Divergence property of Fourier and Ritz expansions

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A divergence property of approximating sequences $\{\psi_n = \sum_{m=1}^{n} c_{nm}\varphi_m\}$ that converge in the norm of the Hilbert space $L_2(\mathbb{R}^N)$ to a fast-decay function ψ is studied. The expansion ψ_n can be a Fourier one or obtained by solving an eigenproblem by the Ritz method and the basis set $\{\varphi_m\}$ need not be orthogonal in $L_2(\mathbb{R}^N)$. The notion of uniform boundedness is used to show that if $\{\psi_n\}$ is nonuniformly bounded, then it diverges from its correct limit ψ in such a way that there is an increasing separation between the asymptotic tails of ψ_n and ψ as n increases. The analytical and numerical examples show that the rate of this divergence may be exponential, hence the divergence of expectation-value sequences $\{S(\psi_n)\}$ is proved for some operators S whose correct expectation value $S(\psi)$ depends mainly on the long-range behavior of ψ. The compatibility between several convergence properties of the approximating sequence $\{\psi_n\}$ and basis set properties with the nonuniform boundedness property is shown. We show that the well-known property of some trial wave functions to generate correct expectation values of some operators and incorrect values for other operators is connected with the property of nonuniformly bounded sequences $\{\psi_n\}$ to converge correctly on a finite region and diverge on its complementary one, hence it is proved that correct expectation values can be obtained from a nonuniformly bounded sequence by using a suitable limiting procedure. As model examples, Fourier and Ritz expansions of the ground state $\psi = 2Z^{3/2}e^{-Zr}$ of a hydrogenlike atom are considered. [S1050-2947(98)07402-2]

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I. INTRODUCTION

The theory of Fourier series with respect to orthogonal basis sets had its origin in the debate concerning the vibrating string two hundred years ago [1]. This theory was completely transformed during the first third of this century and currently several areas such as quantum mechanics, signal analysis, and numerical analysis, have found a rich storehouse in the theory of expansions with respect to systems of functions $\{\varphi_m\}_{m=1}^{\infty}$ [2].

The present article deals with two classes of expansions of fast-decay functions ψ in $\mathbb{R}^N$ with respect to a linearly independent system of functions $\{\varphi_m\}_{m=1}^{\infty}$ that need not be orthogonal in the Hilbert space $L_2(\mathbb{R}^N)$. Let $\langle , \rangle$ and $\|\cdot\|$ denote the scalar product and the norm of $L_2(\mathbb{R}^N)$. The coefficients of the first class of expansions $\psi_n^F = \sum_{m=1}^{n} c_{nm}^F \varphi_m$ are (uniquely) determined by minimizing the distance $\|\psi_n^F - \psi\|$ [3], and the second class is obtained from the variational Ritz method when the expanded function ψ is an eigenfunction of a self-adjoint operator in $L_2(\mathbb{R}^N)$. As is known [4–8], the Ritz method yields expansions $\psi_n^R = \sum_{m=1}^{n} c_{nm}^R \varphi_m$ whose coefficients are obtained by minimizing the so-called *energy* functional $E(\cdot)$ associated to the operator in question. Hereafter the expansions ψ_n^F and ψ_n^R will be referred to as *Fourier* and *Ritz* expansions, respectively.

A deep mathematical study [9] has been devoted to the investigation of connections between the convergence properties of Fourier series $\psi_{n=\infty}^F$ with respect to an orthonormal system of basis functions φ_m, the properties of the expanded function, and the behavior of the expansion coefficients, while the problem of computing Ritz expansions that converge in the norm to the eigenfunctions of self-adjoint operators can be solved by a *completeness argument* alone for many eigenproblems of physical interest particularly in numerical quantum mechanics [4–8]. Improvements in computers, numerical computer programs, and theoretical methods to carry out large scale calculations of eigenfunctions ψ of atomic and molecular Schrödinger operators, suggest that the largest source of error in most *ab initio* methods is now the basis set truncation of Ritz expansions ψ_n^R [10]. However, an old difficulty in numerical quantum mechanics has been the calculation of expectation values $S(\psi) = \langle \psi, S\psi \rangle$ of symmetric operators S since Ritz expansions ψ_n^R that yield sequences $\{S(\psi_n^R)\}$ that converge to their correct limit $S(\psi)$ for some operators S can generate sequences $\{S(\psi_n^R)\}$ for other operators S that converge to a wrong limit or diverge even when $\{\psi_n^R\}$ tends to ψ in the norm [11–14], a problem that has motivated a wide study of criteria for assessing the reliability or accuracy of trial functions [15,16]. The main aim of this article is to show that this convergence problem is connected with an *intrinsic* property of a wide class of sequences of Fourier and Ritz expansions of *fast-decay* functions ψ in *unbounded* regions of configuration space $\mathbb{R}^N$, rather than a result from the basis set truncation or rounding errors.

As model expansions we shall consider one-dimensional Fourier and Ritz expansions of eigenfunctions ψ of the Schrödinger operator in the Hilbert space $L_2(0,\infty)$ for hydrogenlike atoms. In Sec. II we use the notion of uniform boundedness to show that a nonuniformly bounded sequence $\{\psi_n\}$ *diverges* from its correct limit in such a way that there is an increasing separation between the asymptotic tails of ψ_n and ψ as n increases. The analytical and numerical examples of Sec. III indicate that this divergence has an expo-

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nential rate, which in turn generates sequences $\{S(\psi_n)\}$ that diverge or converge to a wrong limit for some operators S (Sec. IV). In Secs. IV A and IV B it is shown that the nonuniform boundedness property is compatible with several convergence properties of an approximating sequence $\{\psi_n\}$ and basis set properties. In Sec. V it is shown that if $\{\psi_n\}$ is nonuniformly bounded, then the integrals $\int_0^{R_n}\psi_n^* S\psi_n dr$ can converge to their correct limit $S(\psi)$ as $n\to\infty$ with an increasing sequence $\{R_n\}$ properly chosen, even when the *complete*-integral sequence $\{S(\psi_n)\}$ does not. The final section VI contains the extrapolation of the main one-dimensional results to high-dimensional expansions and some concluding remarks.

II. NONUNIFORMLY BOUNDED SEQUENCES $\{\psi_n\}$

Hereafter $\langle,\rangle$ and $\|\cdot\|$ denote, respectively, the inner product and the norm of $L_2(0,\infty)$, and $S(f)=\langle f,Sf\rangle$. We will consider ψ's in $L_2(0,\infty)$ with a *fast decay* $[r^k(\psi)=\langle\psi,r^k\psi\rangle<\infty$ for all $k\geqslant 0]$, $\{\psi_n\}_{n=1}^{\infty}$ will be an approximating sequence that tends to ψ in the L_2 norm ($\|\psi_n-\psi\|\to 0$), and by simplicity ψ and each ψ_n are continuous in the whole space.

In this article we say that the sequence $\{\psi_n\}$ is *uniformly bounded* (UB) if there is at least one fast decay function $\psi_{\rm UB}$ such that the inequality $|\psi_n(r)|\leqslant\lambda\psi_{\rm UB}(r)$ holds on a subinterval $[R_0,\infty)$ for $n\geqslant n_0$, where λ and R_0 are independent of n. Following the idea used to show Theorem 5 of [14], we get *Proposition 1*: If $\{\psi_n\}$ converges to ψ in the norm and is UB, then the equation

$$\lim_{n\to\infty} r^k(\psi_n)=r^k(\psi) \quad \text{holds for } k\geqslant 0. \tag{2.1}$$

Intuitively, this result is possible only if ψ_n tends ''correctly'' to ψ in *whole* space so that a correct approximating sequence $\{\psi_n\}$ should be UB [17]. Unfortunately, this property may fail even if $\{\psi_n\}$ tends to ψ in the norm. Accordingly, if $\|\psi_n-\psi\|\to 0$ and Eq. (2.1) fails with one power k, then $\{\psi_n\}$ is *non*uniformly bounded (NUB) and hence cannot be bounded uniformly by *any* fast decay function. This noteworthy property can be characterized geometrically as follows. Suppose that $|\psi|$ and each $|\psi_n|$ with large n are bounded by a fast-decay and continuous function ψ_B on an interval $[R,\infty)$, which is independent of n, that is, there are $\lambda,\lambda_n<\infty$ such that

$$\max_{r\geqslant R}\{|\psi|/\psi_B\}\leqslant\lambda, \quad \max_{r\geqslant R}\{|\psi_n|/\psi_B\}\leqslant\lambda_n .$$

The nonuniform boundedness of $\{\psi_n\}$ implies that $\lambda_n\to\infty$ and by continuity there is an interval $I_n=[a_n,b_n]$ such that $\beta_n\leqslant|\psi_n|/\psi_B$ holds for $r\in I_n$ with $\beta_n\to\infty$ as n increases (see Fig. 2). In geometric terms, this means that there is an increasing separation between the asymptotic tails of ψ_n and its correct limit ψ as $n\to\infty$.

III. EXAMPLES

A simple sequence that, as we shall see later on, exhibits some of the main convergence properties of NUB sequences is the Löwdin's sequence [11] for the function $\psi(r)$ $=(4/\pi)^{1/4}\exp(-r^2/2)$ on $[0,\infty)$:

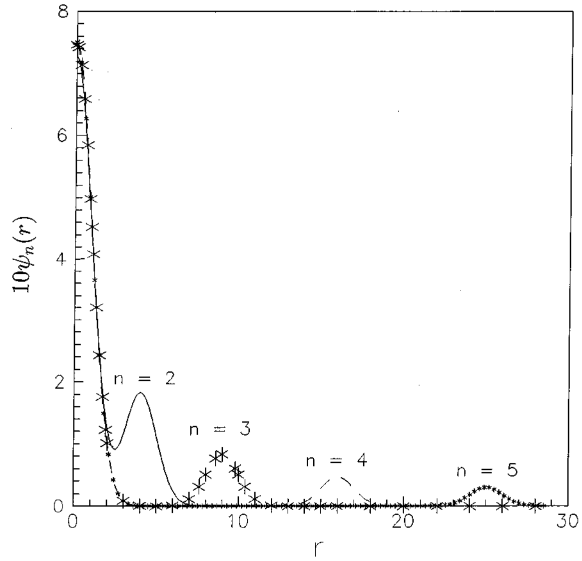

FIG. 1. Graph of $10\psi_n$ for Löwdin's sequence with $\epsilon_n=r_n^{-1}=n^{-2}$.

$$\psi_n(r)=[\psi(r)+\epsilon_n\psi(r-r_n)]c_n , \tag{3.1a}$$

where $\epsilon_n\to 0$ and $r_n\to\infty$ as $n\to\infty$, c_n ($\to 1$) being the normalization constant (see Fig. 1). This sequence converges in the $L_2(0,\infty)$ norm independently of how $\{\epsilon_n\}$ and $\{r_n\}$ are chosen,

$$\|\psi_n-\psi\|^2\leqslant 2[1-c_n-c_n\epsilon_n\exp(-r_n^2/2)(\pi/4)^{1/4}]\to 0, \tag{3.1b}$$

whereas for the moments $r^{2k}(\psi_n)$ we get, after algebraic manipulations, the inequality

$$(c_n\epsilon_n r_n^k)^2\leqslant r^{2k}(\psi_n), \tag{3.1c}$$

which shows that if ϵ_n dies like $r_n^{-k'}$, then $r^{2k}(\psi_n)\to\infty$ for $k>k'$ and therefore $\{\psi_n\}$ is NUB. This is confirmed by the graphs of $\log_{10}\psi/\psi_B$ and $\log_{10}\psi_n/\psi_B$ with $\psi_B=e^{-r}$ and $\epsilon_n=r_n^{-1}=n^{-2}$, plotted in Fig. 2, which shows that there is an interval $I_n=[\overline{r}_n-\delta/2,\overline{r}_n+\delta/2]$ with $\overline{r}_n>r_n$ and $\delta\sim 1$ for which $\beta_n\leqslant\psi_n/\psi_B$ holds on I_n where β_n diverges exponentially as n increases. The consequent increasing separation between the asymptotic tails of ψ_n and ψ is exhibited by the graph of $\log_{10}\psi_n/\psi$ plotted in Fig. 3.

The next Ritz expansions ψ_n^R are obtained by solving the Schrödinger equation for the ground state of hydrogenlike atoms with nuclear charge Z,

$$-\frac{1}{2}\frac{d^2\psi}{dr^2}-\frac{Z}{r}\psi=E\psi, \quad 0<r<\infty \tag{3.2}$$

with $\psi(0)=\psi(\infty)=0$, and the corresponding Fourier series ψ_n^F are computed by direct integration of the eigensolution $\psi=2Z^{3/2}re^{-Zr}$ [18].

Consider the calculation of the eigenstate $\psi=32^{1/2}re^{-2r}$ of He^+ with the basis set

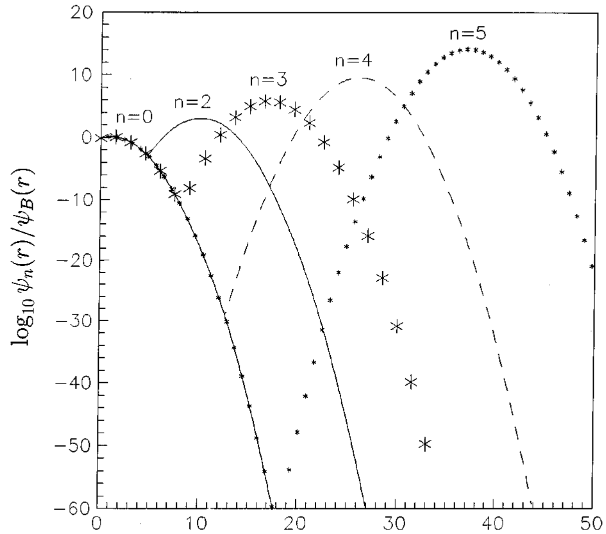

FIG. 2. Graph of $\log_{10}\psi_n/\psi_B$ for Löwdin's sequence and its correct limit $\psi=\psi_{n=0}$ with $\psi_B=e^{-r}$.

$$\varphi_m(r)=r^{2m-1}e^{-r^2/2}, \quad m=1,2,\ldots \tag{3.3}$$

used by Klahn and Morgan [13] in their study of the convergence rate of variational calculations. The $W_{2,1}$ completeness of this basis set ensures the convergence in the L_2 norm of sequences $\{\psi_n^F\}$ and $\{\psi_n^R\}$ toward their correct limit ψ [7]. The Klahn-Morgan's analysis of $\{\psi_n^F\}$ showed that the sequence $\{r^k(\psi_n^F)\}_{n=1}^{\infty}$ diverges with $k\geqslant 7$ (see Table I) so that $\{\psi_n^F\}$ is NUB. This is confirmed by the graph of $\log_{10}|\psi_n^F|/\psi_B$ with $\psi_B=\psi$ plotted in Fig. 4 [19], which shows that the increasing separation between the asymptotic tails of ψ_n^F and ψ has an exponential rate,

$$\max_{r\in[4,b_n)} |\psi_n^F|/\psi_B \sim 10^{\alpha_n}, \quad \alpha_n, b_n\to\infty. \tag{3.4}$$

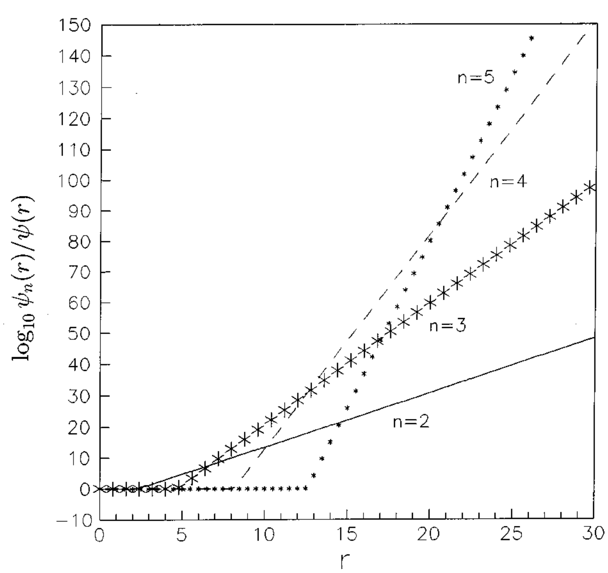

FIG. 3. Graph of $\log_{10}\psi_n/\psi$ for Löwdin's sequence, ψ being its correct limit.

TABLE I. Expectation values (taken from Ref. [13]) $r^k(\psi_n)$ from Fourier ψ_n^F and Ritz ψ_n^R expansions with n basis functions (3.3) for the $1s$ eigenstate of He^+. In this table and the following ones the notation 9.06[−6] (1.4[4]) means 9.06×10^{-6} (1.4×10^4).

n	r^{-2}	r^3	r^6	r^7	r^9
			ψ_n^F		
10	5.9	0.98	11.4	48	14[2]
20	6.8	0.95	10.5	57	32[2]
30	7.1	0.94	9.80	60	51[2]
100	7.7	0.94	7.86	64	18[3]
200	7.9	0.94	7.04	65	37[3]
			ψ_n^R		
10	5.4	1.19	2.5[1]	13[1]	41[2]
20	6.4	1.06	3.7[1]	28[1]	19[3]
30	6.9	1.01	4.3[1]	41[1]	44[3]
100	7.6	0.95	6.1[1]	11[2]	41[4]
200	7.8	0.94	6.8[1]	18[2]	13[5]
ex[a]	8.0	0.94	4.92	11	76

[a]Exact values.

Similar results are obtained with the Ritz sequence $\{\psi_n^R\}$ for which $\{r^k(\psi_n^R)\}_{n=1}^{\infty}$ diverges with $k\geqslant 6$ (see Table I) and the increasing separation between the asymptotic tails obeys a rule like Eq. (3.4) (see Fig. 3 of [14]).

The $W_{2,1}$ completeness of the basis set

$$\varphi_m(r)=r^2e^{-[2+(m-1)/m]r}, \quad m=1,2,\ldots \tag{3.5}$$

follows from Theorem 1 of [7]. Table II reports some expectation values from sequences $\{\psi_n^F\}$ and $\{\psi_n^R\}$ for the eigenstate ψ of He^+ with this basis set. The divergence of sequences $\{r^k(\psi_n^F)\}$ and $\{r^k(\psi_n^R)\}$ with $k\geqslant 6$ indicates that

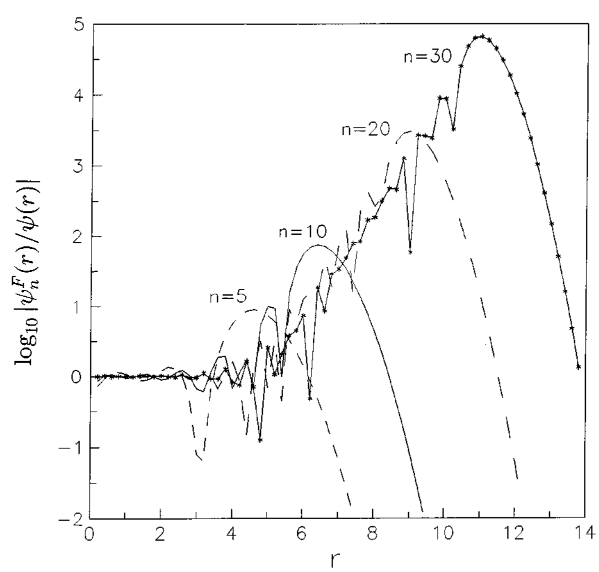

FIG. 4. Graph of $\log_{10}|\psi_n^F/\psi|$ for the $1s$ eigenstate ψ of He^+ approximated by Fourier expansions ψ_n^F with n basis functions (3.3).

TABLE II. Expectation values $r^k(\psi_n)$ from Fourier ψ_n^F and Ritz ψ_n^R expansions with n basis functions (3.5) for the 1s eigenstate of He^+.

n	r^{-2}	r^1	r^3	r^6	r^9
			ψ_n^F		
1	1.3	1.25	3.28	37	99[1]
3	3.7	0.79	1.13	15	77[1]
5	4.8	0.76	1.00	12	12[2]
7	5.5	0.75	0.98	13	24[2]
9	5.9	0.75	0.97	15	48[2]
			ψ_n^R		
1	1.3	1.25	3.33	37	99[1]
3	2.8	1.00	2.39	41	18[2]
5	3.6	0.91	1.79	46	47[2]
6	3.9	0.88	1.67	50	79[2]
ex[a]	8.0	0.75	0.94	4.9	76

[a]Exact values.

$\{\psi_n^F\}$ and $\{\psi_n^R\}$ are NUB, a result supported by the increasing separation between the asymptotic tails of the approximating functions and their correct limit when n increases as Fig. 5 shows.

IV. ADDITIONAL PROPERTIES OF NUB SEQUENCES

The examples show that the nonuniform boundedness is an *intrinsic* property of some sequences $\{\psi_n\}$ that converge to a fast-decay function ψ in the L_2 norm. The divergence of large-k sequences $\{r^k(\psi_n)\}$ from such sets $\{\psi_n\}$ may be attributed basically to the *exponential* rate of separation between the asymptotic tails of ψ_n and its correct limit ψ as $n\to\infty$. In fact, Figs. 2 and 4 show that if ψ_B is a fast-decay bound of each ψ_n, then there is an interval $I_n=[a_n,b_n]$ for which

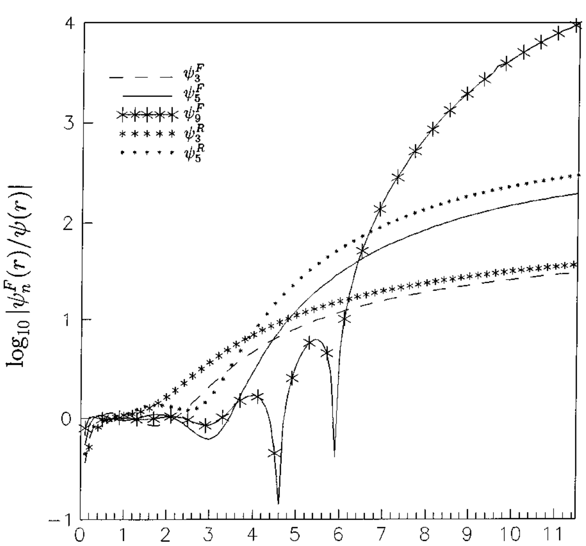

FIG. 5. Graph of $\log_{10}|\psi_n^F/\psi|$ and $\log_{10}|\psi_n^R/\psi|$ for the 1s eigenstate ψ of He^+ and its Fourier and Ritz expansions with basis functions (3.5).

$$\beta_n\leqslant|\psi_n(r)|/\psi_B(r)\quad \text{holds for } r\in I_n, \tag{4.1a}$$

where β_n diverges exponentially as n increases, $a_n\to\infty$ and $b_n-a_n\geqslant\delta>0$. Hence we get the inequality

$$\beta_n^2\int_{a_n}^{b_n}\psi_B^2(r)r^k dr\leqslant r^k(\psi_n), \tag{4.1b}$$

which, by rewriting the left-hand integral as $(b_n-a_n)(r_n^*)^k\psi_B^2(r_n^*)$ with $r_n^*\in I_n$ (mean value theorem for integrals), leads to

$$\delta(r_n^*)^k[\beta_n\psi_B(r_n^*)]^2\leqslant r^k(\psi_n). \tag{4.1c}$$

This clearly shows that the exponential divergence of β_n can compensate the fast decay of the factor $\psi_B(r_n^*)$ as n increases in such a way that for a large enough k the left-hand side and, therefore, $\{r^k(\psi_n)\}$ diverge when $n\to\infty$.

The incorrect convergence of some expectation values from NUB sequences $\{\psi_n\}$ poses the problem of how to avoid the calculation of such sequences. Of course, the nonuniform boundedness property is determined by both the basis set $\{\varphi_m\}$ and the expanded function ψ but since ψ is unknown in general and only few of its properties are known we shall study the connections between (i) the convergence properties of $\{\psi_n\}$ and (ii) the basis set properties with the nonuniform boundedness.

A. Convergence properties of $\{\psi_n\}$

In this section we show the coexistence of the nonuniform boundedness property with the stronger convergence properties that *one*-dimensional Fourier and Ritz expansions may have: the uniform convergence, convergence in the norm, and point-by-point. It should be noted that in bounded intervals there is a hierarchy between these convergence criteria that disappears in unbounded intervals [20].

It is easy to see that the Löwdin's sequence converges to its correct limit (i) uniformly on each finite interval $[0,R]$ $[|\psi_n(r)-\psi(r)|<\epsilon$ holds on $[0,R]$ for $n>n_{\epsilon,R}$ and any small $\epsilon>0$, $n_{\epsilon,R}$ being properly chosen], (ii) point-by-point in whole space $[\lim_{n\to\infty}\psi_n(r)=\psi(r)$ holds for all $r\geqslant0]$, and, obviously, (iii) in the L_2 norm. Nevertheless, $\{\psi_n\}$ is NUB, a result that shows the compatibility of three strong convergence criteria with the nonuniform boundedness property.

Convergence problems with some trigonometric series has motivated a deep mathematical analysis of convergence properties of Fourier series with respect to general orthogonal basis sets in *finite* intervals [9]. For example, it is known the existence of continuous functions whose trigonometric series diverge at some points and, therefore, do not converge uniformly, and to the date several problems concerning the *pointwise* convergence of generalized Fourier series are still unsolved [9]. Of course, the class of open convergence problems of series in unbounded regions and higher-dimensional spaces is greater. To circumvent these problems and study the connections between convergence criteria and the nonuniform boundedness we shall consider Ritz expansions since if the basis set $\{\varphi_m\}$ is complete in the Sobolev space $W_{2,1}$ endowed with the norm $\|\phi\|_1^2=\|\phi\|^2+\|d\phi/dr\|^2$ ($W_{2,1}$ completeness), then the Ritz method provides an approxi-

TABLE III. Coefficients c_{nm} of Fourier expansions ψ_n^F with n basis functions (3.5) for the $1s$ eigenstate of He^+. The values $\overline{c}_{nm}=(-1)^{n+m}c_{nm}$ are reported.

n	$\overline{c}_{n1}$	$\overline{c}_{n2}$	$\overline{c}_{n3}$	$\overline{c}_{n4}$
1	7.5			
3	1.7[1]	6.4[2]	3.9[3]	
5	1.1[2]	4.1[4]	1.2[6]	6.4[6]
7	1.2[3]	3.0[6]	3.2[8]	5.5[9]
9	1.5[4]	2.4[8]	8.4[10]	3.8[12]

mating sequence $\{\psi_n^R\}$ for the hydrogenlike problem (3.2) that converges to the true eigenfunction ψ in the norm $\|\cdot\|_1$ [6], which in turn ensures the uniform convergence of $\{\psi_n^R\}$ on *each* finite interval $[0,R]$ as well as its point-by-point convergence in whole space [21]. In this way, the $W_{2,1}$-complete basis sets (3.3) and (3.5) generate Ritz sequences for the eigenstate ψ of He^+ that have such convergence properties and, however, these sequences are NUB (see Figs. 4 and 5). Thus, the stronger convergence properties that one-dimensional Fourier and Ritz sequences may have are compatible with the nonuniform boundedness property as occurs with the Löwdin's sequence.

B. Basis set properties

To begin the study of basis set properties and the nonuniform boundedness consider the *asymptotic behavior* of the basis functions φ_m. A first question is if φ_m's that decay more rapidly than the expanded function ψ can yield a UB sequence $\{\psi_n\}$. The sequences $\{\psi_n^F\}$ and $\{\psi_n^R\}$ with basis functions (3.3) for the eigenstate ψ of He^+ indicate that the answer is negative because such sequences are NUB whereas the φ_m's and, therefore, ψ_n^F and ψ_n^R decay more rapidly than ψ: for an arbitrarily small $\epsilon>0$ there is an $R(\epsilon,n)$ such that

$$|\psi_n^F|,|\psi_n^R|<\epsilon\psi \quad \text{hold for } r\in[R(\epsilon,n),\infty),$$

where $R(\epsilon,n)$ diverges as n does (see Fig. 4). In this case every φ_m and each finite linear combination ψ_n of the φ_m's are bounded by the correct limit ψ but *not* uniformly since $R(\epsilon,n)$ depends on n; this suggests to see if a basis set $\{\varphi_m\}$ that is UB generates Fourier and Ritz sequences with the same boundedness property. The answer to this question is negative again as is shown by the basis set (3.5), which is uniformly bounded by $\lambda_l r^l\psi$ with $l\geqslant 1$ and a suitable λ_l but yields NUB sequences $\{\psi_n^F\}$ and $\{\psi_n^R\}$ for the eigenstate of He^+ (see Fig. 5 and Table II).

When the coefficients c_{nm} of $\psi_n=\Sigma_{m=1}^n c_{nm}\varphi_m$ are obtained by means of the Ritz method or by direct integration of the expanded function $\{\varphi_m\}$ being a *non*orthogonal system, the c_{nm}'s depend on n. This suggests studying the possible connections between the *behavior of the* c_{nm}*'s as* $n\to\infty$ and the nonuniform boundedness property. Since there is no theory that describes the n dependence of the c_{nm}'s in terms of basis set properties alone we consider some representative cases of coefficients' behavior. Table III shows that for each m value the coefficients c_{nm} of Fourier expansions with basis functions (3.5) for He^+ diverge as n does, an undesired result from the physical point of view that may be connected with the nonuniform boundedness of $\{\psi_n^F\}$ (the corresponding NUB sequence $\{\psi_n^R\}$ has the same coefficients' behavior), but the next example shows that this connection is less obvious. Table IV shows that the Fourier expansion ψ_n^F of the hydrogen-atom eigenstate ψ with basis functions

$$\varphi_m(r)=r\exp[-(1+m/2)r] \quad (m=1,2,\dots) \qquad (4.2)$$

has coefficients c_{nm} that diverge as n does with each m value, whereas Fig. 6 and the correct r^k convergence reported in Table IV indicate that $\{\psi_n^F\}$ is uniformly bounded by ψ.

TABLE IV. Coefficients c_{nm} and expectation values $r^k(\psi_n)$ from Fourier expansions ψ_n^F with n basis functions (4.2) for the $1s$ eigenstate of hydrogen atom.

n	c_{n1}	$-c_{n2}$	c_{n3}	$-c_{n4}$
3	1.3[1]	2.4[2]	9.0[2]	
7	4.3[1]	3.1[3]	6.0[4]	4.8[5]
11	8.8[1]	1.3[4]	5.7[5]	1.1[7]
15	1.5[2]	3.7[4]	2.8[6]	9.7[7]
n	r^{-2}	r^3	r^7	r^9
3	2.49	5.94	4.68[2]	7.15[3]
7	2.08	7.35	1.08[3]	2.24[4]
11	2.03	7.48	1.30[3]	3.11[4]
15	2.01	7.49	1.37[3]	3.51[4]
ex[a]	2.00	7.50	1.42[3]	3.90[4]

[a]Exact values.

Consider now the case for which the coefficients are well behaved. The orthonormality and completeness of the basis set (3.3) guarantee that the coefficients of ψ_n^F for He^+ are n

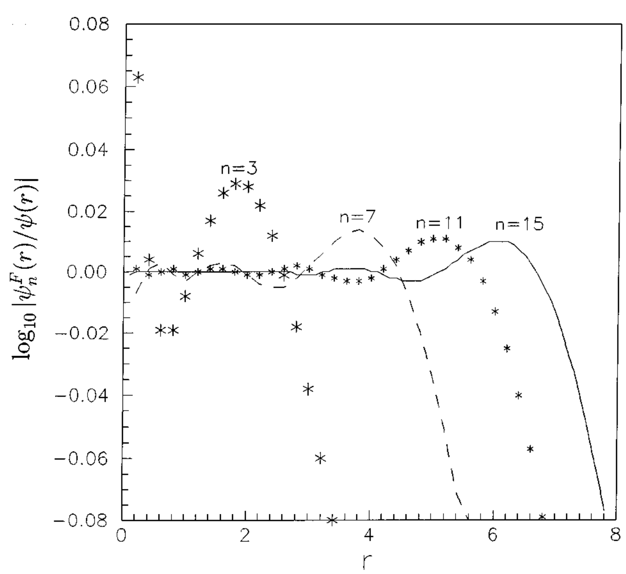

FIG. 6. Graph of $\log_{10}|\psi_n^F/\psi|$ for the $1s$ eigenstate ψ of hydrogen atom approximated by Fourier expansions ψ_n^F with n basis functions (4.2).

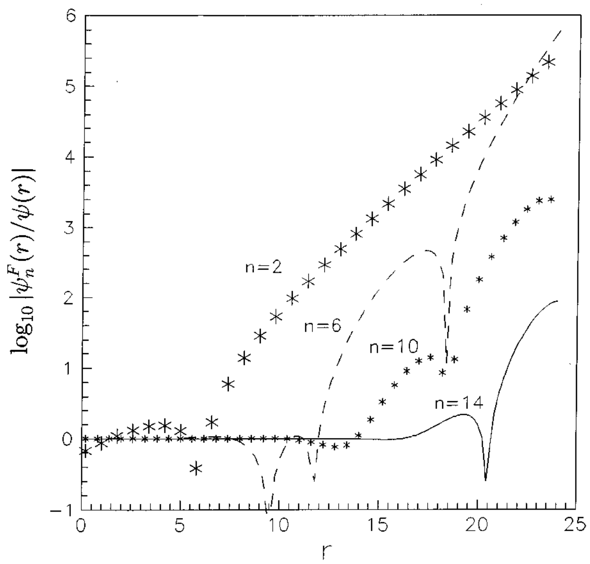

FIG. 7. Graph of $\log_{10}|\psi_n^F/\psi|$ for the 1s eigenstate ψ of hydrogen atom approximated by Fourier expansions ψ_n^F with n basis functions (4.3).

independent and satisfy $\Sigma_{m=1}^{\infty}c_m^2=1$, a result with physical sense in the frame of quantum mechanics, but $\{\psi_n^F\}$ is NUB (see Fig. 4). It should be noted that this nonuniform boundedness cannot be attributed to the powers r^m of basis functions (3.3) alone since the basis functions

$$\varphi_m(r)=r^m e^{-r/2} \quad (m=1,2,\dots), \tag{4.3}$$

which also have increasing powers r^m, generate a sequence $\{\psi_n^F\}$ for the hydrogen-atom eigenstate ψ that is uniformly bounded by it, as follows from Fig. 7 [22] and the correct r^k convergence exhibited by Table V, and whose coefficients c_{nm} converge to a value c_m, which in turn decreases when m increases as Table VI shows.

In summary, the results above indicate that there is *no* apparent connection between the uniform or nonuniform boundedness of a sequence $\{\psi_n\}$ and the behavior of its expansion coefficients c_{nm} as n increases.

The concepts of *overcompleteness* (when the completeness of $\{\varphi_m\}_{m=1}^{\infty}$ remains unchanged after deleting any finite set of elements) and *exact completeness* (when the completeness of $\{\varphi_m\}_{m=1}^{\infty}$ is lost by omission of a single arbitrarily chosen element) provide a first general classification of basis sets. The nonuniform boundedness of the He^+ sequences $\{\psi_n^F\}$ and $\{\psi_n^R\}$ from basis sets (3.5) and (3.3), which are respectively overcomplete and exactly complete [7], indicates that these concepts do not play a significant role in the nonuniform boundedness of such sequences.

In infinite-dimensional Hilbert spaces, no standard criterion of linear independence can be given, instead of this there is *hierarchy* of nonequivalent criteria, each of which defines a kind of linear independence property (see, e.g., [8]). It is easy to see that these *linear independence properties* of a basis set $\{\varphi_m\}$ do not play a significant role in the boundedness properties: Consider a basis set $\{\varphi_m\}$ that generates a UB (or NUB) sequence $\{\psi_n=\Sigma_{m=1}^{n}c_{nm}\varphi_m\}$ and let $\{\phi_m\}$ be the corresponding orthonormal system obtained by the Gram-Schmidt procedure, then

$$\psi_n=\sum_{m=1}^{n}\langle\phi_m,\psi\rangle\phi_m \qquad (n=1,2,\dots).$$

The orthonormality of $\{\phi_n\}$ implies that it has the main Hilbert-space linear independence properties such as ω linear independence, minimality, uniform minimality, the Bessel and Riez properties, and the γ linear independence [8]. Thus, we get an orthonormal basis set that generates a UB (or NUB) sequence $\{\psi_n\}$ and therefore any one of the mentioned linear independence properties is compatible with the uniform (or nonuniform) boundedness property. In particular, we have that the Gram-Schmidt procedure preserves both the uniform and nonuniform boundedness properties.

TABLE V. Expectation values $r^k(\psi_n)$ from Fourier expansions ψ_n^F with n basis functions (4.3) for the 1s eigenstate of hydrogen atom.

n	r^{-2}	r^3	r^5	r^7
2	1.05	2.9[1]	24.4[2]	380[3]
4	1.79	1.0[1]	96.2[1]	345[3]
6	1.97	7.66	18.5[1]	780[2]
8	2.00	7.51	85.98	9827
10	2.00	7.50	79.10	2019
12	2.00	7.50	78.76	1450
14	2.00	7.50	78.75	1419
ex[a]	2.00	7.50	78.75	1418

[a]Exact values.

V. CORRECT EXPECTATION VALUES FROM NUB SEQUENCES

We have not attempted to yield an exhaustive discussion about the factors connected with either the uniform or nonuniform boundedness of an approximating sequence $\{\psi_n\}$, in part, because of the absence of a theory to estimate the behavior of expansion coefficients c_{nm} as $n\to\infty$ when $\{\psi_n\}$ is a Fourier sequence and the basis set is nonorthogonal or $\{\psi_n\}$ is a Ritz sequence and the limit function is unknown. Of course, the difficulty in carrying out such an analysis with variational calculations that optimize several nonlinear parameters [23] or employ n-dependent sets $\{\varphi_{nm}\}_{m=1}^{n}$ that become complete in the limit $n\to\infty$ [24] is greater. In general, we can say that a unique way to see if a basis set $\{\varphi_m\}$ generates a NUB sequence $\{\psi_n\}$ is by calculating it and determining its nonuniform boundedness (i) by monitoring the behavior of large-k moments $r^k(\psi_n)$ as n increases, or (ii) by using an upper bound ψ^{ub} of the true limit function ψ and verifying that the graph of $|\psi_n|/\psi^{\mathrm{ub}}$ behaves as those of Figs. 3–5 when n increases, although these ways may not be satisfactory if a large n that exceeds the computational resources is required to observe a clear tendency toward either uniform or nonuniform boundedness.

The remarks above pose the problem of how to get correct or, at least, reliable expectation values from a sequence $\{\psi_n\}_{n=1}^{N}$ that may be NUB in the limit $N\to\infty$ in order to

TABLE VI. Coefficients c_{nm} of Fourier expansions ψ_n^F with n basis functions (4.3) for the 1s eigenstate of the hydrogen atom.

n	c_{n1}	$-c_{n2}$	c_{n3}	$-c_{n4}$	c_{n5}	$-c_{n6}$	c_{n7}
4	1.8	1.3	0.4	0.04			
8	1.993	1.80	0.92	0.31	0.067	0.009	7.0[−4]
12	1.9998	1.832	0.988	0.381	0.113	0.026	4.6[−3]
14	1.99998	1.8327	0.9909	0.3864	0.118	0.029	5.77[−3]
16	1.999997	1.83285	0.9915	0.3877	0.1191	0.030	6.32[−3]
18	1.9999995	1.83287	0.99162	0.38793	0.1194	0.0303	6.52[−3]
20	1.99999997	1.83288	0.99164	0.38798	0.1195	0.0304	6.59[−3]

compensate part of the computational work that was done. The answer to this question will clarify the apparent contradiction between the title of this section and the property of NUB sequences to generate nonconvergent sequences $\{S(\psi_n)\}$. Figures 3, 4, and 5 show that NUB sequences can ''converge correctly'' in a finite interval $[0,R]$ even when they ''diverge'' in the complement $[R,\infty)$, this observation can be formalized as follows. Let $\chi_R(r)$ be the characteristic function of the interval $[0,R]$, $\chi_R=1$ for $r\in[0,R]$ and $\chi_R=0$ otherwise, and let χ_R^c be the corresponding function of $[R,\infty)$. Since the local fit of ψ_n in the interval $[a-\sigma,a+\sigma]$ can be gauged by the error $|S(\chi_R\psi_n)-S(\chi_R\psi)|$ with an operator $S=s(r)$ such as $s(r)=10^{N(\geqslant 1)}\exp[-(r-a)^2/2\sigma^2]$, we can say that $\{\psi_n\}$ tends ''correctly'' to ψ in $[0,R]$ if the equation

$$\lim_{n\to\infty} S(\chi_R\psi_n)=S(\chi_R\psi) \tag{5.1}$$

holds for each operator $S=s(r)$ where $s(r)$ is continuous in $[0,R]$. Thus, *if* $\{\psi_n\}$ *converges to* ψ *in the* $L_2(0,\infty)$ *norm, then* ψ_n *tends correctly to* ψ *in* each *finite interval* $[0,R]$! since the convergence in the norm guarantees the correctness of Eq. (5.1) for all continuous functions $s(r)$ in $[0,R]$, a result that includes *any* NUB sequence [25]. From this it follows that if $\{\psi_n\}$ is NUB, then we can choose an increasing sequence $\{R_n\}$ for which every interval $[0,R_n]$ includes (excludes) the region where the relative error of $\psi_n(r)$ is small (large) in such a way that the equation

$$\lim_{n\to\infty} S(\chi_{R_n}\psi_n)=S(\psi) \tag{5.2}$$

holds true for many operators $S=s(r)$ including r^k with $k\geqslant 0$, a result that validates the title of this section. Additionally, from the equation

$$S(\psi_n)=S(\chi_{R_n}\psi_n)+S(\chi_{R_n}^c\psi_n) \tag{5.3}$$

it follows that if $\{\psi_n\}$ is NUB, then the convergence of the complete-integral sequence $\{S(\psi_n)\}$ is determined by the competition between the convergence rate of *locally* correct sequence $\{S(\chi_{R_n}\psi_n)\}$ and the incorrect convergence of $S(\chi_{R_n}^c\psi_n)$. This provides an explanation of the well-known fact that trial wave functions that yield a correct expectation value of one physical property, may fail utterly if they are used to compute another property. In fact, as occurs with the sequences of Figs. 3–5, if $\{\psi_n\}$ converges correct but slowly to ψ in $[0,R]$ and there is an increasing separation between the asymptotic tails in $[R,\infty)$, then the expectation values insensitive to the tail, such as the energy $E(\psi_n)$ and the small-k moments $r^k(\psi_n)$, converge to their correct limit while the sensitive-tail expectation values do not converge to their correct limit as occurs with the large-k moments (see Tables I and II).

VI. CONCLUDING REMARKS

The results of Secs. II–V show that if $\{\psi_n\}$ converges to a fast decay ψ and is NUB, then ψ_n diverges from ψ in such a way that there is an increasing separation between the tails of ψ_n and ψ as n increases, and if this divergence has an exponential rate then the sequence $\{S(\psi_n)\}$ diverges with some operators S whose expectation value $S(\psi)$ depends mainly on the long-range behavior of ψ [Eqs. (4.1a)–(c)]. This includes both Fourier and Ritz sequences with respect to a complete basis set $\{\varphi_m\}$ that need not be orthogonal. Although there is no obvious criterion that allows us to know *a priori* the boundedness property of an approximating sequence $\{\psi_n=\sum_{m=1}^n c_{nm}\varphi_m\}$ by means of the basis set properties or the stronger convergence properties of $\{\psi_n\}$ alone, correct expectation values can be obtained with the limiting procedure (5.2) with an increasing sequence $\{R_n\}$ properly chosen.

The extrapolation of the results above to high-dimensional expansions is immediate. Let Ω and $\psi_{\rm UB}$ denote a bounded region of configuration space $\mathbb{R}^N$ and a fast decay function in $\mathbb{R}^N$, if $\{\psi_n\}$ converges to a fast-decay function ψ in the norm of the Hilbert space $L_2(\mathbb{R}^N)$, then we say that the sequence $\{\psi_n\}$ is NUB when it cannot be bounded uniformly by any $\psi_{\rm UB}$ in the region $\mathbb{R}^N\backslash\Omega$ for each Ω. An N-dimensional NUB sequence $\{\psi_n\}$ can be described geometrically by means of the increasing separation between the asymptotic tails of ψ_n and its correct limit ψ as n increases, a property that can yield incorrect convergence of some sensitive-tail expectation values $S(\psi_n)=\langle\psi_n,S\psi_n\rangle$, $\langle,\rangle$ being the inner product of $L_2(\mathbb{R}^N)$. Nonuniform boundedness of large-scale variational calculations for atoms has been pointed out in [14] where the convergence problem of expectation values was attributed to the incapability of the Ritz method to control the long-range behavior of a trial function ψ_n^R, while the results of previous sections show that such a problem is connected with an intrinsic property that an approximating sequence $\{\psi_n\}$ may have, namely, the nonuniform boundedness property.

Although the problem of determining *a priori* the uniform or nonuniform boundedness property of N-dimensional Fourier and Ritz sequences, is a nontrivial one, we can take into account that the $L_2(\mathbb{R}^N)$ convergence guarantees the correctness of the equation

$$\lim_{n\to\infty} S(\Omega,\psi_n)=S(\Omega,\psi) \tag{6.1}$$

$[S(\Omega,\phi)=\int_\Omega \phi^* S\phi d\overline{r}_1,\ldots,d\overline{r}_N$ for $\phi\in L_2(\mathbb{R}^N)]$ for any operator S defined by a continuous function $s(\overline{r}_1,\ldots,\overline{r}_N)$ on Ω [26], to obtain correct expectation values by means of the limiting procedure

$$\lim_{n\to\infty} S(\Omega_n,\psi_n)=S(\psi) \tag{6.2}$$

with an increasing sequence $\Omega_1\subset\Omega_2\subset\ldots$ where each Ω_n includes (excludes) the region where the relative error of ψ_n is small (large). It is not hard to extend this result to the calculation of transition values $\langle\psi^{(i)},S\psi^{(j)}\rangle$, although the problem of determining the *reliability* region Ω_n of a given ψ_n remains as an open problem that will be studied in a forthcoming work.

In Sec. V we used the L_2 convergence to define a notion of correct *local* convergence in spite of the fact that, for example, one-dimensional variational sequences converge uniformly in any finite interval. The motivation lies in the fact that the $L_2(\mathbb{R}^N)$ convergence of Fourier and Ritz sequences can be guaranteed by a completeness argument alone whereas other convergence criteria such as the uniform one require the L_2 convergence of high derivatives of the approximating functions toward those of the expanded function, a requirement that fails in general because of the convergence in the energy norm for Schrödinger operators, for example, includes at most the first derivatives [6,21]. Thus the pointwise convergence or equivalently the calculation of the expectation value of a *high*-dimensional δ function remains as an open problem in general.

In the context of numerical quantum mechanics several authors have pointed out that the calculation of a function ψ_n by means of the energy optimization does not yield the best trial function to compute other property (see, e.g., [11–13]). This deficiency of energy calculations can, at least in principle, be eliminated in the limit $E(\psi_n)\to E(\psi)$ because Eckart's inequality $\|\psi_n-\psi\|\leqslant\gamma[E(\psi_n)-E(\psi)]$ [5] implies that correct expectation values of many operators S can be obtained by means of the limiting procedure (6.2), which can be complemented with the use of criteria for assessing the accuracy or reliabilty of approximating trial wave functions in position space [15] and momentum space [16].

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[17] A notion of ''correct'' convergence is given in Sec. V.

[18] All calculations were done in a 32-digit precision machine.

[19] The cusps observed in Figs. 4, 5, and 7 are generated by the zeros of ψ_n.

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[22] It is not hard to see that if $|\psi_n|<\psi_B$ on $[0,R_n)$ and $|\psi_{n+1}|\leqslant|\psi_n|$ on $[R_n,\infty)$ with $R_n\to\infty$ as $n\to\infty$, then $\{\psi_n\}_{n=j+1}^{\infty}$ is uniformly bounded by ψ_j, as occurs with the sequence of Fig. 7 for which $\psi_B=\lambda\psi$ with a suitable constant λ.

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[26] See, e.g., Secs. 2–3 of Ref. [14].