Radius of convergence and analytic behavior of the $1/Z$ expansion

Jonathan D. Baker, David E. Freund,* Robert Nyden Hill, and John D. Morgan III
Department of Physics, University of Delaware, Newark, Delaware 19716
(Received 29 June 1989)

We have performed a 401-order perturbation calculation to resolve the controversy over the radius of convergence of the $1/Z$ expansion for the ground-state energy $E(\lambda)$ of heliumlike ions, where $\lambda=1/Z$ and $H(\lambda)=-\frac{1}{2}\nabla_1^2-1/r_1-\frac{1}{2}\nabla_2^2-1/r_2+\lambda/r_{12}$. Such high-order calculations followed by Neville-Richardson extrapolation of the ratios of the coefficients are necessary to study the asymptotic behavior of the perturbation series. We find (i) that λ_c, the critical value of λ for which $H(\lambda)$ has a bound state with zero binding energy, is approximately 1.097 66, (ii) that λ^*, the radius of convergence of the perturbation series, is equal to λ_c, and (iii) that the nearest singularity of $E(\lambda)$ in the complex plane, which determines λ^*, is on the positive real axis at λ_c. Thus our results confirm Reinhardt's analysis [Phys. Rev. A **15**, 802 (1977)] of this problem using the theory of dilatation analyticity (complex scaling). We also find that the perturbation series for $E(\lambda)$ is convergent at $\lambda=\lambda_c$. The same statements hold for the perturbation series for the square of the norm of the corresponding eigenfunction $\|\psi(\lambda)\|^2$. We find numerically that $E(\lambda)$ has a complicated branch-point singularity at $\lambda=\lambda_c$ of the same type as the function $(1-\lambda/\lambda^*)^{-a}U(a,c;x/(1-\lambda/\lambda^*))$, where U is the irregular solution of the confluent hypergeometric equation, and that $\|\psi(\lambda)\|^2$ has a similar but even more complicated singularity at λ^*. We also discuss the $1/Z$ expansions for excited states of the helium isoelectronic sequence and for states of multielectron atomic ions. By-products of our calculation include the most accurate estimates so far of the nonrelativistic ground-state energies of the H^- ion and of the helium atom, as well as the most accurate upper bound ever obtained to the second-order energy coefficient E_2.

I. INTRODUCTION

In 1930 Hylleraas[1] observed that the scaling transformation $\mathbf{r}\rightarrow\mathbf{r}/Z$ applied to the Hamiltonian of a two-electron atomic ion of nuclear charge Z (in atomic units)

$$-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_{12}} \tag{1}$$

yielded the scaled Hamiltonian

$$Z^2\left[-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-\frac{1}{r_1}-\frac{1}{r_2}+\frac{1}{Z}\frac{1}{r_{12}}\right]. \tag{2}$$

Hence Rayleigh-Schrödinger perturbation theory can be applied to this Hamiltonian by letting the unperturbed Hamiltonian be

$$H_0=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-\frac{1}{r_1}-\frac{1}{r_2}\ , \tag{3}$$

the perturbing operator W be $1/r_{12}$, and the perturbation parameter λ be $1/Z$. Then an eigenvalue $E(\lambda)$ and an eigenvector $\psi(\lambda)$ of $H(\lambda)=H_0+\lambda W$ can be expressed as power series in λ,

$$E(\lambda)=\sum_{n=0}^{\infty}E_n\lambda^n\ , \tag{4}$$

$$\psi(\lambda)=\sum_{n=0}^{\infty}\lambda^n\psi_n\ . \tag{5}$$

Kato[2,3] proved that these series have a nonzero radius of convergence. We shall always employ the convention that

$$\langle\psi_n|\psi_0\rangle=\delta_{0,n}\ . \tag{6}$$

Hylleraas developed a variation-perturbation procedure to calculate numerically the coefficients E_n. For the ground state $E(\lambda)$, E_0 of course is just twice the ground-state energy of the hydrogen atom, -1.0 a.u., and E_1 is the first-order perturbation correction, $\frac{5}{8}=0.625$ a.u., which is evaluated in many quantum-mechanics textbooks. The higher E_n's cannot be evaluated in closed form. Using eight basis functions, Hylleraas found

$$\begin{aligned}E_2&\cong-0.157\,44\ ,\\ E_3&\cong+0.008\,76\ ,\\ E_4&\cong-0.002\,74\ ,\end{aligned} \tag{7}$$

in a.u.

Some 30 years later Knight and Scherr[4–6] used 100 basis functions of the type introduced by Kinoshita[7] to calculate E_2 through E_{13}. Their results in Ref. 6 for the E_n's and the ratios $r_n=E_n/E_{n-1}$ are given in Table I. (One may incidentally note from Knight and Scherr's results that Hylleraas's value for E_2 was accurate to 1 part in 750 and his value for E_3 to 1 part in 150, but his value for E_4 was wrong by a factor of 3. This example is a striking illustration of how rapidly the accuracy of numerical estimates of higher E_n's can deteriorate if one is not using enough basis functions which are concentrated

TABLE I. Knight and Scherr's E_n's and r_n's.

n	E_n	r_n
2	−0.157 666 405	
3	0.008 698 991	
4	−0.000 888 587	
5	−0.001 036 372	
6	−0.000 612 917	0.5914
7	−0.000 372 187	0.6072
8	−0.000 242 872	0.6526
9	−0.000 165 651	0.6821
10	−0.000 116 157	0.7012
11	−0.000 083 281	0.7170
12	−0.000 060 866	0.7309
13	−0.000 045 213	0.7428

in the right regions of configuration space to describe the higher ψ_n's.)

In Ref. 5 Knight and Scherr had calculated the first 11 E_n's and had suggested that they "had the appearance of converging toward a ratio of the coefficients of about +0.75," which would imply that the radius of convergence λ^*, which is determined by the singularity in $E(\lambda)$ nearest to 0 in the complex λ plane, would be $\frac{1}{0.75} \simeq 1.33$. However, in Ref. 6 with two more E_n's they suggested that the ratios "probably extrapolate to some value for r_∞ lying between +0.78 and +0.80," which would imply that $\lambda^* = 1/r_\infty$ would lie between 1.250 and 1.282.

Within the next three years the estimate for r_∞ had been increased still further by Stillinger's analysis[3] of the first 21 E_n's which had been calculated by Midtdal[9] using 203 Hylleraas basis functions. Stillinger observed that the ratios r_n seemed to be behaving as $n \to \infty$ like

$$r_n \simeq r_\infty + \frac{c}{n} . \tag{8}$$

Stillinger therefore did a least-squares fit of the r_n's for $14 \leq n \leq 21$ as a function of $1/n$ and obtained an estimate of $r_\infty \cong 0.8941$ and $\lambda^* \simeq 1.1184$. From the energy series Stillinger estimated λ_c, the maximum value of λ for which $H(\lambda)$ has a bound state, as 1.0975, implying that $Z_c = 1/\lambda_c$, the minimum charge necessary to bind two electrons, is about 0.911 16(10).

In 1969 Sanders and Scherr[10] computed the E_n's up to $n = 25$ for the ground state of helium, using a basis of 100 Hylleraas functions with a single "open-shell" exponential.

In the same year Midtdal, Lyslo, and Aashamar[11] published tables of the first 41 E_n's calculated using 204 Hylleraas basis functions and of the first 81 E_n's using 140 such functions. They also used the corresponding 20th-order wave functions to estimate that the radius of convergence was between 1.20 and 1.23.[12] However, as was apparent at the time, their values for higher-order E_n's obtained using 140 and 204 basis functions showed oscillatory behavior and were in serious disagreement with each other. As we shall see, their results with 140 basis functions for the E_n's for $n \geq 30$ are completely unreliable. For example, their estimate for E_{81} is too small by two orders of magnitude and has the wrong sign. These papers illustrate how easy it is for an iterative computer program to spew out long tables of unreliable numbers, and how necessary it is for a scientist to determine how well converged are his output data before drawing dramatic conclusions from them. In particular, the suggestion by Midtdal and his co-workers that the conventional definition of a bound or "closed" state as one with a square-integrable eigenfunction is in need of modification will turn out to rest on a very shaky foundation.

In 1970 Brändas and Goscinski[13] applied Padé analysis to Midtdal's E_n's for n up to 20 (which are reliable) and estimated $Z_c = 1/\lambda_c \simeq 0.911\,246$ and $\lambda^* = 1/r_\infty = 1/0.894 = 1.118$, in agreement with Stillinger's result. However, they also observed on the basis of their Padé analysis that one could not exclude the possibility that $E(\lambda)$ has a branch point at λ_c, and a further Padé analysis of the logarithmic derivatives of $E(\lambda)$ seemed to indicate that the singularity was more complicated than a simple branch point. Subsequently, Brändas and Goscinski[14] applied a Darboux function ansatz, which assumes that $E(\lambda)$ has a simple branch point singularity, to the E_n's of Midtdal *et al.* up to $n = 27$ and found the same value of Z_c and $\lambda^* = 1/r_\infty \cong \frac{1}{0.893} \cong 1.119$. Very recently Arteca, Fernández, and Castro[15] have applied a rather different analysis using the Darboux function ansatz to the ground state of the helium isoelectronic sequence and have obtained an estimate of $Z^* = 0.9045 \pm 0.0035$, which in turn would imply that $\lambda^* = 1/Z^* = 1.1056 \pm 0.0040$.

A major breakthrough in improving the understanding of the singularities of $E(\lambda)$ was provided by Reinhardt's use of the theory of dilatation analyticity (complex scaling) to show that "if the radius of convergence [of an eigenvalue $E(1/Z)$ corresponding a normalizable eigenfunction] is determined by a singularity on the positive real Z axis, it will occur for a value of Z such that $E(1/Z)$ becomes degenerate with a threshold."[16] Reinhardt's observation implies that Stillinger's interpretation of $E(\lambda)$ for $\lambda_c < \lambda < \lambda^*$ as a bound state imbedded in a continuum[8] could not be right. However, in his reply to Reinhardt's comment, Stillinger[17] observed that the nearest singularity λ^* which determines the radius of convergence of $E(\lambda)$ need not in general be at a threshold because it is possible that the corresponding eigenfunction $\psi(\lambda)$ loses its square integrability at a threshold while $E(\lambda)$ remains analytic at the threshold. Stillinger pointed out that this behavior, which may seem anomalous, occurs in the case where $H_0 = -\frac{1}{2}\nabla^2$ and W is the three-dimensional negative square-well potential. The energy $E(\lambda)$ of $H(\lambda) = H_0 + \lambda W$ remains analytic at the critical value of λ below which $H(\lambda)$ ceases to have a normalizable eigenfunction $\psi(\lambda)$, and $E(\lambda)$ possesses an analytic continuation down to $\lambda = 0$, where it has a logarithmic branch-point singularity. Examples of such behavior are actually quite common. For example, Klaus and Simon[18] have shown that in $\mathbb{R}^3$ if $H_0 = -\frac{1}{2}\nabla^2$ and $W = V(\mathbf{r})$ is in C_0^∞ (the set of infinitely differentiable functions different from 0 on a compact set), then the ground-state eigenvalue $E(\lambda)$ of $H(\lambda) = H_0 + \lambda W$ defines an analytic function for $0 < \lambda < \infty$ even though that eigenvalue is absorbed by the continuum at a strictly posi-

tive value of λ. Of course, neither the square-well potential nor a C_0^∞ potential is dilatation analytic. However, the same phenomenon occurs in the case of the Hulthén potential

$$W=-\frac{e^{-r/a}}{1-e^{-r/a}}\ , \tag{9}$$

which is dilatation analytic. The nth s-state eigenvalue $E_n(\lambda)$ of $-\frac{1}{2}\nabla^2+\lambda W$ is given by

$$E_n(\lambda)=-\frac{(2\lambda a^2-n^2)^2}{8n^2a^2} \tag{10}$$

provided that $n^2<2\lambda a^2$.[19] Clearly for each n the formula for $E_n(\lambda)$ defines an entire function of λ (i.e., a function analytic in the entire complex plane) even though the corresponding eigenfunction ceases to be normalizable at $\lambda=n^2/2a^2$. A less esoteric example is the Coulomb potential, for if $W=-1/r$, then as is well known the nth eigenvalue $E_n(\lambda)$ of $-\frac{1}{2}\nabla^2+\lambda W$ is

$$-\frac{1}{2}\frac{\lambda^2}{n^2}\ , \tag{11}$$

which clearly defines an entire function of λ even though the corresponding eigenfunctions are unnormalizable if $\mathrm{Re}\lambda\le 0$. This last case might be regarded as yet another freak of the two-body Coulomb problem, for if $W=-1/r^\alpha$ with $0<\alpha<2$, then a simple scaling argument shows that an eigenvalue $E_n(\lambda)$ of $H(\lambda)=-\frac{1}{2}\nabla^2+\lambda W$ behaves as

$$E_n(\lambda)=c_n\lambda^{2/(2-\alpha)} \tag{12}$$

(where c_n is an n-dependent constant), which generically *does* have a singularity at $\lambda=0$, the point where the bound states are absorbed by the continuum. Nonetheless, even this family of Hamiltonians illustrates how the disappearance of an eigenvalue need not be accompanied by a singularity in that eigenvalue. Since by the theory of complex scaling the bound eigenvalues of

$$e^{-2\theta}(-\tfrac{1}{2}\nabla^2)-\frac{e^{-\alpha\theta}}{r^\alpha} \tag{13}$$

disappear when $\mathrm{Im}\theta=\pm\pi/2$, it follows that the bound eigenvalues of

$$-\tfrac{1}{2}\nabla^2-\frac{e^{(2-\alpha)\theta}}{r^\alpha} \tag{14}$$

also disappear when $\mathrm{Im}\theta=\pm\pi/2$, and hence that the bound eigenvalues of

$$H(\lambda)=-\tfrac{1}{2}\nabla^2-\frac{\lambda}{r^\alpha} \tag{15}$$

disappear when $\arg\lambda=\pm\pi(1-\alpha/2)$. Thus, as illustrated in Fig. 1, a bound eigenstate of $H(\lambda)$ will vanish whenever $\arg\lambda=\pm\pi(1-\alpha/2)$, but

$$E_n(\lambda)=c_n\lambda^{2/(2-\alpha)} \tag{16}$$

has no singularity except at $\lambda=0$.

However, as Simon has emphasized to us, these results for two-body Schrödinger operators in which $E(\lambda)$ remains analytic at a threshold do *not* resolve the paradox of having $\lambda_c<\lambda^*$ in the case of the $1/Z$ expansion. From the proof of Theorem 2.3 of Klaus and Simon's article,[18] it follows that if $E(\lambda)$ is analytic at λ_c and $E(\lambda)$ approaches $E(\lambda_c)$ linearly in $\lambda_c-\lambda$ (as is the case with the $1/Z$ expansion), then for λ slightly larger than λ_c, $H(\lambda)$ has a genuine bound state imbedded in the continuum, and the content of Reinhardt's argument[16] is that this cannot happen because a bound state cannot penetrate the continuum at λ_c and then disappear at some larger λ^* which is not a threshold. [Note that our λ_c-λ corresponds to Klaus and Simon's λ-λ_0, and that our threshold energy $E(\lambda_c)$ corresponds to their $e(\lambda_0)=0$.]

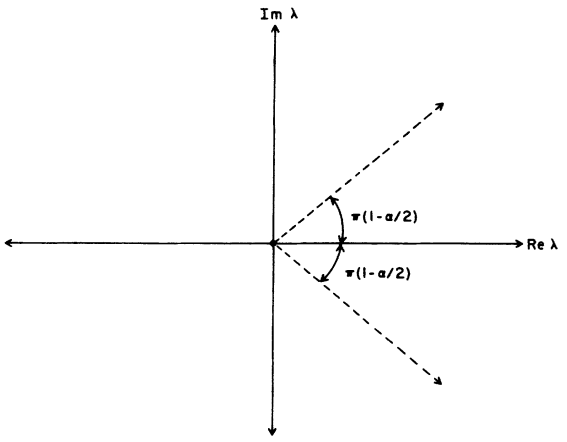

FIG. 1. A bound state eigenvalue $E(\lambda)$ of $H(\lambda)=-\frac{1}{2}\nabla^2-\lambda/r^\alpha$ disappears when $\arg\lambda=\pm\pi(1-\alpha/2)$, but $E(\lambda)$ is singular only at $\lambda=0$.

Although there are a wealth of results on threshold behavior in two-body Schrödinger operators, the only rigorous results for three-body problems seem to be those of Klaus and Simon,[20] who, after separating out the three degrees of freedom associated with center-of-mass motion, considered the Hamiltonian

$$H(\lambda)=-\tfrac{1}{2}\nabla^2+\lambda V\ , \tag{17}$$

where $-\frac{1}{2}\nabla^2$ is the kinetic energy operator in $\mathbb{R}^6$ and V is a sum of pair potentials $V_{ij}(\mathbf{r}_i-\mathbf{r}_j)$ which are negative and in $C_0^\infty(\mathbb{R}^3)$. Klaus and Simon proved that if the ground-state energy $E(\lambda)$ becomes degenerate with a unique two-body threshold at $\lambda=\lambda_c$, then $E(\lambda)$ is analytic at λ_c. However, no analogous rigorous results have been published for three-body problems with pair potentials which are not in C_0^∞.

Stillinger[17] concluded his reply to Reinhardt's comment with a plea for further analysis of the enigmatic problem of the radius of convergence of the $1/Z$ expansion:

"It seems obvious that more information is needed for full understanding of the analytic behavior of atomic perturbation problems. More than a decade has passed since publication of Midtdal's perturbation coefficients for the

two-electron problem, upon which the conclusions of Ref. [8] were based. It is timely and appropriate to turn present computing power to redetermination of the two-electron perturbation coefficients. This can surely be done to higher order than before, with scrupulous attention to convergence of individual coefficients with respect to basis-set size. The results could substantially sharpen our knowledge of the singularities of $E(\lambda)$."

In view of the continuing interest in the $1/Z$ expansion (over 100 publications on it are cited in a recent article by Silverman[21]), which is one of the very few perturbation expansions in atomic and molecular physics which is actually convergent and not merely asymptotic, the determination of the radius of convergence of the power series for $E(1/Z)$ is particularly worthwhile, since knowledge of how the analytic structure of $E(\lambda)$ determines λ^* in the case of the ground state of heliumlike ions should provide insight which is generalizable to other atoms and molecules.

II. SURVEY OF MATHEMATICALLY RIGOROUS RESULTS ON THE GROUND STATE

Before describing our variational procedure, we shall first survey what is rigorously known about the properties of the ground-state eigenvalue and eigenfunction of the operator

$$H(1/Z)=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-\frac{1}{r_1}-\frac{1}{r_2}+\frac{1}{Z}\frac{1}{r_{12}}\ . \tag{18}$$

Using techniques which he had developed for studying the perturbations of unbounded linear operators, Kato[2,3] showed that the $1/Z$ expansion is convergent, and for the ground state of heliumlike ions he derived a lower bound to the radius of convergence of $\frac{1}{7.7}\cong 0.13$. Subsequently Ahlrichs[22] derived an improved lower bound to λ^* of $\frac{1}{1.98}\cong 0.505$, which is sufficient to prove that the $1/Z$ expansion for the ground state converges in the physically important case of $Z=2$ (helium).

Recently M. and T. Hoffmann-Ostenhof and B. Simon[23] have proved that $H(\lambda_c)$ has a square-integrable eigenfunction corresponding to a threshold bound state with ionization potential 0. (This result had earlier been inferred in a nonrigorous way by Stillinger and Stillinger.[8]) In fact, as noted by the Hoffmann-Ostenhof's and Simon, the one-electron density $\rho(r)$ associated with this threshold bound state obeys (in atomic units)

$$C_-(\delta)(r+1)^{-(3/4)-\delta}e^{-[8(\lambda_c-1)r]^{1/2}} \le\sqrt{\rho(r)}\le C_+(\delta)(r+1)^{-(3/4)+\delta}e^{-[8(\lambda_c-1)r]^{1/2}}\ , \tag{19}$$

where δ is an arbitrarily small positive constant and $C_\pm(\delta)$ are constants depending on δ. These inequalities show that the square-integrable eigenfunction of $H(\lambda_c)$ actually has a modified exponential decrease over not too long a length scale [note that $8(\lambda_c-1)\cong 0.78$] even though its binding energy is zero. As we shall see, this has important consequences for our ability to calculate accurately high-order perturbation coefficients. Furthermore, the Hoffmann-Ostenhof's and Simon noted that by an earlier theorem of Simon,[24(a)] the existence of a bound state at the critical coupling constant λ_c implies that for $\lambda<\lambda_c$, $E(\lambda)$ approaches $E(\lambda_c)=-\frac{1}{2}$ *linearly* in $\lambda-\lambda_c$ as $\lambda-\lambda_c\to 0^-$. Explicitly, as $\lambda\to\lambda_c^-$,

$$E(\lambda)=E(\lambda_c)+E'(\lambda_c)(\lambda-\lambda_c)+o(\lambda-\lambda_c)\ , \tag{20}$$

where

$$E'(\lambda_c)=\frac{\left\langle\psi(\lambda_c)\left|\frac{1}{r_{12}}\right|\psi(\lambda_c)\right\rangle}{\langle\psi(\lambda_c)|\psi(\lambda_c)\rangle}\ , \tag{21}$$

as would be expected from the Hellmann-Feynman theorem.

Finally, we may mention the general result that if the family of operators $H(\lambda)=A+\lambda B$ is self-adjoint on the domain of A, then a simple application of the Rayleigh-Ritz variational principle shows that the lowest eigenvalue $E(\lambda)$ is a concave function of λ. This is a generalization of the well-known result that in perturbation theory the second-order correction to the ground-state energy is always negative.

III. NUMERICAL PROCEDURE

We have employed the standard Hylleraas-Knight-Scherr (HKS) variational perturbation method described in detail by these authors;[1,6] hence we need not duplicate their presentations. The only minor difference is that since we use the convention $\langle\psi_0|\psi_n\rangle=\delta_{0,n}$, we replace Knight and Scherr's[6] operator $G_0=H_0-E_0$ with $G_0'=H_0-E_0+CP_0$, where P_0 is the projection onto ψ_0 and C is an arbitrary nonzero real constant which we take to be 1. G_0' is a little easier to use numerically since it has a genuine inverse, whereas G_0 has only a generalized inverse because $G_0\psi_0=0$. In the HKS perturbation equations for $n\ge 1$, G_0 always multiplies a ψ_n with $n\ge 1$, so G_0 may freely be replaced by G_0' since $G_0'\psi_n=G_0\psi_n+CP_0\psi_n$ and $P_0\psi_n\equiv 0$.[24(b)]

As basis functions for the HKS variational procedure we initially tried using the modified Frankowski-Pekeris[25] (FP) basis set which we have recently used in a variational calculation of the ground states of the helium isoelectronic sequence.[26] These basis functions are of the form $\phi(2ks,2kt,2ku)$, where

$$\phi(s,t,u)=s^n t^l u^m(\ln s)^j e^{-s/2}\ . \tag{22}$$

Here s, t, and u are the Hylleraas coordinates

$$s=r_1+r_2,\quad t=r_2-r_1,\quad u=r_{12}\ , \tag{23}$$

n is allowed to be negative if $n+l+m\ge 2j+2$, and k is a flexible scaling parameter. The key idea behind Frankowski and Pekeris's introduction and our subsequent modification of this basis is that vastly accelerated convergence of a variational calculation can be obtained by using basis functions with the same analytic structure (cusp behavior) as the exact function one is trying to ap-

proximate.[27] Indeed, our initial results for the first few E_n's using 256 such basis functions were more accurate than even the extrapolated values for the E_n's which Midtdal *et al.*[11] had obtained using 204 Hylleraas functions. However, it became obvious to us that our values for the E_n's for $n \gtrsim 15$ were not reliable enough to use for extrapolation of the ratios $r_n = E_{n+1}/E_n$ as $n \to \infty$. A little reflection made the reason quite clear. Our estimates of E_{2n} and E_{2n+1} depend on how well we have determined ψ_n. Since

$$\psi(\lambda) = \sum_{n=0}^{\infty} \lambda^n \psi_n \ , \tag{24}$$

we see that for λ slightly less than λ_c, the higher order ψ_n's make a relatively large contribution to the exact eigenfunction $\psi(\lambda)$. Since for λ slightly less than λ_c, the eigenfunction $\psi(\lambda)$ is concentrated heavily in that region of configuration space where one electron is close to the nucleus and the other is much further away (consider H^-, for which $\lambda = 1$), we would expect that the higher-order ψ_n's are also concentrated heavily in this region of configuration space. However, the FP basis functions, with their common length scale factor in the exponential $\exp(-ks)$, are not concentrated very much in this region of configuration space except for those whose power of t is very large. It was clear that it would be advantageous to use basis functions which had a "split" or "open-shell" exponential, as well as the correct analytic structure at $s = 0$, and so we tried those developed by Frankowski[28] of the form $\phi(2ks, 2kt, 2ku)$, where

$$\phi(s,t,u) = s^n t^l u^m (\ln s)^j (e^{ct} \pm e^{-ct}) e^{-s/2} \ . \tag{25}$$

(The $\pm$ sign depends on whether l is even or odd to assure the proper exchange symmetry.) With a moderately large value of c these basis functions introduced by Frankowski could be expected to do a better job than the FP ones of duplicating the higher-order ψ_n's; unfortunately, they did a significantly less accurate job of duplicating the lower-order ψ_n's, such as ψ_0, ψ_1, etc., which are needed to obtain E_2, E_3, etc., and which must be known accurately to obtain by iteration the higher-order E_n's and ψ_n's. Again our hopes had been disappointed, but the road to success was now clearly visible.

We combined our modified FP basis and Frankowski's basis into one composite basis, which could be expected to duplicate accurately both the low-order and the high-order ψ_n's. (A similar composite basis has recently been used by Kono and Hattori[29] in their variational calculations on excited states of helium.) We excluded high powers of t from the FP basis to avoid excessive overlaps with the members of the Frankowski basis. The numbers of elements selected for each basis were progressively increased to find a composite basis which did not suffer from problems with numerical linear dependence. We finally settled on using 244 FP basis functions and 232 Frankowski basis functions for a grand total of 476 basis functions.

IV. SUBTLETIES AT LARGE ORDER: FINITE VERSUS INFINITE-DIMENSIONAL EIGENVALUES AND PERTURBATION SERIES

In approximating the eigenvalue(s) $E(\lambda)$ of the unbounded linear operator

$$H(\lambda) = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{\lambda}{r_{12}} \tag{26}$$

by the eigenvalue(s) $E_N(\lambda)$ of finite $N \times N$ matrix approximants $H_N(\lambda)$ to $H(\lambda)$, one needs to be aware of several subtleties. For example, it is well known that whereas for any given N $H_N(\lambda)$ has only discrete eigenvalues, $H(\lambda)$ has a continuous spectrum. It is less well known (at least among chemists and physicists) that a singularity of an eigenvalue $E(\lambda)$ of the unbounded operator $H(\lambda)$ can have a quite different nature from that of any singularity of an eigenvalue $E_N(\lambda)$ of any finite matrix approximant $H_N(\lambda)$, and hence that the large-order behavior of the perturbation series for $E(\lambda)$ can be quite different from the large-order behavior of the perturbation series for $E_N(\lambda)$. To illustrate these points, we briefly review some results which can be found in Kato's book on perturbation theory.[3]

Suppose that $H(\lambda) = A + \lambda B$ is a self-adjoint operator for all λ in some interval which contains the point $\lambda = 0$. Then it is quite possible that an eigenvalue $E(\lambda)$ of $H(\lambda)$ has a singularity on the real axis [e.g., consider the eigenvalues in Eq. (12)]. However, the eigenvalues $E_N(\lambda)$ of any finite matrix approximant $H_N(\lambda)$ to $H(\lambda)$ are holomorphic on the real axis; singularities of $E_N(\lambda)$ must occur at points where $\mathrm{Im}\lambda \neq 0$. At these points $E_N(\lambda)$ has at worst algebraic branch-point singularities, whereas the exact $E(\lambda)$ can have a more complicated singularity. The singularities of $E_N(\lambda)$ occur at complex values of λ where two or more eigenvalues of $H_N(\lambda)$ are degenerate. If an eigenvalue is p-fold degenerate at a complex value of λ, then the order of the branch-point singularity of $E_N(\lambda)$ does not exceed $p-1$. If A_N and B_N are Hermitian, then the singular points of a given eigenvalue $E_N(\lambda)$ come in pairs which are complex conjugates of each other, as is illustrated in Fig. 2. It is quite possible that as $N \to \infty$ the imaginary parts of some of the singular points of $E_N(\lambda)$ tend to 0 if $E(\lambda)$ has a singularity on the real axis.

The radius of convergence of the power series for $E_N(\lambda)$ is determined by the distance to the nearest singularities in the complex plane. Since these singularities occur pairwise at values of λ and λ^* where eigenvalues $E_N(\lambda)$ and $E_N(\lambda^*)$ are degenerate, and since generically twofold degeneracies are more frequent than multiple degeneracies, generically we would expect that the singularities of $E_N(\lambda)$ which determine the radius of convergence of the power series for $E_N(\lambda)$ are a complex conjugate pair $\lambda_r \pm i\lambda_i$ associated with twofold degeneracies. Such degeneracies can give rise to only a square-root branch point. Thus typically the behavior of the nearest singularities of $E_N(\lambda)$ will be that of

$$\sqrt{(\lambda_r + i\lambda_i - \lambda)(\lambda_r - i\lambda_i - \lambda)} \ . \tag{27}$$

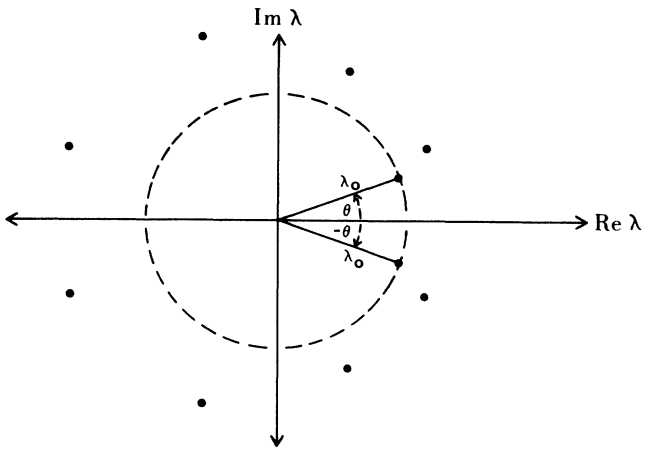

FIG. 2. Typical singular points in the complex λ plane of an eigenvalue $E_N(\lambda)$ of a finite $N\times N$ matrix $H_N(\lambda)=A_N+\lambda B_N$, where A_N and B_N are Hermitian. λ_0 and $\pm\theta$ are the moduli and the arguments of the pair of singular points closest to 0.

These remarks can be illustrated by considering the prototypical problem of the perturbation theory of 2×2 Hermitian matrices. Without loss of generality, consider $H_2(\lambda)=A_2+\lambda B_2$, where

$$A_2=\begin{bmatrix} a_{11} & 0 \\ 0 & a_{22} \end{bmatrix},$$
$$B_2=\begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix}, \tag{28}$$

where all diagonal matrix elements are real, $b_{12}=b_{21}^*\neq 0$, and $a_{11}\neq a_{22}$. Then the two eigenvalues $E_\pm(\lambda)$ of $H_2(\lambda)=A_2+\lambda B_2$ are given by

$$E_\pm(\lambda)=\tfrac{1}{2}(a_{11}+\lambda b_{11}+a_{22}+\lambda b_{22} \pm\{[a_{11}-a_{22}+\lambda(b_{11}-b_{22})]^2+4\lambda^2 b_{12}b_{21}\}^{1/2}). \tag{29}$$

These eigenvalues have square-root branch points at those values of λ for which the discriminant vanishes; i.e., for which

$$\lambda=(a_{11}-a_{22})\frac{-(b_{11}-b_{22})\pm 2i|b_{12}|}{(b_{11}-b_{22})^2+4|b_{12}|^2}. \tag{30}$$

The radius of convergence λ_0 of the power series for $E_\pm(\lambda)$ is thus given by

$$\lambda_0=\frac{|a_{11}-a_{22}|}{[(b_{11}-b_{22})^2+4|b_{12}|^2]^{1/2}}. \tag{31}$$

Thus Eq. (29) can be rewritten as

$$E_\pm(\lambda)=\frac{1}{2}\left\{a_{11}+a_{22}+\lambda(b_{11}+b_{22}) \pm|a_{11}-a_{22}|\left[1-2\frac{\lambda}{\lambda_0}\cos\theta+\left[\frac{\lambda}{\lambda_0}\right]^2\right]^{1/2}\right\}, \tag{32}$$

where

$$\cos\theta=-\frac{b_{11}-b_{22}}{[(b_{11}-b_{22})^2+4|b_{12}|^2]^{1/2}}\operatorname{sgn}(a_{11}-a_{22}) \tag{33}$$

is the cosine of the argument of the singular points of $E_\pm(\lambda)$. Thus the radical in Eq. (32) can be expanded in a series of Legendre polynomials of $\cos\theta$:

$$\left[1-2\frac{\lambda}{\lambda_0}\cos\theta+\left[\frac{\lambda}{\lambda_0}\right]^2\right]^{1/2} = 1-\frac{\lambda}{\lambda_0}\cos\theta + \sum_{n=2}^{\infty}\left[\frac{\lambda}{\lambda_0}\right]^n\frac{P_{n-2}(\cos\theta)-P_n(\cos\theta)}{2n-1}, \tag{34}$$

which is straightforward to derive from the generating function and the recurrence relations for Legendre polynomials. Hence for $n\geq 2$ the nth-order coefficient in the perturbation series for $E_\pm(\lambda)$ is proportional to

$$\pm\lambda_0^{-n}\frac{P_{n-2}(\cos\theta)-P_n(\cos\theta)}{2n-1}. \tag{35}$$

The formula of Laplace for the asymptotic behavior of Legendre polynomials as $n\to\infty$

$$P_n(\cos\theta)=2^{1/2}(\pi n\sin\theta)^{-1/2}\cos\left[(n+\tfrac{1}{2})\theta-\frac{\pi}{4}\right]+O(n^{-3/2}), \tag{36}$$

which is valid for $n\gg 1/\theta$ (cf. Szegö,[30(a)] Theorem 8.21.2), shows that as $n\to\infty$,

$$P_{n-2}(\cos\theta)-P_n(\cos\theta)=2^{1/2}(\pi n\sin\theta)^{-1/2}\left[\cos\left[(n-\tfrac{3}{2})\theta-\frac{\pi}{4}\right]-\cos\left[(n+\tfrac{1}{2})\theta-\frac{\pi}{4}\right]\right]+O(n^{-3/2}) \tag{37}$$

The formula

$$\cos\alpha-\cos\beta=-2\sin\frac{\alpha+\beta}{2}\sin\frac{\alpha-\beta}{2} \tag{38}$$

for the difference of the cosines of two angles shows that as $n\to\infty$,

$$P_{n-2}(\cos\theta)-P_n(\cos\theta)=2^{3/2}(\pi n\sin\theta)^{-1/2}\sin\left[(n-\tfrac{1}{2})\theta-\frac{\pi}{4}\right]\sin\theta+O(n^{-3/2}). \tag{39}$$

Thus as $n \to \infty$, the nth-order coefficient of the perturbation series of $E_{\pm}(\lambda)$ behaves as

$$\pm\lambda_0^{-n}\left[\left[\frac{2}{\pi n}\sin\theta\right]^{1/2}\frac{\sin\left[(n-\frac{1}{2})\theta-\frac{\pi}{4}\right]}{n-\frac{1}{2}}+O(n^{-5/2})\right]. \tag{40}$$

Since $\sin\theta \neq 0$, it is evident that as $n \to \infty$ the perturbation coefficients oscillate with period $2\pi/\theta$. This will be true for any eigenvalue whose nearest singularities are square-root-type branch points of the type in Eq. (32). Since generically the nearest singularities of finite-matrix eigenvalues will be of precisely this form, we may expect that generically the nth-order perturbation coefficients for an eigenvalue $E_N(\lambda)$ of a finite-dimensional matrix $A_N+\lambda B_N$ will asymptotically oscillate periodically as $n \to \infty$. However, the nth-order perturbation coefficients of an eigenvalue $E(\lambda)$ of an infinite-dimensional self-adjoint operator $H(\lambda)=A+\lambda B$ in general need not oscillate as $n \to \infty$. Thus when one is trying to approximate the perturbation coefficients for an infinite-dimensional operator $H(\lambda)=A+\lambda B$ by solving for those of a finite-dimensional matrix $H_N(\lambda)=A_N+\lambda B_N$, periodic oscillatory behavior of the finite-dimensional perturbation coefficients at large order must be viewed with suspicion (until proven otherwise) as possibly a *finite-basis effect* of no physical significance, which is present for all finite N but disappears at a fixed order n in the limit as $N \to \infty$.[30(b)] Before credence can be put in periodic oscillatory behavior at large order, it must first be determined how stable are the coefficients E_n to changes in the basis, such as increasing the number of basis functions or shifting nonlinear variational parameters.

To avoid misunderstanding, we hasten to add that oscillatory behavior in the first few E_n's is hardly suspicious, and even very common. For example, if $H(\lambda)=H_0+\lambda W$ is the Hamiltonian of an atomic ion, where W is the sum of the interelectronic Coulomb potentials, then E_0 is negative for any bound state, $E_1=\langle W\rangle$ is positive, and E_2 is negative at least for the ground state of a given symmetry.

We also emphasize that asymptotic oscillatory behavior with indefinitely increasing "period" of a function's Taylor series coefficients is *not* inconsistent with the nearest singularity of that function being on the positive real axis. Consider, for example, the function

$$(1-\lambda/\lambda^*)^{-\beta}\exp[-\xi/(1-\lambda/\lambda^*)], \tag{41}$$

where ξ is a positive real number. This function has an essential singularity at $\lambda=\lambda^*$, and if β is not an integer, it also has a branch point at $\lambda=\lambda^*$. This function can be expanded as a power series in λ/λ^*:

$$(1-\lambda/\lambda^*)^{-\beta}\exp[-\xi/(1-\lambda/\lambda^*)]=\sum_{n=0}^{\infty}C_n(\lambda/\lambda^*)^n, \tag{42}$$

where asymptotically

$$C_n=\pi^{-1/2}\xi^{1/4-\beta/2}e^{-\xi/2}n^{\beta/2-3/4}\times\left[\cos\left[2(\xi n)^{1/2}+\frac{\pi}{4}-\frac{\pi\beta}{2}\right]+O(n^{-1/2})\right] \tag{43}$$

as Perron[31] showed in 1921. Hence as $n \to \infty$, the coefficients C_n oscillate, but with a steadily increasing "period" proportional to $2\pi(n/\xi)^{1/2}$. Thus we see that a function whose nearest singularity is on the positive real axis can still have oscillatory Taylor-series coefficients.

V. NUMERICAL RESULTS FOR THE GROUND STATE

All of our calculations were performed in quadruple precision ($\sim$30 decimal digits) on the University of Delaware's IBM 3081D computer.

The first order of business is to pin down the critical value λ_c, the maximum value of λ for which $H(\lambda)$ has a bound state. Using our 476 basis functions in a *variational* calculation with $k=0.606\,72$ and $c=0.448$ we still have a bound state, with binding energy 2.0×10^{-7} a.u., at $\lambda=1.097\,66$. This is a lower bound (within a round-off error which experience strongly suggests is negligible) to λ_c. Obtaining a useful rigorous upper bound to λ_c is unfeasible; however, comparison of the close agreement of (i) Stillinger's estimate $\lambda_c \simeq 1.0975$, (ii) our results with approximately 250 FP-type basis functions which still gave binding at $\lambda=1.0976$, and (iii) our result $\lambda_c > 1.097\,66$, leads us to believe that the exact λ_c does not exceed our lower bound by more than a few units in the last digit. From our results in Table II and Fig. 3 one may see that $E(\lambda)$ approaches $E(\lambda_c)=-\frac{1}{2}$ like

$$E(\lambda)\simeq E(\lambda_c)+0.235(\lambda-\lambda_c), \tag{44}$$

in agreement with the observation of the Hoffmann-Ostenhof's and Simon[23] that $E(\lambda)-E(\lambda_c)$ is linear in $(\lambda-\lambda_c)$. As mentioned previously, by Simon's[24(a)] proof of the Hellmann-Feynman theorem at thresholds, the coefficient of the linear term equals

$$\frac{\left\langle\psi(\lambda_c)\left|\frac{1}{r_{12}}\right|\psi(\lambda_c)\right\rangle}{\langle\psi(\lambda_c)|\psi(\lambda_c)\rangle}. \tag{45}$$

The reciprocal of 1.097 66 is 0.911 03, which provides an upper bound to and an accurate estimate of the minimum nuclear charge $Z_c=1/\lambda_c$ necessary to bind two electrons.

Having obtained an accurate knowledge of λ_c (prob-

TABLE II. $E(\lambda)$'s for λ slightly less than $\lambda_c \cong 1.097\,66$.

λ	$E(\lambda)$
1.0960	−0.500 409 3
1.0970	−0.500 162 3
1.0974	−0.500 064 0
1.0975	−0.500 039 4
1.0976	−0.500 014 9
1.097 66	−0.500 000 2

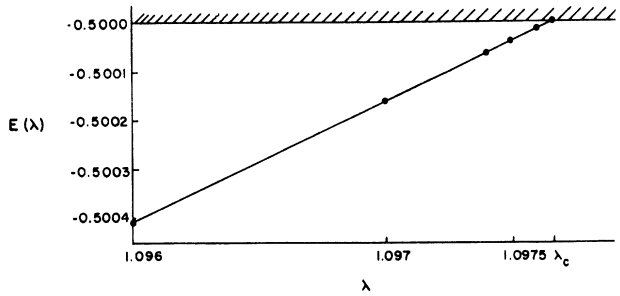

FIG. 3. The ground state $E(\lambda)$ approaches the continuum linearly in $\lambda-\lambda_c$.

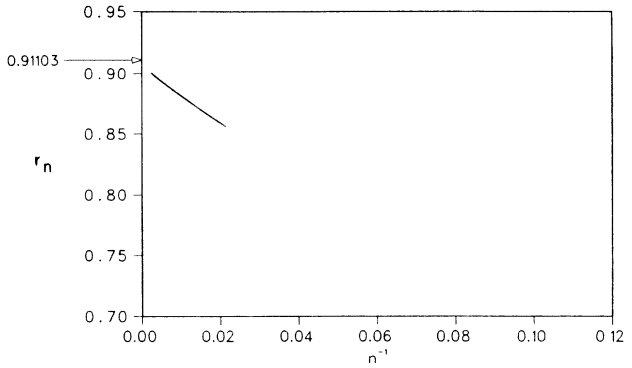

FIG. 4. The r_n's for $11 \le n \le 400$ vs n^{-1}, obtained with $c=0.425$ and $k=0.80$.

ably to within a few parts in 10^5), we may now proceed with the much more difficult task of estimating λ^*. Since we could not be sure how representative are the first 21 E_n's, we decided to calculate the ψ_n's for n up to 200 and hence the E_n's for n up to 401. Our results with $k=0.80$ and $c=0.425$ are presented in the second column of Table III. The ratios $r_n=E_{n+1}/E_n$ for n up to 400 are graphed versus $1/n$ in Fig. 4. The results of other runs with $k=0.85$ and $c=0.420$, $k=0.80$ and $c=0.425$, and $k=0.85$ and $c=0.425$ suggest that even our higher-order E_n's are accurate to a few parts in 10^5 and our high-order r_n's to a few parts in 10^6. The lower-order E_n's are of course much more accurate. In view of the recent resurgence of interest in calculating E_2,[32] we may mention our estimate of

$$-0.157\,666\,429\,469\,14$$

obtained with $k=1$ and $c=0.40$. Since ψ_0 is included exactly in the basis with $k=1$, the HKS variational principle implies that this estimate is an upper bound (within a negligible round-off error) to the exact E_2.

The sum of the E_n's for n running from 0 to 401 is

$$-0.527\,751\,016\,544\,266$$

which at the time we did our calculations was the most accurate estimate of the energy of the ground state of H^-; by comparison, Frankowski and Pekeris's variational upper bound[25] was

$$-0.527\,751\,016\,35\ .$$

Our perturbational result is only slightly above Drake's recent value

$$-0.527\,751\,016\,544\,306(85)$$

obtained by extrapolation of results with up to 616 Hylleraas-type functions with multiple exponential scale parameters.[33] A variational calculation with our 476 basis functions, but using the nonlinear variational parameters $k=0.73, c=0.40$, yields an upper bound of

$$-0.527\,751\,016\,544\,375\ ,$$

which is the most accurate estimate to date of the nonrelativistic energy of H^-.

For $Z=2$ the corresponding weighted sum of coefficients with $k=0.80$ and $c=0.425$ yields an estimate of

$$-2.903\,724\,377\,034\,116\,7$$

for the ground-state energy of helium, which may be compared with the variational upper bound of

$$-2.903\,724\,377\,034\,07$$

obtained recently with 230 FP basis functions by Freund, Huxtable, and Morgan.[26] (In that article, we conservatively reported one fewer digit, and we rounded our result upward to ensure that we still had an upper bound.) It may also be compared with the estimate

$$-2.903\,724\,377\,034\,105(28)$$

which Drake obtained by systematic extrapolation of results with up to 616 basis functions.[33] A variational calculation using our 476 basis functions, but with $k=0.96$ and $c=0.40$, yields an upper bound of

$$-2.903\,724\,377\,034\,118\,4\ .$$

At first it might seem puzzling that the optimal nonlinear parameters for calculating the large-order series coefficients do not optimize the energy for various values of Z. However, it can be readily understood in the light of the fact that changing $Z=1/\lambda$ changes the weighting of the energy coefficients E_n in the power series (4) for $E(\lambda)$. As λ decreases, the higher-order coefficients E_n are weighted less and less, and so they count less heavily in the optimization of the total energy. Hence in optimizing $E(\lambda)$ for a given $\lambda<\lambda_c$, it pays to use nonlinear variational parameters which do a better job of optimizing the lower-order than the higher-order coefficients.

To hasten the convergence of the ratio's r_n to their limiting value $r_\infty=1/\lambda^*$, we tried Neville-Richardson extrapolation. Stillinger[8] had already observed that for $10 \le n \le 20$ the ratios r_n seemed to be behaving like

$$r_n \simeq C_0+\frac{C_1}{n}\ . \tag{46}$$

If one has a sequence of numbers r_n such that

$$r_n=C_0+\frac{C_1}{n}+\frac{C_2}{n^2}+\cdots\ , \tag{47}$$

TABLE III. The E_n's, their estimates from Eq. (82), the differences, and the relative errors. The numbers in square brackets are powers of 10.

Order	Perturbation	Asymptotic	Difference	Diff/Pert
0	-0.1000000000[+01]	-0.2595640918[+00]	0.74044[+00]	-0.74044[+00]
1	0.6250000000[+00]	0.3259805486[+00]	-0.29902[+00]	-0.47843[+00]
2	-0.1576664295[+00]	-0.2525179810[-01]	0.13241[+00]	-0.83984[+00]
3	0.8699031528[-02]	-0.6013542672[-02]	-0.14713[-01]	-0.16913[+01]
4	-0.8887072842[-03]	-0.2396454007[-02]	-0.15077[-02]	0.16966[+01]
5	-0.1036371848[-02]	-0.1187795186[-02]	-0.15142[-03]	0.14611[+00]
6	-0.6129405205[-03]	-0.6662091795[-03]	-0.53269[-04]	0.86907[-01]
7	-0.3721755765[-03]	-0.4048954453[-03]	-0.32720[-04]	0.87915[-01]
8	-0.2428779732[-03]	-0.2603934115[-03]	-0.17515[-04]	0.72116[-01]
9	-0.1656610547[-03]	-0.1746575755[-03]	-0.89965[-05]	0.54307[-01]
10	-0.1161792026[-03]	-0.1210292671[-03]	-0.48501[-05]	0.41746[-01]
11	-0.8330135003[-04]	-0.8607582425[-04]	-0.27745[-05]	0.33306[-01]
12	-0.6088027632[-04]	-0.6253109599[-04]	-0.16508[-05]	0.27116[-01]
13	-0.4523072242[-04]	-0.4623754169[-04]	-0.10068[-05]	0.22260[-01]
14	-0.3407966122[-04]	-0.3470536215[-04]	-0.62570[-06]	0.18360[-01]
15	-0.2599106570[-04]	-0.2638615630[-04]	-0.39509[-06]	0.15201[-01]
16	-0.2003307002[-04]	-0.2028589931[-04]	-0.25283[-06]	0.12621[-01]
17	-0.1558537543[-04]	-0.1574893218[-04]	-0.16356[-06]	0.10494[-01]
18	-0.1222584280[-04]	-0.1233255310[-04]	-0.10671[-06]	0.87283[-02]
19	-0.9661636835[-05]	-0.9731698647[-05]	-0.70062[-07]	0.72515[-02]
20	-0.7686162634[-05]	-0.7732355162[-05]	-0.46193[-07]	0.60098[-02]
21	-0.6151468041[-05]	-0.6181986228[-05]	-0.30518[-07]	0.49611[-02]
22	-0.4950169803[-05]	-0.4970327043[-05]	-0.20157[-07]	0.40720[-02]
23	-0.4003380609[-05]	-0.4016654833[-05]	-0.13274[-07]	0.33158[-02]
24	-0.3252508668[-05]	-0.3261196278[-05]	-0.86876[-08]	0.26710[-02]
25	-0.2653603522[-05]	-0.2659231329[-05]	-0.56278[-08]	0.21208[-02]
26	-0.2173399140[-05]	-0.2176986636[-05]	-0.35875[-08]	0.16506[-02]
27	-0.1786506716[-05]	-0.1788736465[-05]	-0.22297[-08]	0.12481[-02]
28	-0.1473400370[-05]	-0.1474730616[-05]	-0.13302[-08]	0.90284[-03]
29	-0.1218957262[-05]	-0.1219696595[-05]	-0.73933[-09]	0.60653[-03]
30	-0.1011388955[-05]	-0.1011745577[-05]	-0.35662[-09]	0.35261[-03]
31	-0.8414513883[-06]	-0.8415656039[-06]	-0.11422[-09]	0.13574[-03]
32	-0.7018554629[-06]	-0.7018213114[-06]	0.34151[-10]	-0.48659[-04]
33	-0.5868237564[-06]	-0.5867036377[-06]	0.12012[-09]	-0.20469[-03]
34	-0.4917547384[-06]	-0.4915894451[-06]	0.16529[-09]	-0.33613[-03]
35	-0.4129667397[-06]	-0.4127823950[-06]	0.18434[-09]	-0.44639[-03]
36	-0.3475015037[-06]	-0.3473143657[-06]	0.18714[-09]	-0.53852[-03]
37	-0.2929725474[-06]	-0.2927923204[-06]	0.18023[-09]	-0.61517[-03]
38	-0.2474474379[-06]	-0.2472795345[-06]	0.16790[-09]	-0.67854[-03]
39	-0.2093558999[-06]	-0.2092029705[-06]	0.15293[-09]	-0.73048[-03]
40	-0.1774177169[-06]	-0.1772806705[-06]	0.13705[-09]	-0.77245[-03]
41	-0.1505858883[-06]	-0.1504645673[-06]	0.12132[-09]	-0.80566[-03]
42	-0.1280016120[-06]	-0.1278952324[-06]	0.10638[-09]	-0.83108[-03]
43	-0.1089584800[-06]	-0.1088659164[-06]	0.92564[-10]	-0.84953[-03]
44	-0.9287388845[-07]	-0.9279385636[-07]	0.80032[-10]	-0.86173[-03]
45	-0.7926612330[-07]	-0.7919729437[-07]	0.68829[-10]	-0.86833[-03]
46	-0.6773592858[-07]	-0.6767700218[-07]	0.58926[-10]	-0.86994[-03]
47	-0.5795163168[-07]	-0.5790137769[-07]	0.50254[-10]	-0.86717[-03]
48	-0.4963709996[-07]	-0.4959438280[-07]	0.42717[-10]	-0.86059[-03]
49	-0.4256196029[-07]	-0.4252575051[-07]	0.36210[-10]	-0.85075[-03]
50	-0.3653363293[-07]	-0.3650301056[-07]	0.30622[-10]	-0.83820[-03]
51	-0.3139082506[-07]	-0.3136497750[-07]	0.25848[-10]	-0.82341[-03]
52	-0.2699820214[-07]	-0.2697641866[-07]	0.21783[-10]	-0.80685[-03]
53	-0.2324201270[-07]	-0.2322367686[-07]	0.18336[-10]	-0.78891[-03]
54	-0.2002648718[-07]	-0.2001106803[-07]	0.15419[-10]	-0.76994[-03]
55	-0.1727086666[-07]	-0.1725790972[-07]	0.12957[-10]	-0.75022[-03]
56	-0.1490694605[-07]	-0.1489606419[-07]	0.10882[-10]	-0.72999[-03]
57	-0.1287703797[-07]	-0.1286790282[-07]	0.91351[-11]	-0.70941[-03]
58	-0.1113228206[-07]	-0.1112461601[-07]	0.76660[-11]	-0.68863[-03]
59	-0.9631238139[-08]	-0.9624807072[-08]	0.64311[-11]	-0.66773[-03]
60	-0.8338713427[-08]	-0.8333320252[-08]	0.53932[-11]	-0.64676[-03]
61	-0.7224783083[-08]	-0.7220262085[-08]	0.45210[-11]	-0.62576[-03]
62	-0.6263970780[-08]	-0.6260182702[-08]	0.37881[-11]	-0.60474[-03]
63	-0.5434562009[-08]	-0.5431389847[-08]	0.31722[-11]	-0.58370[-03]
64	-0.4718027681[-08]	-0.4715373108[-08]	0.26546[-11]	-0.56264[-03]
65	-0.4098539575[-08]	-0.4096319923[-08]	0.22197[-11]	-0.54157[-03]
66	-0.3562562376[-08]	-0.3560708102[-08]	0.18543[-11]	-0.52049[-03]
67	-0.3098509705[-08]	-0.3096962274[-08]	0.15474[-11]	-0.49941[-03]
68	-0.2696453705[-08]	-0.2695163818[-08]	0.12899[-11]	-0.47836[-03]
69	-0.2347879506[-08]	-0.2346805626[-08]	0.10739[-11]	-0.45738[-03]
70	-0.2045477367[-08]	-0.2044584491[-08]	0.89288[-12]	-0.43651[-03]
71	-0.1782966493[-08]	-0.1782225123[-08]	0.74137[-12]	-0.41581[-03]
72	-0.1554945518[-08]	-0.1554330803[-08]	0.61471[-12]	-0.39533[-03]
73	-0.1356765460[-08]	-0.1356256478[-08]	0.50898[-12]	-0.37514[-03]
74	-0.1184421664[-08]	-0.1184000814[-08]	0.42085[-12]	-0.35532[-03]
75	-0.1034461773[-08]	-0.1034114264[-08]	0.34751[-12]	-0.33593[-03]
76	-0.9039072781[-09]	-0.9036206995[-09]	0.28658[-12]	-0.31704[-03]
77	-0.7901865701[-09]	-0.7899505242[-09]	0.23605[-12]	-0.29872[-03]
78	-0.6910777500[-09]	-0.6908835411[-09]	0.19421[-12]	-0.28102[-03]
79	-0.6046597253[-09]	-0.6045000951[-09]	0.15963[-12]	-0.26400[-03]
80	-0.5292703540[-09]	-0.5291392565[-09]	0.13110[-12]	-0.24769[-03]
81	-0.4634705874[-09]	-0.4633629972[-09]	0.10759[-12]	-0.23214[-03]
82	-0.4060137233[-09]	-0.4059254722[-09]	0.88251[-13]	-0.21736[-03]
83	-0.3558190191[-09]	-0.3557466575[-09]	0.72362[-13]	-0.20337[-03]
84	-0.3119490281[-09]	-0.3118897071[-09]	0.59321[-13]	-0.19016[-03]
85	-0.2735901158[-09]	-0.2735414873[-09]	0.48628[-13]	-0.17774[-03]
86	-0.2400356987[-09]	-0.2399958316[-09]	0.39867[-13]	-0.16609[-03]
87	-0.2106718132[-09]	-0.2106391216[-09]	0.32692[-13]	-0.15518[-03]
88	-0.1849646810[-09]	-0.1849378649[-09]	0.26816[-13]	-0.14498[-03]
89	-0.1624499872[-09]	-0.1624279824[-09]	0.22005[-13]	-0.13546[-03]
90	-0.1427236294[-09]	-0.1427055657[-09]	0.18064[-13]	-0.12656[-03]
91	-0.1254337293[-09]	-0.1254188956[-09]	0.14834[-13]	-0.11826[-03]
92	-0.1102737305[-09]	-0.1102615460[-09]	0.12184[-13]	-0.11049[-03]
93	-0.9697643063[-10]	-0.9696642132[-10]	0.10009[-13]	-0.10321[-03]
94	-0.8530881854[-10]	-0.8530059717[-10]	0.82214[-14]	-0.96372[-04]
95	-0.7506760448[-10]	-0.7506085463[-10]	0.67498[-14]	-0.89917[-04]
96	-0.6607534835[-10]	-0.6606981120[-10]	0.55371[-14]	-0.83801[-04]
97	-0.5817710380[-10]	-0.5817256737[-10]	0.45364[-14]	-0.77976[-04]
98	-0.5123750794[-10]	-0.5123379834[-10]	0.37096[-14]	-0.72400[-04]
99	-0.4513825588[-10]	-0.4513523018[-10]	0.30257[-14]	-0.67032[-04]
100	-0.3977590813[-10]	-0.3977344858[-10]	0.24596[-14]	-0.61835[-04]
101	-0.3505998589[-10]	-0.3505799527[-10]	0.19906[-14]	-0.56778[-04]
102	-0.3091131557[-10]	-0.3090971341[-10]	0.16022[-14]	-0.51831[-04]
103	-0.2726058924[-10]	-0.2725930879[-10]	0.12804[-14]	-0.46971[-04]
104	-0.2404711213[-10]	-0.2404609788[-10]	0.10142[-14]	-0.42178[-04]
105	-0.2121771238[-10]	-0.2121691806[-10]	0.79432[-15]	-0.37437[-04]
106	-0.1872579156[-10]	-0.1872517855[-10]	0.61301[-15]	-0.32736[-04]
107	-0.1653049741[-10]	-0.1653003342[-10]	0.46400[-15]	-0.28069[-04]
108	-0.1459600269[-10]	-0.1459566067[-10]	0.34202[-15]	-0.23432[-04]
109	-0.1289087625[-10]	-0.1289063358[-10]	0.24266[-15]	-0.18825[-04]
110	-0.1138753438[-10]	-0.1138737211[-10]	0.16226[-15]	-0.14249[-04]
111	-0.1006176182[-10]	-0.1006166411[-10]	0.97713[-16]	-0.97113[-05]
112	-0.8892293565[-11]	-0.8892247157[-11]	0.46407[-16]	-0.52188[-05]
113	-0.7860449467[-11]	-0.7860443324[-11]	0.61423[-17]	-0.78142[-06]
114	-0.6949814948[-11]	-0.6949839895[-11]	-0.24947[-16]	0.35897[-05]
115	-0.6145961819[-11]	-0.6146010261[-11]	-0.48442[-16]	0.78818[-05]
116	-0.5436204106[-11]	-0.5436269785[-11]	-0.65678[-16]	0.12082[-04]
117	-0.4809384397[-11]	-0.4809462188[-11]	-0.77792[-16]	0.16175[-04]
118	-0.4255686832[-11]	-0.4255772574[-11]	-0.85742[-16]	0.20148[-04]
119	-0.3766473360[-11]	-0.3766563697[-11]	-0.90338[-16]	0.23985[-04]
120	-0.3334140293[-11]	-0.3334232556[-11]	-0.92264[-16]	0.27672[-04]
121	-0.2951992627[-11]	-0.2952084720[-11]	-0.92093[-16]	0.31197[-04]
122	-0.2614133867[-11]	-0.2614224171[-11]	-0.90305[-16]	0.34545[-04]
123	-0.2315369423[-11]	-0.2315456721[-11]	-0.87298[-16]	0.37704[-04]
124	-0.2051121873[-11]	-0.2051205277[-11]	-0.83404[-16]	0.40663[-04]
125	-0.1817356614[-11]	-0.1817435507[-11]	-0.78892[-16]	0.43411[-04]
126	-0.1610516602[-11]	-0.1610590587[-11]	-0.73985[-16]	0.45939[-04]
127	-0.1427465056[-11]	-0.1427533915[-11]	-0.68859[-16]	0.48239[-04]
128	-0.1265435134[-11]	-0.1265498790[-11]	-0.63656[-16]	0.50304[-04]
129	-0.1121985729[-11]	-0.1122044217[-11]	-0.58488[-16]	0.52129[-04]
130	-0.9949626143[-12]	-0.9950160531[-12]	-0.53439[-16]	0.53709[-04]
131	-0.8824642950[-12]	-0.8825128679[-12]	-0.48573[-16]	0.55042[-04]
132	-0.7828119767[-12]	-0.7828559131[-12]	-0.43936[-16]	0.56126[-04]
133	-0.6945231546[-12]	-0.6945627153[-12]	-0.39561[-16]	0.56961[-04]

TABLE III. (*Continued*).

Order	Perturbation	Asymptotic	Difference	Diff/Pert
134	-0.6162883760[-12]	-0.6163238415[-12]	-0.35465[-16]	0.57547[-04]
135	-0.5469507912[-12]	-0.5469824520[-12]	-0.31661[-16]	0.57886[-04]
136	-0.4854881522[-12]	-0.4855163016[-12]	-0.28149[-16]	0.57982[-04]
137	-0.4309969633[-12]	-0.4310218910[-12]	-0.24928[-16]	0.57837[-04]
138	-0.3826785214[-12]	-0.3827005096[-12]	-0.21988[-16]	0.57459[-04]
139	-0.3398266193[-12]	-0.3398459388[-12]	-0.19320[-16]	0.56851[-04]
140	-0.3018167088[-12]	-0.3018336170[-12]	-0.16908[-16]	0.56022[-04]
141	-0.2680963505[-12]	-0.2681110897[-12]	-0.14739[-16]	0.54977[-04]
142	-0.2381767935[-12]	-0.2381895900[-12]	-0.12796[-16]	0.53727[-04]
143	-0.2116255509[-12]	-0.2116366142[-12]	-0.11063[-16]	0.52278[-04]
144	-0.1880598504[-12]	-0.1880693739[-12]	-0.95235[-17]	0.50641[-04]
145	-0.1671408577[-12]	-0.1671490182[-12]	-0.81606[-17]	0.48824[-04]
146	-0.1485685773[-12]	-0.1485755361[-12]	-0.69588[-17]	0.46839[-04]
147	-0.1320773537[-12]	-0.1320832569[-12]	-0.59032[-17]	0.44695[-04]
148	-0.1174318984[-12]	-0.1174368777[-12]	-0.49794[-17]	0.42402[-04]
149	-0.1044237821[-12]	-0.1044279562[-12]	-0.41740[-17]	0.39972[-04]
150	-0.9286833743[-13]	-0.9287181214[-13]	-0.34747[-17]	0.37415[-04]
151	-0.8260192161[-13]	-0.8260479145[-13]	-0.28698[-17]	0.34743[-04]
152	-0.7347949878[-13]	-0.7348184760[-13]	-0.23488[-17]	0.31966[-04]
153	-0.6537250299[-13]	-0.6537440497[-13]	-0.19020[-17]	0.29094[-04]
154	-0.5816694939[-13]	-0.5816846990[-13]	-0.15205[-17]	0.26140[-04]
155	-0.5176176429[-13]	-0.5176296072[-13]	-0.11964[-17]	0.23114[-04]
156	-0.4606730848[-13]	-0.4606823105[-13]	-0.92257[-18]	0.20027[-04]
157	-0.4100407125[-13]	-0.4100476372[-13]	-0.69247[-18]	0.16888[-04]
158	-0.3650151503[-13]	-0.3650201542[-13]	-0.50039[-18]	0.13709[-04]
159	-0.3249705326[-13]	-0.3249739445[-13]	-0.34119[-18]	0.10499[-04]
160	-0.2893514575[-13]	-0.2893535608[-13]	-0.21033[-18]	0.72691[-05]
161	-0.2576649809[-13]	-0.2576660188[-13]	-0.10379[-18]	0.40282[-05]
162	-0.2294735286[-13]	-0.2294737089[-13]	-0.18033[-19]	0.78582[-06]
163	-0.2043886209[-13]	-0.2043881204[-13]	0.50051[-19]	-0.24488[-05]
164	-0.1820653153[-13]	-0.1820642835[-13]	0.10318[-18]	-0.56669[-05]
165	-0.1621972836[-13]	-0.1621958465[-13]	0.14371[-18]	-0.88600[-05]
166	-0.1445124522[-13]	-0.1445107152[-13]	0.17370[-18]	-0.12020[-04]
167	-0.1287691379[-13]	-0.1287671885[-13]	0.19493[-18]	-0.15138[-04]
168	-0.1147526245[-13]	-0.1147505351[-13]	0.20894[-18]	-0.18208[-04]
169	-0.1022721285[-13]	-0.1022699581[-13]	0.21704[-18]	-0.21222[-04]
170	-0.9115810857[-14]	-0.9115590507[-14]	0.22035[-18]	-0.24172[-04]
171	-0.8125988120[-14]	-0.8125768285[-14]	0.21984[-18]	-0.27053[-04]
172	-0.7244350579[-14]	-0.7244134272[-14]	0.21631[-18]	-0.29859[-04]
173	-0.6458990909[-14]	-0.6458780460[-14]	0.21045[-18]	-0.32582[-04]
174	-0.5759322166[-14]	-0.5759119330[-14]	0.20284[-18]	-0.35219[-04]
175	-0.5135930200[-14]	-0.5135736254[-14]	0.19395[-18]	-0.37763[-04]
176	-0.4580442711[-14]	-0.4580258535[-14]	0.18418[-18]	-0.40209[-04]
177	-0.4085413044[-14]	-0.4085239194[-14]	0.17385[-18]	-0.42554[-04]
178	-0.3644217054[-14]	-0.3644053821[-14]	0.16323[-18]	-0.44792[-04]
179	-0.3250961563[-14]	-0.3250809024[-14]	0.15254[-18]	-0.46921[-04]
180	-0.2900403077[-14]	-0.2900261142[-14]	0.14194[-18]	-0.48936[-04]
181	-0.2587875633[-14]	-0.2587744078[-14]	0.13156[-18]	-0.50835[-04]
182	-0.2309226703[-14]	-0.2309105204[-14]	0.12150[-18]	-0.52614[-04]
183	-0.2060760285[-14]	-0.2060648444[-14]	0.11184[-18]	-0.54272[-04]
184	-0.1839186344[-14]	-0.1839083708[-14]	0.10264[-18]	-0.55805[-04]
185	-0.1641575895[-14]	-0.1641481977[-14]	0.93918[-19]	-0.57212[-04]
186	-0.1465321098[-14]	-0.1465235389[-14]	0.85709[-19]	-0.58491[-04]
187	-0.1308099795[-14]	-0.1308021777[-14]	0.78018[-19]	-0.59642[-04]
188	-0.1167843994[-14]	-0.1167773148[-14]	0.70845[-19]	-0.60663[-04]
189	-0.1042711852[-14]	-0.1042647669[-14]	0.64183[-19]	-0.61554[-04]
190	-0.9310627789[-15]	-0.9310047605[-15]	0.58018[-19]	-0.62314[-04]
191	-0.8314352894[-15]	-0.8313829558[-15]	0.52334[-19]	-0.62944[-04]
192	-0.7425273210[-15]	-0.7424802130[-15]	0.47108[-19]	-0.63443[-04]
193	-0.6631787249[-15]	-0.6631364061[-15]	0.42319[-19]	-0.63812[-04]
194	-0.5923556954[-15]	-0.5923177537[-15]	0.37942[-19]	-0.64052[-04]
195	-0.5291369198[-15]	-0.5291029680[-15]	0.33952[-19]	-0.64165[-04]
196	-0.4727012569[-15]	-0.4726709329[-15]	0.30324[-19]	-0.64150[-04]
197	-0.4223167746[-15]	-0.4222897416[-15]	0.27033[-19]	-0.64011[-04]
198	-0.3773309961[-15]	-0.3773069416[-15]	0.24054[-19]	-0.63749[-04]
199	-0.3371622189[-15]	-0.3371408544[-15]	0.21365[-19]	-0.63366[-04]
200	-0.3012917896[-15]	-0.3012728492[-15]	0.18940[-19]	-0.62864[-04]
201	-0.2692572269[-15]	-0.2692404667[-15]	0.16760[-19]	-0.62246[-04]
202	-0.2406461000[-15]	-0.2406312967[-15]	0.14803[-19]	-0.61515[-04]
203	-0.2150905789[-15]	-0.2150775287[-15]	0.13050[-19]	-0.60673[-04]
204	-0.1922625813[-15]	-0.1922510986[-15]	0.11483[-19]	-0.59724[-04]
205	-0.1718694516[-15]	-0.1718593678[-15]	0.10084[-19]	-0.58671[-04]
206	-0.1536501123[-15]	-0.1536412747[-15]	0.88377[-20]	-0.57518[-04]
207	-0.1373716362[-15]	-0.1373639066[-15]	0.77296[-20]	-0.56268[-04]
208	-0.1228261934[-15]	-0.1228194472[-15]	0.67463[-20]	-0.54925[-04]
209	-0.1098283311[-15]	-0.1098224560[-15]	0.58751[-20]	-0.53493[-04]
210	-0.9821255006[-16]	-0.9820744530[-16]	0.51048[-20]	-0.51977[-04]
211	-0.8783114560[-16]	-0.8782672074[-16]	0.44249[-20]	-0.50379[-04]
212	-0.7855228316[-16]	-0.7854845724[-16]	0.38259[-20]	-0.48705[-04]
213	-0.7025828348[-16]	-0.7025498417[-16]	0.32993[-20]	-0.46960[-04]
214	-0.6284409414[-16]	-0.6284125694[-16]	0.28372[-20]	-0.45147[-04]
215	-0.5621592713[-16]	-0.5621349465[-16]	0.24325[-20]	-0.43270[-04]
216	-0.5029004434[-16]	-0.5028796555[-16]	0.20788[-20]	-0.41336[-04]
217	-0.4499167467[-16]	-0.4498990434[-16]	0.17703[-20]	-0.39348[-04]
218	-0.4025404859[-16]	-0.4025254667[-16]	0.15019[-20]	-0.37311[-04]
219	-0.3601753722[-16]	-0.3601626832[-16]	0.12689[-20]	-0.35230[-04]
220	-0.3222888454[-16]	-0.3222781746[-16]	0.10671[-20]	-0.33109[-04]
221	-0.2884052269[-16]	-0.2883962996[-16]	0.89273[-21]	-0.30954[-04]
222	-0.2580996118[-16]	-0.2580921866[-16]	0.74252[-21]	-0.28769[-04]
223	-0.2309924213[-16]	-0.2309862865[-16]	0.61348[-21]	-0.26558[-04]
224	-0.2067445417[-16]	-0.2067395121[-16]	0.50296[-21]	-0.24327[-04]
225	-0.1850529890[-16]	-0.1850489029[-16]	0.40861[-21]	-0.22081[-04]
226	-0.1656470394[-16]	-0.1656437558[-16]	0.32836[-21]	-0.19823[-04]
227	-0.1482847770[-16]	-0.1482821734[-16]	0.26036[-21]	-0.17558[-04]
228	-0.1327500129[-16]	-0.1327479830[-16]	0.20299[-21]	-0.15291[-04]
229	-0.1188495354[-16]	-0.1188479871[-16]	0.15483[-21]	-0.13027[-04]
230	-0.1064106557[-16]	-0.1064095097[-16]	0.11460[-21]	-0.10769[-04]
231	-0.9527901728[-17]	-0.9527820528[-17]	0.81200[-22]	-0.85223[-05]
232	-0.8531664030[-17]	-0.8531610362[-17]	0.53668[-22]	-0.62904[-05]
233	-0.7640017543[-17]	-0.7639986389[-17]	0.31153[-22]	-0.40777[-05]
234	-0.6841934515[-17]	-0.6841921598[-17]	0.12917[-22]	-0.18879[-05]
235	-0.6127555180[-17]	-0.6127556865[-17]	-0.16853[-23]	0.27503[-06]
236	-0.5488063463[-17]	-0.5488076676[-17]	-0.13212[-22]	0.24074[-05]
237	-0.4915575981[-17]	-0.4915598129[-17]	-0.22149[-22]	0.45058[-05]
238	-0.4403042901[-17]	-0.4403071814[-17]	-0.28913[-22]	0.65666[-05]
239	-0.3944159397[-17]	-0.3944193265[-17]	-0.33868[-22]	0.85868[-05]
240	-0.3533286556[-17]	-0.3533323878[-17]	-0.37322[-22]	0.10563[-04]
241	-0.3165380719[-17]	-0.3165420262[-17]	-0.39543[-22]	0.12492[-04]
242	-0.2835903358[-17]	-0.2835971116[-17]	-0.40758[-22]	0.14372[-04]
243	-0.2540899681[-17]	-0.2540940842[-17]	-0.41161[-22]	0.16199[-04]
244	-0.2276678237[-17]	-0.2276719153[-17]	-0.40916[-22]	0.17972[-04]
245	-0.2040035893[-17]	-0.2040076056[-17]	-0.40163[-22]	0.19687[-04]
246	-0.1828082589[-17]	-0.1828121607[-17]	-0.39017[-22]	0.21343[-04]
247	-0.1638232381[-17]	-0.1638269959[-17]	-0.37578[-22]	0.22938[-04]
248	-0.1468171296[-17]	-0.1468207221[-17]	-0.35925[-22]	0.24469[-04]
249	-0.1315828605[-17]	-0.1315862732[-17]	-0.34128[-22]	0.25936[-04]
250	-0.1179351144[-17]	-0.1179383383[-17]	-0.32239[-22]	0.27336[-04]
251	-0.1057080356[-17]	-0.1057110661[-17]	-0.30306[-22]	0.28669[-04]
252	-0.9475317669[-18]	-0.9475601294[-18]	-0.28363[-22]	0.29933[-04]
253	-0.8493766383[-18]	-0.8494030769[-18]	-0.26439[-22]	0.31127[-04]
254	-0.7614255588[-18]	-0.7614501152[-18]	-0.24556[-22]	0.32251[-04]
255	-0.6826137747[-18]	-0.6826365075[-18]	-0.22733[-22]	0.33303[-04]
256	-0.6119880706[-18]	-0.6120090514[-18]	-0.20981[-22]	0.34283[-04]
257	-0.5486950373[-18]	-0.5487143465[-18]	-0.19309[-22]	0.35191[-04]
258	-0.4919705785[-18]	-0.4919883027[-18]	-0.17724[-22]	0.36027[-04]
259	-0.4411305261[-18]	-0.4411467556[-18]	-0.16229[-22]	0.36791[-04]
260	-0.3955622457[-18]	-0.3955770722[-18]	-0.14826[-22]	0.37482[-04]
261	-0.3547171270[-18]	-0.3547306422[-18]	-0.13515[-22]	0.38101[-04]
262	-0.3181038664[-18]	-0.3181161609[-18]	-0.12294[-22]	0.38649[-04]
263	-0.2852824572[-18]	-0.2852936192[-18]	-0.11162[-22]	0.39126[-04]
264	-0.2558588125[-18]	-0.2558689273[-18]	-0.10115[-22]	0.39533[-04]
265	-0.2294799543[-18]	-0.2294891037[-18]	-0.91494[-23]	0.39870[-04]
266	-0.2058297087[-18]	-0.2058379704[-18]	-0.82618[-23]	0.40139[-04]
267	-0.1846248533[-18]	-0.1846323012[-18]	-0.74478[-23]	0.40340[-04]

TABLE III. (*Continued*).

Order	Perturbation	Asymptotic	Difference	Diff/Pert	Order	Perturbation	Asymptotic	Difference	Diff/Pert
268	-0.1656116705[-18]	-0.1656183736[-18]	-0.67032[-23]	0.40475[-04]	335	-0.1240380561[-21]	-0.1240379763[-21]	0.79793[-28]	-0.64329[-06]
269	-0.1485628611[-18]	-0.1485688847[-18]	-0.60236[-23]	0.40546[-04]	336	-0.1115276336[-21]	-0.1115275428[-21]	0.90796[-28]	-0.81412[-06]
270	-0.1332747842[-18]	-0.1332801888[-18]	-0.54046[-23]	0.40552[-04]	337	-0.1002818354[-21]	-0.1002817388[-21]	0.96581[-28]	-0.96309[-06]
271	-0.1195649847[-18]	-0.1195698267[-18]	-0.48420[-23]	0.40497[-04]	338	-0.9017252806[-22]	-0.9017242966[-22]	0.98404[-28]	-0.10913[-05]
272	-0.1072699811[-18]	-0.1072743129[-18]	-0.43317[-23]	0.40382[-04]	339	-0.8108459233[-22]	-0.8108449504[-22]	0.97287[-28]	-0.11998[-05]
273	-0.9624328557[-19]	-0.9624715526[-19]	-0.38697[-23]	0.40207[-04]	340	-0.7291459792[-22]	-0.7291450387[-22]	0.94052[-28]	-0.12899[-05]
274	-0.8635363038[-19]	-0.8635708247[-19]	-0.34521[-23]	0.39976[-04]	341	-0.6556961370[-22]	-0.6556952435[-22]	0.89358[-28]	-0.13628[-05]
275	-0.7748338107[-19]	-0.7748645640[-19]	-0.30753[-23]	0.39690[-04]	342	-0.5896613926[-22]	-0.5896605554[-22]	0.83723[-28]	-0.14199[-05]
276	-0.6952711529[-19]	-0.6952985125[-19]	-0.27360[-23]	0.39351[-04]	343	-0.5302914547[-22]	-0.5302906792[-22]	0.77555[-28]	-0.14625[-05]
277	-0.6239035038[-19]	-0.6239278115[-19]	-0.24308[-23]	0.38961[-04]	344	-0.4769121294[-22]	-0.4769114177[-22]	0.71164[-28]	-0.14922[-05]
278	-0.5598840411[-19]	-0.5599056087[-19]	-0.21568[-23]	0.38521[-04]	345	-0.4289175829[-22]	-0.4289169351[-22]	0.64786[-28]	-0.15104[-05]
279	-0.5024537447[-19]	-0.5024728557[-19]	-0.19111[-23]	0.38035[-04]	346	-0.3857633936[-22]	-0.3857628077[-22]	0.58594[-28]	-0.15189[-05]
280	-0.4509322603[-19]	-0.4509491724[-19]	-0.16912[-23]	0.37505[-04]	347	-0.3469603110[-22]	-0.3469597839[-22]	0.52711[-28]	-0.15192[-05]
281	-0.4047097181[-19]	-0.4047246646[-19]	-0.14946[-23]	0.36931[-04]	348	-0.3120686518[-22]	-0.3120681796[-22]	0.47218[-28]	-0.15131[-05]
282	-0.3632394045[-19]	-0.3632525966[-19]	-0.13192[-23]	0.36318[-04]	349	-0.2806932654[-22]	-0.2806928437[-22]	0.42168[-28]	-0.15023[-05]
283	-0.3260311994[-19]	-0.3260428277[-19]	-0.11628[-23]	0.35666[-04]	350	-0.2524790131[-22]	-0.2524786373[-22]	0.37584[-28]	-0.14886[-05]
284	-0.2926456972[-19]	-0.2926559338[-19]	-0.10237[-23]	0.34979[-04]	351	-0.2271067068[-22]	-0.2271063721[-22]	0.33475[-28]	-0.14740[-05]
285	-0.2626889416[-19]	-0.2626979411[-19]	-0.89995[-24]	0.34259[-04]	352	-0.2042894609[-22]	-0.2042891626[-22]	0.29832[-28]	-0.14603[-05]
286	-0.2358077079[-19]	-0.2358156093[-19]	-0.79014[-24]	0.33508[-04]	353	-0.1837694156[-22]	-0.1837691493[-22]	0.26637[-28]	-0.14495[-05]
287	-0.2116852779[-19]	-0.2116922060[-19]	-0.69281[-24]	0.32728[-04]	354	-0.1653147934[-22]	-0.1653145548[-22]	0.23864[-28]	-0.14435[-05]
288	-0.1900376539[-19]	-0.1900437203[-19]	-0.60664[-24]	0.31922[-04]	355	-0.1487172545[-22]	-0.1487170397[-22]	0.21483[-28]	-0.14446[-05]
289	-0.1706101666[-19]	-0.1706154713[-19]	-0.53047[-24]	0.31092[-04]	356	-0.1337895213[-22]	-0.1337893267[-22]	0.19461[-28]	-0.14546[-05]
290	-0.1531744371[-19]	-0.1531790693[-19]	-0.46322[-24]	0.30241[-04]	357	-0.1203632442[-22]	-0.1203630666[-22]	0.17763[-28]	-0.14758[-05]
291	-0.1375256528[-19]	-0.1375296921[-19]	-0.40393[-24]	0.29371[-04]	358	-0.1082870842[-22]	-0.1082869207[-22]	0.16353[-28]	-0.15102[-05]
292	-0.1234801283[-19]	-0.1234836455[-19]	-0.35172[-24]	0.28484[-04]	359	-0.9742498999[-23]	-0.9742483800[-23]	0.15199[-28]	-0.15601[-05]
293	-0.1108731187[-19]	-0.1108761768[-19]	-0.30582[-24]	0.27582[-04]	360	-0.8765465015[-23]	-0.8765450748[-23]	0.14267[-28]	-0.16276[-05]
294	-0.9955685996[-20]	-0.9955951503[-20]	-0.26551[-24]	0.26669[-04]	361	-0.7886610250[-23]	-0.7886596724[-23]	0.13526[-28]	-0.17150[-05]
295	-0.8939881327[-20]	-0.8940111488[-20]	-0.23016[-24]	0.25745[-04]	362	-0.7096048434[-23]	-0.7096035487[-23]	0.12947[-28]	-0.18245[-05]
296	-0.8028009102[-20]	-0.8028208311[-20]	-0.19921[-24]	0.24814[-04]	363	-0.6384890957[-23]	-0.6384878452[-23]	0.12504[-28]	-0.19584[-05]
297	-0.7209404633[-20]	-0.7209576776[-20]	-0.17214[-24]	0.23878[-04]	364	-0.5745145965[-23]	-0.5745133791[-23]	0.12174[-28]	-0.21190[-05]
298	-0.6474500866[-20]	-0.6474649377[-20]	-0.14851[-24]	0.22938[-04]	365	-0.5169627687[-23]	-0.5169615752[-23]	0.11934[-28]	-0.23086[-05]
299	-0.5814715059[-20]	-0.5814842963[-20]	-0.12790[-24]	0.21997[-04]	366	-0.4651874949[-23]	-0.4651863183[-23]	0.11767[-28]	-0.25294[-05]
300	-0.5222347183[-20]	-0.5222457147[-20]	-0.10996[-24]	0.21056[-04]	367	-0.4186077948[-23]	-0.4186066295[-23]	0.11654[-28]	-0.27839[-05]
301	-0.4690488862[-20]	-0.4690583230[-20]	-0.94368[-25]	0.20119[-04]	368	-0.3767012438[-23]	-0.3767000857[-23]	0.11581[-28]	-0.30743[-05]
302	-0.4212941719[-20]	-0.4213022550[-20]	-0.80831[-25]	0.19186[-04]	369	-0.3389980583[-23]	-0.3389969047[-23]	0.11536[-28]	-0.34029[-05]
303	-0.3784144188[-20]	-0.3784213288[-20]	-0.69100[-25]	0.18260[-04]	370	-0.3050757802[-23]	-0.3050746294[-23]	0.11508[-28]	-0.37722[-05]
304	-0.3399105885[-20]	-0.3399164835[-20]	-0.58950[-25]	0.17343[-04]	371	-0.2745544990[-23]	-0.2745533502[-23]	0.11489[-28]	-0.41844[-05]
305	-0.3053348764[-20]	-0.3053398948[-20]	-0.50183[-25]	0.16436[-04]	372	-0.2470925570[-23]	-0.2470914100[-23]	0.11470[-28]	-0.46420[-05]
306	-0.2742854365[-20]	-0.2742896989[-20]	-0.42624[-25]	0.15540[-04]	373	-0.2223826898[-23]	-0.2223815451[-23]	0.11446[-28]	-0.51471[-05]
307	-0.2464016496[-20]	-0.2464052614[-20]	-0.36118[-25]	0.14658[-04]	374	-0.2001485562[-23]	-0.2001474150[-23]	0.11413[-28]	-0.57022[-05]
308	-0.2213598813[-20]	-0.2213629342[-20]	-0.30529[-25]	0.13791[-04]	375	-0.1801416202[-23]	-0.1801404836[-23]	0.11366[-28]	-0.63096[-05]
309	-0.1988696777[-20]	-0.1988722513[-20]	-0.25736[-25]	0.12941[-04]	376	-0.1621383464[-23]	-0.1621372160[-23]	0.11304[-28]	-0.69715[-05]
310	-0.1786703531[-20]	-0.1786725166[-20]	-0.21634[-25]	0.12109[-04]	377	-0.1459376805[-23]	-0.1459365581[-23]	0.11223[-28]	-0.76904[-05]
311	-0.1605279303[-20]	-0.1605297435[-20]	-0.18132[-25]	0.11295[-04]	378	-0.1313587833[-23]	-0.1313576709[-23]	0.11124[-28]	-0.84684[-05]
312	-0.1442323961[-20]	-0.1442339109[-20]	-0.15148[-25]	0.10502[-04]	379	-0.1182389942[-23]	-0.1182378936[-23]	0.11006[-28]	-0.93079[-05]
313	-0.1295952397[-20]	-0.1295965008[-20]	-0.12611[-25]	0.97309[-05]	380	-0.1064319996[-23]	-0.1064309128[-23]	0.10868[-28]	-0.10211[-04]
314	-0.1164472446[-20]	-0.1164482906[-20]	-0.10459[-25]	0.89820[-05]	381	-0.9580618691[-24]	-0.9580511578[-24]	0.10711[-28]	-0.11180[-04]
315	-0.1046365085[-20]	-0.1046373725[-20]	-0.86395[-26]	0.82567[-05]	382	-0.8624316452[-24]	-0.8624211085[-24]	0.10537[-28]	-0.12217[-04]
316	-0.9402666621[-21]	-0.9402737665[-21]	-0.71043[-26]	0.75557[-05]	383	-0.7763643068[-24]	-0.7763539618[-24]	0.10345[-28]	-0.13325[-04]
317	-0.8449529608[-21]	-0.8449587739[-21]	-0.58131[-26]	0.68798[-05]	384	-0.6989017717[-24]	-0.6988916341[-24]	0.10138[-28]	-0.14505[-04]
318	-0.7593249020[-21]	-0.7593296324[-21]	-0.47304[-26]	0.62297[-05]	385	-0.6291821333[-24]	-0.6291722176[-24]	0.99157[-29]	-0.15760[-04]
319	-0.6823957166[-21]	-0.6823995422[-21]	-0.38256[-26]	0.56061[-05]	386	-0.5664299870[-24]	-0.5664203060[-24]	0.96809[-29]	-0.17091[-04]
320	-0.6132794363[-21]	-0.6132825085[-21]	-0.30722[-26]	0.50095[-05]	387	-0.5099477310[-24]	-0.5099382962[-24]	0.94348[-29]	-0.18501[-04]
321	-0.5511805679[-21]	-0.5511830152[-21]	-0.24473[-26]	0.44401[-05]	388	-0.4591077439[-24]	-0.4590985652[-24]	0.91788[-29]	-0.19993[-04]
322	-0.4953848284[-21]	-0.4953867596[-21]	-0.19312[-26]	0.38985[-05]	389	-0.4133453509[-24]	-0.4133364364[-24]	0.89145[-29]	-0.21567[-04]
323	-0.4452508314[-21]	-0.4452523385[-21]	-0.15070[-26]	0.33847[-05]	390	-0.3721524975[-24]	-0.3721438540[-24]	0.86435[-29]	-0.23226[-04]
324	-0.4002026273[-21]	-0.4002037874[-21]	-0.11602[-26]	0.28990[-05]	391	-0.3350636941[-24]	-0.3350636941[-24]	0.83672[-29]	-0.24971[-04]
325	-0.3597230084[-21]	-0.3597238866[-21]	-0.87820[-27]	0.24413[-05]	392	-0.3016927360[-24]	-0.3016846488[-24]	0.80872[-29]	-0.26806[-04]
326	-0.3233475019[-21]	-0.3233481524[-21]	-0.65049[-27]	0.20117[-05]	393	-0.2716444300[-24]	-0.2716366253[-24]	0.78047[-29]	-0.28731[-04]
327	-0.2906589785[-21]	-0.2906594465[-21]	-0.46798[-27]	0.16101[-05]	394	-0.2445941287[-24]	-0.2445866077[-24]	0.75210[-29]	-0.30749[-04]
328	-0.2612828133[-21]	-0.2612831363[-21]	-0.32297[-27]	0.12361[-05]	395	-0.2202421727[-24]	-0.2202349354[-24]	0.72373[-29]	-0.32861[-04]
329	-0.2348825433[-21]	-0.2348827522[-21]	-0.20893[-27]	0.88950[-06]	396	-0.1983189105[-24]	-0.1983119557[-24]	0.69548[-29]	-0.35069[-04]
330	-0.2111559697[-21]	-0.2111560900[-21]	-0.12034[-27]	0.56989[-06]	397	-0.1785816874[-24]	-0.1785750130[-24]	0.66744[-29]	-0.37375[-04]
331	-0.1898316592[-21]	-0.1898317118[-21]	-0.52542[-28]	0.27678[-06]	398	-0.1608121378[-24]	-0.1608057408[-24]	0.63971[-29]	-0.39780[-04]
332	-0.1706658038[-21]	-0.1706658054[-21]	-0.16394[-29]	0.96061[-08]	399	-0.1448137490[-24]	-0.1448076254[-24]	0.61236[-29]	-0.42286[-04]
333	-0.1534394015[-21]	-0.1534393659[-21]	0.35643[-28]	-0.23229[-06]	400	-0.1304096702[-24]	-0.1304038155[-24]	0.58547[-29]	-0.44895[-04]
334	-0.1379557263[-21]	-0.1379556642[-21]	0.62032[-28]	-0.44965[-06]	401	-0.1174407416[-24]	-0.1174351505[-24]	0.55911[-29]	-0.47608[-04]

then one can readily see that the weighted differences

$$s_n=(n+1)r_{n+1}-nr_n$$
$$=(n+1)C_0+C_1+\frac{C_2}{n+1}+\cdots-nC_0-C_1-\frac{C_2}{n}-\cdots$$
$$=C_0-\frac{C_2}{n(n+1)}+\cdots \tag{48}$$

converge to the same limit C_0 as the r_n's but faster by a power of $1/n$. However, as illustrated in Figs. 5 and 6, we found that the s_n's were *not* converging like $1/[n(n+1)]$, but rather like $1/\sqrt{n}$. We can now retrace our steps to see what has happened. If the r_n's are behaving like

$$r_n=C_0+\frac{C_{1/2}}{n^{1/2}}+\frac{C_1}{n}+\frac{C_{3/2}}{n^{3/2}}+\cdots, \tag{49}$$

then the s_n's are behaving as

$$s_n=(n+1)C_0+(n+1)^{1/2}C_{1/2}+C_1+\frac{C_{3/2}}{(n+1)^{1/2}}+\cdots-nC_0-n^{1/2}C_{1/2}-C_1-\frac{C_{3/2}}{n^{1/2}}-\cdots$$
$$=C_0+n^{1/2}[(1+1/n)^{1/2}-1]C_{1/2}+n^{-1/2}[(1+1/n)^{-1/2}-1]C_{3/2}+\cdots$$
$$=C_0+\frac{1}{2}\frac{C_{1/2}}{n^{1/2}}+O(n^{-3/2}). \tag{50}$$

Thus even in this case Neville-Richardson extrapolation has helped accelerate the convergence by eliminating the $1/n$ term completely and reducing by $\frac{1}{2}$ the coefficient of the $n^{-1/2}$ term. Graphs of the s_n's calculated with $k=0.80$ and $c=0.425$ and with $k=0.85$ and $c=0.420$ as a function of $n^{-1/2}$ for $50\le n\le 399$ are presented in Figs. 5 and 6. The linear dependence of the s_n's on $n^{-1/2}$ is evident. We regard the slight c- and k-dependent oscillation of the s_n's as an incipient indication of the periodic oscillation which must asymptotically occur in the coefficients E_n of the perturbation series for any finite Hermitian matrix problem as $n\to\infty$.

It is clear from the graphs that the intercept as $n\to\infty$ is entirely consistent (within finite-basis set errors) with $Z_c=1/\lambda_c=0.911\,03$. A least-squares fit of the s_n's to the formula

$$s_n\simeq 0.911\,03+\frac{c_{1/2}}{n^{1/2}}+\frac{c_{3/2}}{n^{3/2}}+\frac{c_2}{n^2} \tag{51}$$

yielded unreliable values of $c_{3/2}$ and c_2 but a value of

$$c_{1/2}\simeq -0.062, \tag{52}$$

which is probably accurate to one unit in the last digit.

We can also examine the limit of the r_n's as $n\to\infty$ by removing the $n^{-1/2}$ term by forming the weighted differences

$$t_n=2[(n+\tfrac{1}{2})r_{n+1}-nr_n]. \tag{53}$$

If one assumes that the r_n's have an asymptotic expansion given by Eq. (49), then it is a little tedious but quite straightforward to verify that the t_n's obey

$$t_n=C_0-\frac{C_1}{n}+O(n^{-3/2}). \tag{54}$$

Graphs of the t_n's calculated with $k=0.80$ and $c=0.425$ and with $k=0.85$ and $c=0.420$ are presented in Figs. 7 and 8. The linear dependence of the t_n's on $1/n$ is evident, and again it is clear that the intercept is consistent with $0.911\,03=Z_c=1/\lambda_c$. Least-squares fitting indicates that the value of C_1 in Eq. (54) is about -1.76. Hence we see that the ratios obey

$$r_n\simeq C_0+\frac{C_{1/2}}{n^{1/2}}+\frac{C_1}{n}+O(n^{-3/2}), \tag{55}$$

where

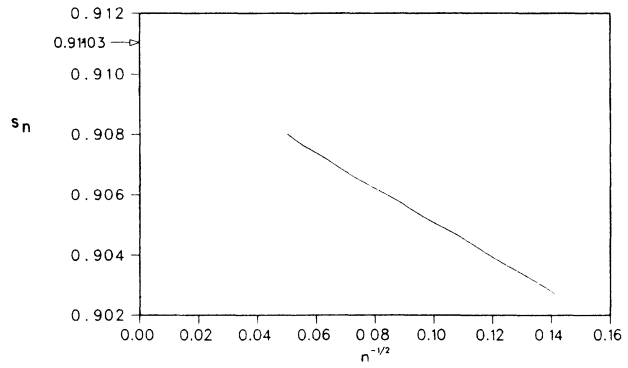

FIG. 5. The s_n's for $50\le n\le 399$ obtained with $k=0.80$ and $c=0.425$ vs $n^{-1/2}$.

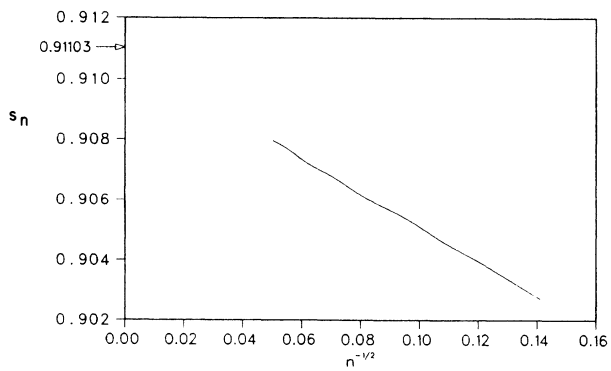

FIG. 6. The s_n's for $50\le n\le 399$ obtained with $k=0.85$ and $c=0.420$ vs $n^{-1/2}$.

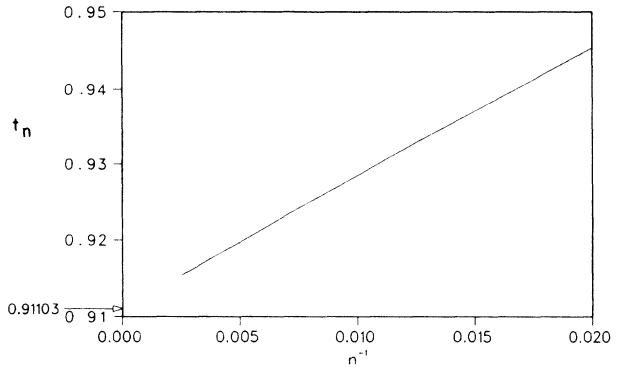

FIG. 7. The t_n's for $50 \le n \le 399$ obtained with $k=0.80$ and $c=0.425$ vs n^{-1}.

$$C_0 = 1/\lambda_c = Z_c \simeq 0.911\,03 , \tag{56a}$$

$$C_{1/2} = 2c_{1/2} \simeq -0.124 , \tag{56b}$$

$$C_1 \simeq -1.76 . \tag{56c}$$

Whether $C_{1/2}$ is exactly $-\frac{1}{8}$ we are unable to say. Thus we conclude that the radius of convergence of the $1/Z$ expansion for the ground state of the helium isoelectronic sequence is indeed determined by a singularity in $E(\lambda)$ at a distance λ_c from the origin, as Reinhardt[16] had surmised.

The 2% discrepancy between λ^* and λ_c which first Stillinger[8] and later Brändas and Goscinski[13,14] and quite recently Anno and Teruya[34] and Arteca, Fernández, and Castro[15] had found was due not to errors in the calculation of the E_n's by Midtdal,[9] but to the anomalous fact that at $n=21$ one is still very far from the region where the asymptotic behavior of the r_n's is manifest. Since $C_1/C_{1/2} \cong 14$, it is only for $n \ge (C_1/C_{1/2})^2 \cong 200$ that the leading $n^{-1/2}$ term in the asymptotic expansion for r_n exceeds the higher-order n^{-1} term, and the region where the $n^{-1/2}$ term dominates the n^{-1} term is much further out indeed. For example, the $n^{-1/2}$ term exceeds the n^{-1} term by a factor of 10 only for $n \ge (10C_1/C_{1/2})^2 \cong 20\,000$. Hence the range $10 \le n \le 20$ is very, very far from the asymptotic region, and it is this circumstance which is responsible for the discrepancy between λ_c and λ^* found by Stillinger,[8] by Brändas and Goscinski,[13,14] by Anno and Teruya,[34] and by Arteca, Fernández, and Castro.[15] This point is illustrated in Fig. 4, a graph of the r_n's for $11 \le n \le 400$ versus $1/n$. For $n \le 20$ the r_n's are approximately linear in n^{-1}, but straight-line extrapolation yields a misleading value of the intercept.

To provide further evidence that λ_c and λ^* are identical, we investigated the power series for $\|\psi(\lambda)\|$:[2]

$$\begin{aligned}\|\psi(\lambda)\|^2 &= \left\| \sum_{n=0}^{\infty} \lambda^n \psi_n \right\|^2 \\ &= \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} \lambda^{n+n'} \langle \psi_n | \psi_{n'} \rangle \\ &= \sum_{n=0}^{\infty} \lambda^n \sum_{m=0}^{n} \langle \psi_m | \psi_{n-m} \rangle . \end{aligned} \tag{57}$$

Our 200th-order wave function

$$\sum_{n=0}^{200} \lambda^n \psi_n \tag{58}$$

will provide the coefficients of the powers of λ in Eq. (57) up to $n=201$. The ratios R_n of the norm coefficients were found to have the same qualitative behavior as the ratios of the energy coefficients. The same kind of Neville-Richardson extrapolation yielded weighted differences S_n, which in Figs. 9 and 10 are graphed versus $n^{-1/2}$ for the two pairs of values $k=0.80$, $c=0.425$ and $k=0.85, c=0.420$. Although it is more difficult to estimate the intercept because of the curvature of the graphs, clearly an intercept of $Z_c = 1/\lambda_c = 0.911\,03$ would be consistent with the graphs. Least-squares fitting of the S_n's suggests that

$$S_n \simeq c_0 + \frac{c_{1/2}}{n^{1/2}} + o(n^{-1/2}) , \tag{59}$$

where

$$c_0 = 1/\lambda_c \simeq 0.911\,03 , \tag{60a}$$

$$c_{1/2} \simeq -0.062 , \tag{60b}$$

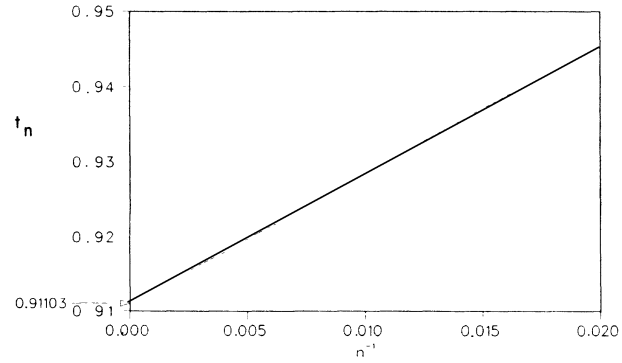

FIG. 8. The t_n's for $50 \le n \le 399$ obtained with $k=0.85$ and $c=0.420$ vs n^{-1}.

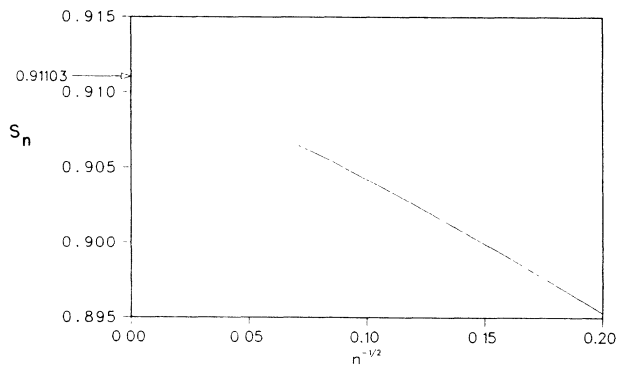

FIG. 9. The S_n's for $25 \le n \le 199$ obtained with $k=0.80$ and $c=0.425$ vs $n^{-1/2}$.

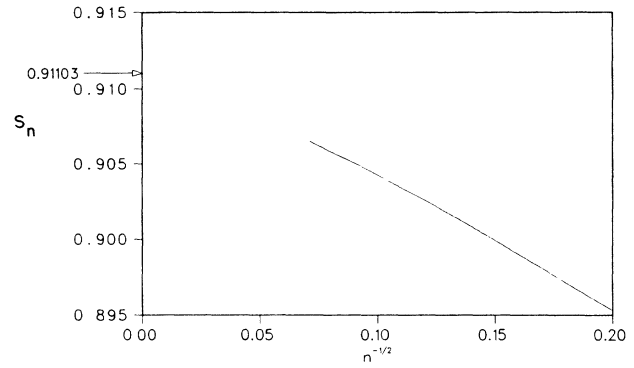

FIG. 10. The S_n's for $25 \leq n \leq 199$ obtained with $k=0.85$ and $c=0.420$ vs $n^{-1/2}$.

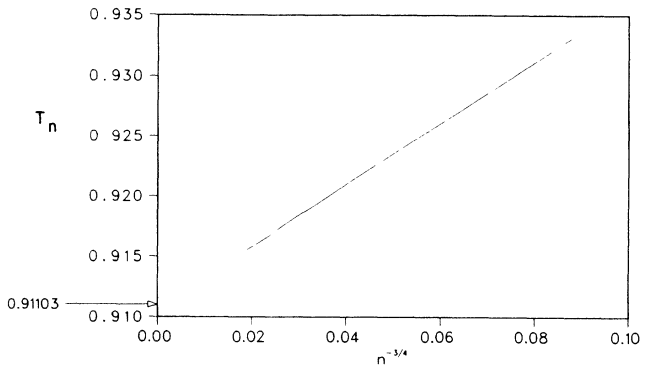

FIG. 12. The T_n's for $25 \leq n \leq 199$ obtained with $k=0.85$ and $c=0.420$ vs $n^{-3/4}$.

which are *identical* with the values for the weighted differences of the energy coefficients. However, our analysis of weighted differences

$$T_n = 2[(n+\tfrac{1}{2})R_{n+1} - nR_n] , \tag{61}$$

in which the $n^{-1/2}$ term is eliminated, revealed a surprise. Whereas the corresponding quantities t_n for the energy series converge like $1/n$ as $n \to \infty$, the T_n's for $\|\psi(\lambda)\|^2$ converge like $n^{-3/4}$, as can be seen in Figs. 11 and 12. Least-squares fitting suggests that

$$T_n \simeq c_0 + \frac{c_{3/4}}{n^{3/4}} + o(n^{-3/4}) , \tag{62}$$

where

$$c_0 = 1/\lambda_c \simeq 0.911\,03 , \tag{63a}$$

$$c_{3/4} \simeq 0.25 . \tag{63b}$$

Combining the results for the T_n's and the S_n's suggests that the ratios R_n of perturbation coefficients for $\|\psi(\lambda)\|^2$ obey

$$R_n = C_0 + \frac{C_{1/2}}{n^{1/2}} + \frac{C_{3/4}}{n^{3/4}} + O\left[\frac{1}{n}\right] , \tag{64}$$

where

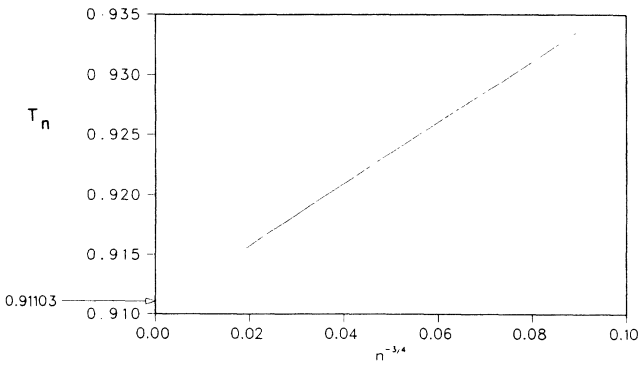

FIG. 11. The T_n's for $25 \leq n \leq 199$ obtained with $k=0.80$ and $c=0.425$ vs $n^{-3/4}$.

$$C_0 = c_0 = 0.911\,03 , \tag{65a}$$

$$C_{1/2} = 2c_{1/2} = -0.124 , \tag{65b}$$

$$C_{3/4} = -2c_{3/4} = -0.50 . \tag{65c}$$

Whether $C_{1/2}$ and $C_{3/4}$ are exactly $-\frac{1}{8}$ and $-\frac{1}{2}$, respectively, is an interesting question which the uncertainty in our estimates does not allow us to answer.

Thus far we have established that both $E(\lambda)$ and $\|\psi(\lambda)\|^2$ have singularities in the complex plane at a distance λ_c from the origin. Since all but the first few coefficients of the series for the *exact* $E(\lambda)$ and $\|\psi(\lambda)\|^2$ have the same sign, we may conclude from a theorem of Vivanti[35] (see Dienes, Ref. 36, for a more accessible proof in the English language) that the perturbation series for the *exact* $E(\lambda)$ and $\|\psi(\lambda)\|^2$ have singularities directly on the positive real axis at $\lambda = \lambda_c$.

Having determined that the singularities in $E(\lambda)$ and $\|\psi(\lambda)\|^2$ are both located on the positive real axis at λ_c, we may next investigate their nature. As Stillinger[8] observed, a simple branch point singularity of the type $(\lambda^* - \lambda)^\eta$ will produce ratios of coefficients which behave like

$$r_n = C_0 + \frac{C_1}{n} + \cdots , \tag{66}$$

where $C_0 = 1/\lambda^*$ and $C_1/C_0 = -(1+\eta)$. Since we have found that in fact

$$\frac{E_{n+1}}{E_n} = r_n = C_0 + \frac{C_{1/2}}{n^{1/2}} + \frac{C_1}{n} + \cdots \tag{67}$$

with a nonzero $C_{1/2}$, we conclude that the singularities in $E(\lambda)$ and $\|\psi(\lambda)\|^2$ at λ_c are more complicated than a simple branch point. To proceed further, we take the logarithm of Eq. (67) to obtain

$$\ln(-E_{n+1}) - \ln(-E_n) = \ln\left[C_0 + \frac{C_{1/2}}{n^{1/2}} + \frac{C_1}{n} + \cdots\right] . \tag{68}$$

Equation (68) is a first-order finite difference equation for $\ln(-E_n)$ which can be solved by analogy with the corresponding differential equation. The result yields the fol-

lowing large-n asymptotic expansion for E_n:

$$E_n \simeq -\text{const}\times C_0^n n^{\beta}\exp(-\alpha n^{1/2}) \times(1+\gamma_{1/2}n^{-1/2}+\gamma_1 n^{-1}+\cdots), \tag{69}$$

where

$$C_0=1/\lambda^*\simeq 0.911\,03, \tag{70a}$$

$$\alpha=-2C_{1/2}/C_0\simeq 0.272, \tag{70b}$$

and

$$\beta=-\tfrac{1}{2}(C_{1/2}/C_0)^2+(C_1/C_0)\simeq -1.94. \tag{70c}$$

Term by term differentiation of (4) yields for the kth derivative of $E(\lambda)$ the expansion

$$\frac{d^kE(\lambda)}{d\lambda^k}=\sum_{n=0}^{\infty}\frac{(n+k)!}{n!}E_{n+k}\lambda^n. \tag{71}$$

The asymptotic expansion (69) with $\alpha>0$ implies that for each positive integer k the series in (71) converges uniformly and absolutely for all λ for which $|\lambda|\le\lambda^*$. This in turn implies that $E(\lambda)$ and its derivatives have asymptotic expansions in powers of $(\lambda-\lambda^*)$ which are valid as $\lambda-\lambda^*$ from within the interior of the circle of convergence $|\lambda|\le\lambda^*$. To show this, we first record the appropriate version of Poincaré's definition of an asymptotic expansion, and then state the result as a theorem.

Definition. $d^jE(\lambda)/d\lambda^j$ has an asymptotic expansion

$$d^jE(\lambda)/d\lambda^j\sim\sum_{m=0}^{\infty}a_m^{(j)}(\lambda-\lambda^*)^m \tag{72}$$

as $\lambda\to\lambda^*$ in $|\lambda|\le\lambda^*$ means that for each positive integer M

$$\frac{d^jE(\lambda)}{d\lambda^j}=\sum_{m=0}^{M}a_m^{(j)}(\lambda-\lambda^*)^m+(\lambda-\lambda^*)^M\varepsilon_M^{(j)}(\lambda), \tag{73}$$

where the remainder obeys

$$\lim_{\lambda\to\lambda^*}\varepsilon_M^{(j)}(\lambda)=0,$$

with the understanding that the limit is to be taken with λ approaching λ^* from the interior of the disk defined by $|\lambda|\le\lambda^*$.

Theorem. If the asymptotic behavior of the coefficients is given by (69) with $\alpha>0$, then $d^jE(\lambda)/d\lambda^j$ has an asymptotic power series of the form (71) as $\lambda\to\lambda^*$ in $|\lambda|\le\lambda^*$.

Proof of Theorem. Taylor's theorem with remainder yields an expansion of the form (73) with

$$a_m^{(j)}=\frac{1}{m!}\left[\frac{d^{j+m}E(\lambda)}{d\lambda^{j+m}}\right]_{\lambda=\lambda^*} \tag{74}$$

and

$$\varepsilon_M^{(j)}(\lambda)=\frac{(\lambda-\lambda^*)}{(M+1)!}\left[\frac{d^{j+M+1}E(\lambda)}{d\lambda^{j+M+1}}\right]_{\lambda=\tilde{\lambda}}, \tag{75}$$

where $\tilde{\lambda}=\theta\lambda+(1-\theta)\lambda^*$ for some θ in $0\le\theta\le 1$. Convergence of the series in (71) for $\lambda=\lambda^*$ implies that the derivatives in (71) all exist. For all λ in $|\lambda|\le\lambda^*$, (71) and (75) imply the bound

$$|\varepsilon_M^{(j)}(\lambda)|\le\frac{|\lambda-\lambda^*|}{(M+1)!}\sum_{n=0}^{\infty}\frac{(n+j+M+1)!}{n!}|E_{n+j+M+1}|\times(\lambda^*)^n, \tag{76}$$

where the series in (76) converges as a consequence of (69). The bound (76) implies that $\varepsilon_M^{(j)}(\lambda)\to 0$ as $\lambda\to\lambda^*$ in $|\lambda|\le\lambda^*$, thus completing the proof.

To elucidate further the nature of the singularity, we next examine a known, well-studied function whose expansion coefficients have the behavior (69) for large n. Consider the function U defined by the integral representation

$$U(a,c;x)=\frac{1}{\Gamma(a)}\int_0^{\infty}e^{-xt}t^{a-1}(1+t)^{c-a-1}dt, \quad \mathrm{Re}a>0,\ \mathrm{Re}x>0. \tag{77}$$

$U(a,c;x)$ is the second solution of the confluent hypergeometric equation. (Ref. 37, p. 277; Ref. 38, Eq. (2), p. 255). The restrictions $\mathrm{Re}a>0$, $\mathrm{Re}x>0$ in (77) can be removed by using other representations for U. We will show that the function

$$S(a,c,x,\lambda^*;\lambda)=\left[1-\frac{\lambda}{\lambda^*}\right]^{-a}U(a,c;x/(1-\lambda/\lambda^*)), \tag{78}$$

with

$$\lambda^*=1/C_0, \tag{79a}$$

$$x=(\alpha/2)^2, \tag{79b}$$

$$a=\tfrac{1}{2}c+\beta+\tfrac{3}{4}, \tag{79c}$$

$$c=1\pm[\tfrac{1}{4}+\alpha^2(\beta+\tfrac{3}{4})+\tfrac{1}{48}\alpha^4+2\alpha\gamma_{1/2}]^{1/2}, \tag{79d}$$

has a power series in powers of λ whose coefficients have a large-n asymptotic expansion which agrees with (69) through the $\gamma_{1/2}n^{-1/2}$ term. Additional terms in the expansion (69) can be fitted by appropriate choice of the coefficients b_k in the function

$$T_K(a,c,x,\lambda^*;\lambda)=\sum_{k=0}^{K}b_kS(a,c+k,x,\lambda^*;\lambda). \tag{80}$$

The derivation of these results begins with the asymptotic formula

$$\Gamma(a+n)U(a+n,c;x)=\pi^{1/2}x^{(1-2c)/4}n^{(2c-3)/4}\exp[-2(nx)^{1/2}+\tfrac{1}{2}x]$$
$$\times\{1+(nx)^{-1/2}[\tfrac{1}{4}(c-\tfrac{1}{2})(c-\tfrac{3}{2})+(\tfrac{1}{2}c-a)x-\tfrac{1}{12}x^2]+O(n^{-1})\}\ , \tag{81}$$

which is valid as $n\to\infty$ when x is real, positive, and bounded away from zero and infinity. Define the coefficient a_n by

$$a_n=\frac{\Gamma(a+n)}{\Gamma(a)}\begin{bmatrix}c-a-1\\ n\end{bmatrix}U(a+n,c;x)(-\lambda^*)^{-n}\ . \tag{82}$$

Equation (81) and the asymptotic formula

$$(-1)^n\begin{bmatrix}p\\ n\end{bmatrix}=\frac{\Gamma(n-p)}{\Gamma(-p)\Gamma(n+1)}=\frac{1}{\Gamma(-p)n^{p+1}}[1+O(n^{-1})]\ , \tag{83}$$

which follows from the Stirling approximation to the Γ function, can be inserted in (82) to show that

$$a_n=\frac{\pi^{1/2}x^{(1-2c)/4}\exp(x/2)}{\Gamma(a)\Gamma(a-c+1)}(\lambda^*)^{-n}\exp[-2(nx)^{1/2}]n^{(4a-2c-3)/4}$$
$$\times\{1+(nx)^{-1/2}[\tfrac{1}{4}(c-\tfrac{1}{2})(c-\tfrac{3}{2})+(\tfrac{1}{2}c-a)x-\tfrac{1}{12}x^2]+O(n^{-1})\}\ . \tag{84}$$

Formulas (79a)–(79d) are obtained by comparing (84) with (69). Equations (77), (78), and (82) can be used along with Eq. 6.14.6 in Ref. 38 to show that

$$S(a,c,x,\lambda^*;\lambda)=\sum_{n=0}^{\infty}a_n\lambda^n\ . \tag{85}$$

The fact that additional terms in the expansion (69) can be fitted by using the function T_K defined in (80) follows from the fact that the factor $n^{(4a-2c-3)/4}$ in (84) decreases by $n^{-1/2}$ when c is increased by 1.

The next question obviously is uniqueness: what other functions have power series whose expansion coefficients have the asymptotic behavior (69) for large n? We do not know how to give a definitive answer to this question. However, a better understanding of how the asymptotic behavior (84) arises can be gained by examining the derivation of the asymptotic formula (81). It follows from (77) that

$$\Gamma(a+n)U(a+n,c;x)=\int_0^{\infty}g(t)\exp[h(t)]dt\ , \tag{86}$$

where

$$g(t)=t^{a-1}(1+t)^{c-a-1} \tag{87}$$

and

$$h(t)=-xt+n[\ln t-\ln(1+t)]\ . \tag{88}$$

For n large, the major contribution to the integral in (86) comes from the neighborhood of a saddle point at

$$t_0=-\frac{1}{2}+\left[\frac{n}{x}+\frac{1}{4}\right]^{1/2}\ , \tag{89}$$

which is the positive root of $h'(t_0)=0$. The integral (86) can then be approximated by the saddle-point formula

$$\int_0^{\infty}g(t)\exp[h(t)]dt\sim\left[\frac{2\pi}{-h''(t_0)}\right]^{1/2}g(t_0)\exp[h(t_0)]\ , \tag{90}$$

which is accurate enough to reproduce the first term of the expansion (81); additional terms can be obtained by expanding about the neighborhood of t_0 to obtain a more accurate approximation.[39] Most of the contribution to the integral occurs for $|t-t_0|\lesssim x^{-3/4}n^{1/4}$; modifications to $g(t)$ which do not change $g(t)$ much in this range, and which leave $g(t)\exp[h(t)]$ small outside this range, will not change the asymptotic behavior.

The parameter values which give the best fit to the expansion coefficients E_n have been determined by least-squares fitting. Make the definition

$$\sigma=\sum_{n=n_{\min}}^{n_{\max}}\left[\frac{Ca_n}{E_n}-1\right]^2\ , \tag{91}$$

where a_n is given by (82). Using the E_n's for $k=0.80$, $c=0.425$ and minimizing σ with respect to C, a, c, and x for $n_{\min}=99$ and $n_{\max}=399$ yields

$$\begin{aligned}C&\simeq-0.059\,021\,207\,52\ ,\\ a&\simeq-1.179\,890\ ,\\ c&\simeq-0.120\,103\ ,\\ x&\simeq0.018\,446\ ,\end{aligned} \tag{92}$$

at the minimum, with a residual $\sigma\simeq0.3343\times10^{-6}$.

These values of the parameters were then used in Eq. (82) to generate estimates of the E_n's. In Table III we have listed the E_n's as computed numerically using the HKS procedure, the values of the E_n's as predicted by Eq. (82) using the parameters in (92), their differences, and the relative error. One can see that for $n\geq94$ we have agreement to better than 1 part in 10^4, for $n\geq28$ to better than 1 part in 10^3, for $n\geq18$ to better than 1 part in 10^2, and for $n\geq6$ to better than 1 part in 10. This is spectacular agreement for a four-parameter fit, especially since E_n's with $n\leq98$ were excluded from our optimization of the four parameters. Since the slight oscillatory behavior of the E_n's for large n in an unphysical basis-dependent effect, it is likely that for very large n our estimates using Eq. (82), in which the wiggles have been

averaged out, are actually more accurate approximations to the exact E_n's than are our values of the E_n's calculated using a finite basis.

The structure of the singularity at λ_c in $\|\psi(\lambda)\|^2$ is even more complicated. If the ratios R_n of the coefficients in the expansion (57) behave as

$$R_n = C_0 + \frac{C_{1/2}}{n^{1/2}} + \frac{C_{3/4}}{n^{3/4}} + \frac{C_1}{n} + O(n^{-5/4}) , \tag{93}$$

then the nth coefficient behaves as

$$\begin{aligned} &\text{const} \times \exp\left[\int dn \ln(R_n)\right] \\ &\quad = \text{const} \times C_0^n \exp(-\alpha n^{1/2} - \gamma n^{1/4}) n^{\beta} \\ &\qquad \times [1 + O(n^{-1/4})] , \end{aligned} \tag{94}$$

where

$$\begin{aligned} C_0 &= 1/\lambda^* = 0.911\,03 , \\ \alpha &= -2C_{1/2}/C_0 \simeq 0.272 , \\ \gamma &= -4C_{3/4}/C_0 \simeq 2.195 , \\ \beta &= \frac{C_1}{C_0} - \frac{1}{2}\left[\frac{C_{1/2}}{C_0}\right]^2 . \end{aligned} \tag{95}$$

The same argument which proved that the series (72) for $E(\lambda)$ and all its derivatives are asymptotic as $\lambda \to \lambda^*$ for all $|\lambda| < \lambda^*$ also shows that the corresponding series for $\|\psi(\lambda)\|^2$ and all its derivatives are asymptotic.

The singularity at λ^* in $\|\psi(\lambda)\|^2$ is not quite of the form

$$(1-\lambda/\lambda^*)^{-a} U(a,c;x/(1-\lambda/\lambda^*)) \tag{96}$$

which was obtained for $E(\lambda)$. However, a slight modification suffices. Consider the function defined by the integral representation

$$V(a,c;x,y) = \frac{1}{\Gamma(a)} \int_0^{\infty} e^{-xt - yt^{1/2}} t^{a-1} (1+t)^{c-a-1} dt . \tag{97}$$

A saddle-point analysis similar to that used for $\Gamma(a+n)U(a+n,c;x)$ can be applied to

$$\Gamma(a+n)V(a+n,c;x,y) = \int_0^{\infty} g(t) \exp[h(t)] dt , \tag{98}$$

where

$$g(t) = t^{a-1}(1+t)^{c-a-1} \tag{99}$$

and

$$h(t) = -xt + n[\ln t - \ln(1+t)] - yt^{1/2} . \tag{100}$$

The saddle-point t_0, which is a root of the equation $h'(t_0) = 0$, is given by

$$t_0 = \left[\frac{n}{x}\right]^{1/2} - \frac{1}{4}\frac{y}{x}\left[\frac{n}{x}\right]^{1/4} + \frac{1}{16}\left[\frac{y}{x}\right]^2 - \frac{1}{2} + O(n^{-1/4}) . \tag{101}$$

Hence

$$g(t_0) = \left[\frac{n}{x}\right]^{c/2-1} [1 + O(n^{-1/4})] , \tag{102}$$

$$h(t_0) = -2(nx)^{1/2} - y\left[\frac{n}{x}\right]^{1/4} + x\left[\frac{1}{16}\left[\frac{y}{x}\right]^2 + \frac{1}{2}\right] + O(n^{-1/4}) . \tag{103}$$

and

$$h''(t_0) = -2n^{-1/2}x^{3/2} + O(n^{-3/4}) . \tag{104}$$

Thus by Eq. (90),

$$\Gamma(a+n)V(a+n,c;x,y) = \pi^{1/2} x^{-1/2} \left[\frac{n}{x}\right]^{c/2-3/4} \exp\left\{-2(nx)^{1/2} - y\left[\frac{n}{x}\right]^{1/4} + x\left[\frac{1}{16}\left[\frac{y}{x}\right]^2 + \frac{1}{2}\right]\right\} [1 + O(n^{-1/4})] , \tag{105}$$

which corresponds to Eq. (81), to which Eq. (105) reduces when $y = 0$.

By using the integral representation (97) for V, interchanging summation and integration, and rescaling t by a factor $1-\lambda/\lambda^*$, it can be shown that

$$(1-\lambda/\lambda^*)^{-a} V(a,c;x/(1-\lambda/\lambda^*), y/(1-\lambda/\lambda^*)^{1/2}) = \sum_{n=0}^{\infty} \frac{\Gamma(a+n)}{\Gamma(a)} \binom{c-a-1}{n} V(a+n,c;x,y) \left[-\frac{\lambda}{\lambda^*}\right]^n , \tag{106}$$

which yields a function with the same kind of singularity at $\lambda = \lambda^*$ as is present in $\|\psi(\lambda)\|^2$. Unfortunately, the complexity of the function V has so far deterred us from fitting the coefficients of the series for $\|\psi(\lambda)\|^2$ to the coefficients of the series (106).

The singularities at $\lambda = \lambda^*$ which are possessed by the functions $(1-\lambda/\lambda^*)^{-a}U$ and $(1-\lambda/\lambda^*)^{-a}V$ will now be discussed in more detail. The formula

$$U(a,c;z) = \frac{\Gamma(1-c)}{\Gamma(a-c+1)} {}_1F_1(a,c;z) + \frac{\Gamma(c-1)}{\Gamma(a)} z^{1-c} {}_1F_1(a-c+1,2-c;z) \tag{107}$$

[Ref. 37, p. 264; Ref. 38, Eq. (7), p. 257] can be used to show that

$$\left[1-\frac{\lambda}{\lambda^*}\right]^{-a} U(a,c;x/(1-\lambda/\lambda^*))=\frac{\Gamma(1-c)}{\Gamma(a-c+1)}\left[1-\frac{\lambda}{\lambda^*}\right]^{-a} {}_1F_1(a,c;x/(1-\lambda/\lambda^*))$$
$$+\frac{\Gamma(c-1)}{\Gamma(a)}x^{1-c}\left[1-\frac{\lambda}{\lambda^*}\right]^{c-a-1} {}_1F_1(a-c+1,2-c;x/(1-\lambda/\lambda^*))\,, \tag{108}$$

where ${}_1F_1$ is the confluent hypergeometric function (Kummer's function). ${}_1F_1(a,c;z)$ is an entire function of z with an essential singularity at $z=\infty$. Thus the function

$$(1-\lambda/\lambda^*)^{-a}U(a,c;x/(1-\lambda/\lambda^*))$$

which we have used for $E(\lambda)$ is a sum of two terms, each of which is a function with a branch point at $\lambda=\lambda^*$ multiplied by a function with an essential singularity at $\lambda=\lambda^*$. The analysis of

$$(1-\lambda/\lambda^*)^{-a}V(a,c;x/(1-\lambda/\lambda^*),y/(1-\lambda/\lambda^*)^{1/2})$$

at $\lambda=\lambda^*$ is similar but somewhat more complicated. It can be shown from the integral representations (77) and (97) of U and V that $V(a,c;z_1,z_2)$ is an entire function of z_2 with the series representation

$$V(a,c;z_1,z_2)=\sum_{n=0}^{\infty}\frac{z_2^{2n}}{(2n)!}U(a+n,c+n;z_1)$$
$$-\sum_{n=0}^{\infty}\frac{z_2^{2n+1}}{(2n+1)!}$$
$$\times U(a+\tfrac{1}{2}+n,c+\tfrac{1}{2}+n;z_1)\,. \tag{109}$$

It follows from (107) and (109) that

$$\left[1-\frac{\lambda}{\lambda^*}\right]^{-a} V(a,c;x/(1-\lambda/\lambda^*),y/(1-\lambda/\lambda^*)^{1/2})$$
$$=\left[1-\frac{\lambda}{\lambda^*}\right]^{-a}\omega_1(\lambda)+\left[1-\frac{\lambda}{\lambda^*}\right]^{-a-1/2}\omega_2(\lambda)$$
$$+\left[1-\frac{\lambda}{\lambda^*}\right]^{c-a-1}\omega_3(\lambda)\,, \tag{110}$$

where

$$\omega_1(\lambda)=\sum_{n=0}^{\infty}\frac{y^{2n}}{(2n)!}\frac{\Gamma(1-c-n)}{\Gamma(a-c+1)}\left[1-\frac{\lambda}{\lambda^*}\right]^{-n}$$
$$\times {}_1F_1(a+n,c+n;x/(1-\lambda/\lambda^*))\,, \tag{111a}$$

$$\omega_2(\lambda)=-\sum_{n=0}^{\infty}\frac{y^{2n+1}}{(2n+1)!}\frac{\Gamma(\frac{1}{2}-c-n)}{\Gamma(a-c+1)}\left[1-\frac{\lambda}{\lambda^*}\right]^{-n}$$
$$\times {}_1F_1(a+\tfrac{1}{2}+n,c+\tfrac{1}{2}+n;x/(1-\lambda/\lambda^*))\,, \tag{111b}$$

and

$$\omega_3(\lambda)=\sum_{n=0}^{\infty}\left[\frac{y^{2n}}{(2n)!}\frac{\Gamma(c+n-1)}{\Gamma(a+n)}x^{1-c-n}{}_1F_1(a-c+1,2-c+n;x/(1-\lambda/\lambda^*))\right.$$
$$\left.-\frac{y^{2n+1}}{(2n+1)!}\frac{\Gamma(c-\frac{1}{2}+n)}{\Gamma(a+\frac{1}{2}+n)}x^{1/2-c-n}{}_1F_1(a-c+\tfrac{3}{2},\tfrac{3}{2}-c-n;x/(1-\lambda/\lambda^*))\right]\,. \tag{111c}$$

Each of the three functions ω_1, ω_2, and ω_3 can be seen to have an essential singularity at $\lambda=\lambda^*$. Thus the function $(1-\lambda/\lambda^*)^{-a}V$ which we have used for $\|\psi(\lambda)\|^2$ is a sum of *three* terms, each of which is a function with a branch point at $\lambda=\lambda^*$ multiplied by a function with an essential singularity at $\lambda=\lambda^*$.

It is enlightening to compare our expression (108) for the form of the singularity in $E(\lambda)$ at $\lambda=\lambda^*$ with the

$$\text{const}\times(1-\lambda/\lambda^*)^{-a}$$

form deduced by Stillinger,[8] where $-a\simeq 1.2057$. We saw in Eq. (92) that the parameter

$$x=(C_{1/2}/C_0)^2\simeq 0.018\,45$$

is extremely small. If it were exactly zero, then the coefficient $C_{1/2}$ of the $n^{-1/2}$ term in the asymptotic expansion of the ratio r_n of energy coefficients would also vanish, and Stillinger's analysis of the ratios would have led him to what would have been the true behavior of $E(\lambda)$ at $\lambda=\lambda^*$. Now if in Eq. (108) we set $x=0$, the ${}_1F_1$'s are just 1 and the second term vanishes, and we would find that the singular part of $E(\lambda)$ would behave as

$$\text{const}\times(1-\lambda/\lambda^*)^{-a}\,,$$

where from Eq. (92) $-a\simeq 1.1799$, which is quite close to Stillinger's estimate 1.2057. Thus to some extent one could say that Stillinger found a rather good approximation to the form of the branch-point singularity at $\lambda=\lambda^*$, but missed the underlying essential singularity, which rears its head only when λ is extraordinarily close to λ^*.

We may now discuss the results for λ_c and λ^* which Brändas and Goscinski obtained using Padé approximants[13] and a Darboux function ansatz.[14] In the Padé method, one approximates a function $f(\lambda)$ with a sequence of rational functions (i.e., ratios of polynomials), which are single-valued functions, and whose worst

singularities are multiple poles. In the Darboux function method, one assumes that the function $f(\lambda)$ has a simple branch-point singularity at λ^*; i.e., $f(\lambda)=(\lambda-\lambda^*)^\alpha g(\lambda)+h(\lambda)$, where $g(\lambda)$ and $h(\lambda)$ are not singular at $\lambda=\lambda^*$. However, as we have determined, at $\lambda=\lambda^*=\lambda_c$ both $E(\lambda)$ and $\|\psi(\lambda)\|^2$ have singularities which are sums of products of branch point singularities (in the sense that following a contour which encloses λ^* through an angle 2π yields different values of the functions) and essential singularities (in the sense that within any arbitrarily small neighborhood of λ^*, the functions assume an infinitely wide range of values). Thus $E(\lambda)$ and $\|\psi(\lambda)\|^2$ have quite different singularities from that of any Padé approximant or Darboux function. Hence in retrospect it is perhaps not surprising that the use of these techniques does not lead to improved estimates of λ_c and λ^*. In fact, Brändas and Goscinski's use of Padé approximants yielded estimates of λ_c and λ^* which were actually slightly *worse* than Stillinger's estimates using just the pedestrian ratio test:

Brändas and Goscinski		Stillinger		This work	
1.0974	<	1.0975	<	1.097 66	for λ_c
0.893	<	0.894	<	0.911 03	for $1/\lambda^*$.

(112)

We are able to offer a qualitative analysis of the initially surprising phenomenon of Padé analysis yielding slightly *worse* results than those obtained from a simple power series. The critical point λ_c is determined by the equation $E(\lambda_c)=-\frac{1}{2}$. Now on the one hand, a Padé approximant $[L/M]_E(\lambda)$ to $E(\lambda)$ wants to equal $-\frac{1}{2}$ at λ_c in order to yield a good estimate of λ_c. On the other hand, $[L/M]_E(\lambda)$ wants to have a cluster of poles near λ_c in order to approximate the branch-point singularity in $E(\lambda)$ at λ_c. Since a rational function cannot be both finite and infinite at the same point, a compromise is made: the Padé approximants do a relatively poor job of approximating both the zero of $E(\lambda)-(-\frac{1}{2})$ at λ_c and the singularity of $E(\lambda)$ at λ_c. Thus the approximate $\tilde{\lambda}_c$ determined from the Padé approximant by the equation

$$[L/M]_E(\tilde{\lambda}_c)=-\tfrac{1}{2} \tag{113}$$

and the approximate $\tilde{\lambda}^*$ determined from the Padé approximant by the equation

$$[L/M]_E(\tilde{\lambda}^*)=\pm\infty \tag{114}$$

will both be rather inaccurate.

Indeed, as Baker and Graves-Morris observed in their review of the Padé approximation,[40] a case where the Padé method is inappropriate is a function "$f(z)=\sum_{i=0}^{\infty}c_i z^i$ [that] has a branch point at $z=1$ and yet $f(1)$ is well-defined. One expects the poles of the Padé approximants to accumulate at $z=1$ and convergence to be slow;" correspondence with our case is achieved by setting $z=\lambda/\lambda^*$. One may also compare the logarithmically slow convergence of Padé approximants to the function $-x/\ln(1-x)$ at the branch point $x=1$, which was discussed a quarter-century ago by Baker.[41]

The Darboux function ansatz suffers from similar problems of slow convergence of the estimates of λ_c and λ^* because the exact $E(\lambda)$ is not of the Darboux class.

Thus we have another illustration of the general phenomenon that the convergence of a sequence of approximants to a given function can be rather slow if the approximants have an analytic structure different from that of the exact function being approximated.[42] This convergence can be particularly slow in the vicinity of a singular point of the exact function. In general, one would expect to find very slow convergence of the singular points of the approximants to the singular points of the exact function if the singularities of the approximants are quite different from the singularities of the exact function. Hence although Padé approximants have proven very useful in a wide variety of situations, they are not a universal panacea (nor would an expert on the Padé approximation claim that they are[40]), and there are times when refinements of the ratio test (such as the employment of Neville-Richardson extrapolation) yield more accurate and reliable results.

VI. EXCITED STATES OF THE HELIUM ISOELECTRONIC SEQUENCE

Having presented our results for the ground state of the helium isoelectronic sequence, we may now consider other states of this two-electron system and other ions with more than two electrons. We may start with a survey of rigorous results and then proceed to more general speculations.

To begin, Kato's estimates (Ref. 3, pp. 404–406) of the radii of convergence of the perturbation series for isolated states of finite multiplicity of $H(\lambda)=H_0+\lambda W$, where H_0 is self-adjoint and W is Hermitian and relatively bounded by H_0, will show that the $1/Z$ expression has a nonzero radius of convergence for any energy level which arises from a discrete eigenvalue of H_0, where

$$H_0=\sum_{i=1}^{N}\left[-\tfrac{1}{2}\nabla_i^2-\frac{1}{r_i}\right] \tag{115}$$

restricted to an appropriate symmetry subspace, and

$$W=\sum_{\substack{i,j\\ i>j}}\frac{1}{r_{ij}} \tag{116}$$

restricted to the same subspace.

Next, it is implicit in Kato's[43] proof that the helium atom with infinite nuclear mass has infinitely many bound states, and in Hunziker's generalization[44] that a neutral atom has an infinite number of Rydberg states, that the N-electron Hamiltonian $H(\lambda)=H_0+\lambda W$ has a full Rydberg series for $\lambda=1/Z<1/(N-1)$. The physical reason behind this is that the "outermost" electron sees a screened charge of $Z-(N-1)$, and as long as this quantity is positive, the ion will have a full Rydberg series.

During the last 15 years there have been a number of rigorous results on the numbers of bound states of nega-

tive ions. In 1969 Uchiyama[45] showed that the two-electron Hamiltonian

$$-\frac{1}{2}\nabla_1^2-\frac{1}{r_1}-\frac{1}{2}\nabla_2^2-\frac{1}{r_2}+\frac{\lambda}{r_{12}} \tag{117}$$

has a finite number of discrete eigenvalues if $\lambda>1$. In the early 1970s Zhislin and co-workers[46] and Yafaev[46] generalized Uchiyama's result to show that the multielectron Hamiltonian

$$\sum_{i=1}^{N}\left[-\frac{1}{2}\nabla_i^2-\frac{1}{r_i}\right]+\lambda\sum_{\substack{i,j\\ i>j}}\frac{1}{r_{ij}} \tag{118}$$

has a finite number of discrete eigenvalues if $\lambda\geq 1/(N-1)$; thus the results of Ref. 46 applied for $N=2$ to the borderline case $\lambda=1$ show that the hydride ion H^- has finitely many discrete bound states. More recently Hill[47] proved that the hydride ion H^- has only one discrete energy level, and Hoffman-Ostenhof and Hoffman-Ostenhof[48] showed that H^- has no threshold bound state (with energy $-\frac{1}{2}$ a.u.) in the ^3S symmetry subspace. Hill's theorem implies that whereas

$$-\frac{1}{2}\nabla_1^2-\frac{1}{r_1}-\frac{1}{2}\nabla_2^2-\frac{1}{r_2}+\frac{\lambda}{r_{12}} \tag{119}$$

has infinitely many discrete bound states for any $\lambda<1$, it has only one at $\lambda=1$, so the infinitely many discrete excited Rydberg states for $\lambda<1$ merge into the continuum as $\lambda\rightarrow 1$. Thus $H(\lambda)$ has only one discrete bound state for $1\leq\lambda<\lambda_c$. (H^- also has a bound state of unnatural parity with $E\cong -0.125\,35$ a.u. [the $(2p)^2\,^3P^e$ state] embedded in a continuum of different symmetry, which will be discussed later.)

One might wonder whether any discrete bound states of $H(\lambda)$ merge into the continuum at $E=-\frac{1}{2}$ a.u. for any λ strictly less than 1. If one does, then it must cross infinitely many energy levels of the same symmetry. At the present time this cannot be ruled out, since there are exceptions to the "no crossing" rule (for recent rigorous studies of the genericity of curve crossings, see Friedland and Simon[49] and Waterhouse[50]); however, it does seem most unlikely that infinitely many "forbidden" crossings would occur. Hence it seems most probable that *all* the discrete excited states of $H(\lambda)$ are absorbed by the continuum at $E=-\frac{1}{2}$ a.u. *precisely* at $\lambda=1$. (This analysis also provides an answer to the question "can a bound Rydberg level be pushed into its own continuum?" posed recently by Smid and Hansen:[51] only if that level crosses infinitely many levels of the same symmetry, which seems most improbable.)

Let us now address the question of the radii of convergence of the perturbation series for the $E(\lambda)$'s of the discrete excited states. We know from Kato's work that an isolated eigenvalue $E(\lambda)$ of finite multiplicity is holomorphic for λ real. We also strongly suspect that any discrete excited eigenvalue is absorbed by the continuum at $\lambda=1$, and from our results for the ground state we should presume that $E(\lambda)$ will have a singularity there. Hence we should infer that the radius of convergence λ^* of the perturbation series for a discrete excited eigenvalue $E(\lambda)$ should not exceed 1. If there are no nearer singularities in the complex plane, the radius of convergence λ^* will be exactly 1 for all discrete excited eigenvalues of $H(\lambda)$.

The numerical evidence presently available is insufficient to confirm or to disprove this conjecture. In the late 1960s Midtdal and co-workers[11,52] published tables of the E_n's for n up to 41 for the $2\,^1S$, $2\,^3S$, $2\,^1P$, and the $2\,^3P$ states of the helium isoelectronic sequence, and Sanders and Scherr[10] for n up to 17, 19, and 21 for the $2\,^3S$, $2\,^1P$, and the $2\,^3P$ states, respectively. The results of these two groups agree fairly well up to $n\simeq 15$ for the $2\,^3S$ state, $n\simeq 12$ for the $2\,^3P$ state, and $n\simeq 11$ for the $2\,^1P$ state; however, there are serious discrepancies for higher n, for which neither group's results are reliable. Both Sanders and Scherr[10] and Midtdal and co-workers[11,52] used relatively small numbers of basis functions (100 and 162, respectively), and Midtdal *et al.*'s calculation suffered from their use of basis functions of the form

$$s^n t^l u^m e^{-s/2} \tag{120}$$

with the *same* constant multiplying both r_1 and r_2 in the exponential. Such basis functions of course are inefficient at modeling the in-out correlation which is even more important in these singly excited states than it is in the ground state. In fact, since at the threshold at $\lambda=1$, where we know by the work of Hoffman-Ostenhof and Hoffmann-Ostenhof[48] that there is no bound state in the ^3S subspace and suspect there is no excited bound state in any other subspace, as $\lambda\rightarrow 1^-$ the corresponding excited state wave functions $\psi(\lambda)$ must become more and more distended, for the length scale on which the "outermost" electron moves should go like $1/(1-\lambda)$, the reciprocal of the screened charge. The higher-order corrections ψ_n to the wave function $\psi(\lambda)$ for such an excited state will accordingly be more and more distended, and they cannot be accurately computed with a basis containing only a single "closed-shell" exponential. In fact, with reference to their calculations for these states Midtdal, Aashamar, and Lyslo acknowledged "we will not quite exclude from consideration the possibility that our specific basic set of wave functions is not flexible enough" (Ref. 12, p. 18), and a few years later these authors found that the introduction of a "split-shell" exponential greatly improved the rate of convergence of variational calculations on these states.[53] In 1974 Aashamar, Midtdal, and Lyslo published perturbation calculations through 21st order on the $2\,^3S$ state using up to 235 basis functions with a "split-shell" exponential[54] and on the $3\,^3S$ state using up to 204 such basis functions.[55] These results seem to indicate that for these states all the exact E_n's except for E_1 are negative, and hence that the $E(\lambda)$'s for these states will have a singularity on the positive real axis. Hence the results published by Aashamar, Midtdal, and Lyslo in 1974 show that their earlier oscillatory results for the high-order perturbation coefficients for the $2\,^3S$ and $3\,^3S$ states are artifacts due to the inadequacy of their basis with only a single "closed-shell" exponential. Hence we regard as unreliable the estimates of Midtdal and his co-workers[12] of the radii of convergence of the perturbation

series for singly excited states of helium obtained using a basis with only a single "closed-shell" exponential. For the $1\,^1S$ state, their estimate of $\lambda^* \cong 1.22$ is wrong by about 12% and their E_n's for $n \gtrsim 30$ obtained using 140 basis functions with a single "closed-shell" exponential are devoid of physical significance, so it would not be surprising if their estimates of the λ^*'s for the much more distended $2\,^3S$, $2\,^1S$, $2\,^3P$, and $2\,^1P$ states

State	λ^* (Midtdal, Aashamar, and Lyslo, Ref. 12)
$2\,^3S$	0.93
$2\,^1S$	0.84
$2\,^3P$	0.76
$2\,^1P$	0.78

are in error by 7–24 %. On the other hand, the calculations of Sanders and Scherr are in agreement with those of Midtdal *et al.* in predicting that for the $2\,^1P$ state the E_n's for $3 \le n \le 11$ oscillate in sign with a period Δn of about 5, so if this trend persists in the exact coefficients it would imply that for the $2\,^1P$ state the radius of convergence of the power series for $E(\lambda)$ is determined by a singularity in the complex plane closer than 1 to the origin. However, the E_n's for $n \ge 12$ for the $2\,^1P$ state as calculated by Sanders and Scherr and by Midtdal *et al.* show serious disagreements with each other, which emphasizes the need for more accurate high-order calculations if any definitive conclusions are to be drawn. Furthermore, Sanders and Scherr's results for the E_n's for the $2\,^3P$ state are suggestive of a periodic oscillation with period $\Delta n \simeq 7$, but their results and those of Midtdal *et al.* disagree seriously for $n \ge 13$, so the presently available numerical data do not allow us to proceed beyond speculation for the $2\,^3P$ state.

At this point we issue a reminder that although we expect an eigenvalue $E(\lambda)$ of an atom to have a singularity at a threshold λ_c, there is no *a priori* reason why $E(\lambda)$ could not also have a complex conjugate pair of singularities closer than λ_c, in which case the perturbation series coefficients will oscillate with asymptotically constant period. Furthermore, we direct attention to a point which we made at the end of Sec. IV: a function whose nearest singularity is on the positive real axis can still have oscillatory Taylor series coefficients if the "period" of oscillation increases without limit.

We are planning to carry out high-order perturbation calculations on the excited states of the helium atom to test whether for them $\lambda^* = \lambda_c$. We may observe that a rather more complicated basis will be needed to achieve high-order results for excited states as accurate as those for the ground state since as $\lambda \to 1$ the excited-state eigenfunctions $\psi(\lambda)$ will become progressively more and more distended. In the language of Hilbert space, for the excited states

$$\lim_{\lambda \to 1^-} \frac{\psi(\lambda)}{\|\psi(\lambda)\|} \tag{121}$$

does not exist, whereas for the ground state

$$\lim_{\lambda \to \lambda_c^-} \frac{\psi(\lambda)}{\|\psi(\lambda)\|} \tag{122}$$

does exist and is equal to $\psi(\lambda_c)/\|\psi(\lambda_c)\|$. For the excited states the projection of the normalized $\psi(\lambda)$ onto *any* finite basis tends to 0 as $\lambda \to 1^-$, whereas for the ground state the normalized $\psi(\lambda)$ tends to the normalized $\psi(\lambda_c)$, which can be approximated with arbitrary accuracy as the basis approaches completeness. Hence the accurate calculation of high-order ψ_n's and E_n's for excited states will require the inclusion of basis functions which are concentrated on progressively larger and larger length scales. We plan to try using basis functions of the Frankowski type $\phi(2ks, 2kt, 2ku)$, where

$$\phi(s,t,u) = s^n t^l u^m (lns)^j \times \begin{Bmatrix} \sinh(ct) \\ \cosh(ct) \end{Bmatrix} \times e^{-s/2}, \tag{123}$$

with several different values of the parameter c to represent the progressively more distended ψ_n's.

In the meantime, we have performed a 50th-order perturbation calculation on the $2\,^3S$ state using a rather inadequate basis of 202 functions of the form (22) and 253 functions of the form (25). The nonlinear parameters k and c were 0.60 and 0.4375, respectively. Our energy coefficients E_n begin to oscillate in sign for $n = 47$, and their ratios ceased to be monotone at $n = 27$. Varying k and c showed that the onset of such behavior is a basis-dependent effect. Hence we have presented a table of the E_n's (Table IV) and a graph of their ratios r_n (Fig. 13) only for $n \le 26$; in the graph the incipient oscillatory behavior of the ratios is clearly visible. Nonetheless, our re-

TABLE IV. The E_n's associated with $E(\lambda)$ for the $2\,^3S$ state obtained with $k = 0.60$ and $c = 0.4375$.

N	$E(N)$
0	−0.625 000 000 0
1	0.187 928 669 4
2	−0.474 093 041 7[−01]
3	−0.487 228 008 9[−02]
4	−0.345 780 460 7[−02]
5	−0.202 984 925 3[−02]
6	−0.128 713 537 3[−02]
7	−0.871 415 267 6[−03]
8	−0.618 225 020 9[−03]
9	−0.454 433 311 0[−03]
10	−0.343 492 455 9[−03]
11	−0.265 559 255 4[−03]
12	−0.209 163 203 9[−03]
13	−0.167 330 342 7[−03]
14	−0.135 652 031 2[−03]
15	−0.111 256 107 4[−03]
16	−0.922 115 593 3[−04]
17	−0.771 599 290 9[−04]
18	−0.650 943 608 6[−04]
19	−0.552 523 917 9[−04]
20	−0.470 836 932 4[−04]
21	−0.402 388 493 8[−04]
22	−0.345 324 375 7[−04]
23	−0.298 674 402 6[−04]
24	−0.261 457 949 8[−04]
25	−0.232 058 661 7[−04]
26	−0.208 143 962 6[−04]

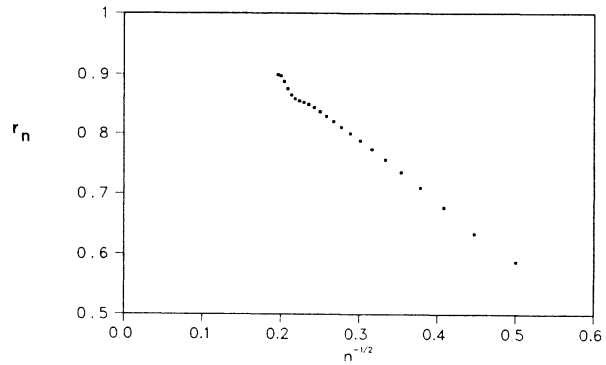

FIG. 13. The r_n's associated with $E(\lambda)$ for the $2\,^3S$ state for $4 \le n \le 26$ obtained with $k=0.60$ and $c=0.4375$ vs $n^{-1/2}$.

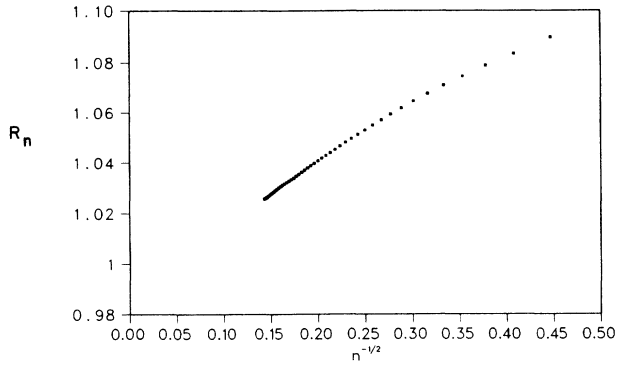

FIG. 14. The R_n's associated with $\|\psi(\lambda)\|^2$ for the $2\,^3S$ state for $5 \le n \le 50$ vs $n^{-1/2}$, obtained with $k=0.60$ and $c=0.4375$.

sults for the $2\,^3S$ state are considerably more stable than those of Sanders and Scherr[10] and of Midtdal *et al.*[11,52,53] We also calculated the perturbation coefficients for $\|\psi(\lambda)\|^2$, and a graph of the ratios of these coefficients for $n \le 50$ is presented in Fig. 14. One can see that the ratios seem to be smoothly converging downward to a limit of about 0.99, which would imply that $\lambda^* \simeq 1/0.99 \simeq 1.01$ would *exceed* $\lambda_c = 1$. In view of our results for the $1\,^1S$ state, it is hard to believe that the perturbation series for the $2\,^3S$ state would not become singular at $\lambda_c = 1$, and given the inadequacy of the basis and the relatively low order, 1.01 is not inconsistent with 1. Hence the radius of convergence of the $1/Z$ expansion for the $2\,^2S$ state of helium probably is determined by a singularity on the real axis at $\lambda = 1/Z = 1$. In any event it seems that the estimate for this state of $\lambda^* \simeq 0.93$ by Midtdal *et al.*[12] is wrong by about 7%.

The H^- ion also has a genuinely bound (square-integrable) doubly excited state, the $(2p)^2\,^3P^e$ state, of unnatural parity imbedded in the natural parity continuum; thus this state is discrete within its symmetry subspace. Using a basis of 50 P-type Hylleraas functions with a "split-shell" exponential, Drake[56] computed an upper bound of $-0.125\,350$ a.u. to the energy of this state, which is very close to the upper bound of $-0.125\,351\,006$ a.u. computed earlier by Midtdal using a basis of 203 P-type Hylleraas functions with a "closed-shell" exponential, and Midtdal's extrapolated estimate $-0.125\,354\,85$ a.u.[9] [Herrick and Stillinger[57] pointed out that the energy of this $(2p)^2\,^3P^e$ state is equal to the ground-state energy of an H^- ion in five dimensions.] Recently Grosse and Pittner[58] proved rigorously that there is no other discrete bound state within the unnatural parity subspace. This doubly excited state is qualitatively similar to the ground state in that it should have a bound state of zero binding energy at its critical coupling constant $\lambda_c = 1/Z_c > 1$. Hence the variational perturbation calculations by Midtdal *et al.*[9,11] on the $(2p)^2\,^3P^e$ state using a Hylleraas basis with a single "closed-shell" exponential should be comparably accurate to their calculations on the $(1s)^2\,^1S$ ground state using an analogous basis. Midtdal *et al.*[11] have calculated the energy perturbation coefficients E_n for this state using up to 204 Hylleraas basis functions. Stillinger[8] analyzed Midtdal's[9] coefficients E_n for n up to 21 obtained using 203 basis functions for this state in the same manner as for the $(1s)^2\,^1S$ ground state and found $\lambda^* \simeq 1.0128$, but he gave no estimate for λ_c. By applying a Darboux function ansatz to the E_n's of Midtdal *et al.*[11] for n up to 27, Brändas and Goscinski[14] found $\lambda_c = 1/Z_c \cong 1/0.9952 \simeq 1.0048$ and $\lambda^* \cong 1/0.990 \cong 1.010$. For the $(1s)^2\,^1S$ state Brändas and Goscinski's estimate of λ_c is too low by only 0.0002, so it would be reasonable to hope that their estimate of λ_c for the $(2p)^2\,^3P^e$ state is comparably accurate. We would not hesitate to attribute the very small discrepancy of about 0.005 between Brändas and Goscinski's estimates of λ_c and λ^* to some combination of small errors in the E_n's calculated by Midtdal *et al.*[11] and to $n=27$ simply not being far enough into the asymptotic region. We plan in the future to calculate the E_n's for this state to high order.

VII. "RADIAL" HELIUMLIKE IONS

A simplified model of the helium atom, which has been studied by several authors,[59] is obtained by replacing the interelectronic Coulomb potential

$$\frac{1}{r_{12}} = \frac{1}{r_>} \sum_{l=0}^{\infty} \left[\frac{r_<}{r_>} \right]^l P_l(\cos\theta) , \tag{124}$$

where

$$\begin{aligned} r_< &= \min(r_1, r_2) , \\ r_> &= \max(r_1, r_2) , \end{aligned} \tag{125}$$

with its spherical average $1/r_>$. For an S state, the Schrödinger equation in $(r_<, r_>)$ coordinates assumes a remarkably simple form reminiscent of the Schrödinger equation for a pair of uncoupled hydrogenic atoms with nuclear charges Z and $Z-1$:

$$\left[-\frac{1}{2} \left[\frac{\partial^2}{\partial r_>^2} + \frac{2}{r_<} \frac{\partial}{\partial r_<} \right] - \frac{Z}{r_<} - \frac{1}{2} \left[\frac{\partial^2}{\partial r_>^2} + \frac{2}{r_>} \frac{\partial}{\partial r_>} \right] - \frac{Z-1}{r_>} \right] \psi = E\psi . \tag{126}$$

This equation, however, is *not* separable in $(r_<, r_>)$ coordinates because of the nonseparable boundary condition at $r_< = r_>$:

$$\frac{\partial\psi}{\partial r_<} = \frac{\partial\psi}{\partial r_>} \quad \text{at } r_< = r_> \ . \tag{127}$$

It may be noted that because of the discontinuity at $r_1 = r_2$ in the first derivative of $1/r_>$ with respect to r_1 or r_2, one would expect that third derivatives of ψ with respect to r_1 or r_2 would not be continuous at $r_1 = r_2$.

For any Z for which the radial Hamiltonian has a bound state, the radial eigenfunction can be used in a Rayleigh-Ritz variational calculation on the full Hamiltonian, and the result of computing that expectation value of the full Hamiltonian is just the radial eigenvalue. Thus the radial energy provides an upper bound to the full energy:

$$E(\lambda) \le E_{\text{rad}}(\lambda) \ . \tag{128}$$

Since the threshold is at $-\frac{1}{2}$ for both systems, the critical value of λ_c for a state of a radial heliumlike ion cannot exceed the critical value λ_c for the corresponding state of the real ion:

$$\lambda_{c,\text{rad}} \le \lambda_c \ . \tag{129}$$

Furthermore, since the ground state of radial H^- is bound,[59(b)] we know that $\lambda_{c,\text{rad}}$ must exceed 1. In fact, combining the definition of $\lambda_{c,\text{rad}}$ $[E_{\text{rad}}(\lambda_{c,\text{rad}}) = -\frac{1}{2}]$ and the numerical results

$$E_{\text{rad}}(1) = -0.514\,494\,0(32) \ ,$$

$$E_{\text{rad}}(\tfrac{1}{2}) = -0.719\,757\,0(5) = -2.879\,028\,0(18)/4 \ ,$$

of Ref. 59(b) with the concavity of $E_{\text{rad}}(\lambda)$

$$\frac{(1-\frac{1}{2})E_{\text{rad}}(\lambda_{c,\text{rad}}) + (\lambda_{c,\text{rad}}-1)E_{\text{rad}}(\frac{1}{2})}{\lambda_{c,\text{rad}}-\frac{1}{2}} \le E_{\text{rad}}(1) \tag{130}$$

implies that

$$\lambda_{c,\text{rad}} \ge \frac{\frac{1}{2}E_{\text{rad}}(1) - E_{\text{rad}}(\frac{1}{2}) - \frac{1}{4}}{E_{\text{rad}}(1) - E_{\text{rad}}(\frac{1}{2})} \simeq \frac{0.212\,510}{0.205\,263} \simeq 1.0353\ldots . \tag{131}$$

Hence for the ground state

$$1.0353 \lesssim \lambda_{c,\text{rad}} \le \lambda_c \simeq 1.097\,66\ldots . \tag{132}$$

We have not performed our own variational or large-order perturbation theory calculations on radial helium, since we would first want to modify our basis by removing all nonzero powers of r_{12} (which is trivial) and including functions with discontinuous third and higher derivatives at $r_1 = r_2$ (which is straightforward but not trivial). However, we can refer to a rather recent large-order perturbation theory study of radial helium by Silverman, Sudhindra, and Olbrich,[60] who used a basis consisting of symmetrized sums of products of Laguerre orthonormal functions of r_1 and r_2:

$$N_{m_1 m_2}[L^{(2)}_{m_1}(r_1)L^{(2)}_{m_2}(r_2) + L^{(2)}_{m_2}(r_1)L^{(2)}_{m_1}(r_2)] \times e^{-(r_1+r_2)/2} \ . \tag{133}$$

By systematically increasing the maximum index m from 0 to 12, they generated bases of dimension $M = \binom{m+2}{2}$ ranging from 1 to 91. Silverman has kindly provided tables of the high-order perturbation coefficients up to $n = 81$ for each value of m. The angle θ^*_m subtended by the nearest pair of complex conjugate square-root branch-point singularities $\lambda^*_m = |\lambda^*_m| e^{\pm i\theta^*_m}$ can be estimated by the techniques described in the appendix. For $m \le 6$, there are sufficiently many oscillations up to order $n = 81$ to allow a reliable estimate of the "period" of oscillation, from which we have estimated θ^*_m using Eq. (A1). For $7 \le m \le 12$, we have instead used Eq. (A7) to estimate θ^*_m from the first sign change in E_n for large n. In Table V we have listed our estimate of the angle θ^*_m for each m. (In each case the value of θ^*_m is probably accurate within several percent.) Clearly there is no reason to think that as $m \to \infty$, the angle θ^*_m would not tend to 0. Hence we would conclude that for the operator problem in the infinite dimensional Hilbert space, the perturbation series for the ground state of the radial heliumlike ion has its nearest singularity on the positive real axis. The estimate $\lambda^*_{\text{rad}} \simeq 1.05$ of Silverman, Sudhindra, and Olbrich[60] agrees remarkably well with our own estimate of $\lambda_{c,\text{rad}}$ in Eq. (131). Hence it is likely that for the operator problem in the infinite-dimensional Hilbert space, $\lambda^*_{\text{rad}} = \lambda_{c,\text{rad}}$, just as for the full helium atom system.

We may note, however, that the method of Silverman, Sudhindra, and Olbrich[60] for estimating the location of the nearest complex-conjugate pair of singularities involves triangulation with very approximate estimates, obtained via a technique due to Silverman,[21] of the radii of convergence of the shifted and unshifted expansions, and hence is susceptible to relatively large errors. This is, we believe, the cause of the strikingly large discrepancy between Silverman, Sudhindra, and Olbrich's estimate $\theta^* \simeq 39°$ for their largest basis and our estimate $\theta^* \simeq 3.6°$. Apparently the quality of Silverman's technique[21] for es-

TABLE V. Apparent convergence of θ^*_m to 0 as $m \to \infty$ for the ground state of radial helium in a Laguerre basis.

m	θ^*_m (rad)	θ^*_m (deg)
2	$2\pi/6$[a]	60
3	$2\pi/10$[a]	36
4	$2\pi/15$[a]	24
5	$2\pi/22$[a]	16
6	$2\pi/30$[a]	12
7	0.166[b]	9.5
8	0.132[b]	7.6
9	0.106[b]	6.1
10	0.089[b]	5.1
11	0.074[b]	4.2
12	0.063[b]	3.6

[a]From Eq. (A1).
[b]From Eq. (A7).

timating $\lambda^*_{\rm rad}$ deteriorates as the origin of the shifted perturbation series moves away from 0, and the zero-order wave function becomes more and more distended. This trend correlates with the decreasing quality of Silverman's estimates of $\lambda^*_{\rm rad}$ for singly excited states of helium,[21] for which the zero-order wave functions are quite distended because of "in-out" correlation.

VIII. MULTIELECTRON ATOMS

Having considered excited states of the helium isoelectronic sequence and the "radial" helium problem, we may now turn our attention to the $1/Z$ expansions for the states of N-electron atoms. We have already mentioned the mathematically rigorous results of Kato[43] and Hunziker[44] which imply that an atom or ion has infinitely many discrete Rydberg states if $Z > N-1$, and the results of Zhislin and co-workers[46] and Yafaev[46] which show that a negative ion has only finitely many discrete states if $Z \le N-1$. Furthermore, experiment has yet to find a stable doubly negative atomic ion (*in vacuo*, not in solution), so it seems very likely, at least for those known atoms in the Periodic Table, that no discrete states exist if $Z \le N-2$. Hence we may infer from this combination of mathematical theorems and experimental results that generically for a discrete atomic state the minimum charge Z_c necessary to bind N electrons obeys

$$N-2 \le Z_c \le N-1 \ . \tag{134}$$

Since $\lambda_c = 1/Z_c$, λ_c generically will obey

$$\frac{1}{N-1} \le \lambda_c \le \frac{1}{N-2} \ . \tag{135}$$

If the radius of convergence λ^* of the perturbation series for $E(\lambda)$ is determined by a singularity at λ_c, then λ^* generically will obey

$$\frac{1}{N-1} \le \lambda^* \le \frac{1}{N-2} \ . \tag{136}$$

Since if $\lambda = 1/Z = 1/(N-1)$ the negative ion has only finitely many discrete states, for most states $\lambda = 1/(N-1)$, and for these one would expect that $\lambda^* \le \lambda_c = 1/(N-1)$.

Currently there is not much reliable numerical evidence for testing these inequalities. Numerical perturbation calculations have been performed on various states of the lithium[61] and the beryllium[62] isoelectronic sequences, but none has been carried out to sufficiently high order, and with sufficient emphasis on obtaining well-converged higher-order coefficients,[63] to obtain a definitive estimate of λ^* for these systems. However, we should mention Herrick and Stillinger's estimates for λ_c and λ^* for the ground state of the neon isoelectric sequence ($N=10$), which were obtained using a superposition of the ground state and singly excited Hartree-Fock determinantal wave functions.[64] They found

$$\begin{aligned} &\lambda_c \simeq 0.114 \ , \\ &\lambda^* \simeq 0.117 \text{ or } 0.118 \ . \end{aligned} \tag{137}$$

Both numbers lie between $\frac{1}{9} = 0.111\ldots$ and $\frac{1}{8} = 0.125$, and the 3% discrepancy between Herrick and Stillinger's estimates for λ_c and λ^* may well be attributable to the very approximate nature of their variational ansatz. [Our analysis of the two-electron case supports Reinhardt's[16] observation that Herrick and Stillinger's attempted calculation of the position and the width of the O^{2-} resonance, which was based on the assumptions that $\lambda^* > \lambda_c$ and that $E(\lambda)$ has a simple branch point singularity at λ^*, rests on an unfirm foundation.]

IX. COMPUTATIONAL DETAILS

All calculations reported in this article were performed in quadruple precision ($\sim$30 decimal digits) on the University of Delaware's IBM 3081D computer. The use of quadruple precision is necessary to control round-off errors in matrix manipulation due to our use of a nonorthogonal basis. The storage requirements of our program are formidable, primarily because of the need to perform algebraic operations on $N \times N$ matrices, where N is slightly less than 500, all of whose entries occupy 4 words. We reduce our storage requirement by about a factor of 2 by using symmetric storage mode for our matrices.

One of our runs would typically use about three hours of CPU time, most of which is spent in multiplying matrices and evaluating expectation values. Such operations, of course, would proceed much more quickly on a vector computer, such as a CRAY or a CYBER 205. Unfortunately, there presently is no easy way to use vector arithmetic in vector double precision, which corresponds to quadruple precision on the IBM 3081. We strongly encourage supercomputer manufacturers to develop an easily accessible way of performing vector operations with about 30 decimal digits.

X. CONCLUSIONS

By performing a 401-order variational perturbational calculation of the coefficients of the $1/Z$ expansion for the ground state of the helium isoelectronic sequence, we have found the following:

(i) As Reinhardt had surmised,[16] the radius of convergence λ^* of the perturbation series for the eigenvalue $E(\lambda)$ and the eigenfunction $\psi(\lambda)$ is equal to $\lambda_c = 1/Z_c$, where Z_c is the minimum nuclear charge necessary to bind two electrons.

(ii) $E(\lambda)$ and $\|\psi(\lambda)\|^2$ have singularities on the positive real axis at λ_c which are more complicated than a simple branch-point singularity; in particular, $E(\lambda)$ has a singularity of the form

$$(1-\lambda/\lambda_c)^{-a} U(a,c;x/(1-\lambda/\lambda_c)) \ ,$$

where U is the second (irregular) solution of the confluent hypergeometric equation.[65] $\|\psi(\lambda)\|^2$ has a similar but even more complicated singularity.

We also found that the perturbation series for the $2\,^3S$ and the $(2p)^2\,^3P^e$ states of helium seem to have radii of convergence λ^*'s equal to the λ_c's for those states. We have also seen that there is a need for more accurate cal-

culations to much higher order if we are to locate definitively the nearest singularities in the $E(\lambda)$'s for other excited states of the helium isoelectronic sequence and for states of multielectron atoms.

Our work has revealed several phenomena which are worthy of investigation by mathematical physicists. There is need for a rigorous theory of coupling constant thresholds in multielectron systems, and for an explanation of why the asymptotic form of the perturbation coefficients manifests itself only in extraordinarily high order. Furthermore, there is a need for a rigorous generalization of our results in Sec. IV on the singularities of the eigenvalues of 2×2 Hermitian matrices to multidimensional Hermitian matrices.

ACKNOWLEDGMENTS

This research was supported in its earlier stages by grants to J.D.M. from the University of Delaware Research Foundation and the Research Corporation, and in its later stages by National Science Foundation Grant Nos. PHY-8317085 and PHY-8608155 to J.D.M. and PHY-8507907 to R.N.H. We thank the University of Delaware for providing extensive amounts of computer time, first on its Burroughs B7700 and then on its IBM 3081D. J.D.M. is especially grateful to R. Stephen Berry for generous sabbatical support and the hospitality of the Department of Chemistry of the University of Chicago. Part of this article was written by J.D.M. in the stimulating environment of the Aspen Center for Physics. J.D.M. is further grateful to Dudley R. Herschbach for the hospitality of the Department of Chemistry at Harvard University, where the final touches were put on this article, and for an illuminating lecture on the asymptotics of Legendre polynomials for small θ, which led to the second technique for estimating θ presented in the Appendix. We are grateful to Barry Simon and Martin Klaus for information about rigorous results on the behavior of eigenvalues near thresholds, and we are further grateful to Barry Simon for asking a probing question which led to our determining the nature of the singularity in $E(\lambda)$ at λ_c. George Baker, Jr. gave us the benefit of his expertise on the Padé approximation, and Jeremiah Silverman kindly provided us with unpublished data from his calculations on the radial helium problem. Finally it is a pleasure to thank William P. Reinhardt, Barry Simon, and Frank Stillinger for numerous helpful and stimulating discussions of this challenging problem.

APPENDIX: LOCATING THE NEAREST COMPLEX-CONJUGATE PAIR OF SQUARE-ROOT BRANCH-POINT SINGULARITIES

Suppose one is studying the perturbation series for an eigenvalue $E(\lambda)$ of a self-adjoint operator $H(\lambda)=A+\lambda B$, where the nearest singularities of $E(\lambda)$ are a complex-conjugate pair of square-root branch-point singularities at $\lambda_0 e^{\pm i\theta}$. Then as $n\to\infty$, the perturbation coefficients E_n will have the behavior described in Sec. IV, with periodic oscillatory behavior of period $2\pi/\theta$. If one wishes to locate the complex-conjugate pair of singularities by determining λ_0 and θ, one could do so from the high-order perturbation coefficients by fitting them to the expression in Eq. (35), or to its asymptotic approximant in Eq. (40). Indeed, Eq. (40) provides a ready estimate of θ from simply knowing the sign behavior of the high-order perturbation coefficients: one counts the "distance" Δn between successive "periods" of oscillation, and then obtains the quick estimate

$$\theta=\frac{2\pi}{\Delta n} . \tag{A1}$$

This technique, however, is valid only if $\theta n \gg 1$, i.e., if n is sufficiently large that there have been several oscillations. If θ is so small that at a given order n there have been few or no complete periodic oscillations, then Eq. (36), the formula of Laplace, and the subsequent derivations based on it, in particular Eq. (40) are not valid. In this case, one must instead retreat to Eq. (35),

$$E_n \sim \pm\lambda_0^{-n}\frac{P_{n-2}(\cos\theta)-P_n(\cos\theta)}{2n-1} \tag{A2}$$

and use the approximation, which is valid for all n for $\theta \ll 1$,

$$P_n(\cos\theta)\simeq J_0((n+\tfrac{1}{2})\theta) , \tag{A3}$$

where J_0 is a Bessel function. Thus we see that for $\theta \ll 1$,

$$E_n \sim \pm\lambda_0^{-n}\frac{J_0((n-\frac{3}{2})\theta)-J_0((n+\frac{1}{2})\theta)}{2n-1} . \tag{A4}$$

Since θ is small, we can approximate the finite difference of the Bessel functions of slightly different arguments by the derivative of the Bessel function times 2θ:

$$J_0((n-\tfrac{3}{2})\theta)-J_0((n+\tfrac{1}{2})\theta)\simeq -2\theta J_0'((n-\tfrac{1}{2})\theta) . \tag{A5}$$

Since $-J_0'=J_1$, we obtain

$$E_n \sim \pm\lambda_0^{-n}\theta\frac{J_1((n-\frac{1}{2})\theta)}{n-\frac{1}{2}} . \tag{A6}$$

To use knowledge of the first sign change of E_n (for large n) to determine θ, observe that the first node of $J_1(z)$ occurs at $z=j_{1,1}=3.831\,71\ldots$. Thus if the first sign change of E_n (for large n) occurs at $\bar{n}$, then θ can be determined from

$$(\bar{n}-\tfrac{1}{2})\theta\simeq j_{1,1}=3.831\,71\ldots . \tag{A7}$$

It is interesting to compare this formula with what would result from the naive and (and improper) use of Eq. (40),

$$E_n \sim \pm\lambda_0^{-n}\left[\left[\frac{2}{\pi n}\sin\theta\right]^{1/2}\frac{\sin\left[(n-\frac{1}{2})\theta-\frac{\pi}{4}\right]}{n-\frac{1}{2}} + O(n^{-5/2})\right] , \tag{A8}$$

outside its region of validity. Since the sine function vanishes at multiples of π, one might conclude that θ is determined from the first positive zero of the sine according to

$$(\tilde{n}-\tfrac{1}{2})\theta=\frac{\pi}{4}\ . \tag{A9}$$

This would be quite wrong. However, if one used the *second* positive zero of the sine, one would find that

$$(\tilde{n}-\tfrac{1}{2})\theta=\frac{\pi}{4}+\pi=\frac{5\pi}{4}\simeq 3.926\,99\ldots\ , \tag{A10}$$

which is remarkably close to $j_{1,1}=3.831\,71\ldots$. The net effect is that if $\theta\ll 1$, then the first sign change of E_n (for large n) occurs at

$$\frac{j_{1,1}}{\theta}=\frac{j_{1,1}}{\pi}\frac{\pi}{\theta}=1.219\,67\frac{\pi}{\theta}\ , \tag{A11}$$

whereas in general the Nth sign change of E_n asymptotically occurs at

$$n\simeq(N+\tfrac{1}{4})\frac{\pi}{\theta}\ . \tag{A12}$$

---

*Present Address: Milton S. Eisenhower Research Center, The Johns Hopkins University Applied Physics Laboratory, Johns Hopkins Road, Laurel, MD 20810.

[1]E. A. Hylleraas, Z. Phys. **65**, 209 (1930).

[2]T. Kato, J. Fac. Sci. Univ. Tokyo Sect. I **6**, 145 (1951).

[3]T. Kato, *Perturbation Theory for Linear Operators,* 2nd ed. (Springer, New York, 1976), pp. 410–413.

[4]R. E. Knight and C. W. Scherr, Phys. Rev. **128**, 2675 (1962).

[5]R. E. Knight and C. W. Scherr, J. Chem. Phys. **37**, 2503 (1962).

[6]R. E. Knight and C. W. Scherr, Rev. Mod. Phys. **35**, 436 (1963).

[7]T. Kinoshita, Phys. Rev. **105**, 1490 (1957); **115**, 366 (1959).

[8]F. H. Stillinger, Jr., J. Chem. Phys. **45**, 3623 (1966). Further analysis along the lines of this article was presented by F. H. Stillinger and D. K. Stillinger, Phys. Rev. A **10**, 1109 (1974), and by F. H. Stillinger and T. A. Weber, Phys. Rev. A **10**, 1122 (1974).

[9]J. Midtdal, Phys. Rev. **138**, A1010 (1965).

[10]F. C. Sanders and C. W. Scherr, Phys. Rev. **181**, 84 (1969).

[11]J. Midtdal, G. Lyslo, and K. Aashamar, Phys. Norv. **3**, 163 (1969), particularly Tables II and III.

[12]J. Midtdal, K. Aashamar, and G. Lyslo, Phys. Norv. **3**, 11 (1968), particularly Table II.

[13]E. Brändas and O. Goscinski, Int. J. Quantum Chem. **4**, 571 (1970).

[14]E. Brändas and O. Goscinski, Int. J. Quantum Chem. Symp. **6**, 59 (1972).

[15]G. A. Arteca, F. M. Fernández, and E. A. Castro, J. Chem. Phys. **84**, 1624 (1986).

[16]W. P. Reinhardt, Phys. Rev. A **15**, 802 (1977).

[17]F. H. Stillinger, Phys. Rev. A **15**, 806 (1977).

[18]M. Klaus and B. Simon, Ann. Phys. (N.Y.) **130**, 251 (1980), particularly Sections 1 and 2.

[19]S. Flügge, *Practical Quantum Mechanics* (Springer, New York, 1971), Vol. 1, pp. 175–178.

[20]M. Klaus and B. Simon, Commun. Math. Phys. **78**, 153 (1980), particularly Theorem 3.2, where they show that for $\lambda>\lambda_c$, $E(\lambda)\to E(\lambda_c)$ like $(\lambda-\lambda_c)^2$ for $V_{ij}\le 0$ and in $C_0^\infty(\mathbb{R}^3)$.

[21]J. N. Silverman, Phys. Rev. A **23**, 441 (1981).

[22]R. Ahlrichs, Phys. Rev. A **5**, 605 (1972).

[23]M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof, and B. Simon, J. Phys. A **16**, 1125 (1983).

[24](a) B. Simon, J. Funct. Anal. **25**, 338 (1977). (b) This simple trick goes back to P.-O. Löwdin, J. Math. Phys. **3**, 969 (1962).

[25]K. Frankowski and C. Pekeris, Phys. Rev. **146**, 46 (1966); **150**, 366(E) (1966).

[26]D. E. Freund, B. D. Huxtable, and J. D. Morgan III, Phys. Rev. A **29**, 980 (1984).

[27]C. Schwartz, Meth. Comput. Phys. **2**, 241 (1963); B. Klahn and J. D. Morgan III, J. Chem. Phys. **81**, 410 (1984); R. N. Hill, *ibid.* **83**, 1173 (1985); J. D. Morgan III, in *Numerical Determination of the Electronic Structure of Atoms, Diatomic and Polyatomic Molecules,* Vol. 271 of *NATO Advanced Study Institute, Series C: Mathematical and Physical Sciences,* edited by M. Defranceschi and J. Delhalle (Kluwer, Dordrecht, 1989), pp. 49–84.

[28]K. Frankowski, Phys. Rev. **160**, 1 (1967).

[29]A. Kono and S. Hattori, Phys. Rev. A **29**, 2981 (1984); **31**, 1199 (1985).

[30](a) G. Szegö, *Orthogonal Polynomials,* 2nd ed. (American Mathematical Society, New York, 1959). (b) Somewhat oddly, Midtdal *et al.*, Ref. 12, pp. 16–17, considered it "unfortunate" that Stillinger's analysis was confined to the nonoscillatory E_n's with $n\le 21$, even though they went on to say "for the state $(1s)^2\,{}^1S$, and the same is true of the state $(2p)^2\,{}^3P$, the oscillations will disappear as the number of terms [in the basis] increases."

[31]O. Perron, Journal für die reine und angewandte Mathematik **151**, 76-77 (1921).

[32]W. Kutzelnigg, Theor. Chim. Acta **68**, 445 (1985); H. M. Schmidt, Phys. Rev. A **34**, 56 (1986); W. R. Johnson and J. Sapirstein, Phys. Rev. Lett. **57**, 1126 (1986); S. Salomonson and P. Öster, Phys. Rev. A **40**, 5559 (1989).

[33]G. W. F. Drake, Nucl. Inst. Meth. Phys. Res. **B31**, 7 (1988).

[34]T. Anno and H. Teruya, Mem. Fac. Sci. Kyushu Univ., Ser. C **15**, 29 (1985).

[35]G. Vivanti, Riv. Mat. **3**, 111 (1893).

[36]P. Dienes, *The Taylor Series* (Clarendon, Oxford, 1931), p. 226.

[37]W. Magnus, F. Oberhettinger, and R. P. Soni, *Formulas and Theorems for the Special Functions of Mathematical Physics,* 3rd ed. (Springer, New York, 1966).

[38]A. Erdelyi, W. Magnus, F. Oberhettinger, and F. G. Tricomi, *Higher Transcendental Functions* (McGraw-Hill, New York, 1953), Vol. 1, Sec. 6.5. This reference uses the symbol Ψ for the function U, so we have chosen to follow Ref. 37 and use the symbol U to avoid confusion with the wave function.

[39]The saddle point method, also known as the method of steepest descent, is discussed in considerable detail in Chaps. 5 and 6 of N. G. De Bruijn, *Asymptotic Methods in Analysis* (Dover, New York, 1981). Briefer discussions can be found on pp. 437–443 of P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), Vol. 1, and on pp. 503–506 of H. Jeffreys and B. Jeffreys, *Methods of Mathematical Physics,* 3rd ed. (Cambridge University Press, Cambridge, 1972).

[40]G. A. Baker, Jr. and P. Graves-Morris, *Padé Approximants, Part II: Extensions and Applications,* Vol. 14 of *Encylopedia*

of Mathematics and its Applications (Addison-Wesley, Reading, MA, 1981), p. 38.
[41]G. A. Baker, Jr., Phys. Rev. **129**, 99 (1963).
[42]For expositions of this intuition in the case of variational calculations on atomic and molecular systems, see Ref. 27.
[43]T. Kato, Trans. Am. Math. Soc. **70**, 212 (1951).
[44]W. Hunziker, Helv. Phys. Acta **48**, 145 (1975).
[45]J. Uchiyama, Publ. Res. Inst. Math. Sci. (Kyoto Univ.) **A5**, 51 (1969).
[46]G. M. Zhislin, Theor. Math. Phys. **7**, 571 (1971); D. R. Yafaev, Funct. Anal. Appl. **6**, 349 (1972); M. A. Antonets, G. M. Zhislin, and I. A. Shereshevskii, Theor. Math. Phys. **16**, 800 (1973); G. M. Zhislin, *ibid.* **21**, 971 (1974).
[47]R. N. Hill, Phys. Rev. Lett. **38**, 643 (1977); J. Math. Phys. **18**, 2316 (1977).
[48]M. Hoffmann-Ostenhof and T. Hoffmann-Ostenhof, J. Phys. A **17**, 3321 (1984).
[49]S. Friedland and B. Simon, Linear Algebra Appl. **44**, 41 (1982).
[50]W. C. Waterhouse, Linear Algebra Appl. **57**, 227 (1984).
[51]H. Smid and J. E. Hansen, J. Phys. B **20**, 6541 (1987).
[52]K. Aashamar, G. Lyslo, and J. Midtdal, J. Chem. Phys. **52**, 3324 (1970).
[53]J. Midtdal, K. Aashamar, and G. Lyslo, Phys. Norv. **6**, 87 (1972).
[54]K. Aashamar, J. Midtdal, and G. Lyslo, J. Chem. Phys. **60**, 3403 (1974).
[55]K. Aashamar, J. Midtdal, and G. Lyslo, J. Chem. Phys. **61**, 1345 (1974).
[56]G. W. F. Drake, Phys. Rev. Lett. **24**, 126 (1970). Cf. the subsequent upper bound of $-0.125\,354\,705\,1$ a.u. obtained using 90 P-type Hylleraas functions with a "split-shell" exponential by A. K. Bhatia, Phys. Rev. A **2**, 1667 (1970).
[57]D. R. Herrick and F. H. Stillinger, Phys. Rev. A **11**, 42 (1975).
[58]H. Grosse and L. Pittner, J. Math. Phys. **24**, 1142 (1983).
[59]See, for example, (a) H. Shull and P.-O. Löwdin, J. Chem. Phys. **30**, 617 (1959); (b) H. L. Davis, *ibid.* **39**, 1827 (1963).
[60]J. N. Silverman, B. S. Sudhindra, and G. Olbrich, Phys. Rev. A **30**, 1554 (1984).
[61]J. S. Onello, L. Ford, and A. Dalgarno, Phys. Rev. A **10**, 9 (1974); J. S. Onello, *ibid.* **11**, 743 (1975). Since the E_2 for the $(1s)^2 2s\ ^2S$ state calculated in these articles differs by about 1% from the "exact" value obtained by Z. J. Horak, M. N. Lewis, A. Dalgarno, and P. Blanchard, Phys. Rev. **185**, 21 (1969), one may wonder how accurate are the higher-order coefficients E_n for n up to 10, and whether their oscillation at higher order is a characterization of the finiteness of the basis.
[62]D. K. Watson and S. V. O'Neil, Phys. Rev. A **12**, 729 (1975). Since these authors note that their value for E_2 for the ground state obtained with 60 configurations differs by 1% from that obtained with 150 configurations, and by $2\frac{1}{2}$% or 3% from semiempirical values obtained from spectroscopic data, one may wonder how well converged are their higher coefficients for n up to 10, and whether the oscillatory behavior at higher n is not a finite-basis effect.
[63]Indeed, A. Dalgarno (private communication) has said "I am sure that much of the oscillation in sign in our lithium and beryllium results is due to the limited basis. I seem to recall in fact that as we increased the basis size, the oscillation moved to higher-order coefficients. A high precision calculation would be very interesting."
[64]D. R. Herrick and F. H. Stillinger, J. Chem. Phys. **62**, 4360 (1975).
[65]On more than one occasion we have been asked how we can be sure that in the asymptotic expansion (55) of the ratios there is not, say, an $n^{-1/4}$ term with a tiny coefficient, which might be numerically detectible only if n is as large as, say, 10^9. We cannot, of course, be absolutely sure that there is not such a term. However, it probably is not a coincidence that the expression we found for the singularity in $E(\lambda)$ at the threshold involves the irregular solution of the confluent hypergeometric equation—the same equation which figures in the description of an electron moving in a Coulomb potential, which is the potential seen by the "outermost" electron at large distances. It would of course be desirable to find a way of making this relation explicit.