Rigorous mathematical study of the He bound states

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(Received 20 October 1999; revised manuscript received 23 March 2000; published 8 September 2000)

A method is proposed for searching the formal solution of the Hylleraas equation for the helium atom. A mathematically rigorous study confirms, in a unified and simpler manner, several results obtained earlier in the literature but not necessarily in the same contexts. We use an adequate transformation of the Schrödinger equation to identify three asymptotic channels. Two of these are considered in detail as physical and are seen to differ from ''traditional'' ones. In particular, we demonstrate that there is no place for the widely used Hylleraas-type exponent. Furthermore, we show how the mathematical presence of logarithms at small hyperradii, first suggested by Bartlett, is linked to the electron-electron interaction. Finally, the study leads to the development of simple procedures for the numerical calculations of energy levels and approximate wave functions.

PACS number(s): 31.15.−p

I. INTRODUCTION

Recent series of $(e,3e)$ experiments on helium [1] clearly demonstrate that simple bound-state wave functions, used with success for calculations of elastic and inelastic scattering, are not necessarily satisfactory to describe the details of many-electron ionization processes. Seeking almost exact solutions is now timely. In this context, many efforts were concentrated to get the proper final-state wave functions close to the formal solution of the Schrödinger equation (named SE hereafter) [2–4]; however, the probing functions used up to now for the bound state are far from the SE formal solution.

The theory of the helium atom has been developed for more than 70 years, starting from the works of Hylleraas [5]. By considering only *S*-state solutions, he reduced the six-dimensional SE into a three-dimensional one (named HE hereafter); from it, basic wave functions were obtained and used in the Ritz variational method to get the helium energy spectrum. However, later on, it was shown that the Hylleraas approximate basis is not a formal solution of the SE [6].

Since then, a great number of papers have been devoted to approximate solutions of SE, the most known approximation being that of Hartree-Fock. The main idea of many other studies is to find series expansions that are somehow close to the formal solution of HE (here we refer only to a few of them [7–13]). This approach is more correct for numerical applications than, say, the choice of a complete basis set consisting of some suitable functions (Sturmian basis, for example), even if highly accurate energy levels can be obtained [14–21].

The minimization of the energy can be done using the conventional variational integral $\langle\Phi|\hat{H}-E|\Phi\rangle$ or by minimizing the following integral [22]:

$$\int [(\hat{H}-E)\Phi]^2 dV.$$

These integrals are both equal to zero for exact solutions, but may yield, for the same probing function Φ, different values of energy levels. The minimization process is therefore not unique and conclusive on the quality of a proposed wave function [22]. One may also consider the simple relation

$$E(\vec{r}_1,\vec{r}_2)=\frac{\hat{H}\Phi}{\Phi},$$

which will give a constant value E over the whole space only for the exact solution. For the six-term Hylleraas wave function, Bartlett [23] has shown that the calculated value E ranged from $-\infty$ to $+\infty$ and was near its true value only in small regions of space.

In his earlier papers [6], Bartlett demonstrated that the helium-atom eigenfunctions cannot be power series of the variables r_1, r_2 and r_{12} (the two radial coordinates and the electron-electron distance), and suggested that a formal solution might contain logarithms. Later on, Fock reached the same proposition [24]. He built a recurrancy system that allows us, in principle, to construct the helium ground-state wave function as a series consisting of products of powers and logarithms. A truncated series yields a fitting function that may be used in variational methods to obtain the ground energy. However, many mathematical questions linked to his investigation were, and are still, left open. For example, one may suggest combinations of powers and, say, exponential integral functions [25] or other variants. Even the pure power expansion cannot be completely rejected; indeed, we know that the exact solution of SE in the absence of the electron-electron interaction has a hyper-radial expansion that does not contain any logarithms. The Temkin-Poet model [26] contains a combination of powers and logarithms that differs from that predicted by Fock, and so on.

Surprising as it may seem, many issues about the helium ground-state wave function are therefore still unclarified. It is important to underline that no probing helium wave function used until now in practical calculations has the correct be-

havior both at small and large hyper-radius ρ. Even the asymptotic behavior is not well established. In this respect, all probing wave functions can be conventionally subdivided into two main groups: the Hartree-Fock type with the binary exponential factor $\exp(-p_1 r_1 - p_2 r_2)$, and the Hylleraas type, which is characterized by the presence of the interelectronic distance r_{12} in the exponential factor [27]. Both groups of wave functions have been and are currently being used in calculations for interpreting cross sections for single and double ionization on He. For example, in the high-energy dipolar regime [28] (small ejected energies and small momentum transfers) one observes in the triple differential cross section a persistent discrepancy in the vicinity of the recoil peak between the experimental data and the results of several calculations (see [29] and references therein). Several models with simple or complicated final-state wave functions and ''traditional'' He ground-state wave functions give results that are practically the same, but differing noticeably from the experiments. Popov *et al.* [30] have investigated this issue and have reached the conclusion that it is the asymptotic behavior of both wave functions (bound and scattered) that is mainly responsible for the ratio of the binary to recoil peak heights. Moreover, recently, surprising results on helium were obtained in a series of $(e,3e)$ experiments [1], and no explanation can be found with conventional wave functions.

Motivated by these considerations, we study here the SE for helium *S*-bound states (and in particular the $_1S^0$ ground state) in an attempt to move ahead as far as possible without any preliminary approximations and simplifications. An original transformation of SE allows us to obtain a system of channeling equations that leads to two results. On one hand, from these, the correct asymptotic solution is derived. Merkuriev and collaborators [31] have intensively studied the asymptotics of many-body wave functions, but mainly for the scattering states. Fock [24] considered the asymptotic behavior of the helium-ground wave function, but derived only the correct exponential index of the binary channel. Here we enlarge his result. On the other hand, these equations make clear the behavior of the helium wave function near the triple collisions point (the hyper-radius $\rho \to 0$). A recurrancy system that gives automatically the proper behavior can then be derived.

In this investigation, we show what the formal solution must look like at small and large hyper-radius and prove that the widely used Sturmian basis is not adequate to represent the HE formal solution. This information should be valuable, for example, to those who make calculations for interpreting $(e,2e)$ and $(e,3e)$ reactions on helium. We also illustrate how the analytical study can further be used for practical calculations of energy levels and construction of an approximate formal bound-state wave function.

II. TRANSFORMATION OF SE

Designing by r_1 and r_2 the two electrons radial coordinates, and $r_{12}=|\vec{r}_1-\vec{r}_2|$ the electron-electron distance, the radial SE for the He atom $(Z=2)$ reads

$$\left[\frac{1}{2}\Delta_1+\frac{1}{2}\Delta_2+\frac{2}{r_1}+\frac{2}{r_2}-\frac{\alpha}{r_{12}}\right]\Phi(\vec{r}_1,\vec{r}_2)=\varepsilon\Phi(\vec{r}_1,\vec{r}_2),$$

$$\varepsilon \geqslant 0, \tag{1}$$

where the quantity α is used here to ''turn on'' (physically $\alpha=1$) or ''switch off'' ($\alpha=0$) the electron-electron interaction. For $\alpha=0$, the elementary partial solution of Eq. (1) for the *S*-bound states of two noninteractive electrons is known:

$$\Phi(\vec{r}_1,\vec{r}_2)=\Phi^{(l)}_{mn}(\vec{r}_1,\vec{r}_2)=\varphi^{(Z=2)}_{ml}(r_1)\varphi^{(Z=2)}_{nl}(r_2)P_l(\cos\theta_{12}), \tag{2}$$

where θ_{12} is the mutual angle between the two vectors $\vec{r}_1$ and $\vec{r}_2$ given by $\cos\theta_{12}=(r_{12}^2-r_1^2-r_2^2)/(2r_1r_2)$, P_l is the Legendre polynomial, $\varphi^{(Z=2)}_{ml}(r)$ is a one-electron Coulombic bound wave function corresponding to charge $Z=2$ and quantum energy ε_m, and $\varepsilon=\varepsilon_m+\varepsilon_n$ $(m,n\geqslant l\geqslant 0)$.

Note that in Eq. (2) we have considered only nonsymmetrized solutions of the SE and shall do similarly below, for the sake of brevity; one should therefore keep in mind to perform at the end proper symmetrization (or antisymmetrization) of the wave functions, in the usual way.

The *S*-state wave function depends on the scalar combinations of variables r_1, r_2, and r_{12}, which are restricted to their physical domains

$$0\leqslant r_1,r_2<\infty,$$

$$|r_1-r_2|\leqslant r_{12}\leqslant(r_1+r_2). \tag{3}$$

We have chosen instead to use the following hyperspherical variables since they are more convenient for three-body problems:

$$r_1=\rho\cos\varphi,\quad r_2=\rho\sin\varphi,\quad r_{12}=\sqrt{2}\rho\cos\xi, \tag{4}$$

with $0\leqslant\rho<\infty$ and $0\leqslant\varphi\leqslant\pi/2$, and the range for the angular variable ξ is fixed by Eq. (3). The asymptotic behavior (hyper-radius $\rho\to\infty$) of the noninteractive solution (2) looks then like

$$\Phi_{as}(\vec{r}_1,\vec{r}_2)\sim\rho^{m+n}(\cos\varphi)^m(\sin\varphi)^n e^{-\sqrt{2\varepsilon}\rho\cos(\varphi-\theta)}$$
$$\times P_l(\cos 2\xi/\sin 2\varphi), \tag{5}$$

where we have set $\sqrt{\varepsilon_m}=\sqrt{\varepsilon}\cos\theta$ and $\sqrt{\varepsilon_n}=\sqrt{\varepsilon}\sin\theta$ $(0\leqslant\theta\leqslant\pi/2)$. The parameter θ is linked to the energy sharing between electrons; in particular for $\theta=\pi/4$ we have equal energy sharing $\varepsilon_m=\varepsilon_n$.

In the new variables, the radial SE (1) reads

$$\left[\frac{1}{2}\frac{\partial^2}{\partial\rho^2}+\frac{5}{2\rho}\frac{\partial}{\partial\rho}+\frac{1}{2\rho^2}\hat{T}(\varphi,\xi)+\frac{1}{\rho}Z(\varphi,\xi)\right]\Phi=\varepsilon\Phi, \tag{6}$$

where the angular operators, in what we call the (φ,ξ) form, are given by

$$\hat{T}(\varphi,\xi)=\frac{\partial^2}{\partial\varphi^2}+\frac{\partial^2}{\partial\xi^2}-2\cot(2\varphi)\cot(2\xi)\frac{\partial^2}{\partial\varphi\partial\xi}+4\cot(2\varphi)\frac{\partial}{\partial\varphi}+4\cot(2\xi)\frac{\partial}{\partial\xi},\tag{7}$$

$$Z(\varphi,\xi)=\frac{2}{\cos\varphi}+\frac{2}{\sin\varphi}-\frac{\alpha}{\sqrt{2}\cos\xi}.$$

Two other equivalent forms, which shall be useful below, are the (x,y) form

$$\hat{T}(x,y)=4\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+1-\left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+1\right)^2\right],\tag{8}$$

$$Z(x,y)=\frac{2\sqrt{2}}{\sqrt{1+x}}+\frac{2\sqrt{2}}{\sqrt{1-x}}-\frac{\alpha}{\sqrt{1+y}},$$

with $x=\cos(2\varphi), y=\cos(2\xi)$, and the (σ,η) form

$$\hat{T}(\sigma,\eta)=4\left[(1-\sigma^2)\frac{\partial^2}{\partial\sigma^2}+\left(\frac{1}{\sigma}-3\sigma\right)\frac{\partial}{\partial\sigma}+\frac{1}{\sigma^2}\frac{\partial^2}{\partial\eta^2}\right],\tag{9}$$

$$Z(\sigma,\eta)=\frac{2\sqrt{2}}{\sqrt{1+\sigma\cos\eta}}+\frac{2\sqrt{2}}{\sqrt{1-\sigma\cos\eta}}-\frac{\alpha}{\sqrt{1+\sigma\sin\eta}}$$

with $x=\sigma\cos\eta$, $y=\sigma\sin\eta\,(0\leqslant\eta\leqslant2\pi)$. The physical domains (3) translate into $\sigma^2=x^2+y^2\leqslant1$. One can easily see from Eq. (9) that the second-order differential angular operator $\hat{T}(\sigma,\eta)$ is invariant with respect to rotations in the (σ,η) space, i.e., if $g(\sigma,\eta)$ is an eigenfunction of this operator, then $g(\sigma,\eta+\gamma)$ with any arbitrary angle $0\leqslant\gamma\leqslant2\pi$ is also an eigenfunction. This property will be used below in the (x,y) form, for which we may write in matricial form the rotation into two new variables u and v:

$$\begin{pmatrix}u\\v\end{pmatrix}=\begin{pmatrix}\cos\gamma & \sin\gamma\\ -\sin\gamma & \cos\gamma\end{pmatrix}\begin{pmatrix}x\\y\end{pmatrix}.\tag{10}$$

Suppose now that the solution of (6) takes the form

$$\Phi(\vec{r}_1,\vec{r}_2)=A(\rho,\varphi,\xi)e^{-\chi(\varphi,\xi)\rho},\tag{11}$$

a decomposition that can be done without loss of generality. Using the (x,y) form for the angular operators and writing for brevity χ instead of $\chi(x,y)$, we transform Eq. (6) into two coupled equations

$$\chi^2+4\left[\left(\frac{\partial\chi}{\partial x}\right)^2+\left(\frac{\partial\chi}{\partial y}\right)^2-\left(x\frac{\partial\chi}{\partial x}+y\frac{\partial\chi}{\partial y}\right)^2\right]=2\varepsilon,\tag{12}$$

$$\left[\frac{\partial^2}{\partial\rho^2}+\frac{5}{\rho}\frac{\partial}{\partial\rho}+\frac{1}{\rho^2}\hat{T}(x,y)\right]A(\rho,x,y)=\frac{1}{\rho}\left[\hat{D}(x,y)-2Z(x,y)+2\chi\rho\frac{\partial}{\partial\rho}\right]A(\rho,x,y),\tag{13}$$

where $\hat{D}(x,y)$ is a first-order differential angular operator given by

$$\hat{D}(x,y)=2\hat{G}(\chi)+[\hat{T}(x,y)+5]\chi\tag{14}$$

with

$$\hat{G}(\chi)=4\left[(1-x^2)\frac{\partial\chi}{\partial x}-xy\frac{\partial\chi}{\partial y}\right]\frac{\partial}{\partial x}+4\left[(1-y^2)\frac{\partial\chi}{\partial y}-xy\frac{\partial\chi}{\partial x}\right]\frac{\partial}{\partial y}.\tag{15}$$

Note that Eq. (12) is also equivalent to

$$\chi^2+\hat{G}(\chi)\chi=2\varepsilon.\tag{16}$$

This choice of decomposition (12) and (13) is guided by the assumption that the exponential behavior of Φ will not be too dissimilar to that of Φ_{as} in Eq. (5). In the following sections, the solutions of these coupled equations are studied for large (Secs. III and IV) and small (Sec. V) hyper-radii, while a procedure to obtain the numerical solutions on the whole space is proposed in Sec. VI.

III. CHANNELS OF THE BOUND STATES

Equation (12) has an infinite number of solutions. The simplest one is

$$\chi_0=\sqrt{2\varepsilon}.\tag{17}$$

Other solutions exist, separately, for $0\leqslant\sigma\leqslant1$ and for $1<\sigma\leqslant\sqrt{2}$. Restricting ourselves to the physical domain ($0\leqslant\sigma\leqslant1$), there exist only two other solutions:

$$\chi_1=\sqrt{\varepsilon}\,(\cos\theta\sqrt{1+u}+\sin\theta\sqrt{1-u})\tag{18}$$

with $u=x\cos\gamma+y\sin\gamma$ [see Eq. (10)], and

$$\chi_2=\sqrt{\varepsilon}\,(\cos\theta\sqrt{1+\sigma}+\sin\theta\sqrt{1-\sigma})\tag{19}$$

with $\sigma^2=x^2+y^2$.

For each χ_i $(i=0,1,2)$, Eq. (13) must be solved to determine, up to a multiplicative factor, the corresponding $A^{(i)}(\rho,x,y)$, which we shall write as $A^{(i)}$ for brevity. The general form of the bound-state wave function can be written as a linear combination of these solutions

$$\Phi(\vec{r}_1,\vec{r}_2)=\alpha A^{(0)}e^{-\chi_0\rho}+A^{(1)}e^{-\chi_1\rho}+\alpha A^{(2)}e^{-\chi_2\rho}.\tag{20}$$

We call each term in Eq. (20) a channel of the bound state. We have artificially multiplied by α the first and third term to emphasize their vanishing at $\alpha=0$. Indeed, only χ_1 can

reduce, for $\alpha=0$, to the noninteractive result $\sqrt{2\varepsilon}\cos(\varphi-\theta)$ given by Eq. (5), and this for $\gamma=0$. We note that the dependence on the mutual angle between the vectors $\vec{r}_1$ and $\vec{r}_2$ is present in both χ_1 and χ_2. It can be removed from χ_1 for $\gamma=0$, but always subsists in χ_2. The third term in Eq. (20) shows therefore very strong electron-electron correlation.

IV. ASYMPTOTIC SOLUTIONS

Let us investigate Eq. (13) in the domain of the so-called global three-body asymptotics ($\rho\to\infty, \varphi\neq 0,\pi/2, \xi\neq\pi/2$), and consider two reasonable asymptotic behaviors for $A^{(i)}$.

The first, which we call the Hylleraas-type asymptotics, has the form

$$A(\rho,\varphi,\xi)\sim a(\varphi,\xi)\rho^{\beta}e^{\mu(\varphi,\xi)\rho} \tag{21}$$

with $\mu(\varphi,\xi)$ a real quantity such that $0<\mu(\varphi,\xi)<\chi<\infty$ in order to keep Eq. (11) physical, i.e., well behaved for $\rho\to\infty$ and any angles (φ,ξ). With this choice and considering only the leading ρ term, one gets from Eq. (13) a first-order nonlinear differential equation for $\mu(\varphi,\xi)$:

$$[\hat{G}(\mu)+\mu](\mu-2\chi)=0. \tag{22}$$

The obvious solution $\mu=2\chi$ leads to a divergent behavior for $\rho\to\infty$. It is unphysical as a solution for the bound state but may appear for continuum states, i.e., when $\varepsilon<0$. To analyze Eq. (22) further, we set $\mu=\chi-\zeta$. Using the property $\hat{G}(\mu)\chi=\hat{G}(\chi)\mu$, we fall back onto Eq. (16) for ζ, i.e., $\zeta^2+\hat{G}(\zeta)\zeta=\chi^2+\hat{G}(\chi)\chi=2\varepsilon$ with again the solutions χ_0, χ_1, and χ_2. Take, for example, $\chi=\chi_1$; then $\mu_0=\chi_1-\chi_0$, $\mu_1=0$, $\mu_2=\chi_1-\chi_2$, and therefore the solutions with the Hylleraas-type of asymptotic behavior (21) are of the same family as those presented in Eq. (20). This proves that all possible physical exponential behaviors are already included in Eq. (20) and hence form (21) can be discarded. Moreover, from the analysis of the χ_i given below, it appears that none of the channels in Eq. (20) contains an exponential of the form $\exp(\delta r_{12})$, with δ a constant: Eq. (22) leaves therefore no place for the pure Hylleraas basis.

Thus, in the general case, the coefficient $A^{(i)}(\rho,\varphi,\xi)$ for large r_1, r_2 and r_{12} contains a growing exponential term that may be larger than the decreasing exponent in Eq. (20). $A^{(i)}(\rho,\varphi,\xi)$ is expressed as a power growth only for definite values of the parameters ε and θ, which will determine the helium bound spectrum in one of the channels. The second type of asymptotics, which we call of the Hartree-Fock type, is then of the form

$$A(\rho,\varphi,\xi)\sim a(\varphi,\xi)\rho^{\beta} \tag{23}$$

with β a real number. Inserting Eq. (23) in Eq. (13), we find that in the right-hand side (rhs) of Eq. (13), the term of asymptotic order ρ^{-1} is eliminated if

$$[\hat{D}(\varphi,\xi)-2Z(\varphi,\xi)+2\chi\beta]a(\varphi,\xi)=0 \tag{24}$$

is satisfied (the left-hand side is of order ρ^{-2}). On the other hand, if β depends on the angular variables, the rhs of Eq. (13) contains an additional term proportional $\ln\rho$, which must be set to zero through

$$\hat{G}(\chi)\beta=0. \tag{25}$$

The asymptotic form (23) is therefore valid if the two coupled linear first-order differential equations [Eqs. (24) and (25)] are both satisfied. Equation (25) can be satisfied if χ is a constant (this is the case for $\chi=\chi_0$), or if β is a function of the integral of motion of operator $\hat{G}(\chi)$ (a particular case being a constant value of β).

The limit $\rho\to\infty$ corresponds to four different asymptotic domains: $r_1,r_2,r_{12}\to\infty$ (global three-body asymptotics); $r_2\to\infty, r_1<\infty$; $r_1\to\infty, r_2<\infty$; $r_1,r_2\to\infty, r_{12}<\infty$. The coefficient $a(\varphi,\xi)$ satisfying Eq. (25) can have presumable singular points at $\varphi=0,\pi/2$ and $\xi=\pi/2$ that mark the boundaries of the domains, but not any other ones. This property will be used when solving Eq. (24).

Let us now look at what happens for the three situations $\chi=\chi_0$, χ_1, and χ_2.

(i) $\chi=\chi_0$: we shall call this channel ''hyperspherical.'' The general solution of Eqs. (24) and (25) takes the form (23) with

$$\beta=\frac{Z(\varphi,\xi)}{\sqrt{2\varepsilon}}-\frac{5}{2}, \tag{26}$$

while the function $a^{(0)}(\varphi,\xi)$ remains undetermined. Note that, if $Z(\varphi,\xi)=0$, this behavior coincides with a well-known result of nuclear physics widely used in practical calculations (see, for example, [32]).

(ii) $\chi=\chi_1(\gamma)$: we shall call this channel ''binary.'' For brevity, we omit the calculation details and simply list the results obtained in solving Eq. (24). In the general case, the solution has a singularity at $u=\pm 1$ inside the domain of physical interest [see also Eq. (10)]. This singularity can be removed if $\gamma=0$; in this particular case, Eq. (24) has the following integral (or constant) of motion:

$$C=-\cos\theta_{12}=\frac{\cos(2\xi)}{\sin(2\varphi)}, \tag{27}$$

where θ_{12} is the mutual angle between the two vectors $\vec{r}_1$ and $\vec{r}_2$. This is a remarkable result since it means that the triangle in the momentum space formed by the two vectors

$$\vec{p}_1=\sqrt{2\varepsilon}\cos\theta\frac{\vec{r}_1}{r_1},\quad \vec{p}_2=\sqrt{2\varepsilon}\sin\theta\frac{\vec{r}_2}{r_2}, \tag{28}$$

with fixed mutual angle θ_{12} fully determines the asymptotic dynamics of both electrons. Since the sides of the triangle are quantum numbers, the angle θ_{12} becomes perhaps the asymptotical quantum number of the system (interesting references to Heisenberg and Sommerfeld correspondence on this subject can be found in [33]).

For $\theta_{12}>0$ $(C>-1)$, the general solution of Eq. (24) takes then the following form:

$$a^{(1)}(\varphi,\xi)=F_1(C)|\sin(\varphi-\theta)|^{\beta+2-2/p_1-2/p_2+\alpha/2p_{12}} \times(\cos\varphi)^{2/p_1-1}(\sin\varphi)^{2/p_2-1} \times\left[\frac{1}{2}(p_1+p_2C)\cos\varphi+\frac{1}{2}(p_2+p_1C)\sin\varphi +\sqrt{2}p_{12}\cos\xi\right]^{-\alpha/2p_{12}}, \tag{29}$$

where $F_1(C)$ is an arbitrary finite function of C, $\vec{p}_{12}=\frac{1}{2}(\vec{p}_1-\vec{p}_2)$ is the relative momentum with $4p_{12}^2=p_1^2+p_2^2+2Cp_1p_2$, and now $\sqrt{2}\cos\xi=\sqrt{1+C\sin 2\varphi}$. We can keep $a^{(1)}(\varphi,\xi)$ finite for all values of φ if the parameters are subject to the following limitations:

$$\frac{2}{p_1}-1\geqslant 0;\quad \frac{2}{p_2}-1\geqslant 0 \tag{30}$$

and

$$\beta+2-\frac{2}{p_1}-\frac{2}{p_2}+\frac{\alpha}{2p_{12}}\geqslant 0. \tag{31}$$

Note that Eq. (30) set an upper limit to the total energy $\varepsilon=\frac{1}{2}(p_1^2+p_2^2)\leqslant 4$, which is a very reasonable physical inequality.

For the special case $\theta_{12}=0$ $(C=-1)$, we have also found a nontrivial solution for $\theta=\pi/4$ (equal energy-sharing $p_1=p_2,p_{12}=0$). However, mathematically such a solution has zero measure.

(iii) $\chi=\chi_2$. For brevity, we omit again the calculation details and list the results. For this channel, Eq. (24) is best studied in the (σ,η) form, and $\eta=C_1$ is the constant of motion. The general solution contains two angular singular points: $\sigma=0$ $(\varphi=\pi/4,\theta_{12}=\pi/2)$ and $\sigma=1$ $(\theta_{12}=0,\ \pi$ and any $\varphi)$. These singularities can be removed if we put $\theta=\pi/4$ $(p_1=p_2=p)$ and $\eta=0$ $(0<\varphi<\pi/4)$ or $\eta=\pi$ $(\pi/4<\varphi<\pi/2)$. These conditions lead to the unique choice of $\theta_{12}=\pi/2$. This angle is generally a continuous function of the (σ,η) variables [see Eq. (27)]; the restriction to a unique value means that it is not possible to find a nonsingular and nontrivial general solution of Eq. (24). In the domain of global asymptotics, this channel has therefore no place, and we exclude it from further investigation, setting $A^{(2)}=0$ in Eq. (20).

Collecting and inserting all the above findings in Eq. (20), we can write, using the more familiar (r_1,r_2) variables, the asymptotic form of the helium bound wave function

$$\Phi_{as}(\vec{r}_1,\vec{r}_2)=\alpha\frac{a^{(0)}(\varphi,\xi)}{\rho^{5/2}}\exp\left(-\sqrt{2\varepsilon}\rho+\frac{Z(\varphi,\xi)}{\sqrt{2\varepsilon}}\ln\sqrt{2\varepsilon}\rho\right) +F_{as}(\vec{r}_1,\vec{r}_2)\exp(-p_1r_1-p_2r_2) \tag{32}$$

with

$$F_{as}(\vec{r}_1,\vec{r}_2)=F_1(C)(2p_1r_1)^{2/p_1-1}(2p_2r_2)^{2/p_2-1} \times\left|\frac{r_1}{p_1}-\frac{r_2}{p_2}\right|^{\beta+2-2/p_1-2/p_2+\alpha/2p_{12}} \times\left[\frac{1}{2}(p_1+p_2C)r_1+\frac{1}{2}(p_2+p_1C)r_2 +p_{12}r_{12}\right]^{-\alpha/2p_{12}}. \tag{33}$$

We reiterate, at this point, that the angular variables appear both directly and via p_{12}, through $C=\cos(2\xi)/\sin(2\varphi)$ $(C>-1)$.

Let us analyze formula (32). First of all, it reproduces the case of ''noninteractive'' electrons $(\alpha=0)$. We may then put $2/p_1-1=m$, $2/p_2-1=n$ and $\beta=m+n$, and regain from Eq. (32) the asymptotic behavior of Eq. (5). In this case we have the strict equality in Eq. (31), a result that leads us to believe (without any rigorous argument though) that perhaps it should always be so for a given value $\beta=\overline{\beta}$,

$$\overline{\beta}+2-\frac{2}{p_1}-\frac{2}{p_2}+\frac{\alpha}{2p_{12}}=0, \tag{34}$$

which indeed depends on the integral of motion C according to Eq. (25). Incidentally, this choice altogether eliminates the power of $|r_1/p_1-r_2/p_2|$ from Eq. (33). If we accept hypothesis (34) also for $\alpha=1$, we may rewrite Eq. (32) in an elegant and compact form:

$$\Phi_{as}(\vec{r}_1,\vec{r}_2)=\frac{a^{(0)}(\varphi,\xi)}{\rho^{5/2}}\exp\left[-\sqrt{2\varepsilon}\rho+\frac{Z(\varphi,\xi)}{\sqrt{2\varepsilon}}\ln\sqrt{2\varepsilon}\rho\right] +\frac{F_1(C)}{r_1r_2}\exp[-(p_1r_1+p_2r_2)+W(\vec{r}_1,\vec{r}_2)] \tag{35}$$

with

$$W(\vec{r}_1,\vec{r}_2)=\frac{2}{p_1}\ln(p_1r_1+\vec{p}_1\vec{r}_1)+\frac{2}{p_2}\ln(p_2r_2+\vec{p}_2\vec{r}_2) -\frac{1}{2p_{12}}\ln(p_{12}r_{12}+\vec{p}_{12}\vec{r}_{12}). \tag{36}$$

This latter result is very satisfactory since it visually reminds us of the asymptotic behavior of two-electron Coulomb converging scattering waves including plane and spherical eikonal waves, which are well known in scattering theory [31]. This observation provides an additional argument for the acceptance of hypothesis (34). Note, however, that the binary term in Eq. (35) cannot be presented as the product of functions depending separately on r_1, r_2, and r_{12} [12].

Expression (35) constitutes then the global asymptotics of all helium S-bound states, both ground and excited, and provides us with the proper boundary conditions for studying the physical solutions of Eq. (1) on the whole space. Any particular bound state may have either the binary asymptot-

ics [the second term in Eq. (35)], the hyperspherical one (the first term), or their sum if both channels correspond to the same energy level. The latter situation is possible for the particular case of equal energy sharing, i.e., $\theta=\pi/4$.

V. SOLUTIONS AT SMALL DISTANCES

Let us now investigate Eq. (13) at small hyper-radii ρ. The (σ,η) representation is best suited for studying operator $\hat{T}(\sigma,\eta)$, since it ''diagonalizes'' this operator. It may be seen that the functions

$$f_{lm}(\sigma,\eta)=\sqrt{\frac{2l+m+1}{\pi}}\sigma^m P_l^{(m,0)}(1-2\sigma^2)\exp(im\eta) \tag{37}$$

($P_l^{(\alpha,\beta)}$ are Jacobian polynomials) are eigenfunctions of this operator with eigenvalues $-4n(n+2)$ with $n=2l+m$ [with no relation with the n, m, and l used in Eq. (2)]. They form a full orthonormal set since

$$\int_0^1 \sigma d\sigma \int_0^{2\pi} d\eta\, f^*_{lm}(\sigma,\eta) f_{l'm'}(\sigma,\eta)=\delta_{ll'}\delta_{mm'}. \tag{38}$$

We would like to note that this operator is also ''diagonalized'' if one uses the full set of hyperspherical harmonics (see, for instance, [24] or [10]), in what we would call the (φ,θ_{12}) form. Although convenient, we opted not to use it here (although the results are equivalent) with the purpose of exhibiting another lesser-known angular representation.

Earlier in this paper, we observed that coefficient $A^{(i)}(\rho,\sigma,\eta)$ in general takes the form $a(\sigma,\eta)\rho^{\beta(\sigma,\eta)}$ for large values of ρ. Any expansion of $A^{(i)}$ on a full set of angular functions is not very effective from the point of view of numerical calculations since it demands to take into account many terms (see, for example, [10] or [34]). The slow rate of convergence results directly from the singular behavior of the Coulomb potential. Perhaps, it is more effective to build a suitable spline; for this, however, we must know the behavior of $A^{(i)}$ at small ρ.

In spite of the above observation, let us expand A with the set of angular functions (37)

$$A(\rho,\sigma,\eta)=\sum_{l,m=0}^{\infty} a_{l,m}(\rho) f_{lm}(\sigma,\eta), \tag{39}$$

where we have omitted the channel index ''i.'' Using $\rho=\exp(-t)$ for the sake of simplicity, we obtain from Eq. (13):

$$\left[\frac{\partial^2}{\partial t^2}-4\frac{\partial}{\partial t}-4n(n+2)\right]a_{l,m}(t) =e^{-t}\sum_{l',m'=0}^{\infty}\left(\hat{D}-2Z-2\chi\frac{\partial}{\partial t}\right)_{(lm);(l'm')} a_{l',m'}(t) \tag{40}$$

with the matrix elements for an operator $\hat{F}$ defined by

$$F_{(lm);(l'm')}=\int_0^1 \sigma d\sigma \int_0^{2\pi} d\eta\, f^*_{l'm'}(\sigma,\eta)\hat{F}(\sigma,\eta) f_{lm}(\sigma,\eta).$$

Since small values of ρ correspond to large t, the rhs of Eq. (40) can be considered as a perturbation and we may write

$$a_{l,m}(t)=\sum_k a^{(k)}_{l,m}(t)$$

with

$$\left[\frac{\partial^2}{\partial t^2}-4\frac{\partial}{\partial t}-4n(n+2)\right]a^{(0)}_{l,m}(t)=0, \tag{41}$$

$$\left[\frac{\partial^2}{\partial t^2}-4\frac{\partial}{\partial t}-4n(n+2)\right]a^{(k+1)}_{l,m}(t) =e^{-t}\sum_{l',m'=0}^{\infty}\left(\hat{D}-2Z-2\chi\frac{\partial}{\partial t}\right)_{(lm);(l'm')} a^{(k)}_{l',m'}(t). \tag{42}$$

It follows that the nonexploding solution is

$$a^{(0)}_{l,m}(t)=\lambda^{(0)}_{l,m}e^{-2nt} \tag{43}$$

and

$$a^{(k+1)}_{l,m}(t)=\lambda^{(k+1)}_{l,m}e^{-2nt}+\sum_{l',m'=0}^{\infty}\int_0^{\infty} G_n(t,\omega)e^{-\omega} \times\left(\hat{D}-2Z-2\chi\frac{\partial}{\partial\omega}\right)_{(lm);(l'm')} a^{(k)}_{l',m'}(\omega)d\omega, \tag{44}$$

where $n=2l+m$, $\lambda_{l,m}$ are some constants, and where we have introduced a Green function

$$G_n(t,\omega)=-\frac{1}{4(n+1)}[\theta(t-\omega)e^{-2n(t-\omega)} +\theta(\omega-t)e^{-2(n+2)(\omega-t)}].$$

We note, for later use, the following formulas:

$$I_n(s)=\int_0^{\infty} G_n(t,\omega)e^{-s\omega}d\omega =\frac{1}{(2n-s)}\left[\frac{\exp(-2nt)}{4(n+1)}-\frac{\exp(-st)}{(2n+s+4)}\right], \tag{45}$$

$$I_n(2n)=-\frac{\exp(-2nt)}{4(n+1)}\left[t+\frac{1}{4(n+1)}\right]. \tag{46}$$

It is obvious from Eq. (45) that each solution of the recurrancy (44) contains terms proportional to $\exp(-2nt)=\rho^{2n}$, which leads us to renormalize the initial arbitrary constants $\lambda^{(0)}_{l,m}$; at each step, we therefore choose $\lambda^{(k)}_{l,m}$ in a such way to remove the terms $\exp(-2nt)$.

Let us illustrate this with an example. Consider for the zeroth approximation the particular solution $n=0$

$$a^{(0)}_{l,m}(\rho)=\lambda_{00}\delta_{l0}\delta_{m0}.$$

Then, using Eqs. (45) and (46) and going back to the notation in ρ, we get for any l and m (with always $n=2l+m$)

$$a^{(1)}_{l,m}(\rho)=-\lambda_{00}\frac{(\hat{D}-2Z)_{(lm);(00)}}{(2n-1)(2n+5)}\rho,$$

$$a^{(2)}_{l,m}(\rho)=\lambda_{00}\gamma_{l,m}\rho^2\left[\frac{1}{4(n-1)(n+3)}(1-\delta_{n1})-\frac{\ln\rho}{8}\delta_{n1}\right]$$

$$\gamma_{l,m}=\sum_{l',m'}\frac{(\hat{D}-2Z+2\chi)_{(lm);(l'm')}(\hat{D}-2Z)_{(l'm');(00)}}{(2n'-1)(2n'+5)}\times\delta_{n',2l'+m'},$$

and so on.

For each particular quantum numbers $l=l_0$ and $m=m_0$, the initial condition of type (43),

$$a^{(0)}_{l,m}(t)=\lambda_{l_0m_0}\delta_{ll_0}\delta_{mm_0}\exp(-2n_0t),$$

may be introduced in the recurrancy (42) opening a new branch of the general function $\Phi(\vec{r}_1,\vec{r}_2)$. In the general case, the sum (39) contains therefore an infinite number of constants.

The present investigation is not unrelated to others that have been proposed in the past (see, for example, the thesis [25] where a rather full review on this subject is presented). In particular, it confirms the presence of weak singularities, such as the logarithmic term in $a^{(2)}_{l,m}(\rho)$, as predicted by Fock [24]. However, our approach is quite different in that we do not assume the ρ structure *ab initio*; rather the behavior at the triple collision point is obtained here automatically from Eqs. (40)–(44), without any preliminary assumptions. Moreover, if we truncate the series (39) we obtain an approximate formal solution of Eq. (13) for finite values of ρ.

Note also that, for the noninteracting case, the logarithmic terms certainly do not appear in expansion (39): indeed, we know that the wave function (2)—formal solution of Eq. (1) for $\alpha=0$—does not contain any. This means that all the angular matrix elements related to the logarithms of ρ somehow conspire to cancel each other. This is not obvious at all, however, from the recurrancy we have constructed. The same observation is valid if we assume a constant value for $Z(\sigma,\eta)$ and consider the hyperspherical channel.

Let us now go back to Eq. (40) written in the ρ representation and consider the diagonalization approximation

$$\left[\frac{\partial^2}{\partial\rho^2}+\left(\frac{5}{\rho}-2\chi_{(lm);(lm)}\right)\frac{\partial}{\partial\rho}-\frac{1}{\rho}(\hat{D}-2Z)_{(lm);(lm)}-\frac{4n(n+2)}{\rho^2}\right]a_{l,m}(\rho)=\frac{1}{\rho}\sum_{l'\neq l,m'\neq m}\left(\hat{D}-2Z+2\chi\rho\frac{\partial}{\partial\rho}\right)_{(lm);(l'm')}a_{l',m'}(\rho). \tag{47}$$

Considering again the rhs of Eq. (47) as a perturbation, we obtain a recurrancy relation similar to Eq. (44).

Finally, as an illustrative example, let us consider the *s* branch (i.e., $l=m=0$) in the binary channel. The zeroth approximation to Eq. (47) reads

$$\left[\frac{\partial^2}{\partial\rho^2}+\left(\frac{5}{\rho}-2\chi^{(1)}_{(00),(00)}\right)\frac{\partial}{\partial\rho}-\frac{1}{\rho}(\hat{D}^{(1)}-2Z)_{(00),(00)}\right]a^{(0)}_{0,0}(\rho)=0. \tag{48}$$

Its nontrivial solution is a confluent hypergeometrical function

$$a^{(0)}_{0,0}(\rho)=\lambda_0F_1(\gamma,5;2\chi^{(1)}_{(00),(00)}\rho) \tag{49}$$

with $\gamma=(\hat{D}^{(1)}-2Z)_{(00),(00)}/2\chi^{(1)}_{(00),(00)}$. To have a power-growth solution, we must demand γ to be a negative integer or $\gamma=0$ for the lowest state. For equal energy-sharing $p_1=p_2=p$, one finds $p=\sqrt{\varepsilon}=2-1/2\sqrt{2}=1.65$. This is a reasonable prediction of the experimental ground-state energy ($\sqrt{\varepsilon_{\rm exp}}=1.704$), considering that Eq. (49) does not obey the proper asymptotics predicted in Eq. (29).

VI. RESULTS AND DISCUSSION

With an original approach based on the splitting of the HE into the two equations (12) and (13) we have confirmed—in a more unified manner—many results presented in various forms in the literature, and found some new ones. The principals are as follows.

The solutions of Eq. (22) indicate that there is no place for the Hylleraas type exponent.

The existence of two physical channels is identified; they coincide with those in nuclear physics, if $Z(\varphi,\xi)=0$, and determine the exact global asymptotics of the helium bound wave functions given by expression (35). The binary channel visually coincides with the traditional global asymptotics of the convergent wave function of fully stripped helium. It is interesting to note that, for this channel, the plane angle θ_{12} between electrons is a constant of motion of the first-order partial differential [Eq. (24)] that determines this asymptotics. This may have unexpectable physical consequences and applications for simplified models.

The recurrancy (44) supports the *ab initio* assumption of Bartlett [6] and Fock [24]: the formal helium bound-state wave function includes logarithmic terms at small hyperradii; they are seen here to be a result of the electron-electron

interaction. Contrary to Fock's scheme, our recurrancy is much simpler, and provides automatically the necessary hyper-radius form and a relatively easier procedure for numerical implementation.

It is shown that the Sturmian basis is not adequate for describing the formal solution of helium bound states. Even the well-known binary channel wave function cannot be represented as the product $f(r_1)f(r_2)g(r_{12})$. The electron-electron interaction manifests itself also through the appearance of a new hypersherical channel and therefore new collective energy levels.

To conclude, let us briefly discuss possible numerical methods for getting approximate energy levels and the full solutions of Eq. (13). A widely used approach starts from a truncated series (39) containing a large number of unknown constants; upon substitution into the variational integral, optimal values of these constants are sought to obtain the minimal energy. We discussed the disadvantages of this approach in the Introduction. Certainly, taking a probing wave function close to the formal solution is a judicious choice.

Another method, which uses the knowledge of the asymptotic boundary conditions, consists in constructing a suitable spline and can be done, for example, in the following way. Consider a truncated solution of Eq. (39) at small hyper-radii ρ:

$$A(\rho,\sigma,\eta;N,K)=\sum_{l,m=0}^{N}\sum_{k=0}^{K}a_{l,m}^{(k)}(\rho)f_{lm}(\sigma,\eta). \qquad (50)$$

Taking into account the general asymptotic behavior of $A(\rho,\sigma,\eta)$ at large ρ [Eq. (23)], we connect both limiting parts at a large arbitrary value ρ_0. Equalling the logarithmic derivatives (a known technique widely used in quantum mechanics), we obtain the constraint

$$\rho_0\left[\frac{\partial}{\partial\rho}\ln A(\rho,\sigma,\eta;N,K)\right]_{\rho=\rho_0}=\beta(\sigma,\eta) \qquad (51)$$

with β taken from Eq. (26) or Eq. (34).

For the binary channel, Eq. (51) is equivalent to writing $F^{(N,K)}(p_1,p_2;\rho_0;\sigma,\eta)=0$. From the numerical point of view, the sought values p_i should not depend on the parameters σ, η, N, K, and ρ_0. A numerical algorithm should allow one to find stable values of p_i; the latter can then be minimized by searching the absolute minima in the ''space of physical constants'' contained in Eq. (50). In doing so, the approximate function $A^{(1)}$ is also determined. For the hyperspherical channel, only the value ε is to be found.

Based on the analytical study of the asymptotic behavior presented in this contribution, such a numerical approach should give us the energy spectrum and a very good approximation to the formal solution of HE for the helium atom.

ACKNOWLEDGMENTS

This work was partially supported by the Russian Ministry of Science and Technologies (scientific program ''Physics of Quantum and Wave Processes''). We are grateful to Professor V. G. Sushko for the mathematical help, Professor A. Mikhalev, Professor V. Shablov, and Professor C. Tavard for their permanent interest in the work, and Professor M. Zhukov, Dr. B. Danilin, and Dr. S. Vinitsky for helpful discussions. One of us (Yu.V.P.) would also like to thank Professor C. Dal Cappello for his hospitality in Metz, where the main part of this work was conducted.

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