameters $\alpha_{jl}^{(i)}$ used in the calculation is large [$\sim 3N$, where $N \sim 100$ is the number of basis functions in (9)], the final answer, i.e., the calculated energy, is almost independent of the specific values of the nonlinear parameters, and is determined by their total number ($\sim 3N$), i.e., characteristic statistical regularities arise in calculations using (9). This means that, for high values of N, we can abandon the repeated solution of the eigenvalue problem and generate the $\alpha_{jl}^{(i)}$ *a priori* (before the calculation), i.e., for large N we can use the global chaos method for the nonlinear parameters. A detailed comparison of the possibilities of the stepwise optimization and global chaos techniques in relation to the nonlinear parameters is given in Refs. 4 and 5.

We have followed Refs. 4, 5, and 25 in the specific selection of the $\alpha_{jl}^{(i)}$. In particular, in the first stage, they were chosen from the constant interval $(0, A_2]$:

$$\alpha_1^{(i)}=\langle i(i+1)/2^{1/2}\rangle A_2,$$

where $\langle \ldots \rangle$ represents the fractional part of a number. In the second stage, we selected the $\alpha_2^{(i)}$ from the interval $[B_1^{(i)}, B_2]$:

$$\alpha_2^{(i)}=\langle i(i+1)/2\cdot 3^{1/2}\rangle (B_2-B_1^{(i)})+B_1^{(i)},$$

where $B_1^{(i)} = -\delta\alpha_1^{(i)}$. We note that, in contrast to the preceding stage, the $B_1^{(i)}$ are functions of i and may assume negative values. In the third stage, we select

$$\alpha_3^{(i)}=\langle i(i+1)/2\cdot 5^{1/2}\rangle (C_2-C_1^{(i)})+C_1^{(i)},$$

where $c_1^{(i)} = -\varkappa \min\{\alpha_1^{(i)}, \alpha_2^{(i)}\}$. The true nonlinear parameters of the method are, as already mentioned, the quantities A_2, B_2, C_2, δ, and $\varkappa$. The number of nonlinear parameters can, in fact, be increased, but the very high rate of convergence of (9) for the bound states of Coulomb systems enables us to perform successful calculations by assigning relatively arbitrary values to A_2, B_2, C_2, δ, and $\varkappa$, i.e., without using a single nonlinear parameter. For example, in the work reported here, $\delta = 0$ and $\varkappa = 0$ in practically all the calculations. The care that must be taken in optimizing A_2, B_2, C_2, δ and $\varkappa$ in specific calculations is discussed in detail in Ref. 4. Other strategies for choosing the $\alpha_j^{(i)}$ in the method of variational exponential expansion are given in Refs. 7 and 31. Although, in the work presented here, the implementation of the method of global chaos generally follows Ref. 7, we recall Ref. 32 which may be regarded as the beginning of precision calculations of the bound states of Coulomb systems using a large number of exponential basis functions in terms of relative coordinates. The ideas, conclusions, and results of Ref. 32 for $pp\mu$ ($L = 0$) have not lost their validity, but more accurate values are now available for the constants m_μ, m_p, and Ry.

To evaluate the matrix elements of the Hamiltonian and the weights at the next stage of the method, we have to take into account the explicit form of $Y_{LM}^{l,L-l}(r_{31},r_{32})$ for $L = 1$ and $L = 2$ (for $L = 0$, we have the identity $Y_{00}^{00} = 1$). For $L = 1$, there are two systems of angular functions:

$$Y_{10}^{10}(\mathbf{r}_{31}, \mathbf{r}_{32})=\mathbf{k}\cdot\mathbf{r}_{31},$$
$$Y_{10}^{01}(\mathbf{r}_{31}, \mathbf{r}_{32})=\mathbf{k}\cdot\mathbf{r}_{32},$$

where $\mathbf{k}$ is the unit vector along the Z axis.

For $L = 2$, there are three systems of angular functions:

$$Y_{20}^{20}(\mathbf{r}_{31}, \mathbf{r}_{32})=3(\mathbf{k}\cdot\mathbf{r}_{31})^2-r_{31}^2,$$
$$Y_{20}^{11}(\mathbf{r}_{31}, \mathbf{r}_{32})=3(\mathbf{k}\mathbf{r}_{31})(\mathbf{k}\cdot\mathbf{r}_{32})-\mathbf{r}_{31}\cdot\mathbf{r}_{32},$$
$$Y_{20}^{02}(\mathbf{r}_{31}, \mathbf{r}_{32})=3(\mathbf{k}\cdot\mathbf{r}_{32})^2-r_{32}^2.$$

In these expressions, $\mathbf{k}$ is again the unit vector along the Z axis. The formulas for averaging the matrix elements over the orientations of the Z axis are as follows[33]:

$$\oint(\mathbf{a}\cdot\mathbf{b})\,d\Omega_{\mathbf{k}}=4\pi\,(\mathbf{a}\cdot\mathbf{b}),\qquad \oint(\mathbf{a}\cdot\mathbf{k})(\mathbf{b}\cdot\mathbf{k})\,d\Omega_{\mathbf{k}}=\frac{4\pi}{3}\,(\mathbf{a}\cdot\mathbf{b}),$$

$$\oint(\mathbf{a}\cdot\mathbf{k})(\mathbf{b}\cdot\mathbf{k})(\mathbf{c}\cdot\mathbf{k})(\mathbf{d}\cdot\mathbf{k})\,d\Omega_{\mathbf{k}}$$

$$=\frac{4\pi}{15}\,[(\mathbf{a}\cdot\mathbf{b})(\mathbf{c}\cdot\mathbf{d})+(\mathbf{a}\cdot\mathbf{c})(\mathbf{b}\cdot\mathbf{d})+(\mathbf{a}\cdot\mathbf{d})(\mathbf{b}\cdot\mathbf{c})].$$

After averaging over the directions of $\mathbf{k}$, the matrix elements become functions of only the powers of the scalar variables r_{31}, r_{32}, and r_{21}. We must then remember that, for example,

$$\mathbf{r}_{31}\mathbf{r}_{32}={}^1/_2(r_{31}^2+r_{32}^2-r_{21}^2)$$

and so on for the other scalar products.[4] The concluding stage in the evaluation of the matrix elements involves Laplace transforms and integration over all space. The variables r_{31}, r_{32}, and r_{21} are not convenient in this integration because the triangle condition must be satisfied for them, e.g.,

$$|r_{31}-r_{32}|\leqslant r_{21}\leqslant r_{31}+r_{32}.$$

It is better to introduce the three independent perimetric coordinates:

$$u_1={}^1/_2(r_{31}+r_{21}-r_{32}),\qquad r_{21}=u_1+u_2,$$
$$u_2={}^1/_2(r_{32}+r_{21}-r_{31}),\qquad r_{31}=u_1+u_3,$$
$$u_3={}^1/_2(r_{31}+r_{32}-r_{21}),\qquad r_{32}=u_2+u_3.$$

In terms of these perimetric coordinates, the integrals can be evaluated independently, which introduces a significant simplification when the Laplace transform is performed, i.e., when we transform from the polynomial in u_1, u_2, u_3 to the polynomial in the conjugate variables

$$X_1=(\alpha_2^p+\alpha_2^q+\alpha_3^p+\alpha_3^q)^{-1},$$
$$X_2=(\alpha_1^p+\alpha_1^q+\alpha_3^p+\alpha_3^q)^{-1},$$
$$X_3=(\alpha_1^p+\alpha_1^q+\alpha_2^p+\alpha_2^q)^{-1}$$

for the (p,q)-matrix element. After the matrix elements have been averaged over the orientations of the vector **k** (the directions of the Z axis), the subsequent steps are relatively simple and consist of the following stages. The first is to replace r_{32}, r_{31}, r_{21} with u_1, u_2, u_3 and to multiply the corresponding initial ("basis") polynomials in the perimetric coordinates. The second stage is to collect together similar terms in the resulting polynomials in u_1, u_2, u_3. The third and concluding stage is to perform the Laplace transform, i.e., transform to the polynomial in the conjugate variables X_1, X_2, X_3. The program of operations is very simple and the analytic evaluation of the polynomials in X_1, X_2, X_3 is performed on a computer. We shall now reproduce the formulas for the matrix elements, using $\langle ... \rangle$ to indicate the application of the above program for the evaluation of the polynomials in X_1, X_2, X_3 to the expression within the brackets. We also reproduce the formulas for the matrix elements (weights) of the overlap integral of the basis functions (exponentials) in (9). In this procedure, it is convenient to transfer to the matrix element the product $r_{32}r_{31}r_{21}$ from the volume element in terms of the relative coordinates, i.e., $dV \simeq r_{32}r_{31}r_{21}dr_{32}dr_{31}dr_{21}$. For $L = 0$, the overlap matrix element (weight) can be written in terms of the above notation as follows:

$$N = \langle r_{32}r_{31}r_{21} \rangle.$$

For $L = 1$, there are two types of expression, namely, the two "diagonal" matrix elements

$$N_d = \langle r_{3i}^2 r_{31}r_{32}r_{21} \rangle,$$

where i can be 1 or 2, and the "off-diagonal" matrix elements

$$N_{\mathrm{H}} = \langle (\mathbf{r}_{31}\cdot\mathbf{r}_{32}) r_{31}r_{32}r_{21} \rangle.$$

For $L = 2$, there are four types of expression, namely, the two "diagonal" expressions

$$N_{d,a} = \langle r_{3i}^4 r_{31}r_{32}r_{21} \rangle,$$
$$N_{d,b} = {}^1/_4(3S+V),$$

where i can be 1 or 2, $S = \langle (r_{31}r_{32})^2 r_{31}r_{32}r_{21} \rangle$, and $V = \langle (r_{31}r_{32})^2 r_{31}r_{32}r_{21} \rangle$, and the two "off-diagonal" expressions

$$N_{\mathrm{H},a} = \langle (\mathbf{r}_{31}\mathbf{r}_{32})^2 r_{3i}^2 r_{31}r_{32}r_{21} \rangle,$$
$$N_{\mathrm{H},b} = {}^1/_4(3V-S),$$

where $i = 1, 2$ and S and V are the same as above. The expressions for the matrix elements of the potential energy are obtained in a trivial manner from the matrix elements of the overlap integral by replacing the product $r_{32}r_{31}r_{21}$ with the product

$$e_1e_2r_{31}r_{32} + e_1e_3r_{32}r_{21} + e_2e_3r_{31}r_{21}.$$

In the kinetic energy, the terms that are quadratic in the $\alpha_j^{(i)}$ split into two types, the first of which is proportional to the corresponding weight matrix elements

$$(T_a)_{p,q} = \left\{ \sum_{i=1}^{3} \frac{1}{m_i} (\alpha_j^p \alpha_j^q + \alpha_k^p \alpha_k^q) \right\} N_{p,q},$$

where $(i,j,k) = 1,2,3$.

The second type is simply obtained from $N_{p,q}$ by replacing the product $r_{32}r_{31}r_{21}$ with the products $r_{32}(\mathbf{r}_{31}\cdot\mathbf{r}_{21})$, $r_{31}(\mathbf{r}_{32}\cdot\mathbf{r}_{12})$, and $r_{21}(\mathbf{r}_{32}\cdot\mathbf{r}_{31})$, e.g., for $L = 0$,

$$(T_b)_{p,q} = \frac{1}{m_1} (\alpha_2^p \alpha_3^q + \alpha_2^q \alpha_3^p) \langle r_{31}(\mathbf{r}_{32}\cdot\mathbf{r}_{12}) \rangle$$
$$+ \frac{1}{m_2} (\alpha_1^p \alpha_3^q + \alpha_1^q \alpha_3^p)$$
$$\times \langle r_{32}(\mathbf{r}_{21}\cdot\mathbf{r}_{31}) \rangle + \frac{1}{m_3} (\alpha_1^p \alpha_2^q + \alpha_1^q \alpha_2^p) \langle r_{21}(\mathbf{r}_{31}\cdot\mathbf{r}_{32}) \rangle.$$

When $L \geqslant 1$, the expressions for T_b are obtained in a completely analogous manner. A more detailed description of the procedure used to obtain the matrix elements is given in Ref. 4, together with the expression for the matrix elements of the kinetic energy that are linear in $\alpha_j^{(i)}$. The approach presented in Ref. 4 is preferable to the method used in Ref. 27 for calculating the matrix elements because the expressions are much simpler. We also note that earlier attempts to calculate the bound D-states ($L = 2$) of three-particle systems using high-accuracy Hylleraas or variational exponential expansions were unsuccessful.

The solution of the generalized eigenvalue problems

$$(\hat{H} - \varepsilon \hat{N})\mathbf{c} = 0$$

is the concluding stage of the method. The determination of the corresponding ε and $\mathbf{c}$ is not trivial because the matrix $\hat{N}$ is poorly conditioned and the conventional methods of solving the eigenvalue problem cannot be used. To determine the accurate value ε_a, we use the bisectional subdivision of the interval $[\varepsilon_l, \varepsilon_u]$ between the lower and upper limits for ε_a that definitely contains ε_a. The first step is to specify $\varepsilon_0 = (\varepsilon_l + \varepsilon_u)/2$ and to reduce the matrix $\hat{H} - \varepsilon_0\hat{N}$ to the LDU form,[34] where L and U are, respectively, the lower and upper triangular matrices with units along the diagonal and D is the diagonal matrix. When all the elements of the matrix D are positive, the upper limit is shifted: $\varepsilon_u^{(\text{new})} = \varepsilon_0$ and the segment $[\varepsilon_l, \varepsilon_u^{(\text{new})}]$ is again divided in two, which determines ε_1. The procedure is then repeated. When at least one of the elements of D is negative, we shift the lower limit $\varepsilon_1^{(\text{new})} = \varepsilon_0$, the interval $[\varepsilon_1^{(\text{new})}, \varepsilon_u]$ is again divided in two, and ε_1 is determined. The procedure is then repeated. The result of an n-fold repetition of this technique yields an interval $[\varepsilon_l^{(n)}, \varepsilon_u^{(n)}]$, such that $\varepsilon_l^{(n)} \leqslant \varepsilon_a \leqslant \varepsilon_u^{(n)}$ and $|\varepsilon_u^{(n)} - \varepsilon_l^{(n)}| < \delta$ (in our calculations, $\delta \simeq 10^{-13} - 10^{-14}$). Thus, after n steps, the quantity $\varepsilon_{n+1} = (\varepsilon_l^{(n)} + \varepsilon_u^{(n)})/2$ differs from ε_a by an amount smaller than δ. Inverse iteration is then used to determine the eigenvector. The matrix $\hat{H} - \varepsilon_{n+1}\hat{N}$ is reduced to the LDU form and is inverted. Next, the operator $U^{-1}D^{-1}L^{-1}$ is applied to an arbitrary normalized vector $\mathbf{x}_0$ and the following quantity is calculated:

$$\mathbf{y}_1 = U^{-1}D^{-1}L^{-1}\mathbf{x}_0,$$

which is again normalized, taking $\mathbf{x}_1 = \mathbf{y}_1/\|\mathbf{y}_1\|$. The operator $U^{-1}D^{-1}L^{-1}$ is then applied to $\mathbf{x}_1$, which yields $\mathbf{y}_2$. The latter is again normalized, and so on. When ε_{n+1} is close to ε_a, we can start with an arbitrary vector $\mathbf{x}_0$ and, in a relatively small number of iterations (m less than 20), we obtain a vector $\mathbf{x}_{m+1}$ that closely approximates the true eigenvector $\mathbf{x}_a$ corresponding to the eigenvalue ε_a. A modification of this procedure capable of dealing with the excited states is given in Ref. 4.

Having presented the computational scheme for the bound states of three-particle Coulomb systems, we now

TABLE I. The states of $^{\infty}$He, ^{3}He, and ^{4}He (in atomic units). The table lists the better variational results for the exponential expansion (over 350 basis functions; 300 functions when the 1^1S state is excluded). The asymptotic results are also given for $^{\infty}$He (in parentheses) together with the isotopic shifts calculated relative to $^{\infty}$He.

State	$^{\infty}$He	$^4\text{He}\cdot 10^4$	$^3\text{He}\cdot 10^4$
1^1S	−2.903724376435 (−2.9037243768)	4.19821	5.57168
2^3S	−2.175229378234 (−2.175229378240)	2.99189	3.90707
2^1P	−2.12384308601 (−2.123843087)	2.97433	3.94742
2^3P	−2.133164190701 (−2.133164192)	2.83550	3.76317
3^1D	−2.055629022 (−2.055635)	2.817	3.738
3^3D	−2.055629037 (−2.055635)	2.816	3.738

turn to the results obtained using the expansion (9) for atomic, mesomolecular, and exotic systems.

a. Atomic systems

The variational exponential expansion has been used[8,23,35] to determine the energies of the 1^1S, 2^3S, 2^1P, and 2^3P states of helium and helium-like ions. The precision attained in Ref. 35 for the calculated energies and isotopic shifts in these states of helium-like systems was significantly higher, and it was found that the exponential expansion yielded very high precision for these systems (much higher than in the Hylleraas case). Similar calculations have now been carried out for the D-states of helium-like systems. The results for the $^{\infty}$He atom (and the isotopes ^{3}He and ^{4}He) are listed in Table I (see Refs. 4, 35, and 36 for details), where the better variational results are given for $^{\infty}$He in the upper line and the asymptotic values (in parentheses) in the second line in each row. Only the better variational results are shown for ^{3}He and ^{4}He.

We have carried out calculations on $e^-e^+e^-$, $e^-\mu^+e^-$, and $^{\infty}\text{He}^-$, in which only the 1^1S ground state is a bound state. Earlier calculations on these systems were reported in Ref. 25 and efficient algorithms, capable of accelerating such calculations and increasing their precision, were subsequently developed. The results are listed in Table II and, judging by the stability of the intermediate figures after the decimal point, they are the most accurate among those cited in the literature. Table II also lists the results of calculations on the model systems $e^-(2e)^+e^-$, $e^-(3e)^+e^-$, which are similar to the positronium ion $e^-e^+e^-$, except that the mass of the positron has been increased by a factor of two and three, respectively (the charge is $+1$, as before). Calculations on model Coulomb systems are important for studies of the analytic dependence of the energy $\varepsilon(m)$ of the three-body system on the mass of the central particle [the two other particles with lower (unit) masses are identical]. The availability of simple interpolation formulas for $\varepsilon(m)$ enables us to predict with high accuracy the energy of such systems without performing specific calculations, and thus economize on computational time and resources.[37,38] The constants used in the calculations on atomic, mesomolecular, and exotic systems are listed in Table III. The same values of the nonlinear parameters (chosen without optimization) were used in the calculations on $e^-(2e)^+e^-$ and $e^-(3e)^+e^-$: $A_2 = 1.15$, $B_2 = 0.71$, $C_2 = 0.77$, $\delta = 0.4$, $\varkappa = 1$.

b. Mesomolecular systems

Table IV summarizes the results of our calculations on the bound $S\ (L = 0)$, $P(L = 1)$, and $D(L = 2)$ states of mesic molecules, performed using the expansion given by (9). They are among the most accurate available at present. For most of the states of the mesic molecules, the problem of calculating the Coulomb binding energies can now be regarded as completely solved (these energies are available to better than 10^{-14}–10^{-5} eV). More accurate values of the pure Coulomb binding energy in these mesomolecular states are not of any practical value because the corrections for vacuum polarization, the strong interaction between nuclei, relativistic effects, etc., limit the final accuracy to 10^{-3}–10^{-4} eV. A consistent theory of these corrections in the higher orders is not as yet available. Moreover, all the mesomolecular parameters, including the binding energies in the individual levels, have finite widths due to the decay of the muon, possible nuclear reactions, radiative and radiationless

TABLE II. Total energies of the systems $e^-e^+e^-$, $^{\infty}\text{H}^-$, $e^-\mu^+e^-$, $e^-(2e)^+e^-$, $e^-(3e)^+e^-$ (in atomic units).

N_i	$e{-}e{+}e{-}$	$e{-}(2e){+}e{-}$	$e{-}(3e){+}e{-}$	$^{\infty}\text{H}^-$	$e{-}\mu{+}e{-}$
175	−0,26200506403	−0,34837166167	−0.39214100163	−0.52775101364	−0,52505481343
225	−0,26200506930	−0,34837166380	−0.39214100679	−0,52775101481	−0.52505481515
275	−0,26200507008	−0,34837166456	−0.39214100914	−0.52775101597	−0,52505481524
325	−0.26200507020	−0,34837166498	−0.39214101028	−0,52775101621	−0.52505481531
375	–	–	–	−0.52775101637	–
∞	−0,26200507030	−0,3483716652	−0,3921410104	−0.52775101650	−0.5250548154

TABLE III. Constants used in the calculations.

Ry	13.6058041 eV	$E(p\mu)$	−2528.52171042 eV
m_p	1836.151527 m_e	$E(d\mu)$	−2663.23087278 eV
m_d	3670.481 m_e	$E(t\mu)$	−2711.27278388 eV
m_t	5496.918 m_e	$m\mu$	206.769 m_e
$m_{^3\mathrm{He}}$	5495.87015 m_e		
$m_{^4\mathrm{He}}$	7294.2618241 m_e		

transitions in the mesic molecule and the mesic complex, and collisions with other molecules and complexes.

The first calculations on the S state ($L = 0$) of mesic molecules using the vibrational exponential expansion are reported in Refs. 32, 39, and 19). The first high-accuracy calculations on the S and P states of mesic molecules are reported in Ref. 8, including the first variational determinations of the weakly-bound states of $dt\mu^*$ ($L = 1$) and $dd\mu^*$ ($L = 1$). Accurate calculations of the S and P states have been subsequently reported in Refs. 4, 5, and 25 and of the D states in Ref. 35. In our own calculations, we have concentrated our attention on asymmetric mesic molecules (S and P states). The results are reported in mesoatomic units, for which $\hbar = 1$, $m_\mu = 1$, and $e^2 = 1$. The values of the constants employed in the calculations are listed in Table III. Table V shows the results. Their accuracy is sufficiently high and can readily be estimated from the stability of the intermediate values after the decimal point, and with the help of the asymptotic formula given by (10). The parameter values used in these calculations were not optimized and assumed equal values for $L = 0$: $A_2 = 1.37713$, $B_2 = 1.45581$, and $C_2 = 2.04747$. In all the calculations shown in Table V, the nonlinear parameters were taken to be $\delta = 0$ and $\varkappa = 0$. For $L = 1$, we took $A_2 = 1.15$, $B_2 = 1.17$, $C_2 = 2.27$ in the case of $dt\mu$ and $A_2 = 1.11$, $B_2 = 1.137$, and $C_2 = 1.805$ for $dp\mu$ and $tp\mu$.

The fact that calculations with constant values of A_2, B_2, C_2, δ and $\varkappa$ have yielded very high accuracy for these states is undoubtedly an indication of the considerable promise of our method. The accuracy that has been attained can be readily increased still further merely by approximately optimizing A_2, B_2, C_2, δ and $\varkappa$ or by increasing the attained dimensionality. Table V shows that the accuracy of the calculated binding energy of the mesic molecules decreases with increasing degree of adiabaticity in the system. This is discussed in greater detail in the next Section.

c. Exotic three-particle Coulomb systems

Exotic three-particle Coulomb systems are usually taken to be three-body systems with two-body Coulomb interaction between the particles, for which formation of the system and an appreciable lifetime are exceedingly unlikely. In the work reported here, we calculated the Coulomb binding energies of the mesic molecule $pp\pi$ (two bound S and P states) and the bound states of the systems $\pi\pi K$, $KK\pi$, KKp, and ppK. It is clear that the strong interaction plays a significantly more important role than does the Coulomb interaction in these formations, but estimates of the maximum Coulomb binding energy are not entirely without interest. Moreover, such calculations are important because of the interest, mentioned above, in the dependence of the binding energy on the masses of the particles in the system. In this approach, the results listed in Table VI can serve as reference points that can be used to improve the analytic formulas for the function $\varepsilon(m)$. These formulas can then be used to estimate, with high precision, the binding energies of systems of arbitrary mass m, without performing numerical calculations. The following constants were used in the calculations: $m_{\pi^-} = 273.12695 m_e$, $m_{K^-} = 966.1521$, $E(p\pi) = -3234.91866367$ eV, $E(pK) = -8613.17056305$ eV, and $E(K\pi) = -2897.11118439$ eV; Ry and m_p are listed in Table IV. The nonlinear parameters A_2, B_2, C_2, δ, and $\varkappa$ in the case of $\pi\pi K$, ppK, and pKK were not varied and were assumed to be the same as for $e^-(2e)^+e^-$ (see above); $A_2 = B_2 = 1.5$, $C_2 = 2$, and $\delta = \varkappa = 0$ in all other cases.

The mesic Coulomb molecule $pp\pi$ has two bound states, namely, the ground states in the S and P series. The other systems have only one bound state in the S series.

4. UNIVERSALITY OF THE VARIATIONAL EXPONENTIAL EXPANSION

A number of examples was given above of high-precision solutions, based on the expansion (9) of the nonrelati-

TABLE IV. Binding energy of mesic molecules in eV. Ground and excited (*) states.

System	$L=0$	$L=0$ (*)	$L=1$	$L=1$ (*)	$L=2$
$pp\mu$	$-253.152616\pm$ $\pm 1\cdot 10^{-6}$		$-107.26587\pm$ $\pm 3\cdot 10^{-5}$	–	–
$dd\mu$	$-325.07399\pm$ $\pm 1\cdot 10^{-5}$	$-35.84424\pm$ $\pm 2\cdot 10^{-5}$	$-116.68181\pm$ $\pm 3\cdot 10^{-5}$	$-1.9745\pm$ $\pm 1\cdot 10^{-3}$	$-86.45\pm$ $\pm 2\cdot 10^{-2}$
$tt\mu$	$-362.91031\pm$ $\pm 2\cdot 10^{-5}$	$-83.77115\pm$ $\pm 1\cdot 10^{-4}$	$-289.14210\pm$ $\pm 7\cdot 10^{-5}$	$-45.2057\pm$ $\pm 1\cdot 10^{-4}$	$-172.65\pm$ $\pm 5\cdot 10^{-2}$
$dp\mu$	$-221.54955\pm$ $\pm 2\cdot 10^{-5}$	–	$-97.4987\pm$ $\pm 4\cdot 10^{-4}$	–	–
$tp\mu$	$-213.84028\pm$ $\pm 2\cdot 10^{-5}$	–	$-99.1267\pm$ $\pm 4\cdot 10^{-4}$	–	–
$dt\mu$	$-319.14020\pm$ $\pm 1\cdot 10^{-4}$	$-34.8346\pm$ $\pm 2\cdot 10^{-4}$	$-232.4719\pm$ $\pm 4\cdot 10^{-4}$	$-0.655\pm$ $\pm 1.5\cdot 10^{-2}$	$-102.65\pm$ $\pm 2\cdot 10^{-2}$

TABLE V. Binding energies of the *S* and *P* states of asymmetric mesic molecules.

S state

N_i	$pd\mu$	$pt\mu$	N_i	$dt\mu$	$dt\mu$ *
250	−221.54926	−213.83996	300	−319.13950	−34,83171
275	−221.54943	−213,84012	325	−319.13985	−34,83293
300	−221,54949	−213.84021	350	−319,13998	−34.83356
325	−221.54952	−213,84025	375	−319.14004	−34.83390
350	−221,54953	−213,84026	400	−319.14007	−34,83404
Estimated binding energy, eV	−221,54955± ±2·10^{-5}	−213.84028± ±2·10^{-5}		−319.14025± ±1·10^{-4}	−34,83430± ±2·10^{-4}

P state

N_i	$pd\mu$	$pt\mu$	$dt\mu$
300	−97.49605	−99,12363	−232.46561
375	−97,49753	−99,12554	−232,47043
450	−97.49822	−99,12632	−232,47123
525			−232,47157
Estimated binding energy, eV	−97.4987±4·10^{-4}	−99,1267±4·10^{-4}	−232,4719±4·10^{-4}

vistic Schrödinger equation, for a relatively wide range of bound states of different systems. It might be considered that the expansion given by (9) yields high precision in the case of arbitrary three-particle Coulomb systems. However, this proposition is not entirely valid for adiabatic and similar systems, i.e., when $\min(m_1,m_2) \gg m_3$. This slowing down in the rate of convergence is typical for all expansions in which the relative coordinates r_{31}, r_{32}, and r_{21} are explicitly used. For the variational exponential expansion, this was found in Ref. 4 and, in terms of the asymptotic equation (10), signifies a reduction in γ with increasing degree of adiabaticity in the system. For example, for systems such as $e^-e^+e^-$ and ${}^\infty H_2^+$, considered above, it turns out that $\gamma \simeq 12.5$–10; for $pp\mu$ we have $\gamma \simeq 8.5$; and for $tt\mu$ the result is approximately 5–5.5. Finally, for the purely adiabatic system ${}^\infty H_2^+$ we have $\gamma \simeq 1$. The results of calculations on ${}^\infty H_2^+$ are listed in Table VII. These calculations did not yield even four significant figures in the total energy (-0.602 a.u.) because the rate of convergence in (9) was very low in this case.

Of course, the rate of convergence of the variational expansion (9) may be affected by the spin symmetry of the states under consideration (singlet or triplet), the value of the total angular momentum L, the type of state (excited or ground) under consideration, and so on. However, even the combined effect of these factors on the rate of convergence of the data obtained from the variational expansions [including (9)] is several orders of magnitude lower than the effect of the particle masses. The effect of the particle masses on the

TABLE VI. Binding energies of exotic mesic molecules (in eV).

N_i	$pp\pi$ $(L=0)$	N_i	$pp\pi$ $(L=1)$
150	−294.858724	200	−80,21895
200	−294.858904	250	−80,22860
250	−294.858920	300	−80,23005
300	−294.858921	350	−80,23014
Estimated binding energy, eV	−294.858925±4·10^{-6}		−80,2305±4·10^{-4}

N_i	$\pi\pi K$	ppK
150	−133,93315	−491,46380
200	−133,93327	−491.46429
250	−133,93330	−491.46437
300	−133.93332	−491,46439
Estimated binding energy, eV	−133,93332±2·10^{-5}	−491,46440±2·10^{-5}

N_i	πKK	pKK
150	−207,93475	−388.75253
200	−207.93574	−388,75273
250	−207,93604	−388,75277
300	−207.93605	−388.75280
Estimated binding energy, eV	−207.93608±3·10^{-5}	−388.75282±2·10^{-5}

TABLE VII. The molecular ion $^\infty H_2^+$.

N_i	$E(N_i)$, a.u.	N_i	$E(N_i)$, a.u.
125	−0.57882721	250	−0.58846504
150	−0.58122450	275	−0.58943784
175	−0.58357163	300	−0.59055603
200	−0.58611882	325	−0.59117395
225	−0.58717281	350	−0.59201046

convergence of methods used in the three-body Coulomb problem must therefore be examined first. Thus, for example, for excited states, the convergence of (9) can be substantially improved by optimizing the parameters A_2, B_2, C_2, δ, and $\varkappa$, but an improvement in convergence does not result even from careful optimization in the case of adiabatic systems.

Let us examine the slowing down of convergence of the expansion given by (9) in the case of adiabatic systems. We start by writing out the Hamiltonian for the three-particle Coulomb system in relative coordinates (in view of the foregoing discussion, it will be sufficient[40] to confine our attention to $L = 0$):

$$\begin{aligned}
H = & -\frac{1}{2}(m_1^{-1}+m_2^{-1})\left(\frac{\partial^2}{\partial r_{21}^2}+\frac{2}{r_{21}}\frac{\partial}{\partial r_{21}}\right) \\
& -m_3^{-1}\cos\theta_{31,32}\frac{\partial^2}{\partial r_{31}\,\partial r_{32}} \\
& -\frac{1}{2}(m_1^{-1}+m_3^{-1})\left(\frac{\partial^2}{\partial r_{31}^2}+\frac{2}{r_{31}}\frac{\partial}{\partial r_{31}}\right) \\
& -m_2^{-1}\cos\theta_{21,32}\frac{\partial^2}{\partial r_{21}\,\partial r_{32}} \\
& -\frac{1}{2}(m_2^{-1}+m_3^{-1})\left(\frac{\partial^2}{\partial r_{32}^2}+\frac{2}{r_{32}}\frac{\partial}{\partial r_{32}}\right) \\
& -m_1^{-1}\cos\theta_{21,31}\frac{\partial^2}{\partial r_{31}\,\partial r_{21}} \\
& +\frac{e_1e_2}{r_{12}}+\frac{e_1e_3}{r_{31}}+\frac{e_2e_3}{r_{32}},
\end{aligned} \qquad (11)$$

where $\cos\theta_{21,31} = (r_{21}^2 + r_{31}^2 - r_{32}^2)/2r_{21}r_{31}$, and so on, and e_1, e_2, and e_3 are the particle charges. Let us set the smallest mass (to be specific, m_3) equal to unity, which, together with the conditions $\hbar = 1$, $e^2 = 1$, finally determines the system of units that we are using. We shall examine the Hamiltonian (11) for $m_1 \to \infty$ and, at the same time, for $m_2 \to \infty$, i.e., $m_1^{-1} \to 0$ and $m_2^{-1} \to 0$. In this limit, the Hamiltonian is not a differential operator in the variable r_{21}. In mathematics, it is customary to use the small-parameter method[41] to analyze operators with such singularities in front of the higher-order derivatives. In physics, the small-parameter method is called the Born-Oppenheimer approximation[42] when used in the analysis of adiabatic and similar systems.

In terms of (11), the essence of the adiabatic approximation can be formulated as a significant difference between motion in the variable r_{21} and motions in the variables r_{31} and r_{32} as $(m_1, m_2) \to \infty$. In the limit where $m_1 = m_2 = \infty$, the eigenfunction of the Hamiltonian in r_{21} is the δ-function $\delta(r_{21} - R)$, where R is the separation between the nuclei. The slow convergence of the variational expansion (9) is due to the slow convergence of the expansion of $\delta(r_{21} - R)$ in terms of the basis functions in (9), and is typical for all expansions in terms of relative coordinates, for example, the Hylleraas coordinates. On the other hand, adiabatic methods converge very rapidly for such systems, but they are of no real value for $e^-e^+e^-$, $^\infty H^-$, helium-like systems, and intermediate particle masses (for example, mesic molecules) because of the slow convergence. In view of this, we may conclude that we have a kind of complementarity between adiabatic methods and methods using expansions in relative coordinates. It is still not clear whether this complementarity is fundamental and that at least two types of variational expansion (each in its own mass range) have to be used for three-body problems, or whether there will be a universal expansion which, depending on the particular particle mass values, will transform its basis functions into a form that will be optimal for the analysis of this system.

Another defect of (9) is that the Fock (logarithmic) singularity of the true wave function near the ternary collision between the three Coulomb particles of the system has been ignored. Actually, following Ref. 43, it can be shown that the true wave function of the ground (1^1S) state of the helium atom has a logarithmic singularity in the hyper-radius at the ternary collision point, i.e., it can be written in the form

$$\psi(r_1, r_2, r_{21}) = \sum_{k=0}^{\infty} c_k(r_1, r_2, r_{21})(\ln R)^k,$$

where $\mathbf{r}_1$, $\mathbf{r}_2$ are the position vectors of the two electrons in the $^\infty$He atom, $R = (r_1^2 + r_2^2)^{1/2}$, and r_{21} is the distance between the electrons. The expansion given by (9) does not contain logarithmic terms (in R), so that we may expect a slower rate of convergence of (9) in the case of systems with a significant Fock singularity (or point of ternary collision, $R = 0$, at which the logarithmic distortion is at its maximum). In contrast to adiabatic divergence, this situation is not universal because the effect of the Fock singularity can be ignored (without loss of precision) in the analysis of an arbitrary three-particle Coulomb system, except for the 1^1S state of He and helium-like ions Li$^+$, Be^{2+}, and so on. For systems with other mass values, states with different spin symmetry, and excited states, the logarithmic singularity can be ignored.[4] In the isoelectronic sequence $^\infty H^-$, $^\infty$He, $^\infty$Li$^+$, $^\infty$Be^{2+}..., we may expect a greater departure of the expansion (9) from the true wave function because of the higher probability of ternary collisions in this sequence.

In our calculations, we ignored the logarithmic terms in the hyper-radius and used (3) to calculate the 1^1S, 2^3S, 2^1P, and 2^3P states of $^\infty$He. The results are listed in Table VIII, from which it follows that the accuracy of the calculated S-triplet state is much higher than that of the S-singlet state. Our results on the singlet state are not as good as those re-

TABLE VIII.

The 1^1S and 2^3P states of $^\infty$He.

N_i	Energy 1^1S, a.u.	Energy 2^3S, a.u.
150	−2.903724374135	−2.175228377272
175	−2,903724375435	−2,175229377858
200	−2,903724376006	−2,175229378160
225	−2.903724376119	−2.175229378187
250	−2.903724376232	
300	−2.903724376435	−2.175229378229
350	–	−2.175229378234
∞	−2,9037243768	−2.175229378240

The 2^1P and 2^3P states of $^\infty$He.

N_i	Energy 2^1P, a.u.	Energy 2^3P, a.u.
200	−2,12384308202	−2.133164185925
250	−2,12384308498	−2.133164188054
300	−2.12384308560	−2.133164189634
350	−2,12384308601	−2,133164190801
∞	−2.123843087	−2.133164192

ported in Ref. 44, in which the logarithmic singularity at the ternary collision point was taken into account. Because of the antisymmetry of the spatial part of the wave function in the case of the triplet state, this singularity is of litle significance, so that our results on the 2^3S state were found to be the most accurate of all those obtained for this state.

The author is greatly indebted to N. N. Kolesnikov, V. D. Efros, and V. A. Kopylov for their help at different stages of this research, and thanks V. B. Belyaev, Yu. N. Demkov, and Ya. A. Smorodinskiĭ for their constant interest and numerous valuable suggestions.

APPENDIX

We shall now reproduce the Hamiltonians for the three-body Coulomb system, written in terms of the Bose creation and annihilation operators, which are often convenient in various theoretical treatments. We shall examine the case $L = 0$, for which the Hamiltonian in relative coordinates is given by (11).

Consider the operator r and its conjugate momentum $p_r = (-i)\partial/\partial r$. We then have the obvious commutation relation $[p_r, r] = -i$, and we can use this to verify the validity of following lemma.[45,46]

The operators

$$S=\frac{1}{2}r\left(p_r{}^2+\frac{\hat{l}^2}{r^2}+1\right), \qquad T=rp_r,$$

$$U=\frac{1}{2}r\left(p_r{}^2+\frac{\hat{l}^2}{r^2}-1\right),$$

where $\hat{\mathbf{l}}=\mathbf{r}\times\mathbf{p}$, satisfy the commutation relations of the $O(2,1)$ Lie algebra

$$[S, U]=iT, \quad [U, T]=-iS, \quad [T, S]=iU,$$

and the second-order Casimir operator has the value $C_2 = \hat{l}^2 = l(l+1)$. The fact that C_2 for the $O(2,1)$ algebra is identical with the C_2 for the corresponding $O(3)$ signifies the complementarity of the $O(2,1)$ and $O(3)$ representations in the sense of Moshinsky's definition.[47] A similar lemma can be readily generalized to the case where the dimensionality of space is greater than three.[46] In this case, $\hat{l}^2$ is replaced with $\Delta^2_N(\Omega)$, i.e., the Laplace operator on the surface of a $3N$-dimensional hypersphere.[46]

The transformation of the Hamiltonian (11) is based on this lemma. Let us multiply the Hamiltonian (11) by the product of the relative coordinates:

$$\Theta(r_{31}, r_{32}, r_{21})=r_{31}r_{32}r_{21}H(r_{31}, r_{32}, r_{21}). \tag{A.1}$$

In order to avoid using double indices in the ensuing formulas, we shall use complementary indices, e.g., instead of (21) we use 3, instead of (31) we use 2, and instead of (32) we use 1. In terms of the operators S,T,U defined above and equipped with the previous indices, we now have

$$\Theta(r_{31}, r_{32}, r_{21})=\sum_{i=1}^{3}\left\{(S_j-U_j)(S_k-U_k)\left[\frac{1}{2\mu_i}(S_i+U_i)+e_je_k\right]\right.$$
$$\left.+\frac{1}{2m_i}(\mathbf{n}_j\cdot\mathbf{n}_k)T_jT_k\right\}, \tag{A.2}$$

where $(i,j,k) = 1,2,3$ and $\mu_i^{-1} = m_k^{-1} + m_j^{-1}(i,j,k) = 1,2,3$. The scalar products $(\mathbf{n}_k\cdot\mathbf{n}_j)$ can also be expressed in terms of the corresponding operators S and U:

$$\mathbf{n}_k\mathbf{n}_j=(S_k-U_k)^{-1}(S_j-U_j)^{-1}[(S_k-U_k)^2+(S_j-U_j)^2-(S_i-U_i)^2],$$

where $(i,j,k) = 1,2,3$.

We thus see that the Hamiltonian of an arbitrary three-particle Coulomb system can be expressed in terms of only nine operators S_i, T_i, and U_i, where $i = 1,2,3$ [the generators of the three algebras $O(2,1)_i$] with coefficients that depend on the three particle masses and the three paired products of their charges. It appears that this "closed" expression for the three-particle Coulomb Hamiltonian in the form of the sum of a finite number of terms S_i, T_i, U_i is possible only in relative coordinates, and this is responsible for the high rate of convergence of their variational expansions.

Next, we introduce the Bose operators a_1, a_2, b_1, b_2, c_1, c_2 and transform to the Bose representation for each of the three $O(2,1)$ algebras

$$U_1={}^1/_2(a_2{}^+a_1+a_1{}^+a_2),\quad T_1={}^1/_2i(a_2{}^+a_1-a_1{}^+a_2),$$
$$S_1={}^1/_2i(a_2{}^+a_2-a_1{}^+a_1),$$

and similarly for b_1, b_2 (index 2: S_2, T_2, U_2) and c_1, c_2 (index 3: S_3, T_3, and U_3). This gives us the final form of the Hamiltonian (the operator Θ in the new metric) in terms of the Bose creation and annihilation operators. Each of the a operators commutes with each of the b operators and with each c operator, and each b operator commutes with each c operator (similarly for the creation operators). The commutation relations within the groups are

$$[a_i, a_j{}^+]=\delta_{ij},\quad [a_i, a_j]=0,\quad [a_i{}^+, a_j{}^+]=0,\quad (i, j)=1, 2$$

and similarly for the b and c operators.

The representation of the Coulomb Hamiltonian for the three-body system in terms of the Bose creation and annihilation operators a_i, b_i, c_i $(i=1,2)$ is useful not only in theoretical studies, but also in numerical calculations and estimates of the binding energies of different systems.

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Translated by S. Chomet