Accurate computation of eigenfunctions for Schrödinger operators associated with Coulomb-type potentials

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A numerical method is developed to obtain convergence to the eigenfunctions of the Schrödinger operators associated to singular potentials whose asymptotic behavior is of the Coulomb type. The method consists in solving the Dirichlet problem in a box with radius n by the Ritz method, whose convergence to the eigenfunctions in the norm of the Hilbert space $L_2(0,n)$ is provided. Using a physical argument, we show that the solutions of the Dirichlet problem converge to those of the unbounded system in the norm of the Hilbert space $L_2(0,\infty)$ as $n\to\infty$. This last property guarantees the accurate computation of the expected values for a symmetric operator. The method is applied to the hydrogen atom, Yukawa potential, and Hulten potential; in each case we show the numerical convergence of the eigenfunctions, eigenvalues, and density moments.

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I. INTRODUCTION

In recent years some authors have applied Dirichlet boundary conditions to solve the Schrödinger equation. For example, Ley-Koo and Cruz [1] give the exact eigenfunctions of the ion H_2^+ and the hydrogen atom inside prolate spheroidal boxes, using a functional series, and show that some of the expected values approach those of the unbounded system as the volume of the box is increased. Gorecki and Byers [2] apply the iterative boundary perturbation theory to H_2^+. Marin and Cruz [3] assume a simple form of the eigenfunctions and solve for the hydrogen atom in boxes with finite radius. This last method is similar to the present method. In these works it has been observed that some expected values converge to those of the unbounded system as the boxes are expanded.

The present method guarantees the accurate calculation of the eigenfunctions of the problem

$$\mathcal{H}\psi=-\frac{1}{2}\frac{d^2}{dr^2}\psi+\left\{\frac{l(l+1)}{2r^2}+V(r)\right\}\psi=E\psi\ ,\quad \psi(0)=0 \tag{1.1}$$

for the potentials

$$V(r)=\frac{\chi(r)}{r}\ , \tag{1.2}$$

where $\chi(r)$ is a continuous and bounded function for $r\in[0,\infty)$. The method consists in solving the Dirichlet problem

$$\mathcal{H}_n^0\psi_n=-\frac{1}{2}\frac{d^2}{dr^2}\psi_n+\left\{\frac{l(l+1)}{2r^2}+V(r)\right\}\psi_n=E_n\psi_n\ ,\quad 0\le r\le n\ , \tag{1.3a}$$

with the boundary conditions

$$\psi_n(0)=\psi_n(n)=0 \tag{1.3b}$$

by the Ritz method, whose convergence to the eigenfunctions of $\mathcal{H}_n^0$ in the norm of $L_2(0,n)$ is guaranteed, and we show the convergence in norm of the eigenfunctions of each $\mathcal{H}_n^0$ to those of $\mathcal{H}$ as $n\to\infty$.

In Sec. II we introduce the norm convergence criterion and we show that it guarantees the accurate computation of expected values for a symmetric operator. The Cauchy criterion is especially important to check the convergence of the calculated eigenfunctions when the exact solution is unknown. In Sec. III we give a summary of the compactness condition necessary to assure the norm convergence of the Ritz method and we show that it is satisfied by the operator $\mathcal{H}_n^0$ for the potential (1.2). Using a physical argument we expose the result that guarantees the convergence in norm of the eigenfunctions of $\mathcal{H}_n^0$ to those of $\mathcal{H}$ as $n\to\infty$.

In Sec. IV we apply the method to the potentials

$$V_1(r)=-1/r\ \text{(Coulomb potential)}\ , \tag{1.4a}$$

$$V_2(r)=-e^{-\lambda r}/r\ \text{(Yukawa potential)}\ , \tag{1.4b}$$

$$V_3(r)=-\delta e^{-\delta r}/(1-e^{-\delta r})\ \text{(Hulten potential)}\ . \tag{1.4c}$$

These potentials are representative of the potential (1.2) because they have a simple pole in $r=0$ and are bounded in infinity. On the other hand, they have been studied by some authors in recent works. We use the hydrogen problem to give a method that optimizes the basis and obtain a fast convergence to a particular state. In this paper we shall use atomic units $\hbar=m=e=1$.

II. CONVERGENCE CRITERIA

A. Convergence in the norm of $L_2(0,\infty)$

The condition of normalization that the eigenfunctions must satisfy,

$$\int_0^\infty |\psi(r)|^2 dr = 1 \ , \tag{2.1}$$

sets the problem (1.1) in the Hilbert space $L_2(0,\infty)$ [4], endowed with the inner product

$$\langle f,g \rangle = \int_0^\infty f(r)g(r)dr \tag{2.2}$$

and the norm

$$\|f\| = \langle f,f \rangle^{1/2} \ . \tag{2.3}$$

The norm (2.3) gives a precise meaning to the idea of closeness between two functions $f,g \in L_2(0,\infty)$: we said that $f,g \in L_2(0,\infty)$ are close if their distance given by

$$d(f,g) = \|f-g\| \tag{2.4}$$

is small.

The formula of distance (2.4) introduces the following concept of convergence: the sequence $\{u_n\}_{n=1}^\infty$ in $L_2(0,\infty)$ converges to $u \in L_2(0,\infty)$ in the norm (2.3) if it satisfies

$$\lim_{n\to\infty} \|u_n - u\| = 0 \ . \tag{2.5}$$

The function u is called the *limit function* of $\{u_n\}$.

An equivalent concept of convergence is the Cauchy criterion: the sequence $\{u_n\}$ converges in the Cauchy sense if it satisfies

$$\lim_{n\to\infty} \|u_n - u_{n+1}\| = 0 \ . \tag{2.6}$$

It is well known that if $\{u_n\}$ converges in the Cauchy sense then there exists a unique function $u \in L_2(0,\infty)$ that is the limit of $\{u_n\}$ as is established by (2.5). This criterion has the following advantage: it does not depend on the limit function, hence we shall use it to verify the convergence in norm of a sequence of functions when the exact solutions of the problem (1.1) are unknown.

B. Convergence to the expected values

The convergence in norm is important because it guarantees the accurate computation of the expected values of a symmetric operator, as is established in the following proposition.

Proposition (2.1). Suppose that ψ and ψ_n belong to $L_2(0,\infty)$, with arbitrary n, and S is a symmetric operator. If the sequence $\{\psi_n\}$ converges to ψ in the norm of $L_2(0,\infty)$ then the numerical sequence $\{\langle \psi_n, S\psi_m \rangle\}$ converges to $\langle \psi, S\psi \rangle$:

$$\lim_{m\to\infty}\lim_{n\to\infty} \langle \psi_n, S\psi_m \rangle = \langle \psi, S\psi \rangle \ .$$

Proof. If we apply the Schwarz inequality [it is satisfied by the elements of $L_2(0,\infty)$]

$$|\langle f,g \rangle| \le \|f\|\|g\|$$

we have

$$|\langle \psi_n, S\psi_m \rangle - \langle \psi, S\psi_m \rangle| = |\langle \psi_n - \psi, S\psi_m \rangle| \le \|\psi_n - \psi\|\|S\psi_m\| \ .$$

TABLE I. Convergence of the sequence $\{\psi_{n,m}^{(i)}(\alpha=1,r)\}$ to the exact solutions for the hydrogen atom with $l=0$, Eq. (4.7); n defines the interval $[0,n]$ and m is the number of base functions (4.4) used to compute $\psi_{n,m}^{(i)}$. Exponential notation is used so that [1] means the number preceding is to be multiplied by 10^1.

$[n,m]$	$\|\psi_{n,m}^{(1)} - \psi_{\text{exac}}^{(1)}\|$ State 1s	$\|\psi_{n,m}^{(2)} - \psi_{\text{exac}}^{(2)}\|$ State 2s	$\|\psi_{n,m}^{(3)} - \psi_{\text{exac}}^{(3)}\|$ State 3s
[4,4]	0.165[0]	0.168[1]	0.136[1]
[11,7]	0.482[−3]	0.265[0]	0.116[1]
[18,10]	0.928[−6]	0.270[−1]	0.584[0]
[25,13]	0.500[−7]	0.196[−2]	0.208[0]
[32,16]	0.500[−8]	0.126[−3]	0.561[−1]

Since $\lim_{n\to\infty}\|\psi_n - \psi\| = 0$ we obtain

$$\lim_{n\to\infty} \langle \psi_n, S\psi_m \rangle = \langle \psi, S\psi_m \rangle \ .$$

Now using the symmetry of S,

$$\langle \psi, S\psi_m \rangle = \langle S\psi, \psi_m \rangle \ ,$$

and using Schwarz inequality as above we have

$$\lim_{m\to\infty} \langle S\psi, \psi_m \rangle = \langle S\psi, \psi \rangle \ .$$

From this the assertion follows. QED

In this work we show that the present method provides sequences $\{\psi_n\}$ that converge to the eigenfunctions of $\mathcal{H}$ in the norm of $L_2(0,\infty)$. This guarantees the accurate computation of expected values such as the energy levels and the density moments.

III. METHOD OF CALCULATION

A. Convergence of the Ritz method

For clarity we shall give a brief summary of the Ritz method. It consists in approaching the exact eigenfunctions of $\mathcal{H}$, which we denote $\psi_{\text{exac}}^{(i)}$ for the ith state, by the functions

$$f_m^{(i)}(r) = \sum_{k=1}^m c_k^{(i)} \phi_k(r) \ , \tag{3.1}$$

where $\{\phi_k\}_{k=1}^\infty$ is an orthonormal basis of $L_2(0,\infty)$. The

TABLE II. Convergence of the eigenvalues (in a.u.), for the hydrogen atom, $\{E_{n,m}^{(i)}(\alpha=1)\}$, associated to the eigenfunctions of Table I.

$[n,m]$	$-E_{n,m}^{(1)}$ State 1s	$-E_{n,m}^{(2)}$ State 2s	$-E_{n,m}^{(3)}$ State 3s
[4,4]	0.483	−0.42	−1.98
[11,7]	0.499 999 845	0.118	−0.057
[18,10]	0.499 999 999 999 46	0.124 914	0.042
[25,13]	0.500 000 000 000 000	0.124 999 47	0.054
[32,16]	same	0.124 999 997 6	0.055 43
exact[a]	0.500	0.125	0.055 556

[a]Exact eigenvalues.

TABLE III. Convergence of some density moments (in a.u.) for the hydrogen atom, corresponding to the sequence $\{\psi^{(1)}_{n,m}(\alpha=1,r)\}$ of Table I, state 1s, Eq. (4.10).

$[n,m]$	$\langle r^{-2}\rangle$	$\langle r^{-1}\rangle$	$\langle r^{2}\rangle$
[4,4]	2.200 5	1.068	2.27
[11,7]	2.000 058	1.000 000 27	2.999 85
[18,10]	1.999 999 904	1.000 000 000 017	2.999 999 997 8
[25,13]	2.000 000 000 14	1.000 000 000 000	3.000 000 000 000
[32,16]	1.999 999 999 932	same	same
exact[a]	2.0	1.0	3.0

[a]Exact moments.

TABLE IV. Convergence of the sequence $\{\psi^{(i)}_{n,m}(\alpha,r)\}$ in the Cauchy sense for the hydrogen atom, Eq. (4.8), n defines the interval $[0,n]$ and m is the number of base functions (4.4) used to compute $\psi^{(i)}_{n,m}$, Δn is the increment of the interval $[0,n]$, and α is the exponent of the basis (4.4). The notation [1] signifies $\times 10^1$.

Δn	α	$[k,j]$	$[n,m]$	$\|\psi^{(1)}_{k,j}-\psi^{(1)}_{n,m}\|$	$\|\psi^{(2)}_{k,j}-\psi^{(2)}_{n,m}\|$	$\|\psi^{(3)}_{k,j}-\psi^{(3)}_{n,m}\|$
				State 2p	State 3p	State 4p
7	1.0	[4,4]	[11,7]	0.941[0]	0.134[1]	0.139[1]
		[11,7]	[18,10]	0.183[0]	0.886[0]	0.138[1]
		[18,10]	[25,13]	0.173[−1]	0.414[0]	0.951[0]
		[25,13]	[32,16]	0.122[−2]	0.147[0]	0.610[0]
20	1.0	[4,4]	[24,7]	0.977[0]	0.133[1]	0.139[1]
		[24,7]	[44,10]	0.375[−1]	0.568[0]	0.112[1]
		[44,10]	[64,13]	0.222[−2]	0.220[0]	0.719[0]
		[64,13]	[84,16]	0.126[−3]	0.644[−1]	0.456[0]
20	0.5	[4,4]	[24,7]	0.978[0]	0.135[1]	0.139[1]
		[24,7]	[44,10]	0.157[−2]	0.188[0]	0.921[0]
		[44,10]	[64,13]	0.640[−6]	0.400[−2]	0.206[0]
		[64,13]	[84,16]	0.635[−7]	0.653[−4]	0.238[−1]
				State 3d	State 4d	State 5d
20	0.333	[4,3]	[24,6]	0.134[1]	0.137[1]	0.138[1]
		[24,6]	[44,9]	0.977[−1]	0.758[0]	0.137[1]
		[44,9]	[64,12]	0.819[−3]	0.804[−1]	0.602[0]
		[64,12]	[84,15]	0.378[−5]	0.293[−2]	0.118[0]

TABLE V. Some eigenvalues $E^{(i)}_{n,m}(\alpha)$ (in a.u.), for the hydrogen atom, corresponding to the eigenfunctions $\psi^{(i)}_{n,m}(\alpha,r)$ of Table IV.

α	$[n,m]$	$-E^{(1)}_{n,m}$	$-E^{(2)}_{n,m}$	$-E^{(3)}_{n,m}$
		State 2p	State 3p	State 4p
1.0	[32,16]	0.124 999 999 1	0.055 473	0.025 7
1.0	[84,16]	0.124 999 999 990	0.055 543	0.028 7
0.5	[84,16]	0.125 000 000 000 00	0.055 555 555 07	0.031 249 8
exact[a]		0.125	0.055 555 555 556	0.31 25
		State 3d	State 4d	State 5d
0.333	[84,15]	0.055 555 555 554 99	0.031 249 999 86	0.019 998 5
exact[a]		0.055 555 555 555 56	0.031 25	0.020

[a]Exact eigenvalues.

TABLE VI. Some moments (in a.u.), for the hydrogen atom, corresponding to the eigenfunctions $\psi^{(1)}_{n,m}(\alpha,r)$ of Table IV, Eq. (4.10).

α	$[n,m]$	$\langle r^{-2}\rangle$	$\langle r^{-1}\rangle$	$\langle r^{2}\rangle$
		State $2p$		
1.0	[32,16]	0.083 333 350	0.250 000 023	29.999 956
1.0	[84,16]	0.083 333 335 3	0.250 000 000 28	29.999 999 18
0.5	[84,16]	0.083 333 333 334	0.250 000 000 00	30.000 000 000
exact[a]		0.083 333 333 333	0.250 000 000 00	30.000 000 000
		State $3d$		
0.333	[84,15]	0.014 814 814 815	0.111 111 111 11	126.000 000 000
exact[a]		0.014 814 814 815	0.111 111 111 11	126.0

[a]Exact moments.

coefficients $c_k^{(i)}$ and the eigenvalue $E_m^{(i)}$ associated to $f_m^{(i)}$ satisfy the equation

$$\sum_{k=1}^{m}\{\langle\phi_k,\mathcal{H}\phi_j\rangle-E_m^{(i)}\delta_{kj}\}c_k^{(i)}=0\ ,\quad 1\le j\le m\ . \tag{3.2}$$

The theory of operators in Hilbert spaces gives sufficient conditions for the operator $\mathcal{H}$ in order to guarantee the convergence of the sequence $\{f_m^{(i)}\}$ in the norm of $L_2(0,\infty)$ to the exact eigenfunction $\psi^{(i)}_{\text{exac}}$ as $m\to\infty$; it is established by the following theorem. The spectrum of the operator T is denoted by $\sigma(T)$.

Theorem (3.1). Let T be a Schrödinger operator whose resolvent $(T-z)^{-1}$, for $z\notin\sigma(T)$, is a *compact operator* in the Hilbert space $\mathbb{H}$. Then the sequence $\{f_m^{(i)}\}$, calculated by the Ritz method, converges to the eigenfunction $\psi^{(i)}_{\text{exac}}$ of T in the norm of $\mathbb{H}$ [5].

Instead of defining the concept of compact operator, we give a necessary condition for the operator T in order to have a compact resolvent [6].

Proposition (3.2). Let T be an operator whose resolvent $(T-z)^{-1}$, $z\notin\sigma(T)$, is a compact operator. Then the spectrum $\sigma(T)$ consists only of isolated eigenvalues with finite multiplicity [7].

Proposition (3.2) gives the following rule for showing that an operator has noncompact resolvent.

Corollary (3.3). Assume that the operator T has a nonempty continuous spectrum. Then the resolvent $(T-z)^{-1}$ *is not compact.*

It is well known that the Schrödinger operator $\mathcal{H}$ defined by the problem (1.1) has the continuous spectrum $[0,\infty)$ for the potentials (1.2), hence the convergence of the Ritz method is not secured.

The key of the present method consists in replacing the problem (1.1) by the computation of the eigenfunctions of $\mathcal{H}_n^0$ [associated to the Dirichlet problem (1.3)] whose resolvent $\mathcal{R}_n^0(z)=(\mathcal{H}_n^0-z)^{-1}$ *is compact* in the Hilbert space $L_2(0,n)$ for the potentials (1.2), as we show in Sec. III D. Therefore we can compute the eigenfunctions of $\mathcal{H}_n^0$ with the desired accuracy.

Now using the physical intuition it is clear that the bounded states of $\mathcal{H}_n^0$ are similar to those of $\mathcal{H}$ if the dimensions of the interval $[0,n]$ are greater than the physical dimensions of the unbounded system. Therefore, if the interval $[0,n]$ is expanded as $n\to\infty$, we obtain sequences of approximate eigenfunctions that converge in the norm of $L_2(0,\infty)$ to the eigenfunctions of $\mathcal{H}$. This is explained in the following subsections.

B. Numerical solution of the Dirichlet problem

The inner product and the norm of $L_2(0,n)$ [4] are given by

$$\langle f,g\rangle_{(n)}=\int_0^n f(r)g(r)dr \text{ and } \|f\|_{(n)}=\langle f,f\rangle_{(n)}^{1/2}\ . \tag{3.3}$$

We denote by $\psi_n^{(i)}$ the exact eigenfunction of $\mathcal{H}_n^0$ associated to the ith state. Using the Ritz method, the approximate eigenfunctions of $\mathcal{H}_n^0$ are given by

$$\psi^{(i)}_{n,m}(r)=\sum_{k=1}^{m}c_k^{(i)}\phi_{nk}(r)\ , \tag{3.4}$$

where $\{\phi_{nk}(r)\}_{k=1}^{\infty}$ is an orthonormal basis of $L_2(0,n)$ that satisfies the boundary conditions of Dirichlet type,

TABLE VII. Convergence of the sequence $\{\psi^{(i)}_{n,m}(\alpha=1,r)\}$ in the Cauchy sense for the Yukawa potential with $l=0$ and $\lambda=0.10$, Eq. (4.8); n defines the interval $[0,n]$, m is the number of base functions (4.4) used to compute $\psi^{(i)}_{n,m}(\alpha=1,r)$ by the Ritz method, and α is the exponent of the basis (4.4). The notation $[-6]$ signifies $\times10^{-6}$.

$[k,j]$	$[n,m]$	$\|\psi^{(1)}_{k,j}-\psi^{(1)}_{n,m}\|$ State $1s$	$\|\psi^{(2)}_{k,j}-\psi^{(2)}_{n,m}\|$ State $2s$
[4,4]	[24,7]	0.171[0]	0.119[1]
[24,7]	[44,10]	0.721[−6]	0.108[0]
[44,10]	[64,13]	0.289[−7]	0.149[−1]

TABLE VIII. Convergence of the eigenvalues $E^{(i)}_{n,m}(\alpha=1)$ (in a.u.) corresponding to the eigenfunctions of Table VII, for the Yukawa potential with $l=0$ and $\lambda=0.10$.

$[n,m]$	$-E^{(1)}_{n,m}$ State $1s$	$-E^{(2)}_{n,m}$ State $2s$
[4,4]	0.389	−0.519 111
[24,7]	0.407 058 030 613 07	0.048 92
[44,10]	0.407 058 030 613 401	0.049 907
[64,13]	0.407 058 030 613 403	0.049 927 83

TABLE IX. Convergence of some density moments (in a.u.) corresponding to the sequence $\{\psi^{(1)}_{n,m}(\alpha=1,r)\}$ of Table VII (state 1s), Eq. (4.10).

$[n,m]$	$\langle r^{-2}\rangle$	$\langle r^{-1}\rangle$	$\langle r^{2}\rangle$
[4,4]	2.189	1.065	2.283
[24,7]	1.977 627 26	0.993 305 635 871	3.059 907 685
[44,10]	1.977 627 027 39	0.993 305 635 856	3.059 907 688 608
[64,13]	1.977 627 027 42	same	same

$$\phi_{nk}(0)=\phi_{nk}(n)=0 \ , \tag{3.5}$$

and the coefficients $c^{(i)}_k$ and the eigenvalue $E^{(i)}_{n,m}$ associated to $\psi^{(i)}_{n,m}$ are solutions of the equation

$$\sum_{k=1}^{m}\{\langle\phi_{nk},\mathcal{H}^0_n\phi_{nj}\rangle_{(n)}-E^{(i)}_{n,m}\delta_{kj}\}c^{(i)}_k=0 \ , \quad 1\le j\le m \ . \tag{3.6}$$

According to Theorem (3.1), the *compactness* of the resolvent $\mathcal{R}^0_n(z)$ in $L_2(0,n)$ implies the convergence of the sequence $\{\psi^{(i)}_{n,m}\}^{\infty}_{m=1}$ to the exact eigenfunctions $\psi^{(i)}_n$ in the norm of $L_2(0,n)$:

$$\lim_{m\to\infty}\|\psi^{(i)}_{n,m}-\psi^{(i)}_n\|_{(n)}=0 \ . \tag{3.7}$$

C. Convergence to the eigenfunctions of the unbounded system

Now we study the convergence of the solutions of the Dirichlet problem to those of the unbounded system. If we identify each function $f\in L_2(0,n)$ with the element in $L_2(0,\infty)$ given by

$$\hat{f}=\begin{cases} f(r) & \text{for } 0\le r\le n \\ 0 & \text{otherwise}\end{cases} \tag{3.8}$$

we can apply to the solutions of the Dirichlet problem the rules of convergence in $L_2(0,\infty)$. When we speak of $\psi^{(i)}_n$ and $\psi^{(i)}_{n,m}$ as elements of $L_2(0,\infty)$ we understand the functions defined by (3.8).

The first result that we have is the convergence of $\{\psi^{(i)}_{n,m}\}$ to $\psi^{(i)}_n$ in the norm of $L_2(0,\infty)$.

Proposition (3.4). Suppose that the eigenfunctions $\psi^{(i)}_n$ of $\mathcal{H}^0_n$ and the approximate functions $\psi^{(i)}_{n,m}$ (3.4) are identified as elements of $L_2(0,\infty)$ using (3.8). Then the sequence $\{\psi^{(i)}_{n,m}\}_m$ converges to $\psi^{(i)}_n$ in the norm of $L_2(0,\infty)$.

Proof. The definition (3.8) implies that the inner product $\langle\ ,\ \rangle_{(n)}$ of $L_2(0,n)$ is the restriction of the inner product $\langle\ ,\ \rangle$ of $L_2(0,\infty)$ to the interval $[0,n]$, so we have

$$\begin{aligned}\langle\psi^{(i)}_{n,m}-\psi^{(i)}_n,\psi^{(i)}_{n,m}-\psi^{(i)}_n\rangle&=\int_0^{\infty}|\psi^{(i)}_{n,m}-\psi^{(i)}_n|^2dr\\&=\int_0^{n}|\psi^{(i)}_{n,m}-\psi^{(i)}_n|^2dr\\&=\langle\psi^{(i)}_{n,m}-\psi^{(i)}_n,\psi^{(i)}_{n,m}-\psi^{(i)}_n\rangle_{(n)}\end{aligned}$$

hence $\lim_{m\to\infty}\|\psi^{(i)}_{n,m}-\psi^{(i)}_n\|=\lim_{m\to\infty}\|\psi^{(i)}_{n,m}-\psi^{(i)}_n\|_{(n)}=0$. QED

The fundamental result of the present method, that the physical intuition supports, is the following one.

Theorem (3.5). Assume that each eigenfunction $\psi^{(i)}_n$ of the Dirichlet problem in the interval $[0,n]$ is identified as an element of $L_2(0,\infty)$ using (3.8). If the interval $[0,n]$ is expanded as $n\to\infty$, then the sequence $\{\psi^{(i)}_n\}^{\infty}_{n=1}$ converges to the eigenfunction $\psi^{(i)}_{\text{exac}}$ of the unbounded system in the norm of $L_2(0,\infty)$.

The proof of Theorem (3.5) can be found in [8,9]. Using this theorem we shall prove the convergence in norm of the sequence $\{\psi^{(i)}_{n,m}\}$, computed by the Ritz method, to the eigenfunction $\psi^{(i)}_{\text{exac}}$.

Theorem (3.6). Let the approximate solution $\psi^{(i)}_{n,m}$ (3.4) to the Dirichlet problem be identified as an element of $L_2(0,\infty)$ using (3.8). If the interval $[0,n]$ is expanded as $n\to\infty$ then the sequence $\{\psi^{(i)}_{n,m}\}$ converges to the exact eigenfunction $\psi^{(i)}_{\text{exac}}$ of $\mathcal{H}$ in the norm of $L_2(0,\infty)$.

Proof. If we use the triangle inequality

$$\|\psi^{(i)}_{n,m}-\psi^{(i)}_{\text{exac}}\|\le\|\psi^{(i)}_{n,m}-\psi^{(i)}_n\|+\|\psi^{(i)}_n-\psi^{(i)}_{\text{exac}}\| \ ,$$

and both results Proposition (3.4) and Theorem (3.5),

TABLE X. Accuracy of the eigenfunctions $\psi^{(i)}_{n,m}(\alpha,r)$ for the Yukawa potential, Eq. (4.9); n defines the interval $[0,n]$, m is the number of base functions (4.4) (whose exponent is α) used to solve the Dirichlet problem (4.14) by the Ritz method. The notation $[-7]$ signifies $\times 0^{-7}$.

State	λ	α	$[k,j]$	$[n,m]$	$\|\Delta\psi_{n,m}\|$
1s	0.02	1.0	[34,10]	[49.13]	0.483[−7]
	0.04	0.96	[34,10]	[49,13]	0.500[−7]
	0.06	0.94	[34,10]	[49,13]	0.553[−7]
	0.08	0.92	[34,9]	[49,12]	0.500[−7]
	0.10	1.0	[44,10]	[64,13]	0.289[−7]
	0.20	1.0	[44,10]	[64,13]	0.305[−7]
	0.50	1.0	[64,13]	[84,16]	0.896[−7]
2s	0.02	0.46	[49,13]	[64,16]	0.784[−7]
	0.04	0.42	[49,12]	[64,15]	0.210[−6]
	0.06	0.39	[49,12]	[64,15]	0.187[−6]
	0.08	0.35	[49,12]	[64,15]	0.170[−5]
	0.10	0.316	[64,13]	[84,16]	0.918[−5]
2p	0.02	0.46	[44,10]	[64,13]	0.573[−6]
	0.04	0.42	[44,10]	[64,13]	0.854[−6]
	0.06	0.38	[44,10]	[64,13]	0.163[−5]
	0.08	0.38	[44,10]	[64,13]	0.489[−5]
	0.10	0.305	[64,12]	[84,15]	0.207[−4]

TABLE XI. Some eigenvalues (in a.u.), for the Yukawa potential, corresponding to the eigenfunctions $\psi^{(i)}_{n,m}(\alpha,r)$ of Table X.

State	λ	α	$[n,m]$	$-E^{(i)}_{n,m}(\alpha)$ This work	$-E^{(i)}_{n,m}(\alpha)$ Vrscay (Ref. [12])
1s	0.02	1.0	[49,13]	0.480 296 105 983 78	
	0.04	0.96	[49,13]	0.461 169 636 813 34	
	0.06	0.94	[49,13]	0.442 600 011 473 91	
	0.08	0.92	[49,12]	0.424 568 516 210 45	
	0.10	1.0	[64,13]	0.407 058 030 613 40	0.407 058 030 613 403
	0.20	1.0	[64,13]	0.326 808 511 369 19	0.326 808 511 369 193
	0.50	1.0	[84,16]	0.148 117 021 889 93	0.148 117 021 889 932
2s	0.02	0.46	[64,16]	0.106 148 320 244 70	0.106 148 320 244 695
	0.04	0.42	[64,15]	0.089 414 634 185 15	0.089 414 634 185 159
	0.06	0.39	[64,15]	0.074 578 534 412 68	0.074 578 534 412 709
	0.08	0.35	[64,15]	0.061 464 656 212 24	0.061 464 656 212 300
	0.10	0.316	[84,16]	0.049 928 271 339	0.049 928 271 331 918
2p	0.02	0.46	[64,13]	0.105 963 398 179 94	0.105 963 398 179 939
	0.04	0.42	[64,13]	0.088 729 373 582 88	0.088 729 373 582 879
	0.06	0.38	[64,13]	0.073 149 619 385 86	0.073 149 619 385 860
	0.08	0.38	[64,13]	0.059 112 804 787 02	0.059 112 804 787 031
	0.10	0.305	[84,15]	0.046 534 390 489	0.046 534 390 486 724

$$\lim_{m\to\infty}\|\psi^{(i)}_{n,m}-\psi^{(i)}_n\|=\lim_{n\to\infty}\|\psi^{(i)}_n-\psi_{\text{exac}}\|=0\ ,$$

we have $\lim_{n\to\infty}\lim_{m\to\infty}\|\psi^{(i)}_{n,m}-\psi^{(i)}_{\text{exac}}\|=0$. QED

D. Compactness of the resolvent $(\mathcal{H}^0_n-z)^{-1}$

The theory of elliptic operators provides two conditions on the operator $\mathcal{H}^0_n$ to have a compact resolvent in $L_2(0,n)$. These conditions are defined below [10]. The operator $\mathcal{H}^0_n$ defines the sesquilinear form $h(u,v)$ given by

$$h(u,w)=\left\langle\frac{du}{dr},\frac{dw}{dr}\right\rangle_{(n)}+l(l+1)\langle r^{-2}u,w\rangle_{(n)}+2\langle Vu,w\rangle_{(n)}\ . \tag{3.9}$$

Definition 1. The sesquilinear form $h(\ ,\ )$ is bounded in the norm

$$\|f\|_1=\left\{\|f\|^2_{(n)}+\left|\left|\frac{df}{dr}\right|\right|^2_{(n)}\right\}^{1/2} \tag{3.10}$$

TABLE XII. Density first moments (in a.u.), for the Yukawa potential, corresponding to eigenfunctions $\psi^{(i)}_{n,m}(\alpha,r)$ of Table X, Eq. (4.10).

State	λ	$\langle r^{-2}\rangle$	$\langle r^{-1}\rangle$	$\langle r\rangle$	$\langle r^2\rangle$
1s	0.02	1.999 024 308	0.999 707 629	1.500 583 121	3.002 620 149
	0.04	1.996 187 010	0.998 858 344	1.502 273 030	3.010 205 192
	0.06	1.991 608 142	0.997 488 627	1.504 996 133	3.022 426 518
	0.08	1.985 391 362	0.995 629 097	1.508 696 004	3.039 048 054
	0.10	1.977 627 027	0.993 305 635	1.513 329 978	3.059 907 688
	0.20	1.918 078 726	0.975 394 751	1.549 721 903	3.225 939 441
	0.50	1.576 322 996	0.867 533 084	1.806 554 897	4.533 129 691
2s	0.02	0.247 979 610	0.248 897 280	6.024 283 048	42.357 585 333
	0.04	0.242 495 931	0.245 889 013	6.091 502 572	43.354 356 529
	0.06	0.234 195 36	0.241 286 827	6.197 625 895	44.953 167 05
	0.08	0.223 535 92	0.235 283 436	6.342 688 029	47.191 695 36
	0.10	0.210 862	0.227 996 339	6.529 952 28	50.175 252 1
2p	0.02	0.082 773 742	0.249 068 096	5.022 341 63	30.290 385 15
	0.04	0.081 220 804	0.246 471 505	5.085 323 95	31.115 305 12
	0.06	0.078 806 16	0.242 391 076	5.187 175 10	32.473 488 0
	0.08	0.075 609 41	0.236 896 235	5.330 675 61	34.441 348 8
	0.10	0.071 672 71	0.229 967 849	5.523 282 98	37.186 451

if there exists a constant $k \geq 0$ such that

$$|h(u,u)| \leq k\|u\|_1^2 \tag{3.11}$$

is satisfied for each $u \in W_1^0(0,n)$, where $W_1^0(0,n)$ is a Sobolev space [also denoted by $H_1^0(0,n)$].

Definition 2. The form $h(\ ,\ )$ is coercive (or elliptic) if there exist two constants $\alpha > 0$ and $\mu \in R$ such that

$$h(u,u) \geq \alpha\|u\|_1^2 - \mu\|u\|_{(n)}^2 \tag{3.12}$$

is satisfied for each $u \in W_1^0(0,n)$. The basic result that the theory provides follows.

Theorem (3.7). Let $\mathcal{H}_n^0$ be the operator defined by the Dirichlet problem (1.3). If the form $h(\ ,\ )$ satisfies both (3.11) and (3.12) then the operator $\mathcal{H}_n^0$ has a compact resolvent in $L_2(0,n)$.

We shall show that $h(\ ,\ )$ satisfies both (3.11) and (3.12) for the potentials (1.2) and $l=0$. In the Appendix we demonstrate that for each $\varepsilon > 0$ there exists a constant $C_\epsilon > 0$ such that

$$|2\langle Vu,u\rangle_{(n)}| \leq C_\epsilon\|u\|_{(n)}^2 + \epsilon\left\|\frac{du}{dr}\right\|_{(n)}^2 . \tag{3.13}$$

The condition (3.11) follows from (3.13):

$$\begin{aligned} |h(u,u)| &\leq \left\|\frac{du}{dr}\right\|_{(n)}^2 + |2\langle Vu,u\rangle_{(n)}| \\ &\leq \left\|\frac{du}{dr}\right\|_{(n)}^2 + C_\epsilon\|u\|_{(n)}^2 + \epsilon\left\|\frac{du}{dr}\right\|_{(n)}^2 \\ &\leq k\|u\|_1^2 , \end{aligned}$$

where $k = \max\{C_\epsilon, 1+\epsilon\} \geq 0$. The condition (3.12) also follows from (3.13); this implies

$$-\epsilon\left\|\frac{du}{dr}\right\|_{(n)}^2 - C_\epsilon\|u\|_{(n)}^2 \leq 2\langle Vu,u\rangle_{(n)} .$$

Now if we take $0 < \epsilon < 1$ then

$$\left\|\frac{du}{dr}\right\|_{(n)}^2 (1-\epsilon) - C_\epsilon\|u\|_{(n)}^2 \leq 2\langle Vu,u\rangle_{(n)} + \left\|\frac{du}{dr}\right\|_{(n)}^2 ,$$

$$\left\{\left\|\frac{du}{dr}\right\|_{(n)}^2 + \|u\|_{(n)}^2\right\}(1-\epsilon) - (C_\epsilon + 1 - \epsilon)\|u\|_{(n)}^2 \leq h(u,u) ,$$

therefore

$$\|u\|_1^2(1-\epsilon) - (C_\epsilon + 1 - \epsilon)\|u\|_{(n)}^2 \leq h(u,u) .$$

IV. NUMERICAL EXAMPLES

A. Selection of the basis. Formulas to measure convergence and exactness of eigenfunctions

To solve the Dirichlet problem (1.3) by the Ritz method we have the basis of $L_2(0,n)$,

TABLE XIII. Convergence of the sequence $\{\psi_{n,m}^{(i)}(\alpha=0.47489,r)\}$ in the Cauchy sense for the Hulten potential with $l=0$ and $\delta=0.025$, Eq. (4.8); n defines the interval $[0,n]$, m is the number of base functions (4.4) (whose exponent is α) used to compute $\psi_{n,m}^{(i)}(\alpha,r)$ by the Ritz method. The notation $[-7]$ signifies $\times 10^{-7}$.

$[k,j]$	$[n,m]$	$\|\psi_{k,j}^{(1)} - \psi_{n,m}^{(1)}\|$ State $2p$	$\|\psi_{k,j}^{(2)} - \psi_{n,m}^{(2)}\|$ State $3p$
[4,4]	[19,7]	0.978[0]	0.134[1]
[19,7]	[34,10]	0.960[−2]	0.394[0]
[34,10]	[49,13]	0.204[−4]	0.203[−1]
[49,13]	[64,16]	0.435[−7]	0.550[−3]

$$\xi_{nk}(r) = r(n-r)r^{k-1} = (n-r)r^k , \quad k = 1,2,3,\ldots , \tag{4.1}$$

which satisfies the boundary conditions (3.5).

On the other hand, it is well known that the asymptotic behavior of the eigenfunctions of (1.1) is given by

$$\psi_{\text{exac}}^{(i)} \sim \exp(-\alpha_{\text{exac}}^{(i)} r) , \tag{4.2}$$

where the exponent

$$\alpha_{\text{exac}}^{(i)} = \{2|E_{\text{exac}}^{(i)}|\}^{1/2} \tag{4.3}$$

is *a priori* unknown. Therefore we multiply the basis (4.1) by the factor $e^{-\alpha r}$, where $\alpha > 0$ is an arbitrary parameter. This gives the new basis of $L_2(0,n)$,

$$\varphi_{nk}(\alpha,r) = e^{-\alpha r}(n-r)r^k , \quad k = 1,2,\ldots , \tag{4.4}$$

which is successively orthonormalized by the Gram-Schmidt method, with the inner product (3.3), to obtain an orthonormal basis that we shall denote by $\{\phi_{nk}(\alpha,r)\}$. As both the approximate eigenfunctions and eigenvalues depend on the exponent α, by the basis (4.4), we denote these by $\psi_{n,m}^{(i)}(\alpha,r)$ and $E_{n,m}^{(i)}(\alpha)$.

Remark. For each $\alpha > 0$ the set (4.4) is a basis of $L_2(0,n)$, hence the Ritz method *always converges* to the eigenfunctions $\psi_n^{(i)}$ of $\mathcal{H}_n^0$. This permits us to apply the Ritz method for arbitrary α, for example $\alpha = 1$, and to compute an approximate eigenvalue $E_{n,m}^{(i)}(\alpha)$ which is used in a new basis (4.4) with $\alpha_2 = \{2|E_{n,m}^{(i)}(\alpha)|\}^{1/2}$ to obtain a fast convergence with the same number of base functions. An example of this is found in the hydrogen atom problem in the next subsection.

TABLE XIV. Convergence of the eigenvalues $E_{n,m}^{(i)}(\alpha=0.47489)$ (in a.u.) corresponding to the eigenfunctions of Table XIII for the Hulten potential with $l=1$ and $\delta=0.025$.

$[n,m]$	$-E_{n,m}^{(1)}$ State $2p$	$-E_{n,m}^{(2)}$ State $3p$
[4,4]	−0.156	−1.31
[19,7]	0.112 748	0.038 99
[34,10]	0.112 760 465 50	0.043 688
[49,13]	0.112 760 465 559 344	0.043 706 876
[64,16]	0.112 760 465 559 345	0.043 706 892

TABLE XV. Convergence of some moments (in a.u.) for the Hulten potential, corresponding to the sequence $\{\psi^{(1)}_{n,m}(\alpha=0.474\,89,r)\}$ of Table XIII, state $2p$.

$[n,m]$	$\langle r^{-2}\rangle$	$\langle r^{-1}\rangle$	$\langle r^{2}\rangle$
[4,4]	0.319	0.517	5.18
[19,7]	0.083 25	0.249 90	29.948
[34,10]	0.083 176 990	0.249 739 275	30.081 520 0
[49,13]	0.083 176 977 839	0.249 739 273 381	30.081 523 660 03
[64,16]	0.083 176 977 847	same	30.081 523 660 05

According to Theorem (3.6), the precise computation of the eigenfunctions $\psi^{(i)}_n$ of the Dirichlet problem for fixed n is not sufficient to approach the eigenfunction $\psi^{(i)}_{\text{exac}}$ of the unbounded system; we also must increase the value n. To reduce the computation of $\psi^{(i)}_{n,m}$ with a large basis $\{\varphi_{nk}\}_{k=1}^{m}$ in each interval $[0,n]$ we increase the basis as n grows:

$$m(n)\to\infty \quad \text{as} \quad n\to\infty \ . \tag{4.5}$$

Theorem (4.1). Suppose that the number of base functions $\{\varphi_{nk}\}_{k=1}^{m}$ is increased as the interval $[0,n]$ is expanded, as is established in (4.5). Then the sequence $\{\psi^{(i)}_{n,m(n)}\}_n$ of approximate eigenfunctions (3.4) converges to $\psi^{(i)}_{\text{exac}}$ in the norm of $L_2(0,\infty)$:

$$\lim_{n\to\infty}\|\psi^{(i)}_{n,m(n)}-\psi^{(i)}_{\text{exac}}\|=0 \ .$$

The idea of the proof of Theorem (4.1) is the same as that of Theorem (3.6), except that now we use $\lim_{n\to\infty}\|\psi^{(i)}_{n,m(n)}-\psi^{(i)}_{n}\|=0$.

In all the calculations, both the approximate eigenfunctions $\psi^{(i)}_{n,m(n)}$ and the exact $\psi^{(i)}_{\text{exac}}$ (in the case of the hydrogen atom) are normalized:

$$\int_0^n|\psi^{(i)}_{n,m}|^2dr=\int_0^\infty|\psi^{(i)}_{n,m}|^2dr=\int_0^\infty|\psi^{(i)}_{\text{exac}}|^2dr=1 \ . \tag{4.6}$$

The convergence to the exact solutions is measured by

$$\|\psi^{(i)}_{n,m(n)}-\psi^{(i)}_{\text{exac}}\|=\left\{2\left[1-\int_0^n\psi^{(i)}_{n,m(n)}\psi^{(i)}_{\text{exac}}dr\right]\right\}^{1/2} \tag{4.7}$$

and for the convergence in the Cauchy sense we have

$$\|\psi^{(i)}_{k,j(k)}-\psi^{(i)}_{n,m(n)}\|=\left\{2\left[1-\int_0^{\min(k,n)}\psi^{(i)}_{k,j(k)}\psi^{(i)}_{n,m(n)}dr\right]\right\}^{1/2} . \tag{4.8}$$

If the sequence $\{\psi^{(i)}_{n,m}\}$ converges to $\psi^{(i)}_{\text{exac}}$ then (4.7) gives the accuracy of each $\psi^{(i)}_{n,m}$, but when the exact solution is unknown we define the accuracy of $\psi^{(i)}_{n,m}$ as the distance between it and the function from the previous computation:

$$\|\Delta\psi^{(i)}_{n,m}\|=\|\psi^{(k)}_{k,j(k)}-\psi^{(i)}_{n,m(n)}\| \ . \tag{4.9}$$

For the computation of the density moments we use

$$\langle r^k\rangle=\int_0^\infty|\psi^{(i)}_{n,m}|^2r^kdr=\int_0^n|\psi^{(i)}_{n,m}|^2r^kdr \ . \tag{4.10}$$

B. Hydrogen atom and optimization of the basis

In the solution of

$$-\frac{1}{2}\frac{d^2}{dr^2}\psi^{(i)}_n+\left\{\frac{l(l+1)}{2r^2}-\frac{1}{r}\right\}\psi^{(i)}_n=E^{(i)}_n\psi^{(i)}_n \ ,$$
$$\psi^{(i)}_n(0)=\psi^{(i)}_n(n)=0 \tag{4.11}$$

the calculation of the matrix elements

TABLE XVI. Accuracy of the eigenfunctions $\psi^{(i)}_{n,m}(\alpha,r)$ for the Hulten potential, Eq. (4.9); n defines the interval $[0,n]$, m is the number of base functions (4.4) (whose exponent is α) used to solve the Dirichlet problem (4.15) by the Ritz method. The notation $[-7]$ signifies $\times10^{-7}$.

State	δ	α	$[k,j]$	$[n,m]$	$\|\Delta\psi^{(i)}_{n,m}\|$
$1s$	0.025	0.9875	[34,10]	[49,13]	0.500[−7]
	0.050	0.975	[34,10]	[49,13]	0.500[−7]
	0.075	0.9625	[34,10]	[49,13]	0.473[−7]
	0.100	0.95	[34,10]	[49,13]	0.235[−7]
	0.200	0.90	[34,10]	[49,13]	0.408[−7]
	0.300	0.85	[34,10]	[49,13]	0.737[−7]
$2s$	0.025	0.9875	[49,13]	[64,16]	0.219[−3]
	0.050	0.975	[49,13]	[64,16]	0.218[−3]
	0.075	0.9625	[49,13]	[64,16]	0.236[−3]
	0.100	0.95	[49,13]	[64,16]	0.284[−3]
	0.200	0.90	[49,13]	[64,16]	0.108[−2]
	0.300	0.85	[49,13]	[64,16]	0.732[−2]
$2p$	0.025	0.47489	[49,13]	[64,16]	0.435[−7]
	0.050	0.4495	[49,13]	[64,16]	0.407[−7]
	0.075	0.424	[49,12]	[64,15]	0.134[−6]
	0.100	0.3979	[49,13]	[64,16]	0.500[−5]
	0.200	0.289	[64,12]	[84,15]	0.212[−4]
	0.300	0.25	[49,12]	[64,15]	0.652[−3]
$3p$	0.025	0.30	[49,12]	[64,15]	0.395[−3]
	0.050	0.257	[64,12]	[84,15]	0.167[−4]
	0.075	0.21	[79,12]	[104,15]	0.265[−4]
	0.100	0.18	[94,12]	[124,15]	0.399[−3]
$3d$	0.025	0.20	[79,12]	[104,15]	0.877[−5]
	0.050	0.255	[64,12]	[84,15]	0.892[−5]
	0.075	0.21	[79,12]	[104,15]	0.102[−4]
	0.100	0.17	[94,12]	[124,15]	0.237[−3]
$4d$	0.025	0.20	[79,12]	[104,15]	0.218[−3]
	0.050	0.15	[94,12]	[124,15]	0.161[−3]
	0.075	0.21	[79,12]	[104,15]	0.121[−1]

$$\langle \varphi_{nk}, \varphi_{nj} \rangle_{(n)} = \int_0^n e^{-2\alpha r}(n-r)^2 r^{k+j} dr \ , \tag{4.12}$$

$$\langle \varphi_{nk}, \mathcal{H}_n^0 \varphi_{nj} \rangle_{(n)} = \int_0^n \frac{1}{2} \frac{d\varphi_{nk}}{dr} \frac{d\varphi_{nj}}{dr} dr + \frac{l(l+1)}{2} \int_0^n e^{-2\alpha r}(n-r)^2 r^{k+j-2} dr - \int_0^n e^{-2\alpha r}(n-r)^2 r^{k+j-1} dr \tag{4.13}$$

is analytic. We use the computer program HQR [11] to compute the eigenvalues and the eigenvectors of the matrix $\langle \phi_{nk}, \mathcal{H}_n^0 \phi_{nj} \rangle_{(n)}$, where $\{\phi_{nk}\}_{k=1}^{\infty}$ is the orthonormal basis obtained from (4.4).

Table I shows the convergence in norm of $\{\psi_{n,m}^{(i)}(\alpha=1,r)\}$ to the exact solutions of the hydrogen atom when $l=0$. This implies the convergence of the eigenvalues $E_{n,m}^{(i)}(\alpha=1)$ and the calculated density moments to the exact values, as Proposition (2.1) asserts, which is confirmed by Tables II and III.

It is evident the speed of convergence for the state $1s$, which is explained because the value $\alpha=1$ gives the asymptotic behavior of $\psi_{\text{exac}}^{(1)}$ to the basis (4.4), since $\alpha_{\text{exac}}^{(1)}=1$. For states $2s$ and $3s$ also we observe the convergence to exact solutions, but it is slower.

There are two parameters that we use to obtain a faster convergence without increasing the number of base functions: (a) The increment Δn of the interval $[0,n]$, and (b) the exponent α of the basis. To study the effect of Δn and α on the convergence we compute the states $l=1$.

(1) Increment Δn. Table IV gives the convergence of $\{\psi_{n,m}^{(i)}(\alpha=1,r)\}$ in the Cauchy sense, Eq. (4.8), for $\Delta n=7$ and 20. In both cases we have convergence, hence there exists a unique limit function in $L_2(0,\infty)$ for each sequence, that is precisely the exact solution as Theorem (4.1) asserts. But there is a difference in the convergence. Since the accuracy of eigenfunctions $\psi_{84,16}^{(i)}(1,r)$ is greater than for the eigenfunctions $\psi_{32,16}^{(i)}(1,r)$ it follows that the convergence for $\Delta n=20$ is faster. This coincides with

TABLE XVII. Eigenvalues (in a.u.) for the Hulten potential as obtained by various methods. The energies $E_{n,m}^{(i)}$ corresponding to the eigenfunctions $\psi_{n,m}^{(i)}(\alpha,r)$ of Table XVI.

				$-E_{n,m}^{(i)}(\alpha)$			
State	δ	α	$[n,m]$	This work	Exact (Ref. [15])	Varshni (Ref. [13])	Matthys and De Meyer (Ref. [14])
$1s$	0.025	0.9875	[49,13]	0.487 578 124 999 970	0.487 578 125		0.487 577 7
	0.050	0.975	[49,13]	0.475 312 499 999 962	0.475 312 500		0.475 312 1
	0.075	0.9625	[49,13]	0.463 203 124 999 961	0.463 203 125		
	0.100	0.95	[49,13]	0.451 249 999 999 962	0.451 250		0.451 249 0
	0.200	0.90	[49,13]	0.404 999 999 999 966	0.405 000		0.404 993 0
	0.300	0.85	[49,13]	0.361 249 999 999 950	0.361 250		0.361 231 7
$2s$	0.025	0.9875	[64,16]	0.122 812 499 960	0.112 812 500		0.122 811 5
	0.050	0.975	[64,16]	0.101 249 999 978	0.101 250		0.101 248 5
	0.075	0.9625	[64,16]	0.090 312 499 957	0.090 312 500		
	0.100	0.95	[64,16]	0.079 999 999 955	0.080		0.079 996 9
	0.200	0.90	[64,16]	0.044 999 998 2	0.045		0.045 001 4
	0.300	0.85	[64,16]	0.019 999 864	0.020		0.020 001 4
$2p$	0.025	0.47489	[64,16]	0.122 760 465 559 345		0.122 760 5	0.112 760 4
	0.050	0.4495	[64,16]	0.101 042 452 072 360		0.101 042 5	0.101 042 5
	0.075	0.424	[64,15]	0.089 847 752 885 904		0.089 847 8	
	0.100	0.3979	[64,16]	0.079 179 439 105 15		0.079 179 4	0.079 179 4
	0.200	0.289	[84,15]	0.041 886 049 23		0.041 886 0	0.041 886 0
	0.300	0.25	[64,15]	0.013 790 034 34		0.013 787 8	0.013 790 0
$3p$	0.0250	0.30	[64,15]	0.043 706 891 58		0.043 706 9	0.043 707 1
	0.050	0.257	[84,15]	0.033 164 501 18		0.033 164 5	0.033 165 0
	0.075	0.21	[104,15]	0.023 939 747 26		0.023 939 7	
	0.100	0.18	[124,15]	0.016 053 73		0.016 053 7	0.016 053 7
$3d$	0.025	0.20	[104,15]	0.043 603 050 099		0.043 603 0	0.043 603 0
	0.050	0.255	[84,15]	0.032 753 184 225		0.032 753 2	0.032 753 2
	0.075	0.21	[104,15]	0.023 030 704 076		0.023 030 7	
	0.100	0.17	[124,15]	0.014 484 227 5		0.014 484 2	0.014 484 2
$4d$	0.025	0.20	[104,15]	0.019 846 254		0.019 846 2	0.019 846 2
	0.050	0.15	[124,15]	0.010 667 404		0.010 667 4	0.010 667 4
	0.075	0.21	[104,15]	0.003 834 52		0.003 834 5	0.003 834 6

physical intuition: if the interval $[0,n]$ is greater than the physical dimensions of the unbounded system then the bounded states of $\mathcal{H}_n^0$ are close to those of $\mathcal{H}$, in the sense of the norm of $L_2(0,\infty)$.

According to the accuracy of the eigenfunctions, the expected values of the functions $\psi^{(i)}_{84,16}(1,r)$, as energies and density moments, are more precise than those corresponding to $\psi^{(1)}_{32,16}(1,r)$, as Tables V and VI show.

(2) The exponent α. As Tables IV and V show, the convergence of $\{\psi^{(i)}_{n,m}(\alpha=1,r)\}$ to the exact solutions gives the approximate eigenvalues $E^{(i)}_{n,m}(\alpha=1)$, which we shall use to estimate a value α_2 closer to the exact value $\alpha^{(i)}_{\text{exac}}$ (4.3). Therefore we can give to the basis (4.4) the asymptotic behavior of the state that we desire to know with accuracy and obtain a fast convergence.

For example, we take $E^{(1)}_{84,16}(\alpha=1)$ of Table V and we compute the exponent $\alpha_2=\{2|E^{(1)}_{84,16}(\alpha=1)|\}^{1/2}\sim 0.5$ used in the new basis $\{\varphi_{nk}(\alpha_2,r)\}$ and we repeat the calculations. The increase of the accuracy is evident: in Table IV we see that the accuracy of $\psi^{(1)}_{84,16}(\alpha=0.5,r)$ is 0.635×10^{-7} while $\psi^{(1)}_{84,16}(\alpha=1,r)$ has an accuracy of 0.126×10^{-3}. The accuracy of states $3p$ and $4p$ also increases because $\alpha=0.5$ is more precise than $\alpha=1$. Therefore the energies $E^{(i)}_{n,m}(\alpha=0.5)$ and density moments are more precise, as Tables V and VI show.

Using the previous procedure, we compute states $3d$, $4d$, and $5d$ and the results are shown in Tables IV, V, and VI. The accuracy of state $3d$ is excellent, because $\alpha=0.333$ gives its asymptotic behavior to the basis (4.4).

Remark. As Proposition (2.1) establishes, a convergent sequence $\{\psi^{(i)}_{n,m}\}$ gives a convergent sequence of expected values that is precisely a Cauchy numerical sequence, hence in each stage of the calculation we can know the exact numbers of each expected value, as Tables II and III show. By this fact, we can assert that the reported numbers are exact except the last, which has been rounded.

C. Yukawa potential

In solving the Dirichlet problem

$$-\frac{1}{2}\frac{d^2}{dr^2}\psi^{(i)}_n+\left\{\frac{l(l+1)}{2r^2}+V_2(r)\right\}\psi^{(i)}_n=E^{(i)}_n\psi^{(i)}_n\ ,$$
$$\psi^{(i)}_n(0)=\psi^{(i)}_n(n)=0 \tag{4.14}$$

the calculation of $\langle\varphi_{nk},\varphi_{nj}\rangle_{(n)}$ is given by (4.12) and for $\langle\varphi_{nk},\mathcal{H}^0_n\varphi_{nj}\rangle_{(n)}$ is similar to (4.13.)

Table VII gives an example of the convergence of $\{\psi^{(i)}_{n,m}(\alpha=1,r)\}$ in the Cauchy sense for the Yukawa potential with $\lambda=0.10$ and $l=0$; this implies the convergence in norm to the exact solutions. Therefore both eigenvalues and density moments converge to the exact values, as Tables VIII and IX show.

In Table X we have the accuracy of approximate eigenfunctions $\psi^{(i)}_{n,m}(\alpha,r)$, Eq. (4.9), for some values of λ and l. Table XI gives the energies $E^{(i)}_{n,m}(\alpha)$ calculated by the present method, corresponding to eigenfunctions of Table X, and those calculated by Vrscay [12], who used a method of potential series. The accuracy of the present method is excellent.

We can observe that the expected values are more accurate than the eigenfunctions; for example, the eigenfunction $\psi^{(i)}_{64,13}(\alpha=1,r)$ of Table VII has an accuracy of

TABLE XVIII. Density first moments (in a.u.), for the Hulten potential, corresponding to some eigenfunctions $\psi^{(i)}_{n,m}$ of Table XVI, Eq. (4.10).

State	δ	$\langle r^{-2}\rangle$	$\langle r^{-1}\rangle$	$\langle r\rangle$	$\langle r^2\rangle$
$1s$	0.025	1.999 739 578	0.999 921 871	1.500 156 274	3.000 703 28
	0.050	1.998 958 255	0.999 687 435	1.500 625 391	3.002 815 04
	0.075	1.997 655 854	0.999 296 545	1.501 408 230	3.006 341 00
	0.100	1.995 832 082	0.998 748 957	1.502 506 266	3.011 290 76
	0.200	1.983 313 271	0.994 983 249	1.510 101 010	3.045 658 61
	0.300	1.962 398 038	0.988 664 663	1.523 017 903	3.104 640 21
$2p$	0.025	0.083 176 978	0.249 739 273	5.006 265 870	30.081 523 66
	0.050	0.082 706 634	0.248 953 340	5.025 256 309	30.329 427 50
	0.075	0.081 918 387	0.247 630 674	5.057 568 353	30.754 090 24
	0.100	0.080 805 409	0.245 751 141	5.104 262 636	31.374 164 43
	0.200	0.072 829 17	0.231 840 008	5.481 322 23	36.665 309 8
	0.300	0.057 465 82	0.202 361 1	6.539 44	54.267 1
$3p$	0.025	0.024 430 412	0.110 457 337	12.571 030	182.073 8
	0.050	0.023 641 020	0.108 462 078	12.793 181	188.648 7
	0.075	0.022 301 88	0.105 013 997	13.197 506	200.966 1
	0.100	0.020 371	0.099 888 3	13.852 631	221.913 7
$3d$	0.025	0.014 678 892	0.110 560 811	10.559 796 50	127.530 298 2
	0.050	0.014 264 741	0.108 866 707	10.748 582 72	132.434 202 9
	0.075	0.013 550 636	0.105 880 872	11.099 805 08	141.855 898 5
	0.100	0.012 488 743	0.101 272 792	11.694 295 74	158.720 231

0.289×10^{-7} while their moments $\langle r^{-1}\rangle$ and $\langle r^2\rangle$ have an error lower than 10^{-12}, see Table IX. According to this, the density first moments of the states $1s$ of Table X were calculated with 13 exact numbers. Finally, Table XII gives the first moments of some eigenfunctions of Table X.

We report the moments because these depend on the accurate computation of the eigenfunctions, while the energies can be calculated by other methods that do not give the eigenfunctions, such as the Vrscay method.

D. Hulten potential

To solve the problem

$$-\frac{1}{2}\frac{d^2}{dr^2}\psi_n^{(i)}+\left\{\frac{l(l+1)}{2r^2}+V_3(r)\right\}\psi_n^{(i)}=E_n^{(i)}\psi_n^{(i)}\ ,$$
$$\psi_n^{(i)}=(0)=\psi_n^{(i)}(n)=0 \tag{4.15}$$

by the Ritz method only the calculation of

$$\left\langle\varphi_{nk}\ ,\frac{e^{-\delta r}}{1-e^{-\delta r}}\varphi_{nj}\right\rangle_{(n)}=\int_0^n\frac{e^{-(2\alpha+\delta)r}}{1-e^{-\delta r}}(n-r)^2r^{k+j}dr$$

is numerical and it was made with the Simpson integration method.

The Hulten problem has been studied by some authors [13,14], who have basically calculated the energy levels. For $l=0$ Eq. (1.1) can be solved in closed form [15].

Tables XIII–XV show the convergence of the eigenfunctions, energies, and some moments for the Hulten potential with $\delta=0.025$, $l=1$, and $\alpha=0.474\,89$; this last number gives the asymptotic behavior of state $2p$.

Tables XVI–XVIII give a summary of the accuracy of eigenfunctions, their energies, and density moments for some values of δ. In Table XVII we show the energies calculated by other methods. The accuracy of the present method is excellent. To our knowledge there has been no previous calculation of the density moments.

Varshni [13] has calculated the oscillator strengths, for the $nl\rightarrow n'l'$ transition, given by

$$f=\frac{2}{3}\frac{\max(l,l')}{2l+1}(E_{n'l'}-E_{nl})\left|\int_0^\infty\psi_{nl}r\psi_{n'l'}dr\right|^2 . \tag{4.16}$$

As in Proposition (2.1), we can show that if $\{\psi_{n,m}^{(i)}\}$ and $\{\psi_{k,j}^{(t)}\}$ converge in norm to $\psi_{\text{exac}}^{(i)}$ and $\psi_{\text{exac}}^{(t)}$, respectively, then

$$\lim_{n\rightarrow\infty}\lim_{k\rightarrow\infty}\langle\psi_{n,m(n)}^{(i)},r\psi_{k,j(k)}^{(t)}\rangle=\langle\psi_{\text{exac}}^{(i)},r\psi_{\text{exac}}^{(t)}\rangle\ ,$$

hence the values f calculated by the present method converge to exact values. The accuracy of these values reported in Table XIX was determined following a similar process to the computation of the energies and moments, so all numbers are exact except the last, which has been rounded. Using (3.8) we have

$$\langle\psi_{n,m}^{(i)},r\psi_{k,j}^{(t)}\rangle=\int_0^{\min(n,k)}\psi_{n,m}^{(i)}r\psi_{k,j}^{(t)}dr\ . \tag{4.17}$$

TABLE XIX. Oscillator strengths (in a.u.) for the Hulten potential.

				Oscillator strength	
	δ	$[n,m]$[a]	$[k,j]$[a]	This work[a]	Varshni[b]
$1s\rightarrow2p$	0.025	[49,13]	[64,16]	0.415 494 939	0.415 5
	0.050	[49,13]	[64,16]	0.413 378 829	0.413 4
	0.075	[49,13]	[64,15]	0.409 815 496	0.409 8
	0.100	[49,13]	[64,16]	0.404 748 143	0.404 7
	0.200	[49,13]	[84,15]	0.367 219 5	0.367 1
	0.300	[49,13]	[64,15]	0.289 493	0.288 6
$1s\rightarrow3p$	0.025	[49,13]	[64,15]	0.078 335 1	0.078 34
	0.050	[49,13]	[84,15]	0.075 995 3	0.076 00
	0.075	[49,13]	[104,15]	0.071 954 8	0.071 96
	0.100	[49,13]	[124,15]	0.065 975	0.066 00
$2p\rightarrow3d$	0.025	[64,16]	[104,15]	0.691 611 1	0.691 6
	0.050	[64,16]	[84,15]	0.678 557 5	0.678 5
	0.075	[64,15]	[104,15]	0.654 812 9	0.654 7
	0.100	[64,16]	[124,15]	0.616 433	0.616 1

[a]These values were calculated using $\langle\psi_{n,m}^{(i)}(\alpha_n,r),r\psi_{k,j}^{(i)}(\alpha_k,r)\rangle$, Eqs. (4.16) and (4.17), the exponent α can be found in Table XVI or XVII.
[b] Ref. [13].

V. CONCLUSIONS

Some criteria to assure the accuracy of the eigenfunctions have been developed [16]. In this work we show that the convergence in norm is a *necessary condition* to assure the precise computation of both eigenfunctions and expected values of symmetric operators. The criterion of Cauchy is particularly useful to check the convergence of methods found in expansions of Ritz type, because it does not depend on the limit function. These criteria can be applied to problems with several dimensions, such as atoms.

The conditions that guarantee the convergence of the Ritz method are related to the idea of convergence in norm. The compactness condition, in particular, has been ignored and as we showed, it is not satisfied in important problems: those with a nonempty continuous spectrum. This explains the difficulty in computing expected values different to the energy.

The developed method has the following advantages.

(1) It guarantees the accurate computation of eigenfunctions and expected values.

(2) It does not depend on unknown parameters. The method permits us to compute the exponent α to obtain a fast convergence.

(3) In each stage, we can know the accuracy of the eigenfunctions and expected values. This permits us to stop the computation when the desired accuracy has been obtained.

It is evident that to compute more excited states it is necessary to use a larger basis. Therefore the method is only limited by the computational resources.

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APPENDIX

By hypothesis the potential (1.2) satisfies

$$|2V(r)| = 2\left|\frac{\chi(r)}{r}\right| \le M\frac{1}{r}\ , \tag{A1}$$

where M is a constant that depends only on each potential. The inequality

$$\int_0^\infty r^{-2}|u(r)|^2 dr \le 4\int_0^\infty \left|\frac{du}{dr}\right|^2 dr = 4\left|\left|\frac{du}{dr}\right|\right|^2 \tag{A2}$$

is satisfied for each $u \in W_1(0,\infty)$ [17]. On the other hand, if $\epsilon > 0$ we have

$$0 < r \le \frac{\epsilon}{4M} \text{ implies } \frac{1}{r} \le \frac{\epsilon}{4Mr^2}\ . \tag{A3}$$

Using (A1)–(A3), we have for each $u \in W_1(0,\infty)$

$$\begin{aligned}
&|2\langle V(r)u, u\rangle| \\
&= \left|\int_0^\infty 2V(r)|u(r)|^2 dr\right| \le M\int_0^\infty \frac{1}{r}|u|^2 dr \\
&\le M\int_0^{\epsilon/4M}\frac{1}{r}|u|^2 dr + M\int_{\epsilon/4M}^\infty \frac{1}{r}|u|^2 dr \\
&\le \frac{\epsilon}{4}\int_0^{\epsilon/4M}\frac{1}{r^2}|u|^2 dr + M\int_{\epsilon/4M}^\infty \frac{1}{(\epsilon/4M)}|u|^2 dr \\
&\le \frac{\epsilon}{4}\int_0^\infty \frac{1}{r^2}|u|^2 dr + \frac{4M^2}{\epsilon}\int_0^\infty |u|^2 dr \\
&\le \frac{4M^2}{\epsilon}\|u\|^2 + \epsilon\left|\left|\frac{du}{dr}\right|\right|^2 .
\end{aligned}$$

Consequently, for each $u \in W_1^0(0,n)$ we have

$$|2\langle Vu, u\rangle_{(n)}| \le C_\epsilon \|u\|^2_{(n)} + \epsilon\left|\left|\frac{du}{dr}\right|\right|^2_{(n)}\ , \tag{A4}$$

where $C_\epsilon = 4M^2/\epsilon$.

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