PHYSICAL REVIEW A VOLUME 33, NUMBER 2 FEBRUARY 1986

Hydrogen atom with a Yukawa potential: Perturbation theory and continued-fractions–Padé approximants at large order

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(Received 23 August 1985)

A simple power-series method is developed to calculate to large order the Rayleigh-Schrödinger perturbation expansions for energy levels of a hydrogen atom with a Yukawa-type screened Coulomb potential. Perturbation series for the $1s$, $2s$, and $2p$ levels, shown not to be of the Stieltjes type, are calculated to 100th order. Nevertheless, the poles of the Padé approximants to these series generally avoid the region of the positive real axis $0 < \lambda < \lambda^*$, where λ^* represents the coupling constant threshold. As a result, the Padé sums afford accurate approximations to $E(\lambda)$ in this domain. The continued-fraction representations to these perturbation series have been accurately calculated to large (100th) order and demonstrate a curious "quasioscillatory," but non-Stieltjes, behavior. Accurate values of $E(\lambda)$ as well as λ^* for the $1s$, $2s$, and $2p$ levels are reported.

Here we consider hydrogenlike atoms with a Yukawa[1] or screened Coulomb potential, as given by the Hamiltonian (in atomic units)

$$\hat{H}(Z,\lambda) = -\tfrac{1}{2}\hat{p}^2 - \frac{Ze^{-\lambda r}}{r} \ , \tag{1}$$

where Z is the nuclear charge and λ represents the screening constant. Screened Coulomb potentials of various types have received a great deal of attention, not only in the context of nuclear physics but also from atomic, solid state and plasma physics, and astrophysics. The motivations and a variety of approaches which have been employed to study Eq. (1) are outlined in Ref. 2. In this paper we focus on the properties of the Rayleigh-Schrödinger (RS) perturbation expansions of the energy

$$E_{NLM}(Z,\lambda) = -\frac{Z^2}{2N^2} + \sum_{n=1}^{\infty} E_{NLM}^{(n)}(Z)\lambda^n \ , \tag{2}$$

where N, L, and M denote the usual hydrogen quantum numbers and the dependence of the RS coefficients on the nuclear charge is noted. A scaling transformation of the form $r=\alpha'$, $p=\alpha^{-1}p'$, $\alpha \in \mathbf{R}$, yields the relationship

$$\hat{H}(Z,\lambda) = Z^2\hat{H}(1,\lambda/Z) \ . \tag{3}$$

We therefore need only to study the perturbation expansions for hydrogen atoms, i.e., $Z=1$; the RS coefficients for general Z are then given by

$$E_{NLM}^{(n)}(Z) = Z^{2-n}E_{NLM}^{(n)} \ , \tag{4}$$

where $E^{(n)} \equiv E^{(n)}(1)$. Equation (3) facilitates calculations for screened atomic potentials where Z is varied and λ is assumed Z dependent since the RS coefficients need not be recalculated for each Z value.

Traditional perturbation treatments of hydrogenic problems are complicated by the presence of continuum states. A proper treatment would necessarily involve an integration over the continuum. Methods which have been devised to bypass this difficulty have been applied to Eq. (1) to calculate RS expansions to arbitrary order. They include the Hellman-Feynman and hypervirial theorems[3] and logarithmic perturbation theory.[4] The reformulation of Eq. (1) via a special coordinate realization of the Lie-algebra so(4,2) has also been discussed.[5] [We also mention that a novel variational technique based on the so(4,2) dynamical symmetry group for hydrogen has recently been developed.[6]]

This study was motivated by the work of Lai,[7] who observed that $[N-1,N]$ and $[N,N]$ Padé approximants to the RS series in (2) provide accurate estimates of the eigenvalues $E_{NLM}(\lambda)$. The bounding properties exhibited by these Padé's raised the question of whether or not the perturbation series was Stieltjes. As we report below, a look at the Hadamard determinants associated with (2) as well as its continued fraction representations reveal that the series is *not* Stieltjes. Nevertheless, the poles and zeros of the Padé approximants exhibit an interesting "quasi-Stieltjes" behavior which accounts for the accurate estimates of the eigenvalues.

We first outline a relatively simple power-series method for computing the RS expansion in (2) to arbitrary order. The method has deep connections with the so(4,2) Lie-algebraic reformulation of the Schrödinger equation.[5,8,9] Here, however, no matrix elements need be calculated and the $E^{(n)}$ can be computed in rational form.

Consider the perturbation of a particular reference state ψ_{NLM} and its eigenvalue, $E_{NLM}(\lambda) = E_{NLM}^{(0)} + \Delta E(\lambda)$ [cf. Eq. (2)]. Now introduce the scaling transformation[10] $r = Nr'/Z$, $\hat{p} = Z\hat{p}'/N$ into Eq. (1), drop the primes, and multiply by r to obtain the eigenvalue equation

$$\left\{-\tfrac{1}{2}r\hat{p}^2 + \tfrac{1}{2}r - N\exp\left[-\lambda\left(\frac{N}{Z}\right)r\right] - r\left(\frac{N}{Z}\right)^2\Delta E(\lambda)\right\}\tilde{\psi}(\mathbf{r}) = 0 \ . \tag{5}$$

For $\lambda = 0$, the solutions to Eq. (5) are Coulomb-Sturmian functions,[5,11] which form a complete and discrete basis in the Hilbert space $\mathcal{L}^2(\mathbf{R}^3, 1/r)$. (These functions also span a unitary irreducible representation of the Lie-algebra so(4,2) in the special coordinate realization relevant to the hydrogen atom.) Rather than pursuing traditional RS perturbation theory over this basis, we employ a power-series method analogous to that used by Bender and Wu[12] in their study of anharmonic oscillators. Assume a solution of the form

$$\tilde{\psi}(\lambda,r) = e^{-r}B(r)Y_{LM}(\theta,\phi) \ , \tag{6}$$

where

$$B(r)=\sum_{n=0}\lambda^n B_n(r),\quad B_n(r)=\sum_{j=0} b_{jn}r^j\ . \tag{7}$$

For the ground state of hydrogen, where $N=Z=1$, substitute these series into Eq. (5), expand the exponential, and collect terms in λ^n to obtain the following difference equation for the b_{jn}:

$$b_{jn}=\frac{1}{j}\left[\frac{1}{2}(j+1)(j+2)b_{j+1,n}+\sum_{p=1}^{j}\frac{(-1)^p}{p!}b_{j-p,n-p}+\sum_{m=1}^{n-1}E^{(m)}b_{j-1,n-m}\right],\quad 2\leq j\leq n,\quad n=2,3,4,\ldots, \tag{8}$$

where $b_{00}=1$, $b_{0n}=b_{1n}=0$, $n=1,2,3,\ldots$ and $b_{jn}=0$ if $j>n$. The perturbation coefficients $E^{(n)}$ are given by

$$E^{(1)}=b_{00}=1,\quad E^{(n)}=-3b_{2,n},\quad n=2,3,4,\ldots\ . \tag{9}$$

The b_{jn} coefficients are calculated one row at a time. For each n value, they are calculated inward from the diagonal element b_{nn}. The difference equation is dependent upon the structure of the unperturbed radial function $L_N^{2L+1}L_{L-1}(2r)$ and must be reformulated for each state. The $E^{(n)}$ have been calculated to $n=100$ for the $1s$, $2s$, and $2p$ levels, i.e., $N=1,2$ and $L=0,1$. The first 10 coefficients of the ground-state series are presented in Table I.

If the RS series in (2) is Stieltjes, then its Hadamard determinants, defined by

$$H_m^{(n)}=\begin{vmatrix} a_n & a_{n+1} & \cdots & a_{n+m} \\ a_{n+1} & a_{n+2} & \cdots & a_{n+m+1} \\ \vdots & \vdots & & \vdots \\ a_{n+m} & a_{n+m+1} & \cdots & a_{n+2m} \end{vmatrix}, \tag{10}$$

where $a_k=|E^{(k)}|$, must satisfy the relations[13]

$$H_m^{(1)}>0,\quad H_m^{(2)}>0,\quad m=0,1,2,\ldots\ . \tag{11}$$

For the ground-state series, $H_1^{(1)}=-\frac{1}{16}$, revealing that it is *not* Stieltjes. The same conclusions follow for the $2s$ and $2p$ perturbation series.

We now consider the "RITZ" continued fraction[14] representation of the RS expansions, having the form

$$E(\lambda)=E^{(0)}+\lambda C(\lambda)$$
$$=E^{(0)}+\cfrac{c_1\lambda}{1+\cfrac{c_2\lambda}{1+\cfrac{c_3\lambda}{1+\cdots}}}\ . \tag{12}$$

Quantum number indices have been omitted for notational convenience. The representation generally begins with the first-order term since many nonrelativistic perturbation expansions are negative Stieltjes[15] for $n\geq 1$. In these cases, $C(\lambda)$ *is necessarily an S fraction*, i.e., $c_n>0$ for $n\geq 1$.

If the continued fraction $C(z)$ is truncated by setting $c_k=0$ for $k>n$, $n=1,2,3,\ldots$, a sequence of rational functions $w_n(z)$, called the nth *convergents* or *approximants* to $C(z)$, are produced. Their numerators and denominators obey the recursion relations

$$w_n(z)=\frac{A_n(z)}{B_n(z)}=\frac{A_{n-1}(z)+c_nzA_{n-2}(z)}{B_{n-1}(z)+c_nzB_{n-2}(z)}\ , \tag{13}$$

with initial conditions $A_0=0$, $B_0=1$, $A_1=c_1$, and $B_1=1$. The $w_{2N}(z)$ and $w_{2N+1}(z)$ are, respectively, the $[N-1,N]$ and $[N,N]$ Padé approximants to the series being represented. For S fractions, all zeros of the $A_n(z)$ and $B_n(z)$ lie on the negative real interval $(-\infty,0)$. Furthermore, the $[N-1,N]$ and $[N,N]$ Padé approximants provide lower and upper bounds, respectively, on $\mathbf{R}^+$ to the Stieltjes function being represented.

The coefficients c_n have been computed accurately to $n=100$ for $1s$, $2s$, and $2p$ states using the quotient-difference algorithm.[16] Since this algorithm is numerically unstable, the RS calculation of the $E^{(n)}$ and subsequent quotient-difference procedure were performed in multiple precision[17] to ensure that all the c_n be accurate to at least 32 digits. The first ten values of the ground state c_n are presented in Table II. The negativity of c_3 and c_4 is a consequence of the non-Stieltjes nature of the perturbation series, since the c_i are expressible in terms of the Hadamard determinants.[14]

For Stieltjes perturbation series, where $E^{(n)}\sim(-1)^n(pn)!$, it is found[18,19] that $c_n\sim n^p$ as $n\to\infty$.

TABLE I. Coefficients $E^{(n)}$, to tenth order, of the Rayleigh-Schrödinger perturbation expansion, Eq. (2), for ground-state hydrogen with a Yukawa potential.

n	$E^{(n)}$
0	−1/2
1	1
2	−3/4
3	1/2
4	−11/16
5	21/16
6	−145/48
7	757/96
8	−69 433/3072
9	321 449/4608
10	−2 343 967/102 40

TABLE II. The first 10 coefficients c_n of the continued fraction representation, Eq. (12), of the ground-state Yukawa perturbation series.

n	c_n
1	1.0
2	0.75
3	−0.083 333 333 333 333 3
4	−5.666 666 666 666 666 7
5	7.411 764 705 882 352 7
6	0.125 933 706 816 059 8
7	2.021 152 375 068 037 7
8	0.648 642 832 216 536 2
9	1.806 723 381 062 811 1
10	0.959 545 902 592 448 2

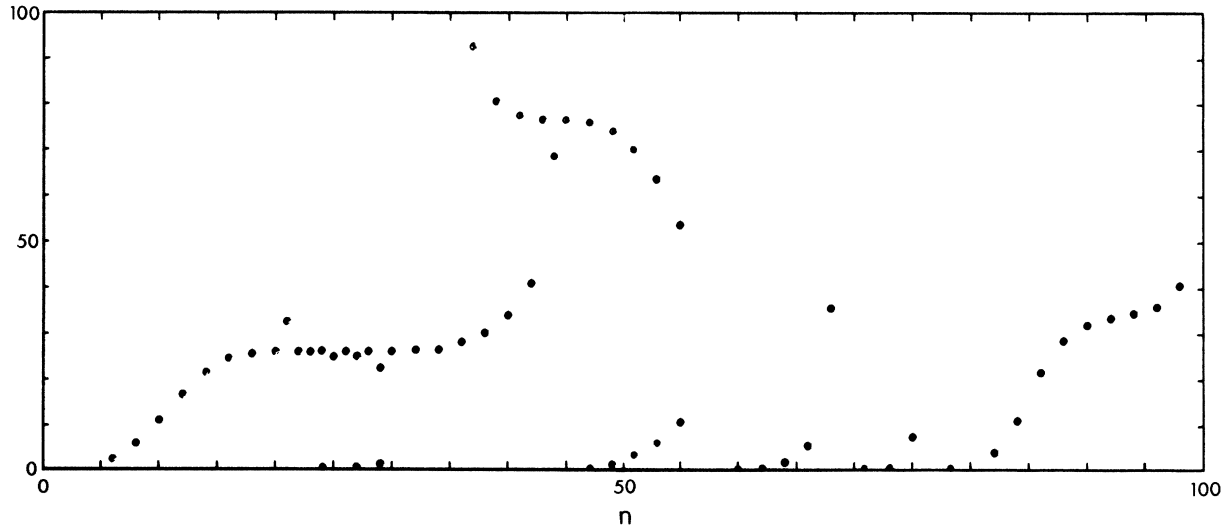

FIG. 1. The poles of the ground-state convergents $w_n(\lambda)$, $1 \leq n \leq 100$, which lie on the positive real-λ axis. (Some isolated poles lying outside the interval [0, 100] have been omitted.)

Such monotonic behavior is not observed for the Yukawa coefficients c_n. For the states examined here, the coefficients c_n demonstrate a curious oscillatory behavior, resembling a beat phenomenon. Periodic "eruptions" of the c_n, where large positive and negative values are assumed, occur regularly but are *not* a consequence of numerical round-off error.

The complete sets of poles and zeros of the convergents $w_n(\lambda)$ of $C(\lambda)$ have been computed for $n \leq 25$ for the continued-fraction representations, using the International Mathematical and Statistical Libraries subroutine ZPOLR.[20] (The procedure is unstable for higher n.) For the ground state, *all* poles and zeros lie on the real λ axis. At most two poles are situated on the positive real axis for various n values. Poles on the negative real axis exhibit the interlacing behavior characteristic of the Stieltjes case. Similar results are obtained for the excited states, with the exception that sets of complex conjugate poles appear sporadically.

The positive poles for convergents $w_n(\lambda)$, $25 \leq n \leq 100$, have been located by first computing explicitly the coefficients of $A_n(\lambda)$ and $B_n(\lambda)$, using Eq. (13). A crude search for changes in sign of the polynomials, followed by Newton-Raphson iteration, located the roots to within 10^{-7}. The locations of the poles for the ground-state representation are plotted in Fig. 1. As n increases, a single pole moves away from the origin until it appears to stabilize at $\lambda \sim 26$. At this time, another pole appears near the origin and moves outward. The stabilization of the outer pole then ceases at $n = 34$. This entire procedure then seems to repeat itself.

The Yukawa potential supports only a finite number of

TABLE III. The eigenvalues $E(\lambda)$ for $1s$, $2s$, and $2p$ levels of hydrogen with a Yukawa potential, as yielded by the convergents $w_n(\lambda)$ of the continued-fraction representation, Eq. (12), of the Rayleigh-Schrödinger perturbation series. The values are accurate to all digits presented.

λ	$E_{1s}(\lambda)$	λ	$E_{2s}(\lambda)$	λ	$E_{2p}(\lambda)$
0.10	−0.407 058 030 613 403 156 75	0.01	−0.115 293 285 167 994 256 22	0.01	−0.115 245 224 090 564 185 89
0.20	−0.326 808 511 369 193 384 88	0.02	−0.106 148 320 244 695 503 25	0.02	−0.105 963 398 179 939 904 76
0.30	−0.257 638 586 303 054 148 88	0.03	−0.097 531 786 134 660 862 77	0.03	−0.097 131 366 795 691 310 67
0.40	−0.198 376 083 361 850 216 61	0.04	−0.089 414 634 185 159 188 42	0.04	−0.088 729 373 582 879 526 29
0.50	−0.148 117 021 889 932 616 71	0.05	−0.081 771 195 795 253 124 17	0.05	−0.080 740 387 037 784 609 71
0.60	−0.106 135 907 505 814 193 00	0.06	−0.074 578 534 412 709 709 69	0.06	−0.073 149 619 385 860 625 02
0.70	−0.071 833 555 904 512 213 04	0.07	−0.067 815 959 981 462 181 22	0.07	−0.065 944 176 996 156 573 38
0.80	−0.044 704 304 497 359 663 20	0.08	−0.061464 656 212 300 385 91	0.08	−0.059 112 804 787 031 234 64
0.90	−0.024 314 193 827 502 054 89	0.09	−0.055 507 388 553 290 736 39	0.09	−0.052 645 701 331 584 274 46
1.00	−0.010 285 789 990 017 696 80	0.10	−0.049 928 271 331 918 889 23	0.10	−0.046 534 390 486 724 608 39
1.10	−0.002 287 244 234 053 485 46	0.15	−0.027 222 190 725 688 518 25	0.15	−0.021 104 888 927 736 242 92
1.15	−0.000 455 889 021 355 957 79	0.20	−0.012 107 865 195 440 464 39	0.20	−0.004 101 646 53
1.16	−0.000 258 622 006 376 600 05	0.25	−0.003 395 906 283 239 307 80	0.21	−0.001 808 760
1.17	−0.000 117 073 729 761 480 41	0.30	−0.000 091 602 443 891 899 01	0.22	−0.000 026
1.18	−0.000 030 985 910 874 039 35	0.31	−0.000 000 037 992 565 724 46		
1.19	−0.000 000 103 031 961 498 99				

bound states for $\lambda > 0$. The number of bound states for a given λ as well as the threshold value λ^* for which a given state is no longer bound have been of great interest.[21] The fact that the positive poles of the $w_n(\lambda)$ generally avoid the region $0 < \lambda < \lambda^*$ accounts for the excellent Padé results originally observed in Ref. 7. For virtually all n, the $w_n(\lambda)$ produce an energy curve which increases monotonically from its unperturbed value at $\lambda = 0$ to a maximum value of $E \cong 0$ (never positive), then to begin a monotonic decrease. Numerical scanning of the Padé sums of the series reveals that $\lambda^*(1s, 2s, 2p) \cong 1.9061$, 0.3102, and 0.220, respectively, in excellent agreement with the values reported in Ref. 21. Let us recall that this perturbative method analyzes the Yukawa problem from the hydrogenic limit, where an infinity of states are bound. In essence it is complementary to that of Ref. 21 and similar studies which always preserve the finiteness of bound states in their approaches.

The convergents $w_n(\lambda)$, $n = 1, 2, \ldots, 100$ have been computed for $0 < \lambda < \lambda^*$ to provide extremely accurate values of the eigenvalues. Table III presents values of $E(\lambda)$ corresponding to $1s$, $2s$, and $2p$ levels of the Yukawa problem. These values are accurate to all digits shown—for the ground state, the w_n agree to over 20 digits for $n > 50$. Accurate values of binding energies for variable Z values, such as those reported in Ref. 7, may also be obtained from these perturbation coefficients, using the scaling relations of Eqs. (3) and (4). The power of these simple perturbative techniques for such short-range problems has been demonstrated. The extension of these methods to excited states is straightforward. However, a decreasing accuracy is expected as found in traditional calculations.

The clustering of Padé poles and zeros on the negative real axis suggests the existence of a branch cut. This would be expected from intuitive physical grounds: The potential in Eq. (1) is unstable for $\lambda < 0$. The existence of poles on the positive real λ axis does not necessarily suggest the existence of a branch cut on $\mathbf{R}^+$, even for $\lambda > \lambda^*$. In fact, $E(\lambda)$ may well be analytic on $\mathbf{R}^+$ even though the bound state becomes imbedded in the continuum. Such analyticity exists for other short-range potentials.[22]

The perturbation coefficients $E^{(n)}$ are observed to be growing roughly as $(n/2)!$ as $n \to \infty$, but a detailed numerical analysis has proven to be quite elusive. A Bender-Wu Wentzel-Kramers-Brillouin–type analysis to determine their large order behavior is also currently being investigated. These aspects are quite important for a better understanding of this and related models.

The author wishes to express his sincere thanks to Professor D. Bessis and Professor B. Simon for much helpful advice as well as to Professor E. M. Harrell for discussions. Fruitful discussions with Professor J. Cizek are also appreicated. I gratefully acknowledge support of this work by the Natural Sciences and Engineering Research Council of Canada.

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