Reliability of one-dimensional Dirichlet wave functions

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(Received 1 November 1994)

It has been recently proven that the bound states of the one-dimensional Schrödinger equation $H\psi^{(i)}=E^{(i)}\psi^{(i)}$ in $[0,\infty)$ can be approximated by those of the corresponding Dirichlet eigenproblem $H_R\psi_R^{(i)}=E_R^{(i)}\psi_R^{(i)}$ in a finite box $[0,R]$ when $R\to\infty$. In this paper, we use a set of mathematical criteria that guarantee the correct calculation of expectation values in the frame of Hilbert spaces, to show that correct expectation values of most physical operators S are obtained by using the equation $\lim_{R\to\infty}\langle\psi_R^{(i)},S\psi_R^{(j)}\rangle=\langle\psi^{(i)},S\psi^{(j)}\rangle$, which includes operators not relatively form bounded by the Hamiltonian H. It is shown that standard numerical methods supply approximate wave functions $\psi_{Rm}^{(i)}$ for which the equation $\lim_{m\to\infty}\langle\psi_{Rm}^{(i)},S\psi_{Rm}^{(j)}\rangle=\langle\psi_R^{(i)},S\psi_R^{(j)}\rangle$ holds true. Thus, combining the previous limits we obtain a general approach to compute correct expectation values. It is shown how this approach agrees with the results found by other authors in special cases. In the particular case of computing approximate wave functions $\psi_{Rm}^{(i)}$ with the Ritz method, we show, analytically and numerically, that correct convergence toward the expectation values of high power of moment operators r^k holds even when the basis functions have an analytic structure that substantially differs from that of the exact wave function.

PACS number(s): 03.65.Ge, 03.65.Ca, 03.65.Db

I. INTRODUCTION

It is known that while approximate wave functions ψ_n may be used to compute the expectation value of one physical property, they may fail utterly if used to compute another physical property. Löwdin [1], for example, gave a sequence of energies and wave functions that converge toward their correct limits

$$\lim_{n\to\infty}E_n=E,\quad \lim_{n\to\infty}\psi_n=\psi\ , \tag{1.1}$$

but whose dipole moments do not satisfy

$$\lim_{n\to\infty}\langle\psi_n,S\psi_n\rangle=\langle\psi,S\psi\rangle\ , \tag{1.2}$$

where $\langle f,g\rangle=\int f^*g\,dr$ and the second equality of (1.1) is understood as $\int|\psi_n-\psi|^2dr\to0$ when n increases. Klahn and Morgan [2] studied this problem from a rigorous mathematical point of view and showed in detail how approximate values of high powers of the moment operators r^k, which were obtained from both Fourier and Ritz expansions with a special Gaussian basis, can diverge or even converge to a wrong limit.

It is generally accepted that the correctness of Eq. (1.2) depends on the ability to duplicate the local peculiarities in the exact wave function. For Ritz-type sequences, Klahn and Morgan [2] pointed out that the correct expectation values can be obtained if the rate of convergence of approximate energies E_n is very fast. Schwartz [3] showed how this is determined by the ability to duplicate the analytic structure of the exact wave function in a neighborhood of the points where it is not analytic [4]. Recently, Klopper and Kutzelnigg [5] indicated that Gaussian basis sets, which do not have the correct analytic structure, can nevertheless exhibit rapid convergence if nonlinear parameters appearing in the exponent of the Gaussians are chosen wisely. The aim of this paper is to show that if the approximate wave functions are obtained from the Dirichlet eigenproblem in a box, rather than the Schrödinger equation in $[0,\infty)$, these eigenfunctions have correct convergence properties for a wide class of operators including the moment operators r^k with large enough k. In the particular case of solving the Dirichlet eigenproblem with the Ritz method, it is shown that correct convergence toward the true expectation values holds even when the analytic structure of the basis functions differs substantially from that of the exact states.

Henceforth R is a positive number, $\langle f,g\rangle_R$ [$\langle u,v\rangle$] denotes the usual inner product of the Hilbert space $L_2(0,R)$ [$L_2(0,\infty)$], and $\|f\|_R$ [$\|u\|$] is the corresponding norm. In previous works [6,7] it was shown that for a wide class of potentials $V(r)$, the bound states of the one-dimensional Schrödinger equation

$$-\frac{d^2}{dr^2}\psi^{(i)}+\frac{l(l+1)}{r^2}\psi^{(i)}+2V(r)\psi^{(i)}=2E^{(i)}\psi^{(i)}\ ,$$
$$\psi^{(i)}(0)=0\ \text{ with } 0\le r\le\infty,\ \ 0\le l \tag{1.3}$$

can be approximated by those of the Dirichlet eigenproblem in a box $[0,R]$

$$-\frac{d^2}{dr^2}\psi_R^{(i)}+\frac{l(l+1)}{r^2}\psi_R^{(i)}+2V(r)\psi_R^{(i)}=2E_R^{(i)}\psi_R^{(i)}\ ,$$
$$\psi_R^{(i)}(0)=\psi_R^{(i)}(R)=0\ ,\ \ 0\le r\le R\ , \tag{1.4}$$

as $R\to\infty$, according to

$$\lim_{R\to\infty} E_R^{(i)}=E^{(i)} \text{ with } E^{(i)}\le E_{R'}^{(i)}\le E_R^{(i)} \text{ for } R\le R' \quad (1.5)$$

and

$$\lim_{R\to\infty} \|\psi_R^{(i)}-\psi^{(i)}\|=0 \text{ where } \psi_R^{(i)}(r)=0 \text{ for } r\ge R \ . \quad (1.6)$$

The wave functions $\psi_R^{(i)}$ will subsequently be referred to as Dirichlet wave functions (DWF's). The main result of this work is that correct expectation values of most operators S for which $\langle \psi^{(i)},S\psi^{(j)}\rangle$ exists can be obtained by means of the limiting procedure

$$\lim_{R\to\infty} \langle \psi_R^{(i)},S\psi_R^{(j)}\rangle_R=\langle \psi^{(i)},S\psi^{(j)}\rangle \ , \quad (1.7)$$

a result that includes $S=r^k$ with $k\ge -2$. Furthermore, it is shown that standard numerical methods for solving Eq. (1.4) supply approximate Dirichlet wave functions (ADWF's) $\psi_{Rm}^{(i)}$ that satisfy the equation

$$\lim_{m\to\infty} \langle \psi_{Rm}^{(i)},S\psi_{Rm}^{(j)}\rangle_R=\langle \psi_R^{(i)},S\psi_R^{(j)}\rangle_R \ . \quad (1.8)$$

Thus a combination of (1.7) and (1.8) permits us to compute accurate expectation values $\langle \psi^{(i)},S\psi^{(j)}\rangle$ of most operators of physical interest.

The idea of computing the bound states of Eq. (1.3) by means of the numerical solution of Eq. (1.4) is not new. This approach has been applied in an implicit way by several authors who, to solve Eq. (1.3) with methods such as finite-difference or finite-element methods, use the fact that $\psi^{(i)}(r)$ is infinitesimally small for large r to replace the boundary condition $\lim_{r\to\infty}\psi^{(i)}(r)=0$ by $\psi^{(i)}(R)=0$ with a suitable "large" R [8–12]. Other authors have applied specific techniques to solve (1.4) and found that the energies $E_R^{(i)}$ and other physical quantities tend to the corresponding properties of the unbounded eigenproblem (1.3) as R is made larger [13–16]. As we will see in this work, these results are particular cases of Eqs. (1.5)–(1.8).

The structure of the paper is as follows. In Sec. II we present general reliability criteria that guarantee the correct calculation of properties, which will be used to show the correctness of Eqs. (1.7) and (1.8). These criteria are obtained from rigorous mathematical results, some of which have been used by other authors to study the correctness of Eq. (1.2) [2,17–19]. In Sec. III we show that the ADWFs $\psi_{Rm}^{(i)}$ obtained from several numerical methods are reliable to compute $\langle \psi_R^{(i)},S\psi_R^{(j)}\rangle_R$ [Eq. (1.8)] and in Sec. IV we show the correctness of (1.7). The results are illustrated by calculating the ground state of the He^+ ion with the Ritz-type ADWF obtained from several basis sets, some of which do not have the correct analytic structure. In order to show that correct convergence of properties holds even when the basis functions do not have the correct analytic structure, in Sec. V we make a comparison of the calculations of Klahn and Morgan and those obtained from our Ritz-type ADWF.

II. RELIABILITY CRITERIA

Following Löwdin [1], we say that an approximating sequence $\{\psi_n\}_{n=1}^{\infty}$ is reliable to compute the expectation value $\langle S\rangle=\int \psi^* S\psi\, dx$ if (i) the sequence $\langle S\rangle_n=\int \psi_n S\psi_n dx$ converges to $\langle S\rangle$ as $n\to\infty$ and (ii) upper and lower bounds of the error $\langle S\rangle_n-\langle S\rangle$ can be constructed. Although the error bounds of $\langle S\rangle_n$ do not have much practical value, they represent a good test of the *numerical stability* of the limiting procedure (i).

In this section we give general reliability criteria that guarantee the correct calculation of physical properties in an interval $[0,a]$ that may be bounded or unbounded $(0<a\le\infty)$. These criteria are obtained from rigorous mathematical results, some of which have been used by other authors to study the correctness of (1.2) in the frame of Hilbert spaces [2,17–19]. The inner product of the Hilbert space $L_2(0,a)$ is $\langle f,g\rangle_a=\int_0^a f^* g\, dr$ and the corresponding norm is $\|f\|_a=\langle f,f\rangle_a^{1/2}$. For an operator B in $L_2(0,a)$, $D(B)$ denotes the set of functions f in $L_2(0,a)$ for which Bf belongs to $L_2(0,a)$.

A. Criterion of L_2 convergence

The norm of $L_2(0,a)$ leads to the following concept of convergence between wave functions, which will be referred as L_2 *convergence:* We say that the sequence $\{\psi_n\}$ converges to ψ in the $L_2(0,a)$ *norm* if it satisfies $\|\psi_n-\psi\|_a\to 0$ as $n\to\infty$. The fundamental role of this concept in the calculation of expectation values is given by the following.

Theorem 1. Let S be a symmetric operator in $L_2(0,a)$ and suppose that $\psi_n^{(i)}$ and $\psi^{(i)}$ belong to $D(S)$ $(i=1,2$ and $n\ge 1)$. If $\{\psi_n^{(i)}\}$ converges to $\psi^{(i)}$ in the $L_2(0,a)$ norm, then $\lim_{m\to\infty}\lim_{n\to\infty}\langle \psi_n^{(1)},S\psi_m^{(2)}\rangle_a=\langle \psi^{(1)},S\psi^{(2)}\rangle_a$, where the left-hand term is the so-called *iterated* limit.

This theorem is a consequence of the following inequality, which is obtained by using the symmetry of S and the Schwarz inequality:

$$|\langle \psi_n^{(1)},S\psi_m^{(2)}\rangle_a-\langle \psi^{(1)},S\psi^{(2)}\rangle_a| \le \|\delta\psi_n^{(1)}\|_a\|S\psi_m^{(2)}\|_a+\|\delta\psi_m^{(2)}\|_a\|S\psi^{(1)}\|_a \ , \quad (2.1)$$

where $\delta\psi_n^{(i)}=\psi_n^{(i)}-\psi^{(i)}$. Theorem 1 is analytically true and since to compute $\langle \psi^{(1)},S\psi^{(2)}\rangle_a$ one chooses a method that supplies approximating wave functions $\psi_n^{(i)}$ in $D(S)$, the relevant assumption is the L_2 convergence. Thus we can say that the L_2 convergence is indeed a *sufficient* criterion to converge toward the true expectation values.

The L_2 convergence of approximating sequences $\{\psi_n\}$ obtained from standard numerical methods has been either exhibited or rigorously proven (see, for example, Refs. [20–25]). Assuming that $\{\psi_n\}$ converges to ψ in the $L_2(0,a)$ norm, the question is then how to find an upper bound of the quantity $\|\delta\psi_n\|_a=\|\psi_n-\psi\|_a$, which we will call the *exact* error of ψ_n, since it appears in the calculation of the error bounds of numerical expectation values, as we shall see below. This can be made in terms of eigenvalues by using Eckart's inequality and its generalizations [26] or applying the properties of the $L_2(0,a)$ norm to obtain the following result [27]: If $\{\psi_{n(k)}\}_{k=1}^{\infty}$ is a rapidly convergent subsequence that satisfies

$$\tau=\sup_{k\geq 1}\frac{\|\psi_{n(k+1)}-\psi_{n(k+2)}\|_a}{\|\psi_{n(k)}-\psi_{n(k+1)}\|_a}<1\ , \tag{2.2a}$$

then

$$\|\delta\psi_{n(1)}\|_a\leq(1-\tau)^{-1}\|\psi_{n(1)}-\psi_{n(2)}\|_a\ . \tag{2.2b}$$

Since in practical situations only a finite number of matrix elements $\langle\psi_n^{(1)},S\psi_m^{(2)}\rangle_a$ can be computed, the iterated limiting procedure of Theorem 1 does not have practical value, so one has to be satisfied if $\langle\psi^{(1)},S\psi^{(2)}\rangle_a$ can be reached by the *single* limiting procedure

$$\lim_{n\to\infty}\langle\psi_n^{(1)},S\psi_n^{(2)}\rangle_a=\langle\psi^{(1)},S\psi^{(2)}\rangle_a\ . \tag{2.3}$$

Unfortunately Eq. (2.3) is not generally true even when $\{\psi_n^{(i)}\}$ converges correctly in the norm, as was shown by Löwdin [1] and by Klahn and Morgan [2]. We will give below two additional conditions that together with the L_2 convergence are sufficient to guarantee the correctness of (2.3) and to compute both upper and lower bounds of the error of approximating expectation values

$$\Delta S_n^{12}=\langle\psi_n^{(1)},S\psi_n^{(2)}\rangle_a-\langle\psi^{(1)},S\psi^{(2)}\rangle_a\ . \tag{2.4}$$

B. Boundedness condition

When the sequence $\{\|S\psi_n^{(2)}\|_a\}_{n=1}^{\infty}$ is bounded by some positive constant M, the inequality (2.1) leads immediately to the following.

Theorem 2. If in addition to the hypothesis of Theorem 1 the sequence $\{\|S\psi_n^{(2)}\|_a\}$ is bounded by $M>0$, then the single limit (2.3) is true and the following inequality holds:

$$|\Delta S_n^{12}|\leq M\|\delta\psi_n^{(1)}\|_a+\|S\psi^{(1)}\|_a\|\delta\psi_n^{(2)}\|_a\ . \tag{2.5}$$

This theorem shows that the boundedness of at least one sequence $\{\|S\psi_n^{(i)}\|_a\}$ (subsequently referred as the *boundedness condition*) together with the L_2 convergence is sufficient for assessing the correctness of (2.3) and to obtain a bound of the error ΔS_n^{12}.

The boundedness condition holds when S is a bounded operator in $L_2(0,a)$ since by definition there is a constant c such that $\|Sf\|_a\leq c$ holds for any normalized wave function f in $L_2(0,a)$. For example, if $S=s(r)$ is bounded by c_a on $[0,a]$, then it is a bounded operator in $L_2(0,a)$. Examples of unbounded operators in $L_2(0,\infty)$ are the power moment operators r^k with $k\neq 0$. When S is not bounded in $L_2(0,a)$ the boundedness condition may fail, as showed by Klahn and Morgan [2], who computed variational wave functions ψ_n in $L_2(0,\infty)$ for which $\{\|r^k\psi_n\|\}_{n=1}^{\infty}$ diverges if k is large.

The importance of the boundedness condition is reinforced by the fact that rigorous bounds of the error ΔS_n^{12} have been obtained by some authors starting from the assumption that $\|S\psi_n^{(i)}\|_a$ remains bounded when $\psi_n^{(i)}\to\psi^{(i)}$. For example, Bazley and Fox [17] considered Eq. (1.3) for a potential $V(r)$ that vanishes at infinity and gave an estimate of $\|s(r)\psi^{(i)}\|$ in order to obtain a bound of $|\Delta S_n^{11}|$ from inequality (2.5), assuming *a priori* that $\{\|s(r)\psi_n^{(i)}\|\}_{n=1}^{\infty}$ is a bounded sequence. By using the determinantal inequalities method, Weinhold [19] obtained a general class of upper and lower bounds of ΔS_n^{12}, whose practical application depends primarily on the boundedness of $\{\|S\psi_n^{(i)}\|_a\}_{n=1}^{\infty}$.

C. Relatively form-bounded operators

Another criterion to guarantee the correctness of (2.3) is obtained in terms of sesquilinear forms. Every operator in B in $L_2(0,a)$ defines a sesquilinear form given by $b(f,g)=\langle Bf,g\rangle_a$ for $f,g\in D(B)$. In the particular case of a self-adjoint Hamiltonian $H_a=T+V$ in $L_2(0,a)$, with T and V the kinetic and potential operators, respectively, we have the form

$$h_a(f,g)=\langle Tf,g\rangle_a+\langle Vf,g\rangle_a\quad\text{for } f,g\in D(H_a)\ ,$$

which defines the well-known energy functional $E_a(f)=h_a(f,f)$, so that $E_a(f)$ is the energy associated with f. Suppose that H_a is bounded from below by E_0 [$E_a(f)\geq E_0\|f\|_a^2$ for $f\in D(H_a)$]. A symmetric operator S is said to be *relatively form bounded by* H_a if there exist two positive constants c_1,c_2 such that

$$|\langle Sf,f\rangle_a|\leq c_1\|f\|_a^2+c_2[E_a(f)-E_0\|f\|_a^2]$$
$$\text{holds for all } f\in D(H_a)\ . \tag{2.6}$$

Consider, for example, the Hamiltonian H in $L_2(0,\infty)$ defined by $T=-d^2/dr^2$ and $V(r)=r^{-2}+r^9$. One can prove that the operators T and V as well as the individual terms r^{-2} and r^9 satisfy the inequality (2.6) [18,28].

There exists a set of functions $f(r)$ in $L_2(0,a)$ for which the energy functional $E_a(f)$ is well defined even when $f(r)$ does not belong to $D(H_a)$. This set is denoted by $D(h_a)$ and is called the "domain of h_a." For example, if $H_a=-d^2/dr^2$ and $f(r)$ is a function in $L_2(0,a)$ whose first derivative df/dr has a finite number of discontinuities on $[0,a]$, then $E_a(f)$ exists, but H_af does not belong to $L_2(0,a)$. This is important for assessing, with the aid of Theorem 3 given below, the correct calculation of properties obtained from methods, such as finite-element and finite-difference methods, that supply approximate wave functions $\psi_n^{(i)}$ for which $E_a(\psi_n^{(i)})$ exists even when $\psi_n^{(i)}\notin D(H_a)$. Theorem 3 is a slight generalization of a similar one found by Bazley and Fox [18], who proved it for Ritz-type sequences, but the present formulation allows us to apply this result to approximate wave functions obtained from *nonvariational* methods as well.

Theorem 3. Suppose that the self-adjoint Hamiltonian H_a in $L_2(0,a)$ is bounded from below by E_0 and has the eigenfunction $\psi^{(i)}$ $(i=1,2)$. Let h_a be the sesquilinear form associated with H_a, with $E_a(\ )$ the corresponding energy functional. If S is relatively form bounded by H_a and the sequence $\{\psi_n^{(i)}\}$ in $D(h_a)$ satisfies

$$\lim_{n\to\infty}E_a(\psi_n^{(i)})=E_a(\psi^{(i)}),\quad\lim_{n\to\infty}\|\psi_n^{(i)}-\psi^{(i)}\|_a=0\ , \tag{2.7}$$

where $\psi_n^{(i)}$ and $\psi^{(i)}$ are normalized wave functions, then the single limit (2.3) is true and the following inequality holds:

$$|\Delta S_n^{12}| \leq \|S\psi^{(1)}\|_a \|\delta\psi_n^{(2)}\|_a + (3K+2)[E_a(\psi_n^{(2)})+1-E_0]^{1/2}\{E_a(\psi_n^{(1)})-E_a(\psi^{(1)})+[1-E_0+E_a(\psi^{(1)})]\|\delta\psi_n^{(1)}\|_a^2\}^{1/2} , \tag{2.8}$$

where $K=\max\{c_1+c_2|1-E_0|,c_2\}$. Therefore, approximating sequences $\{\psi_n^{(i)}\}$ that satisfy (2.7) are *always* reliable to compute both expectation and transition values of an operator S in the *class* of operators relatively form bounded by H_a.

D. Calculation of density moments as a reliability criterion

Since standard numerical methods supply approximating sequences that satisfy (2.7) [20–25], the calculation of expectation values of relatively form-bounded operators does not present theoretical difficulties. However, when the same trial functions are used to compute the expectation value of a *nonrelatively* form-bounded operator, they may fail utterly. This can be attributed to the fact that the boundedness condition does not hold, as was shown in Ref. [2], where Ritz-type wave functions for which the sequence $\{\|r^k\psi_n\|\}_{n=1}^{\infty}$ diverges with large k are given. These remarks suggest that the boundedness condition may be used as a general test of reliability in the following sense: A sequence $\{\psi_n\}$ is more reliable than another one $\{\psi_n'\}$ if the class of nonrelatively form-bounded operators for which $\{\|S\psi_n\|_a\}$ is bounded is larger than the corresponding class of $\{\psi_n'\}$. The immediate question is then, *which* is the best set of nonrelatively form bounded operators S useful for testing the boundedness of $\{\|S\psi_n\|_a\}$? The results found by Klahn and Morgan [2] indicate that this set may be the high powers of r, but as we shall see below there is a more basic reason that supports this. Without loss of generality, we deal with the case $[0,a]=[0,\infty)$.

Theorem 4 (Stieltjes's moment problem [28]). (i) The sequence of real numbers a_k $(k\geq 0)$ are the moments of a positive measure $\rho(r)$ on $[0,\infty)$ $[a_k=\int_0^{\infty} r^k d\rho(r)]$ if and only if the a_k satisfy

$$\sum_{n,m=0}^{N} \beta_n^* \beta_m a_{m+n} \geq 0, \quad \sum_{n,m=0}^{N} \beta_n^* \beta_m a_{m+n+1} \geq 0 \tag{2.9}$$

for all N and all $\{\beta_1,\ldots,\beta_n\}$ in C^N. (ii) If in addition to the positivity requirements (2.9) the a_k satisfy the condition

$$|a_k| \leq AD^k(2k)! , \tag{2.10}$$

where A and D are arbitrary constants, then the measure $\rho(r)$ of part (i) is unique.

Since the probability density $|\psi(r)|^2$ defines a positive measure $d\rho(r)=|\psi(r)|^2 dr$, the moments $\langle r^k\rangle$ satisfy (2.9) and thus the relevant result follows from part (ii): If the moments $\langle r^k\rangle$ satisfy (2.10), then they uniquely determine $\rho(r)$. The inequality (2.10) holds in many cases of interest because of the exponential decay of wave functions; for example, a straightforward calculation with the $1s$ state of hydrogenlike ions shows that (2.10) holds. Therefore, to compute the true measure $\rho(r)$ associated with $|\psi(r)|^2$ it is necessary and sufficient that the calculation of every moment $\langle r^k\rangle$ $(k\geq 0)$ turns out to be correct.

Although the calculation of all moments is not possible in practical situations, we can say that a sequence $\{\psi_n\}$ is indeed reliable if every moment can be reached by the limiting procedure (2.3). As we shall see in Secs. III and IV, this is possible with the DWF $\psi_R^{(i)}$ and the ADWF $\psi_{Rm}^{(i)}$ obtained by several methods.

III. COMPUTATION OF EXPECTATION VALUES $\langle\psi_R^{(i)},S_R\psi_R^{(j)}\rangle_R$ IN $[0,R]$

The numerical solution of the Dirichlet eigenproblem (1.4) has been a subject extensively studied in the past. The correct convergence of approximating sequences $\{\psi_{Rm}^{(i)}\}_{m=1}^{\infty}$ and $\{E_{Rm}^{(i)}\}_{m=1}^{\infty}$ obtained from methods such as projection methods (which include the Ritz method), as well as the finite-element and finite-difference methods, has been rigorously proven [22–25]. The basic property of these methods is that they supply numerical solutions of Eq. (1.4) that converge to their correct limits according to

$$\lim_{m\to\infty} E_{Rm}^{(i)} = E_R^{(i)} \tag{3.1a}$$

and

$$\lim_{m\to\infty} \|\psi_{Rm}^{(i)} - \psi_R^{(i)}\|_R = 0 , \tag{3.1b}$$

where $E_{Rm}^{(i)}=E_R(\psi_{Rm}^{(i)})$ and $E_R^{(i)}=E_R(\psi^{(i)})$, E_R being the energy functional defined by the self-adjoint operator H_R associated with Eq. (1.4) in $L_2(0,R)$. Numerous algorithms of the above methods with high computational efficience have been proposed in the literature [8–12]. We can say that the numerical solution of Eq. (1.4) is a not difficult task in this day of high-speed computers.

In this section we apply the results of Sec. II to show that if the numerical solutions of Eq. (1.4) satisfy Eqs. (3.1) and (3.1b), then they are reliable to compute the expectation value $\langle\psi_R^{(i)},S_R\psi_R^{(i)}\rangle_R$ of most operators S_R by means of the limiting procedure

$$\lim_{m\to\infty} \langle\psi_{Rm}^{(i)},S_R\psi_{Rm}^{(j)}\rangle_R = \langle\psi_R^{(i)},S_R\psi_R^{(j)}\rangle_R . \tag{3.2}$$

Our first result is a trivial application of Theorem 2. If $s(r)$ is function in $[0,\infty)$, which is bounded on each finite interval $[0,R]$, then it defines a *bounded* operator S_R in $L_2(0,R)$ $[\|S_R\psi\|_R \leq \max_{r\in[0,R]}|s(r)|^2\|\psi\|_R]$. This, together with Eq. (3.1b), immediately implies (3.2).

To guarantee the correctness of (3.2) with some unbounded operators in $L_2(0,R)$ such as r^{-2} or the momentum operator, we apply Theorem 3. Accordingly, if S_R is relatively form bounded by H_R, then Eqs. (3.1a) and (3.1b) imply (3.2).

Remark 1. Since the correctness of (3.2) with the operators S_R described above is obtained from Theorems 2 and 3, upper and lower bounds of the error

$$\Delta S^{ij}_{Rm} = \langle \psi^{(i)}_{Rm}, S_R \psi^{(j)}_{Rm} \rangle_R - \langle \psi^{(i)}_R, S_R \psi^{(j)}_R \rangle_R \tag{3.3}$$

can be constructed as in Sec. II and clearly this includes *any* positive power of r. Therefore, the numerical solutions of Eq. (1.4) that satisfy Eqs. (3.1a) and (3.1b) are indeed reliable to compute accurate values of most physical operators S_R.

Numerical examples

We now solve the equation (1.4) corresponding to the He^+ ion with the Ritz method. The motivation for using the Ritz method instead of finite-element or finite-difference methods, for example, is twofold: (i) This method can be applied in both finite and semi-infinite intervals $[0,\infty)$, allowing a good comparison with Ritz-type calculations in $[0,\infty)$ as we will see in Sec. V. (ii) As is known [1–5], the calculation of expectation values may be particularly sensitive to the ability of duplicating the local peculiarities in the exact state. Thus a good test of the correctness of Eq. (3.2) is the application of Ritz method with basis functions whose analytic structure substantially differs from that of the exact states.

The basis sets of $L_2(0,R)$ to be used are

$$\varphi_{Rk}(r) = e^{-\alpha r}(R-r)r^k, \quad k=1,2,\ldots \tag{3.4a}$$

$$\varphi_{Rk}(r) = N_k P_k^{(2)}(2r/R-1), \quad k=2,3\ldots \tag{3.4b}$$

$$\varphi_{Rk}(r) = (2/R)^{1/2}\sin(\pi k r/R), \quad k=1,2,\ldots \tag{3.4c}$$

$$\varphi_{Rk}(r) = e^{-\alpha r}(R-r)r^{2k-1}, \quad k=1,2,\ldots \tag{3.4d}$$

$$\varphi_{Rk}(r) = e^{-\alpha r^2}(R-r)r^{2k-1}, \quad k=1,2,\ldots, \tag{3.4e}$$

where $P_k^{(2)}(r)$ denotes the associated Legendre polynomial with normalization constant N_k. The completeness of basis sets (3.4a)–(3.4c) is well known and that of (3.4d) and (3.4e) follows from the completeness of $\{r^{2k}e^{-\alpha r}\}_{k\geq 0}$ and $\{r^{2k}e^{-\alpha r^2}\}_{k\geq 0}$ in $L_2(0,\infty)$ [21]. Every basis set presents numerical difficulties in computing the states of He^+ in $[0,R]$: Since the overlap integral $\langle \varphi_{Rk}, \varphi_{Rk} \rangle_R$ between basis functions of type (3.4a), (3.4d), or (3.4e) increases rapidly as k increases, the overlap matrix $\{\langle \varphi_{Rk}, \varphi_{Rl} \rangle_R\}$ is ill conditioned and this introduces numerical problems in solving the corresponding matrix eigenproblem. In particular, any orthonormalization procedure applied to these basis sets will be numerically unstable. This difficulty is partially solved by using the exponent $\alpha=2$, which gives the correct asymptotic behavior of the $1s$ state $\psi^{(1)}$ of the *free* He^+ ion and increases the rate of convergence of calculations with large R [7]. The basis sets (3.4b) and (3.4c) are orthonormal in $L_2(0,R)$, but they do not have the structural properties that exact states $\psi^{(1)}_R$ and $\psi^{(1)}$ have at $r=0$ (the cusp originated by the Coulomb singularity) as well as their exponential decay for large R. The latter property is particularly strong for the trigonometric basis (3.4c). Furthermore, these basis functions do not have optimization parameters that allow us to increase the rate of convergence.

Matrix elements calculated with the basis sets (3.4a) and (3.4b) are obtained in exact form and those from the basis sets (3.4c)–(3.4e) are calculated by using N-points Gaussian quadrature. The basis sets (3.4a), (3.4d), and (3.4e) are orthonormalized by using the Gram-Schmidt method. All calculations were done in a 16-digit precision machine and every wave function is normalized.

Tables I–V contain numerical results for the $1s$ state of He^+ in the box $[0,R=1]$. As we saw earlier, since correct expectation values are obtained if Eqs. (3.1a) and (3.1b) hold, they will be used to verify the correctness of our calculations. Table I shows the convergence of energies $E^{(1)}_{1m}$ obtained from basis sets (3.4) toward $-0.500\,000\,0$, which can be considered as the exact energy $E^{(1)}_1$ with all its exact figures. The results of Table II require a more detailed explanation. As is known, the Ritz expansion $\psi^{(1)}_{Rm} = \sum_{k=1}^m c^{(1)}_{Rm}\varphi_{Rk}$ obtained from any basis set (3.4) converges to $\psi^{(1)}_R$ in the $L_2(0,R)$ norm as $m\to\infty$. But since the exact function $\psi^{(1)}_R$ is unknown, we compared $\psi^{(1)}_{Rm}$ with the $1s$ state wave function of the *free* He^+ ion, which is given by $\psi^{(1)} = 2Z^{3/2}re^{-Zr}$, through the relation

$$\|\psi^{(1)}_{Rm} - \psi^{(1)}\|_R = \{2(1-\langle \psi^{(1)}_{Rm}, \psi^{(1)} \rangle_R)\}^{1/2}, \tag{3.5a}$$

and by using (3.1b) one has that the equation

$$\lim_{m\to\infty} \|\psi^{(1)}_{Rm} - \psi^{(1)}\|_R = \|\psi^{(1)}_R - \psi^{(1)}\|_R \tag{3.5b}$$

must be true independently of the basis set used. This is confirmed in Table II, which shows that the Ritz expansions $\psi^{(1)}_{1m}$ obtained from the basis sets (3.4a)–(3.4c) yield

TABLE I. Convergence of $1s$ energies $E^{(1)}_{Rm}$ of He^+ in the box $[0,R=1]$, for increasing values of the number m of basis functions (3.4). The values $-10E^{(1)}_{Rm}$ are reported.

m	Basis (3.4a)	m	Basis (3.4b)	m	Basis (3.4c)	m	Basis (3.4d)	m	Basis (3.4e)
2	4.858 710	2	4.833 148	10	4.966 542	5	4.931 488	10	4.981 481
3	4.998 247	3	4.997 973	20	4.995 329	10	4.985 113	20	4.988 236
4	4.999 989	4	4.999 988	30	4.998 565	15	4.989 910	30	4.988 359
5	5.000 000	5	5.000 000	40	4.999 384	20	4.989 942	40	4.988 385
6	5.000 000	6	5.000 000	50	4.999 681	25	4.990 064	50	4.988 423
7	5.000 000	7	5.000 000	60	4.999 814	30	4.990 156	60	4.988 431
8	5.000 000	8	5.000 000	70	4.999 882	35	4.990 190	70	4.988 432
9	5.000 000	9	5.000 000	80	4.999 921	40	4.990 195	80	4.988 445
				90	4.999 944	45	4.990 196	90	4.988 441
				100	4.999 959	50	4.990 200	100	4.988 444

TABLE II. Convergence in the $L_2(0,1)$ norm of eigenfunctions $\psi_{1m}^{(1)}$ corresponding to the eigenvalues $E_{1m}^{(1)}$ of Table I. The values $10\|\psi_{1m}^{(1)}-\psi^{(1)}\|_1$ are reported, where $\psi^{(1)}$ is the $1s$ wave function of the free He^+ ion [Eqs. (3.5)].

m	Basis (3.4a)	m	Basis (3.4b)	m	Basis (3.4c)	m	Basis (3.4d)	m	Basis (3.4e)
2	6.1179	2	6.0499	10	6.0284	5	6.026 89	10	6.028 50
3	6.0324	3	6.0296	20	6.0290	10	6.028 58	20	6.029 36
4	6.0291	4	6.0290	30	6.0290	15	6.028 96	30	6.029 21
5	6.0290	5	6.0290	40	6.0290	20	6.029 02	40	6.029 31
6	6.0290	6	6.0290	50	6.0290	25	6.029 18	50	6.029 31
7	6.0290	7	6.0290	60	6.0290	30	6.029 17	60	6.029 29
8	6.0290	8	6.0290	70	6.0290	35	6.029 12	70	6.029 29
9	6.0290	9	6.0290	80	6.0290	40	6.029 10	80	6.029 30
				90	6.0290	45	6.029 10	90	6.029 31
				100	6.0290	50	6.029 12	100	6.029 31

values of $\|\psi_{Rm}^{(1)}-\psi^{(1)}\|_R$ converging to 0.602 90 and therefore $\psi_{Rm}^{(1)}$ converges correctly in the $L_2(0,R)$ norm. An incorrect L_2 convergence appears with 45 and 40 basis functions of type (3.4d) and (3.4e), respectively, which can be attributed to the numerical errors introduced by the orthonormalization procedure. This is more evident in the calculation of density moments, as we shall see below.

In what follows we will use the notation $\langle r^k\rangle_{Rm}=\langle\psi_{Rm}^{(1)},r^k\psi_{Rm}^{(1)}\rangle_R$ and $\langle r^k\rangle_R=\langle\psi_R^{(1)},r^k\psi_R^{(1)}\rangle_R$. Tables III–V show the convergence of $\{\langle r^k\rangle_{1m}\}_{m\geq 1}$ for $k=-2,5,9$. In agreement with the convergence of energies and wave functions, we observe a correct convergence of moments obtained from basis sets (3.4a)–(3.4e), which give properties that converge toward a limit value that can be considered as the exact moment $\langle r^k\rangle_1$. As occurs with energies and wave functions, the moments obtained from basis sets (3.4d) and (3.4e) do not converge correctly, although the percentage error of the larger basis values with respect to the best (3.4a) value is quite small. The *rate* of convergence of $\langle r^{-2}\rangle_{1m}$ obtained from the basis sets (3.4c)–(3.4e) is slow because these basis functions do not have the analytic structure of $\psi_1^{(1)}$ at $r=0$ originated by the Coulomb singularity [2–5].

Tables VI–XI contain numerical results for He^+ in the box $[0,R=5]$. Table VI shows the convergence of energies $E_{5m}^{(1)}$ obtained from basis sets (3.4a) and (3.4b) toward $-1.999\,997\,053$, which can be considered as the exact value $E_5^{(1)}$ with all its exact figures. In Table VII we have monitored the L_2 convergence as in Table II. Correct L_2 convergence is obtained from the basis sets (3.4a)–(3.4c) and we observe that 9.6×10^{-4} can be considered as the true limit value $\|\psi_5^{(1)}-\psi^{(1)}\|_5$ [Eqs. (3.5)]. An incorrect L_2 convergence appears with 15 and 25 basis functions of type (3.4d) and (3.4e), respectively. This is comprehensible since, for example, the overlaps $\langle\varphi_{5,1},\varphi_{5,1}\rangle_5=1.9\times10^0$ and $\langle\varphi_{5,50},\varphi_{5,50}\rangle_5=2.02\times10^{94}$ obtained from the basis function (3.4e) produce a rapid loss of precise figures in the numerical calculations. The rate of convergence of both energies $E_{5m}^{(1)}$ and wave functions $\psi_{5m}^{(1)}$ obtained from the basis sets (3.4c)–(3.4e) is slower than that with $R=1$ because for $R=5$ these basis sets must now duplicate two structural properties of $\psi_5^{(1)}$: one originated by the Coulomb singularity and the other by the exponential decay of $\psi_R^{(1)}$ (Fig. 1 shows how $\psi_{Rm}^{(1)}$ duplicates the exponential decay of $\psi^{(1)}$ as R increases).

Tables VIII–XI show the convergence of moments $\langle r^k\rangle_{5m}$ for $k=-2,0,5,9$ and confirm the results of Tables VI and VII. The incorrect convergence of moments obtained from the basis sets (3.4d) and (3.4e) becomes more evident. To understand this result it is enough to distinguish between the exact function $\psi_{Rm}^{(1)}$ associated with the basis set $\{\varphi_{Rn}\}_{n=1}^m$ and the function $\bar{\psi}_{Rm}^{(1)}$ obtained numerically with such a basis set. The er-

TABLE III. Convergence of moments $\langle r^{-2}\rangle_{1m}$ corresponding to the eigenfunctions $\psi_{1m}^{(1)}$ of Table II. In the last row the percentage error of the larger basis value with respect to the best (3.4a) value is exhibited.

m	Basis (3.4a)	m	Basis (3.4b)	m	Basis (3.4c)	m	Basis (3.4d)	m	Basis (3.4e)
3	16.4515	3	16.349	20	16.3443	10	16.607 50	20	16.241 350
5	16.4220	5	16.422	40	16.4024	20	16.564 43	40	16.243 021
7	16.4220	7	16.422	60	16.4132	30	16.562 04	60	16.243 550
9	16.4220	9	16.422	80	16.4171	45	16.561 86	80	16.243 558
				100	16.4188	50	16.561 78	100	16.243 641
			0.0		−0.02		0.85		−1.1

TABLE IV. Convergence of moments $\langle r^5 \rangle_{1m}$ corresponding to the eigenfunctions $\psi^{(1)}_{1m}$ of Table II. The values $10^2\langle r^5 \rangle_{1m}$ are reported and the percentage error of the larger basis value with respect to the best (3.4a) value is given in the last row.

m	Basis (3.4a)	m	Basis (3.4b)	m	Basis (3.4c)	m	Basis (3.4d)	m	Basis (3.4e)
3	5.088 99	3	5.0931	20	5.101 55	10	5.102 87	20	5.101 91
5	5.101 00	5	5.1010	40	5.101 06	20	5.102 02	40	5.101 93
7	5.101 00	7	5.1010	60	5.101 01	30	5.101 88	60	5.101 94
9	5.101 00	9	5.1010	80	5.101 00	45	5.101 93	80	5.101 93
				100	5.100 99	50	5.101 92	100	5.101 93
			0.0		0.0		0.02		0.02

TABLE V. Convergence of moments $\langle r^9 \rangle_{1m}$ corresponding to the eigenfunctions $\psi^{(1)}_{1m}$ of Table II. The values $10^2\langle r^9 \rangle_{1m}$ are reported and the percentage error of the larger basis value with respect to the best (3.4a) value is given in the last row.

m	Basis (3.4a)	m	Basis (3.4b)	m	Basis (3.4c)	m	Basis (3.4d)	m	Basis (3.4e)
3	1.424 77	3	1.4348	20	1.434 51	10	1.434 940	20	1.434 650
5	1.434 33	5	1.4343	40	1.434 35	20	1.434 673	40	1.434 657
7	1.434 33	7	1.4343	60	1.434 33	30	1.434 634	60	1.434 659
9	1.434 33	9	1.4343	80	1.434 33	45	1.434 647	80	1.434 656
				100	1.434 33	50	1.434 643	100	1.434 655
			0.0		0.0		0.02		0.02

TABLE VI. Convergence of $1s$ energies $E^{(1)}_{5m}$ of He^+ in the box $[0,R=5]$, for increasing values of the number m of basis functions (3.4). The values $-E^{(1)}_{Rm}$ are reported.

m	Basis (3.4a)	m	Basis (3.4b)	m	Basis (3.4c)	m	Basis (3.4d)	m	Basis (3.4e)
3	1.999 896 785	2	1.222 586 399	20	1.979 759	3	1.997 869	10	1.983 249
6	1.999 995 850	4	1.849 446 033	40	1.997 000	6	1.999 017	15	1.990 117
9	1.999 997 031	6	1.993 305 030	60	1.999 065	9	1.999 397	20	1.990 173
12	1.999 997 053	8	1.999 918 948	80	1.999 595	12	1.999 599	25	1.990 179
15	1.999 997 053	10	1.999 996 699	100	1.999 788	15	1.999 642	30	1.990 227
18	1.999 997 053	12	1.999 997 052	120	1.999 875	18	1.999 644	35	1.990 310
21	1.999 997 053	14	1.999 997 053	140	1.999 920	21	1.999 645	40	1.990 327
24	1.999 997 053	16	1.999 997 053	160	1.999 945	24	1.999 646	45	1.990 328
27	1.999 997 053	18	1.999 997 053	180	1.999 960	27	1.999 647	50	1.990 332
30	1.999 997 053	20	1.999 997 053	200	1.999 970	30	1.999 648		

TABLE VII. Convergence in the $L_2(0,5)$ norm of eigenfunctions $\psi^{(1)}_{5m}$ corresponding to the eigenvalues $E^{(1)}_{5m}$ of Table VI. The values $\|\psi^{(1)}_{5m}-\psi^{(1)}\|_5$ are reported, where $\psi^{(1)}$ is the $1s$ wave function of the free He^+ ion [Eqs. (3.5)]. The notation $6.7[-3]$ signifies 6.7×10^{-3}.

m	Basis (3.4a)	m	Basis (3.4b)	m	Basis (3.4c)	m	Basis (3.4d)	m	Basis (3.4e)
3	6.762 30[−3]	2	6.819[−1]	20	1.606[−2]	3	1.543[−2]	10	2.941[−2]
6	1.284 10[−3]	4	1.704[−1]	40	2.964[−3]	6	6.332[−3]	15	9.072[−3]
9	9.740 94[−4]	6	2.369[−2]	60	1.382[−3]	9	3.981[−3]	20	8.716[−3]
12	9.616 02[−4]	8	2.345[−3]	80	1.072[−3]	12	2.769[−3]	25	8.754[−3]
15	9.615 36[−4]	10	9.695[−4]	100	9.977[−4]	15	2.794[−3]	30	8.554[−3]
18	9.615 26[−4]	12	9.613[−4]	120	9.757[−4]	18	2.820[−3]	35	5.197[−3]
21	9.615 23[−4]	14	9.613[−4]	140	9.679[−4]	21	2.870[−3]	40	2.058[−3]
24	9.615 22[−4]	16	9.613[−4]	160	9.647[−4]	24	2.921[−3]	45	1.711[−3]
27	9.615 21[−4]	18	9.613[−4]	180	9.633[−4]	27	2.961[−3]	50	1.309[−3]
30	9.615 21[−4]	20	9.613[−4]	200	9.625[−4]	30	2.990[−3]		

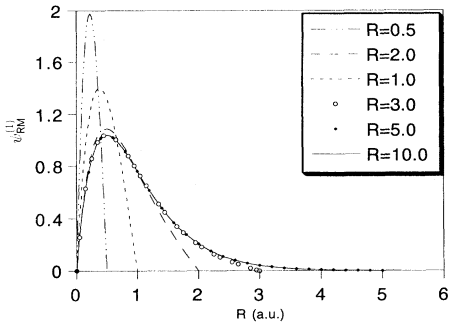

FIG. 1. ADWF $\psi_{Rm}^{(1)}(r)$ of He^+ ion in the box $[0,R]$. Every wave function is obtained from a Ritz-type expansion with a suitable number m of basis functions (3.4a), as in Tables II, VII, and XIII.

ror of $\bar{\psi}_{Rm}^{(1)}$ originated by round-off errors is given by $\|\delta\bar{\psi}_{Rm}^{(1)}\| = \|\psi_{Rm}^{(1)} - \bar{\psi}_{Rm}^{(1)}\|_R$. The increase of $\|\delta\bar{\psi}_{Rm}^{(1)}\|$ as m is made larger follows from Table IX: Each value of $\langle r^0\rangle_{5m}$ obtained from the basis set (3.4d) or (3.4e) might be equal to 1 by the "normalization" of each $\bar{\psi}_{Rm}^{(1)}$, but Table IX shows that this is not the case, since the computed values decrease with (3.4d) and increase with (3.4e) as m increases. The equation

$$|\langle\psi_{Rm}^{(1)}, r^k\psi_{Rm}^{(1)}\rangle_R - \langle\bar{\psi}_{Rm}^{(1)}, r^k\bar{\psi}_{Rm}^{(1)}\rangle_R| = |2\langle\bar{\psi}_{Rm}^{(1)}, r^k\delta\bar{\psi}_{Rm}^{(1)}\rangle_R + O(|\delta\bar{\psi}_{Rm}^{(1)}|^2)|$$

clearly shows how the right-hand term $\langle\bar{\psi}_{Rm}^{(1)}, r^k\delta\bar{\psi}_{Rm}^{(1)}\rangle_R$ increases the round-off error of $\langle\bar{\psi}_{Rm}^{(1)}, r^k\bar{\psi}_{Rm}^{(1)}\rangle_R$ as k increases. The values from the basis sets (3.4d) and (3.4e) reported in Tables X and XI confirm this result. Nevertheless, we see that the percentage of errors with respect to the exact values [obtained from (3.4a)] are quite reasonable.

The above numerical results confirm that correct or reasonable expectation values can be obtained even when the analytic structure of the basis functions radically differs from that of the exact state, provided that Eqs. (3.1) hold (Remark 1).

IV. COMPUTATION OF EXPECTATION VALUES $\langle\psi^{(i)}, S\psi^{(j)}\rangle$ IN $[0,\infty)$

Let H be the Hamiltonian associated with Eq. (1.3) in $L_2(0,\infty)$ and let $h(\,,\,)$ be the corresponding sesquilinear form. In what follows we consider that $\psi_R^{(i)}(r)=0$ for $r \geq R$. It is not difficult to see that this extension of $\psi_R^{(i)}$ belongs to $D(h)$ and satisfies $E_R^{(i)} = h(\psi_R^{(i)}, \psi_R^{(i)})$. As shown in [6], for potentials of physical interest the bound states of Eqs. (1.3) and (1.4) satisfy

$$\lim_{R\to\infty} E_R^{(i)} = E^{(i)} \tag{4.1a}$$

and

$$\lim_{R\to\infty} \|\psi_R^{(i)} - \psi^{(i)}\| = 0 \,. \tag{4.1b}$$

We now show the correctness of equation

$$\lim_{R\to\infty} \langle\psi_R^{(i)}, S\psi_R^{(j)}\rangle = \langle\psi^{(i)}, S\psi^{(j)}\rangle \tag{4.2}$$

for most operators S for which $\langle\psi^{(i)}, S\psi^{(j)}\rangle$ exists, including r^k with $k \geq -2$.

By Theorem 3, if S is relatively form bounded by H, then Eqs. (4.1a) and (4.1b) imply that (4.2) is true, a result that includes r^k with $-2 \leq k \leq 0$ and the momentum operator. This is not a surprise since there are other numerical methods that satisfy conditions (4.1) and therefore guarantee (4.2) for relatively form-bounded operators. The strong result is the correctness of (4.2) with operators S *not* relatively form bounded by H, such as the higher power of moment operators r^k.

For simplicity we consider that $V(r)\to 0$ as $r\to\infty$. Let $s(r)$ be a real-valued function on $[0,\infty)$ that is bounded on each finite interval $[0,R]$ and for which $\|s(r)\psi^{(i)}\|$ exists, for example, r^k with $k \geq 0$. According to Theorem 2, to prove (4.2) with $S = s(r)$ it is enough to show that $\|S\psi_R^{(i)}\|$ remains bounded as $R\to\infty$. This quantity can be expressed as

$$\|S\psi_R^{(i)}\|^2 = \|S\psi_R^{(i)}\|_{R_0}^2 + \int_{R_0}^{R} |s(r)\psi_R^{(i)}|^2 dr \,,$$

where R_0 is a positive constant. From (4.1b) and the boundedness of $s(r)$ on $[0,R_0]$ it follows that $\|S\psi_R^{(i)}\|_{R_0} \to \|S\psi^{(i)}\|_{R_0}$ as $R\to\infty$. It remains to show that the integral is bounded for all R. Intuitively, since the eigenfunctions of Eqs. (1.3) and (1.4) satisfy a differential equation of type

$$\frac{d^2f}{dr^2} + V(r)f = Ef \tag{4.3}$$

and $E_R^{(i)} \to E^{(i)}$, the asymptotic behavior of $\psi_R^{(i)}$ tends to that of $\psi^{(i)}$ as $R\to\infty$ (see, for example, Fig. 1). From this

TABLE VIII. Convergence of moments $\langle r^{-2}\rangle_{5m}$ corresponding to the wave functions $\psi_{5m}^{(1)}$ of Table VII. In the last row the percentage error of the larger basis value with respect to the best (3.4a) value is exhibited.

m	Basis (3.4a)	m	Basis (3.4b)	m	Basis (3.4c)	m	Basis (3.4d)	m	Basis (3.4e)
6	7.999 43	4	4.7296	40	7.7730	6	8.190 42	15	7.470 93
12	8.000 11	8	7.9745	80	7.9446	12	8.104 00	25	7.474 10
18	8.000 11	12	8.0001	120	7.9759	15	8.096 18	35	7.471 82
24	8.000 11	16	8.0001	160	7.8866	24	8.095 53	45	7.471 80
30	8.000 11	20	8.0001	200	7.9916	30	8.095 20	50	7.471 74
			0.0		−0.11		1.2		−6.6

TABLE IX. Convergence of moments $\langle r^0 \rangle_{5m}$ corresponding to the eigenfunctions $\psi^{(1)}_{5m}$ of Table VII.

m	Basis (3.4a)	m	Basis (3.4b)	m	Basis (3.4c)	m	Basis (3.4d)	m	Basis (3.4e)
6	1.000 00	4	1.0000	40	1.000 00	6	1.000 000 0	15	1.000 059
12	1.000 00	8	1.0000	80	1.000 00	12	1.000 000 0	25	1.000 067
18	1.000 00	12	1.0000	120	1.000 00	15	0.999 998 4	35	1.000 061
24	1.000 00	16	1.0000	160	1.000 00	24	0.999 997 6	45	1.000 084
30	1.000 00	20	1.0000	200	1.000 00	30	0.999 997 1	50	1.000 084

idea one can rigorously prove [29] that the set of DWFs $\psi^{(i)}_R$ is bounded basically by the asymptotic form of $\psi^{(i)}$: There exist positive constants $A^{(i)}_0$, $A^{(i)}_1$, b_i, and a large enough R_0 such that the function $g^{(i)}(r)$ given by

$$g^{(i)}(r)=\begin{cases} A^{(i)}_0 & \text{if } r\in[0,R_0] \\ A^{(i)}_1 \exp(-b_i r) & \text{if } r>R_0 \end{cases} \tag{4.4}$$

satisfies the inequality

$$|\psi^{(i)}_R(r)| \le g^{(i)}(r) \quad \text{for all } r\in[0,\infty) \quad \text{with every fixed } R>R_0 \ . \tag{4.5}$$

Now, if $s(r)$ satisfies

$$\int_{R_0}^{\infty} |s(r)g^{(i)}(r)|^2 dr \le M < \infty \ , \tag{4.6}$$

then one immediately obtains that

$$\int_{R_0}^{R} |S\psi^{(i)}_R|^2 dr \le \int_{R_0}^{\infty} |s(r)g^{(i)}(r)|^2 dr < M \ .$$

Thus we conclude that $\lim_{R\to\infty} \|S\psi^{(i)}_R\| \le \|S\psi^{(i)}\|_R + M$ and clearly this includes any positive power of r.

Remark 2. If $V(r)\to\infty$ as $r\to\infty$, the bound states of Eq. (1.3) decay more rapid than $e^{-b_i r}$, so that the *class* of functions $s(r)$ for which Eq. (4.2) holds is larger than the class of functions that satisfy (4.6). For example, if $V(r)\sim r^2$, then $g^{(i)}(r)\sim\exp(-2r^2)$ for large r. In every case, the limiting procedure (4.2) is true for r^k with $k\ge -2$.

Remark 3. Since the correctness of (4.2) with the operators S described above is obtained from Theorems 2 and 3, upper and lower bounds of the error

$$\Delta S^{ij}_R = \langle \psi^{(i)}_R, S\psi^{(j)}_R \rangle - \langle \psi^{(i)}, S\psi^{(j)} \rangle \tag{4.7}$$

can be constructed as in Sec. II. Therefore, the set of DWFs $\psi^{(i)}_R$ is reliable to compute the true expectation value $\langle \psi^{(i)}, S\psi^{(j)} \rangle$.

Equation (4.2) was shown in the particular case of a linear potential $V(r)=r$ by Fernández *et al.* [14], who obtained, in an analytic form, the transition moments $\langle \psi^{(i)}_R, r^k \psi^{(j)}_R \rangle$ and recovered $\langle \psi^{(i)}, r^k \psi^{(j)} \rangle$ when $R\to\infty$.

In the previous section we saw that ADWFs obtained from several numerical methods are reliable to compute the quantity $\langle \psi^{(i)}_R, S_R \psi^{(j)}_R \rangle_R$. We now see how this result allows us to obtain accurate values of $\langle \psi^{(i)}, S\psi^{(j)} \rangle$. Let $\psi^{(i)}_{Rm}$ and $E^{(i)}_{Rm}$ be numerical solutions of Eq. (1.4) that satisfy (3.1). In what follows $\psi^{(i)}_{Rm}(r)=0$ for $r\ge R$, so that $\|\psi^{(i)}_{Rm}-\psi^{(i)}\|_R = \|\psi^{(i)}_{Rm}-\psi^{(i)}\|$. This, together with Eqs. (3.1) and (4.1), leads to

$$\lim_{R\to\infty}\lim_{m\to\infty} E^{(i)}_{Rm} = E^{(i)}, \quad \lim_{R\to\infty}\lim_{m\to\infty} \|\psi^{(i)}_{Rm}-\psi^{(i)}\| = 0 \ . \tag{4.8}$$

Let S be an operator among those described above for which (4.2) is true. It is easy to see the action of S on $\psi^{(i)}_R$ defines an operator S_R [called the restriction of S on $L_2(0,R)$] for which the equations $\langle \psi^{(i)}_R, S\psi^{(j)}_R \rangle = \langle \psi^{(i)}_R, S_R \psi^{(j)}_R \rangle_R$ and (3.2) are true. This, together with (4.2), leads to the correctness of the equation

$$\lim_{R\to\infty}\lim_{m\to\infty} \langle \psi^{(i)}_{Rm}, S\psi^{(j)}_{Rm} \rangle = \langle \psi^{(i)}, S\psi^{(j)} \rangle \ , \tag{4.9}$$

where $S\psi^{(i)}_{Rm} = S_R \psi^{(i)}_{Rm}$. We now show that the error

$$\Delta S^{ij} = \langle \psi^{(i)}_{Rm}, S\psi^{(j)}_{Rm} \rangle - \langle \psi^{(i)}, S\psi^{(j)} \rangle \tag{4.10}$$

can be made arbitrarily small by taking R and m large enough. Let $\epsilon>0$ be a number arbitrarily small. By using (3.3) and (4.7) we obtain

TABLE X. Convergence of moments $\langle r^5 \rangle_{5m}$ corresponding to the eigenfunctions $\psi^{(1)}_{5m}$ of Table VII. In the last row the percentage error of the larger basis value with respect to the best (3.4a) value is exhibited.

m	Basis (3.4a)	m	Basis (3.4b)	m	Basis (3.4c)	m	Basis (3.4d)	m	Basis (3.4e)
6	2.447 48	4	7.0461	40	2.465 94	6	2.467 17	15	2.3887
12	2.451 36	8	2.4527	80	2.453 30	12	2.453 84	25	2.3831
18	2.451 36	12	2.4527	120	2.451 95	15	2.453 45	35	2.4587
24	2.451 36	16	2.4527	160	2.451 61	24	2.453 41	45	2.4769
30	2.451 36	20	2.4527	200	2.451 49	30	2.453 38	50	2.4826
			0.0		0.005		0.08		1.3

TABLE XI. Convergence of moments $\langle r^9 \rangle_{5m}$ corresponding to the eigenfunctions $\psi^{(1)}_{5m}$ of Table VII. In the last row the percentage error of the larger basis value with respect to the best (3.4a) value is exhibited.

m	Basis (3.4a)	m	Basis (3.4b)	m	Basis (3.4c)	m	Basis (3.4d)	m	Basis (3.4e)
6	70.2533	4	1559.6	40	72.5321	6	76.2768	15	54.3812
12	71.8357	8	72.350	80	71.9247	12	72.0219	25	53.8326
18	71.8356	12	71.835	120	71.8624	15	71.9761	35	66.4814
24	71.8357	16	71.835	160	71.8469	24	71.9665	45	70.3595
30	71.8355	20	71.835	200	71.8414	30	71.9602	50	71.9382
			0.0		0.008		0.17		0.14

$$|\Delta S^{ij}| \leq |\Delta S^{ij}_{Rm}| + |\Delta S^{ij}_{R}| \ .$$

From Eq. (4.2) one has that there is a R_1 such that $|\Delta S^{ij}_R| < \epsilon/2$ for all $R > R_1$. On the other hand, from Eq. (3.2) it follows that for every $R > R_1$ there is an $m(R)$ such that $|\Delta S^{ij}_{Rm}| < \epsilon/2$ for all $m > m(R)$. Thus $|\Delta S^{ij}| < \epsilon$ for every $R > R_1$ and $m > m(R)$. Therefore, both the DWF $\psi^{(i)}_R$ and the ADWF $\psi^{(i)}_{Rm}$ that satisfy (3.1) are indeed reliable to compute in $[0, \infty)$ expectation and transition values of most operators S for which $\langle \psi^{(i)}, S\psi^{(j)} \rangle$ exists.

Several authors [8–12] have applied methods, such as finite-element or finite-difference methods, to solve Eq. (1.3) by taking a suitable large R and replacing the boundary condition $\lim_{r\to\infty}\psi^{(i)}(r)=0$ by $\psi^{(i)}(R)=0$, which is an implicit way of using Eqs. (4.8) and (4.9). The classical turning points, given by the equation $E^{(i)}-V(R)=0$, have been used to define a suitable large R. Unfortunately, this definition depends on the exact energy $E^{(i)}$, which is *a priori* unknown, and does not guarantee that the errors $\|\psi^{(i)}_R - \psi^{(i)}\|$ and $E^{(i)}_R - E^{(i)}$ are small. Other authors have applied particular techniques to solve Eq. (1.4) and they found that Eq. (4.9) holds for some operators S [13–16]. It is clear that these results are special cases of Eqs. (4.8) and (4.9).

Since the correct convergence of energies, wave functions, and other properties is guaranteed by Eqs. (4.8) and (4.9), in practical situations it is more convenient to solve Eq. (1.4) in a sequence of boxes $[0,R_n]$ ($R_n \to \infty$ as n increases) until physical properties are obtained with the desired accuracy. For fixed R_n the convergence of numerical solutions of Eq. (1.4) is monitored as in Tables I–V and for increasing values of R_n the convergence can be monitored by comparing the best result in the interval $[0,R_n]$ with that of $[0,R_{n+1}]$. Another way of verifying the L_2 convergence follows from the inequality (2.2b). If $\psi^{(i)}_{R_n m}$ tends to $\psi^{(i)}_{R_n}$ in the $L_2(0,R_n)$ norm then it converges to $\psi^{(i)}$ in the $L_2(0,\infty)$ norm for increasing values of R_n and m; since the quantity $\|\psi^{(i)}_{R_n m} - \psi^{(i)}_{R_{n+1}m'}\|$ ($m' \geq m$) provides a bound of the exact error $\|\psi^{(i)}_{R_n m} - \psi^{(i)}\|$ [Eq. (2.2b)], then $\psi^{(i)}_{R_n m}$ converges in the $L_2(0,\infty)$ norm and is more accurate as $\|\psi^{(i)}_{R_n m} - \psi^{(i)}_{R_{n+1}m'}\|_R \to 0$ [we remark that $\psi^{(i)}_{R_n m}(r)=0$ for $r \geq R_n$]. Examples of this procedure can be found in [7,27]. We now give an example that will be used in our discussion about the analytic structure of approximating sequences.

Numerical example

Continuing with the He^+ ion, in Tables XII–XVIII we give numerical results of the convergence of energies $E^{(i)}_{Rm}$, the ADWF $\psi^{(i)}_{Rm}$, and moments $\langle r^k \rangle_{Rm}$ obtained

TABLE XII. Convergence of $1s$ energies of He^+. The first tree columns are values $-E^{(1)}_{10m}$ obtained from a Ritz-type expansion with m basis functions (3.4) in $[0,R=10]$ and the other columns are the energies from Fourier and Ritz expansions with m Gaussian functions (5.1). The exact energy of the free He^+ ion is $E^{(1)} = -2.000\,000$.

m	Basis (3.4a)	m	Basis (3.4c)	m	Basis (3.4e)	m	Fourier Ref. [2]	m	Ritz Ref. [2]
4	1.999 999 989	20	1.886 170	10	1.980 888	20	1.947 02	20	1.949 73
8	2.000 000 000	40	1.979 062	15	1.988 154	40	1.978 57	40	1.979 20
12	2.000 000 000	60	1.993 099	20	1.988 212	60	1.987 71	60	1.987 96
16	2.000 000 000	80	1.996 948	25	1.988 245	80	1.991 78	80	1.991 91
20	2.000 000 000	100	1.998 396	30	1.988 359	100	1.994 01	100	1.994 09
24	2.000 000 000	120	1.999 056	35	1.988 410	120	1.995 38	120	1.995 43
28	2.000 000 000	140	1.999 399	40	1.988 425	140	1.996 30	140	1.996 33
32	2.000 000 000	160	1.999 594	45	1.988 430	160	1.996 95	160	1.996 97
36	2.000 000 000	180	1.999 713	50	1.988 432	180	1.997 42	180	1.997 44
40	2.000 000 000	200	1.999 790	55	1.988 432	200	1.997 79	200	1.997 80

TABLE XIII. Convergence in the $L_2(0,10)$ norm of the ADWF $\psi^{(1)}_{10m}$ corresponding to the eigenvalues $E^{(1)}_{10m}$ of Table XII. The values $\|\psi^{(1)}_{Rm}-\psi^{(1)}\|_{10}$ are reported, where $\psi^{(1)}$ is the exact 1s state of the free He^+ ion [Eqs. (3.5)]. The notation 8.7[−5] means 8.7×10^{-5}.

m	Basis (3.4a)	m	Basis (3.4c)	m	Basis (3.4e)
4	8.76[−5]	20	8.46[−2]	10	2.89[−2]
8	6.37[−7]	40	1.66[−2]	15	1.14[−2]
12	1.22[−7]	60	5.96[−3]	20	1.25[−2]
16	1.11[−7]	80	2.86[−3]	25	1.28[−2]
20	1.05[−7]	100	1.61[−3]	30	1.19[−2]
24	1.07[−7]	120	1.01[−3]	35	1.02[−2]
28	1.03[−7]	140	6.81[−4]	40	1.01[−2]
32	9.99[−8]	160	4.84[−4]	45	9.89[−3]
36	9.31[−8]	180	3.58[−4]	50	9.87[−3]
40	8.94[−8]	200	2.74[−4]	55	9.88[−3]

from the basis sets (3.4a), (3.4c), and (3.4e) with $R=10$. As in Sec. III, a correct convergence of all quantities from the basis set (3.4a) and (3.4c) holds, whereas the (3.4e) values differ slightly with respect to the best (3.4a) values, which can be considered as the exact ground-state properties of He^+ in the box $[0,R=10]$.

The comparison made in Tables XII and XIII between the energy $E^{(1)}_{10,40}$ and the wave function $\psi^{(1)}_{10,40}$ from the basis set (3.4a) with those of the free He^+ ion shows that the 1s state of He^+ within the box $[0,R=10]$ is essentially the 1s state of the free He^+ ion, in agreement with Eqs. (4.8) and (4.9). This result is reinforced by the convergence of density moments $\langle r^k\rangle_{10m}$ toward the free system values as Tables XIV–XVIII show.

The correct convergence of $E^{(1)}_{Rm}$ and $\psi^{(1)}_{Rm}$ for increasing values of R and m guarantees the convergence of $\langle r^{-2}\rangle_{Rm}$ to the free system value $\langle r^{-2}\rangle$ (Theorem 3) as Table XIV shows. Convergence of $\langle r^k\rangle_{Rm}$ with $k\geq 0$ follows from the L_2 convergence [Eq. (4.8)] and the boundedness of $\{\|r^k\psi^{(1)}_{Rm}\|\}$ as R and m increase (Theorem 2). The latter condition is a consequence of (3.2) and Eq. (4.2), which is determined by the boundedness of $\psi^{(1)}_R$ by $g^{(1)}(r)$ [Eqs. (4.4) and (4.5)]. The manner in which $\psi^{(1)}_{Rm}$ duplicates the asymptotic behavior of $\psi^{(1)}$ is illustrated in Fig. 1, where the best wave functions $\psi^{(1)}_{Rm}$ obtained from the basis set (3.4a) with $R=0.5,1.0,2.0,3.0,5.0,10.0$ are plotted. We observe how $\psi^{(1)}_{Rm}$ tends toward the best $\psi^{(1)}_{10,40}$ which may be considered as the free 1s state since its exact error $\|\psi^{(1)}_{10,40}-\psi^{(1)}\|=8.9\times10^{-8}$ is very small (see Table XIII). The graphs obtained from the basis sets (3.4c) and (3.4e) with the same values of R cannot be distinguished from those of Fig. 1, because of the *pointwise* convergence,

$$\lim_{R\to\infty}\lim_{m\to\infty}\psi^{(i)}_{Rm}(r_0)=\lim_{R\to\infty}\psi^{(i)}_R(r_0)=\psi^{(i)}(r_0)\ , \qquad (4.11)$$

which is shown in Table XIX [a rigorous proof of (4.11) is given in [29]].

V. RITZ-TYPE CALCULATIONS IN $[0,\infty)$

In Ref.[2] Klahn and Morgan undertook a careful convergence analysis of expectation values obtained from both Fourier and Ritz-type expansions with the Gaussian basis functions

$$\varphi_k(r)=e^{-r^2/2}r^{2(k-1)},\quad k=1,2,\ldots . \qquad (5.1)$$

The space in which Klahn and Morgan made their analysis is the weighted Hilbert space $L_2(0,\infty;r^2)$, whose inner product $(\ ,\ )$, in terms of that of $L_2(0,\infty)$, is given by $(\bar f,\bar g)=\langle \bar f,r^2\bar g\rangle$. The convergence analysis for expectation values of operators S not relatively form bounded by the Hamiltonian starts from the inequality

$$|\langle\psi_n,S\psi_n\rangle-\langle\psi,S\psi\rangle| \leq\gamma_E(E_n-E)^{1/2}(\|S\psi_n\|+\|S\psi\|)\ , \qquad (5.2)$$

which shows that incorrect expectation values can be computed when the sequence $\{\|S\psi_n\|\}_{n=1}^{\infty}$ diverges. The calculation of Fourier expansions ψ^F_n for the 1s state of

TABLE XIV. Convergence of approximate values of the 1s moment $\langle r^{-2}\rangle$ of He^+. The first three columns are the values from the ADWF $\psi^{(1)}_{10m}$ of Table XIII and the other columns are the values from Fourier and Ritz expansions with m Gaussian functions (5.1). In the last row the percentage error of the larger basis value with respect to the exact free system value $\langle r^{-2}\rangle=8.0000$ is reported.

m	Basis (3.4a)	m	Basis (3.4c)	m	Basis (3.4e)	m	Fourier Ref. [2]	m	Ritz Ref. [2]
4	7.999 79	20	5.3064	10	7.254 35	20	6.7774	20	6.3997
8	8.000 00	40	7.1153	15	7.404 113	40	7.3280	40	7.1193
12	8.000 00	60	7.5917	20	7.410 288	60	7.5347	60	7.3972
16	8.000 00	80	7.7700	25	7.409 346	80	7.6435	80	7.5436
20	8.000 00	100	7.8537	30	7.407 884	100	7.7107	100	7.6336
24	8.000 00	120	7.8993	35	7.407 310	120	7.7565	120	7.6944
28	8.000 00	140	7.9265	40	7.407 082	140	7.7897	140	7.7382
32	8.000 00	160	7.9441	45	7.407 043	160	7.8149	160	7.7712
36	8.000 00	180	7.9561	50	7.407 073	180	7.8346	180	7.7969
40	8.000 00	200	7.9646	55	7.407 070	200	7.8505	200	7.8175
	0.0		−0.44		−7.4		−1.9		−2.3

TABLE XV. Convergence of approximate values of the $1s$ moment $\langle r^5 \rangle$ of He^+. The first three columns are the values from the ADWF $\psi^{(1)}_{10m}$ of Table XIII and the other columns are the values from Fourier and Ritz expansions with m Gaussian functions (5.1). In the last row the percentage error of the larger basis value with respect to the exact free system value $\langle r^5 \rangle = 2.460\,94$ is reported.

m	Basis (3.4a)	m	Basis (3.4c)	m	Basis (3.4e)	m	Fourier Ref. [2]	m	Ritz Ref. [2]
4	2.459 39	20	5.6640	10	2.0642	20	3.1651	20	6.401
8	2.460 94	40	2.6443	15	2.1436	40	2.8505	40	6.102
12	2.460 94	60	2.5031	20	2.3827	60	2.7297	60	5.803
16	2.460 94	80	2.4774	25	2.3979	80	2.6660	80	5.560
20	2.460 94	100	2.4693	30	2.4533	100	2.6267	100	5.362
24	2.460 94	120	2.4658	35	2.4942	120	2.6001	120	5.198
28	2.460 94	140	2.4639	40	2.5107	140	2.5808	140	5.060
32	2.460 94	160	2.4629	45	2.5189	160	2.5662	160	4.942
36	2.460 94	180	2.4623	50	2.5166	180	2.5548	180	4.839
40	2.460 94	200	2.4620	55	2.5168	200	2.5456	200	4.748
	0.0		0.04		2.3		3.4		94.2

TABLE XVI. Convergence of approximate values of the $1s$ moment $\langle r^6 \rangle$ of He^+. The first three columns are the values from the ADWF $\psi^{(1)}_{10m}$ of Table XIII and the other columns are the values from Fourier and Ritz expansions with m Gaussian functions (5.1). In the last row the percentage error of the larger basis value with respect to the exact free system value $\langle r^6 \rangle = 4.921\,87$ is reported.

m	Basis (3.4a)	m	Basis (3.4c)	m	Basis (3.4e)	m	Fourier Ref. [2]	m	Ritz Ref. [2]
4	4.915 14	20	27.666	10	3.666	20	10.51	20	36.50
8	4.921 87	40	5.8183	15	4.671	40	9.796	40	47.86
12	4.921 87	60	5.0693	20	4.576	60	8.607	60	53.94
16	4.921 87	80	4.9697	25	4.621	80	8.168	80	57.85
20	4.921 87	100	4.9437	30	4.812	100	7.855	100	60.63
24	4.921 87	120	4.9338	35	4.959	120	7.617	120	62.73
28	4.921 87	140	4.9292	40	5.023	140	7.430	140	64.40
32	4.921 87	160	4.9267	45	5.058	160	7.276	160	65.75
36	4.921 87	180	4.9252	50	5.046	180	7.148	180	66.89
40	4.921 87	200	4.9243	55	5.047	200	7.039	200	67.85
	0.0		0.05		2.5		43.0		1278

TABLE XVII. Convergence of approximate values of the $1s$ moment $\langle r^7 \rangle$ of He^+. The first three columns are the values from the ADWF $\psi^{(1)}_{10m}$ of Table XIII and the other columns are the values from Fourier and Ritz expansions with m Gaussian functions (5.1). In the last row the percentage error of the larger basis value with respect to the exact free system value $\langle r^7 \rangle = 11.074\,21$ is reported. The notation 17.53[2] means 17.53×10^2.

m	Basis (3.4a)	m	Basis (3.4c)	m	Basis (3.4e)	m	Fourier Ref. [2]	m	Ritz Ref. [2]
4	11.0452	20	196.917	10	7.0298	20	56.637	20	27.48[1]
8	11.0742	40	17.2937	15	9.9679	40	61.210	40	52.91[1]
12	11.0742	60	11.8642	20	9.6667	60	62.869	60	74.18[1]
16	11.0742	80	11.2761	25	9.8120	80	63.726	80	92.67[1]
20	11.0742	100	11.1517	30	10.4762	100	64.249	100	10.92[2]
24	11.0742	120	11.1122	35	11.0141	120	64.602	120	12.43[2]
28	11.0742	140	11.0959	40	11.2740	140	64.856	140	13.83[2]
32	11.0742	160	11.0879	45	11.4226	160	65.047	160	15.13[2]
36	11.0742	180	11.0835	50	11.3632	180	65.196	180	16.36[2]
40	11.0742	200	11.0808	55	11.3656	200	65.316	200	17.53[2]
	0.0		0.06		2.6		49.0[1]		15.3[3]

TABLE XVIII. Convergence of approximate values of the $1s$ moment $\langle r^9 \rangle$ of He^+. The first three columns are the values from the ADWF $\psi^{(1)}_{10m}$ of Table XIII and the other columns are the values from Fourier and Ritz expansions with m Gaussian functions (5.1). In the last row the percentage error of the larger basis value with respect to the exact free system value $\langle r^9 \rangle = 76.135$ is reported. The notation 13.40[5] means 13.40×10^5.

m	Basis (3.4a)	m	Basis (3.4c)	m	Basis (3.4e)	m	Fourier Ref. [2]	m	Ritz Ref. [2]
4	75.5678	20	14.306[3]	10	30.664	20	32.45[2]	20	19.111[3]
8	76.1340	40	51.871[1]	15	56.877	40	69.98[2]	40	76.717[3]
12	76.1352	60	12.385[1]	20	53.734	60	10.78[3]	60	16.420[4]
16	76.1352	80	85.738[0]	25	55.323	80	14.56[3]	80	27.642[4]
20	76.1352	100	78.950[0]	30	63.830	100	18.35[3]	100	41.018[4]
24	76.1352	120	77.199[0]	35	71.399	120	22.15[3]	120	56.326[4]
28	76.1352	140	76.619[0]	40	75.866	140	25.95[3]	140	73.401[4]
32	76.1352	160	76.388[0]	45	78.862	160	29.73[3]	160	92.115[4]
36	76.1352	170	76.282[0]	50	77.393	180	33.52[3]	180	11.236[5]
40	76.1352	200	76.227[0]	55	77.419	200	37.32[3]	200	13.406[5]
	0.0		0.12		1.7		48.9[3]		17.6[5]

He^+ gives sequences $\{\langle \psi^F_n, r^{k+2}\psi^F_n \rangle\}_{n\geq 1}$, which converge to their correct limit for $k<7$ and diverge for $k>7$ with $k=7$ the crossover from convergence to divergence, and similar results are obtained from the Ritz-type wave functions ψ^R_n with the corresponding crossover value $k=5$ (see Tables XIV–XVIII). The explanation of this result lies in the generally accepted fact that the correctness of the limiting procedure $\lim_{n\to\infty}\langle \psi_n, S\psi\rangle = \langle \psi, S\psi\rangle$ is determined by the *rate* of convergence of approximate energies E_n to the exact one (E convergence) in a manner that the term $\|S\psi_n\|$ is *dominated* by $E_n - E$ on the right-hand side of (5.2). On the other hand, Schwarz [3] pointed out that the rate of E convergence depends on the ability to duplicate the analytic structure of the exact state in the neighborhood of the *cusps* (where the exact state is not analytic in Cartesian coordinates [4]). Thus, if the basis functions have an analytic structure that differs too much from that of the exact state, a slow E convergence occurs and hence the right-hand term of (5.2) may diverge as $n\to\infty$.

TABLE XIX. Pointwise convergence of $\psi^{(1)}_{Rm}$ for increasing values of R. The values $\psi^{(1)}_{Rm}(r_0)$ from the larger basis ADWF of Tables II, VII, and XIII are reported. In the last column the exact value $\psi^{(1)}(r_0)$ of the free system $1s$ state is reported.

R	r_0	Basis (3.4a)	Basis (3.4c)	Basis (3.4e)	Exact free state
1	0.10	0.709 793	0.709 792	0.711 410	
	0.20	1.141 772	1.141 772	1.140 317	
	0.65	1.035 162	1.035 162	1.034 950	
	0.80	0.026 619	0.626 618	0.626 461	
5	0.10	0.463 148	0.463 065	0.444 847	
	0.60	1.022 295	1.022 281	1.026 086	
	1.00	0.765 576	0.765 575	0.770 459	
	1.50	0.422 455	0.422 459	0.427 524	
	2.50	0.095 270	0.095 271	0.098 293	
	4.10	0.006 102	0.006 103	0.008 133	
10	0.10	0.463 144	0.462 561	0.441 921	0.463 144
	0.60	1.022 287	1.022 179	1.026 039	1.022 287
	1.00	0.765 572	0.765 565	0.770 498	0.765 572
	2.50	0.095 289	0.095 294	0.097 770	0.095 289
	4.10	0.006 370	0.006 361	0.005 736	0.006 370
	5.05	0.001 174	0.001 183	0.000 572	0.001 174

Before we compare the numerical results of Klahn and Morgan with those of the ADWF, the following facts should be considered. In Ref. [2] the basis set (5.1) was orthonormalized analytically and integrals were computed through recurrence relations or analytic formulas. Thus numerical instabilities were eliminated as much as possible. Since the exact $1s$ state $\psi^{(1)}$ of He^+ is obtained from $\bar{\psi}^{(1)} = 2Z^{3/2}e^{-Zr}$ of Ref. [2] multiplying by r, the analytic structure of $\psi^{(1)}$ and $\bar{\psi}^{(1)}$ is similar at $r=0,\infty$: they have a discontinuous derivative at $r=0$ because of $e^{-Z|r|}$ and the behavior for large r is similar.

The basis set (3.4e) is as flawed as (5.1) in terms of its ability to duplicate the analytic structure of the exact $1s$ state at $r=0,\infty$. This is obvious for $r\to\infty$ and in the neighborhood of $r=0$ the behavior

$$\varphi_{Rk}(r)\sim Rr^{2k-1},\quad \varphi_k(r)\sim r^{2(k-1)}$$

only differs by the factor r [used to satisfy $\psi^{(i)}_R(0)=0$]. Obviously the analytic structure of the basis set (3.4c) differs completely from that of the exact free system wave function. Thus a slow E convergence holds with these basis sets, as Table XII shows. This is confirmed in Table XIII by the slow L_2 convergence of the $\psi^{(1)}_{Rm}$'s obtained from the basis sets (3.4c) and (3.4e), whose error $\|\psi^{(1)}_{10m} - \psi^{(1)}\|$ is greater than that of $\psi^{(1)}_{Rm}$ obtained from the basis set (3.4a). As expected, a correct, but slow, convergence of the approximating values of $\langle r^{-2}\rangle$ is also observed in Table XIV, since r^{-2} is relatively form bounded by the Hamiltonian.

According to the conjecture that slow E convergence may cause divergences of approximating values of $\langle r^k\rangle$

with large k and the fact that the basis sets (3.4c) and (3.4e) are as flawed as (5.1), we might expect that the variational calculations with these basis sets exhibit similar numerical results with high power moments r^k. Tables XV–XVIII show that this expectation is false, since the basis set (3.4c) gives a completely correct (but slow) convergence toward the true moments and the values from the basis set (3.4e) have a small percentage error (even when the orthonormalization procedure together with the numerical quadrature introduces a rapid loss of precise figures in numerical calculations), whereas the values from the basis set (5.1) diverge. This supports our claim that the possibility of obtaining divergences from the true expectation values or computing wrong limit values because of the nonanalyticities in the exact states can be circumvented by using Dirichlet wave functions and their numerical approximations, provided (3.1) holds.

ACKNOWLEDGMENTS

I wish to thank Professor L. García Colin, Professor Eduardo Piña, and Professor Gustavo Izquierdo from the Universidad Autonoma Metropolitana Iztapalapa for their invaluable help and Alfredo Nicolás and Blanca Bermudez from Mathematics Department (UAMI) for their computational assistance.

APPENDIX: PROOF OF THEOREM 3

A straightforward calculation gives

$$|\Delta S_n^{ij}| \le |\langle \delta\psi_n^{(i)}, S\psi_n^{(j)}\rangle_a| + |\langle S\psi^{(i)}, \delta\psi_n^{(j)}\rangle_a| \ . \tag{A1}$$

Since the second term on the right-hand side is bounded

$$|\langle S\psi^{(i)}, \delta\psi_n^{(j)}\rangle_a| \le \|S\psi^{(i)}\|_a \|\delta\psi_n^{(j)}\|_a \ , \tag{A2}$$

it remains to prove that the first term is bounded. Consider the positive form

$$p(f,g) = h_a(f,g) + (1-E_0)\langle f,g\rangle_a \ . \tag{A3}$$

From Eq. (2.6) it follows that

$$|\langle Sf,f\rangle_a| \le Kp(f,f) \tag{A4}$$

for $K = mx\{c_1 + c_2|1-E_0|, c_2\}$ and hence the form

$$q(f,g) = \langle Sf,g\rangle_a + (1+K)p(f,g) \tag{A5}$$

is positive, so that the Schwarz inequality holds

$$|q(f,g)| \le q(f,f)^{1/2} q(g,g)^{1/2} \ , \tag{A6}$$

where, by using Eq. (A4), one has that

$$\begin{aligned} q(f,f)^{1/2} &\le [|\langle Sf,f\rangle_a|(1+K)p(f,f)]^{1/2} \\ &\le [(2K+1)p(f,f)]^{1/2} \ . \end{aligned} \tag{A7}$$

From Eqs. (A5)–(A7) we obtain

$$|\langle Sf,g\rangle_a| \le (3K+2)p(f,f)^{1/2} p(g,g)^{1/2} \ ,$$

where $|p(f,g)| \le p(f,f)^{1/2} p(g,g)^{1/2}$ was used. This leads to

$$\begin{aligned} |\langle \delta\psi_n^{(i)}, S\psi_n^{(j)}\rangle_a| &\le (3K+2)p(\delta\psi_n^{(i)}, \delta\psi_n^{(i)})^{1/2} \\ &\quad \times p(\psi_n^{(j)}, \psi_n^{(j)})^{1/2} \ . \end{aligned} \tag{A8}$$

Since $\psi^{(i)}$ is an eigenfunction of H_a, one easily obtains

$$\begin{aligned} p(\delta\psi_n^{(i)}, \delta\psi_n^{(i)}) &= E_a(\psi_n^{(i)}) - E_a(\psi^{(i)}) \\ &\quad + [1 - E_0 + E_a(\psi^{(i)})]\|\delta\psi_n^{(i)}\|_a^2 \end{aligned}$$

and $p(\psi_n^{(j)}, \psi_n^{(j)}) = E_a(\psi_n^{(j)}) + 1 - E_0$. These equations, together with Eqs. (A1), (A2), and (A8), immediately lead to the assertion of Theorem 3.

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