Planck's-constant expansions for bound states

Frank H. Stillinger
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 19 October 1990)

Planck's constant h is a fundamental physical parameter that establishes the scale of quantum phenomena. Bound-state energy eigenvalues for several well-known systems (e.g., harmonic oscillators, Morse oscillators, and square-well potentials) are formally analytic functions of h in the neighborhood of $h=0$, and any "physical" state can be reached in principle by analytic continuation. This paper explores the possibility of developing power series in h for atomic and molecular energies, with analytic continuation to access physical states. For this purpose it is necessary to modify Coulomb interactions at short range to keep the potential bounded below. As a result the h expansions appear naturally as Rayleigh-Schrödinger perturbation series in anharmonicity about collective harmonic-oscillator states. Physical eigenvalues emerge in the strong-coupling limit, and Padé approximants seem to be analytical tools well suited for entering this regime. Some basic implementation details are presented for application to the modified hydrogen atom, the two-electron isoelectronic atomic sequence, and many-electron atoms.

I. INTRODUCTION

The importance and difficulty of most physically relevant eigenvalue problems in quantum mechanics demand powerful analytical and computational tools. For this reason we have seen the emergence of several independent techniques to supplement conventional basis-set expansions, such as quantum Monte Carlo[1] and Green's-function methods,[2] density-functional approaches,[3] semiclassical quantization procedures with systematic corrections,[4] and interdimensional interpolations.[5]

This paper is devoted to initial development of yet another systematic approach. Nominally it involves the generation of power series in Planck's constant h for both eigenfunctions and eigenvalues of the time-independent Schrödinger equation. On this account it bears a close relationship to the semiclassical quantization methods,[4] yet it differs from them in at least three key aspects. First, classical orbits and their quantization rules which often appear in semiclassical analyses play no part in the present development. Second, in order to generate solutions for realistic atomic and molecular systems the present approach introduces and exploits a modification of the Coulomb interaction operators. Third, the formal series expansion in h is treated not as an end in itself but as the starting point for analytic continuation throughout the complex h plane (or its equivalent) to access the desired "physical" state with unmodified interactions. It should be stressed at the outset that this technique applies with equal force to ground and excited states.

Section II sets the stage for the general procedure by revisiting some familiar one-dimensional examples. The hydrogen atom with modified Coulomb operator appears in Sec. III, while Sec. IV examines the more challenging case of the helium atom and its isoelectronic sequence. The general atomic case receives scrutiny in Sec. V.

Some closing remarks appear in Sec. VI. Analysis of the multinuclear case, involving aspects of chemical bonding and molecular structure, has been reserved for a planned sequel.

II. ONE-DIMENSIONAL EXAMPLES

In spite of its simplicity the one-dimensional harmonic oscillator illustrates some important points for the present approach. The time-independent Schrödinger equation for this case is

$$-\tfrac{1}{2}\eta^2\psi_n''(x)+\tfrac{1}{2}Kx^2\psi_n(x)=E_n\psi_n(x) \ ; \tag{2.1}$$

the harmonic force constant has been denoted by K, and

$$\eta=\hbar m^{-1/2} \ . \tag{2.2}$$

The solutions of course are well known[6] ($n=0,1,2,\ldots$):

$$E_n(\eta)=(n+\tfrac{1}{2})K^{1/2}\eta \ ; \tag{2.3}$$

$$\psi_n(x)=N_n\exp(-\tfrac{1}{2}s^2)H_n(s) \ ,$$

$$s=K^{1/4}\eta^{-1/2}x \ . \tag{2.4}$$

Here the H_n are Hermite polynomials, and N_n is a normalizing factor for the ψ_n:

$$N_n=(2^n\pi^{1/2}n!)^{-1/2}K^{1/8}\eta^{-1/4} \ . \tag{2.5}$$

All of the harmonic-oscillator eigenvalues E_n are analytic functions of the scaled Planck constant η, indeed just trivial linear functions of this variable. Changing the sign of η leaves the wave equation unchanged, but the eigenvalue functions (2.3) are *not* invariant to this sign change. Analytic continuation of the normalized wave functions from positive real η encounters an essential

singularity at $\eta=0$ and produces complex wave functions along the negative real axis.

If the quadratic potential term in Eq. (2.1) is replaced by the more general $|x|^p$, $p>0$, one easily verifies that the eigenvalues will be proportional to $\eta^{2p/(p+2)}$, an integral power *only* for the harmonic case $p=2$. Consequently this type of anharmonicity destroys analyticity of energy eigenvalues at the η origin. However it is important to realize that anharmonicity *per se* need not eliminate analyticity, as the following well-known example demonstrates.

The wave equation

$$-\tfrac{1}{2}\eta^2\psi_n''(x)+[V(x)-E_n]\psi_n(x)=0 \tag{2.6}$$

can be solved in closed form for bound states in the case of the Morse potential[7]

$$V(x)=A\,[\exp(-2\alpha x)-2\exp(-\alpha x)]\ . \tag{2.7}$$

The eigenvalues now have the form

$$E_n(\eta)=-A\,[1-(n+\tfrac{1}{2})\alpha(2A)^{-1/2}\eta]^2\ , \tag{2.8}$$

where physically realizable states require that n be a non-negative integer subject to the upper limit

$$n+\tfrac{1}{2}<(2A)^{1/2}(\alpha\eta)^{-1}\ . \tag{2.9}$$

Once again the eigenvalues are analytic functions of η, but are not even in η. The eigenfunctions can be expressed in terms of confluent hypergeometric functions, and as in the previous harmonic-oscillator case they become complex when positive η is continued onto the negative real axis.

The existence of eigenfunctions analytic in the scaled Planck constant η in the neighborhood of $\eta=0$ is not contingent on analyticity in x of the potential $V(x)$. Consider the square-well potential with width $2a$:

$$V(x)=\begin{cases}-U & (|x|\le a)\\ 0 & (a<|x|)\ ,\end{cases} \tag{2.10}$$

which obviously is not analytic. By applying the usual wave-function-matching conditions across the discontinuities in V, one finds that energy eigenvalues are given by

$$E=U\,[w^2(y)y^2-1]\ , \tag{2.11}$$

where

$$y=\eta/[(2U)^{1/2}a]=\hbar/[(2mU)^{1/2}a]\ . \tag{2.12}$$

For even-parity states, including the ground state, $w(y)$ is a solution to

$$y^2=\cos^2 w/w^2 \tag{2.13}$$

in any one of the ranges

$$n\pi\le w\le(n+\tfrac{1}{2})\pi,\quad n=0,1,2,3,\dots\ ; \tag{2.14}$$

for odd-parity states $w(y)$ is determined by

$$y^2=\sin^2 w/w^2 \tag{2.15}$$

in any one of the ranges

$$(n+\tfrac{1}{2})\pi\le w\le(n+1)\pi,\quad n=0,1,2,3,\dots\ . \tag{2.16}$$

Exclusion of intervening w intervals in (2.14) and (2.15) stems from the requirement of wave-function normalizability.

In order to investigate analyticity of the square-well energies in η or equivalently in y, we can first take the appropriate square root in Eq. (2.13) or Eq. (2.14). Concentrating on the ground state for illustration we therefore examine

$$y=\cos w/w\ . \tag{2.17}$$

The implicit function theorem[8] guarantees that for real positive y the function $w(y)$ exists and has a well-defined derivative (i.e., is analytic). Leading terms in the convergent power series for w are easily found to be

$$w(y)=\frac{\pi}{2}\left[1-y+y^2-\left(1+\frac{\pi^2}{24}\right)y^3+O(y^4)\right]\ . \tag{2.18}$$

The ground-state energy eigenvalue has the corresponding expansion

$$\frac{E(y)}{U}=-1+\frac{\pi^2 y^2}{4}\left[1-2y+3y^2-\left(4+\frac{\pi^2}{12}\right)y^3\right]$$
$$+O(y^6)\ . \tag{2.19}$$

As was the case with the preceding examples, this is not an even function of the appropriately scaled Planck constant y in spite of occurrence only of y^2 in the wave equation. $E(y)$ can be analytically continued across the origin to the negative real y axis (a regime in which the wave function is un-normalizable). The radii of convergence of both series (2.18) and (2.19) are determined by the presence of a square-root branch point singularity on the negative y axis. It is associated with the first minimum of the function $\cos w/w$ along the positive axis, which occurs at

$$w_c\cong 2.798\,39,\quad y_c\cong-0.336\,508\ . \tag{2.20}$$

The presence of a square-root singularity at y_c in the energy function determines the asymptotic large-order behavior of its power series coefficients.[9] Similar considerations apply to the square-well excited states of both parities.

Before passing on to atomic systems, it is worth pointing out that symmetric double-well potentials will not possess eigenvalues analytic in Planck's constant. The reason resides in the phenomenon of tunneling. Each eigenvalue is expected to contain a tunneling-splitting contribution that should be essentially singular in $\hbar$ at the origin. However, note that double-well asymmetry removes this feature.

III. MODIFIED HYDROGEN ATOM

The time-independent Schrödinger equation for hydrogenic atoms or ions can be written

$$[\tfrac{1}{2}\eta^2\nabla_r^2+Ze^2v(r)+E]\psi(\mathbf{r})=0\ , \tag{3.1}$$

where Z is the atomic number of the nucleus, and v is the

Coulomb potential

$$v(r) = r^{-1} . \tag{3.2}$$

The scaled Planck constant η is still defined by Eq. (2.2) provided m represents the reduced mass. The spectrum of hydrogenic eigenvalues is of course well known

$$E = -Z^2 e^4 / (2n^2 \eta^2) , \tag{3.3}$$

where $n = 1, 2, 3, \ldots$ is the total quantum number. In contrast to the analytic eigenvalues discussed in Sec. II, each of these exhibits a double pole at the origin, a feature associated with divergence of the Coulomb potential.

A simple modification of the Coulomb potential can be introduced which in principle restores origin-neighborhood analyticity to the eigenvalues of Eq. (3.1), while still permitting extraction of physically relevant energies. In place of Eq. (3.2) we instead use

$$v(r) = r^{-1} f(l^{-1} r) , \tag{3.4}$$

where l is an as-yet arbitrary scale parameter, and where the function f obeys the following conditions.

(a) $f(u)$ is continuous, differentiable, and bounded above and below on the real line $-\infty < u < +\infty$.

(b) $f'(u) > 0$ for $-\infty < u < +\infty$.

(c) f is odd: $f(-u) = -f(u)$.

(d) There exist positive numbers A, a such that

$$|f(u) - 1| < A \exp(-au^2)$$

for real positive u.

(e) $f(u)$ is analytic throughout the u plane.

(f) The power series

$$f(u) = \sum_{n=0}^{\infty} (-1)^n f_{2n+1} u^{2n+1} \tag{3.5}$$

has coefficients

$$f_1 = 1, \quad f_{2n+1} > 0 \quad (n > 1) . \tag{3.6}$$

These conditions can easily be met by using familiar standard functions. A specific example might be

$$f(u) = \mathrm{erf}(\pi^{1/2} u / 2)$$

$$= \sum_{n=0}^{\infty} \frac{1}{(2n+1)n!} \left[-\frac{\pi}{4} \right]^n u^{2n+1} . \tag{3.7}$$

As a result of the preceding conditions imposed on f, the modified Coulomb potential (3.4) will be bounded, monotonic, and representable as a convergent expansion in even powers of r:

$$v(r) = \sum_{n=0}^{\infty} (-1)^n f_{2n+1} l^{-(2n+1)} r^{2n} . \tag{3.8}$$

Condition D implies that the Coulomb interaction has been substantially modified only within a distance of order l of the origin, and at large distance it behaves as before

$$v(r) \sim r^{-1} . \tag{3.9}$$

Our modified hydrogenic problem takes on an especially useful form after making the following substitutions:

$$\mathbf{r} = \left[\frac{l^3 \eta^2}{2f_3 Z e^2} \right]^{1/4} \mathbf{s} ,$$

$$\psi(\mathbf{r}) = \phi(\mathbf{s}) , \tag{3.10}$$

along with the introduction of a "coupling constant"

$$\lambda = \frac{\eta}{(2f_3 Zl)^{1/2} e} . \tag{3.11}$$

As a result the Schrödinger equation (3.1) can be transcribed into that for a three-dimensional harmonic oscillator with anharmonic perturbation

$$[-\tfrac{1}{2}\nabla_s^2 + \tfrac{1}{2} s^2 + V(s,\lambda) - \varepsilon]\phi(\mathbf{s}) = 0 . \tag{3.12}$$

The perturbing potential V is

$$V(s,\lambda) = -(2f_3)^{-1}\lambda^{-3/2}[s^{-1}f(\lambda^{1/2}s) - \lambda^{1/2}$$
$$+ f_3 \lambda^{3/2} s^2]$$

$$= (2f_3)^{-1} \sum_{n=2}^{\infty} (-1)^{n-1} f_{2n+1} \lambda^{n-1} s^{2n} . $$

$$\tag{3.13}$$

The eigenvalue ε in the transformed equation is related to the energy eigenvalue E as follows:

$$\varepsilon = \frac{\eta^2 E}{(2f_3 Z e^2)^2 \lambda^3} + \frac{1}{2f_3 \lambda} , \tag{3.14}$$

or equivalently

$$E = 2f_3 Z^2 e^4 \eta^{-2} \lambda^2 [2f_3 \lambda \varepsilon(\lambda) - 1] . \tag{3.15}$$

Taking the point of view that the artificially introduced length $l > 0$ is fixed, Eq. (3.11) shows that coupling constant λ is proportional to η and thus to Planck's constant. Since the perturbation V has a series (3.13) in positive integer powers of λ, one expects ε to have a perturbation series in positive integer powers of λ for any eigenstate

$$\varepsilon(\lambda) = \sum_{n=0}^{\infty} \varepsilon_n \lambda^n , \tag{3.16}$$

with coefficients ε_n accessible through an extended version of Rayleigh-Schrödinger perturbation theory.[10] This series then must be the systematic Planck's-constant expansion for ε, which leads through Eq. (3.15) to the corresponding Planck's-constant expansion for E.

Energy eigenvalues of direct physical interest require fixing η, and then passing to the limit $l \to 0+$. Equation (3.11) demands that $\lambda \to +\infty$, so that physical eigenstates correspond to a strong-coupling limit in the perturbation problem (3.12). In that strong-coupling limit the total interaction present in Eq. (3.12) approaches the following asymptote $(s \gg \lambda^{-1/2})$:

$$\tfrac{1}{2} s^2 + V(s,\lambda) \sim (2f_3\lambda)^{-1} - (2f_3\lambda^{3/2}s)^{-1} ; \tag{3.17}$$

aside from a constant energy shift and a distance scaling

this is just the physical hydrogenic problem. One can easily show that in this asymptotic regime the ground state behaves as follows:

$$\varepsilon(\lambda) = \frac{1}{2f_3\lambda} - \frac{1}{8f_3^2\lambda^3} + \frac{C_7}{\lambda^7} + \ldots , \qquad (3.18)$$

where

$$C_7 = \frac{1}{8f_3^4} \int_0^\infty u^2 f'(u)du . \qquad (3.19)$$

The unperturbed version of Eq. (3.12) is

$$(-\tfrac{1}{2}\nabla_s^2 + \tfrac{1}{2}s^2 - \varepsilon^0)\phi^0(s) = 0 , \qquad (3.20)$$

the wave equation for an isotropic three-dimensional harmonic oscillator. The ϕ^0 form a natural complete basis for solving the perturbed problem. For s states of the modified hydrogenic problem the spherically symmetric basis functions suffice; these and their corresponding unperturbed eigenvalues are the following ($n = 0,1,2,\ldots$):

$$\phi_n^0(s) = A_n s^{-1} H_{2n+1}(s)\exp(-s^2/2) , \qquad (3.21)$$

$$A_n = \frac{(-1)^n}{2^{n+1}\pi^{3/4}[(2n+1)!]^{1/2}} ;$$

$$\varepsilon_n^0 = 2n + \tfrac{3}{2} . \qquad (3.22)$$

Here the H_m are the Hermite polynomials.[11] Using straightforward perturbation theory, one calculates the following low-order coefficients for the eigenvalue series (3.16):

$$\varepsilon_0 = \tfrac{3}{2}, \quad \varepsilon_1 = -\frac{15f_5}{8f_3} ,$$

$$\varepsilon_2 = \frac{105f_7}{16f_3} - \frac{165f_5^2}{32f_3^2} , \qquad (3.23)$$

$$\varepsilon_3 = -\frac{945f_9}{32f_3} + \frac{945f_7f_5}{16f_3^2} - \frac{3915f_5^3}{128f_3^3} .$$

Integer powers of λ have been found to occur both in the small-λ expansion (3.16) and in the large-λ expansion (3.18). This suggests that it may be useful to approximate the function $\varepsilon(\lambda)$ throughout the complex plane by rational functions of λ, i.e., Padé approximants.[12] Specifically this entails

$$\varepsilon(\lambda) \cong P(\lambda)/Q(\lambda) , \qquad (3.24)$$

where P and Q are polynomials whose orders and coefficients must be chosen to agree with (3.16) and (3.18). The more expansion coefficients that are available the higher the degrees of P and Q can be, so presumably the better the approximation will be to $\varepsilon(\lambda)$.

Figure 1 presents a plot of a Padé approximant for $\varepsilon(\lambda)$, where $P(\lambda)$ and $Q(\lambda)$ in Eq. (3.24), respectively, have degrees 3 and 4. These polynomials were fixed by requiring that the four perturbation coefficients, Eq. (3.23), be reproduced as well as the four leading orders in the asymptotic expansion (3.18). The error-function form shown in Eq. (3.7) was employed for f. This approxi-
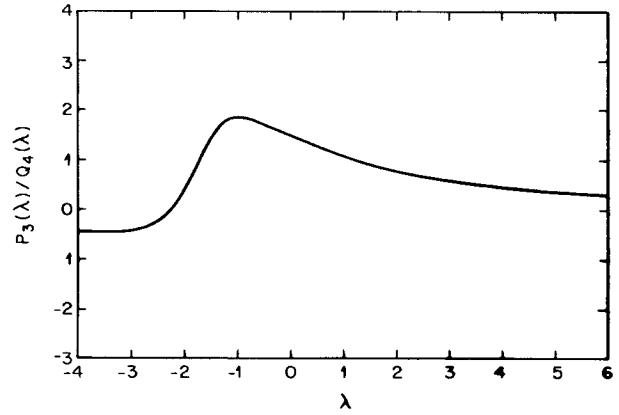

FIG. 1. Padé approximant for $\varepsilon(\lambda)$, the eigenvalue of Eq. (3.12) associated with the ground state of the modified hydrogen atom.

mant possesses two complex-conjugate pairs of simple poles in the complex λ plane, with approximate positions $-1.603\pm0.925i$ and $-0.230\pm1.918i$.

Considering the examples cited in Sec. II as well as the Padé approximant shown in Fig. 1, it seems reasonable to suppose that the exact $\varepsilon(\lambda)$ is analytic at the origin for appropriate f choices. Hence perturbation series (3.16) would have a positive radius of convergence for those choices.

The modified hydrogen atom obviously has little physical significance by itself since the unmodified version has a well-known exact solution.[13] However this case provides a natural starting point for subsequent use of the same approach for many-electron atoms and ions.

IV. HELIUM ISOELECTRONIC SEQUENCE

Two-electron bound states in the isoelectronic sequence H^-, He, Li^+, Be^{2+},... afford a relatively simple, yet nontrivial, testing ground for the expansion technique. As was the case for hydrogenic atoms in Sec. III, it is necessary to modify the interactions so that they are bounded below. This requirement could be met by invoking Eq. (3.4) for the electron-nucleus attraction, while leaving the electron-electron repulsion unchanged. But to generate a computationally convenient format it is useful to modify the latter interaction as well. Consequently the wave equation for the spatial part of the eigenfunction will formally be written as follows:

$$\{\tfrac{1}{2}\eta^2(\nabla_1^2+\nabla_2^2)+Ze^2[r_1^{-1}f(l^{-1}r_1)+r_2^{-1}f(l^{-1}r_2)]$$

$$-e^2r_{12}^{-1}f(\xi^{-1}l^{-1}r_{12})+E\}\psi(\mathbf{r}_1,\mathbf{r}_2)=0 . \qquad (4.1)$$

As was the case previously, f obeys conditions (A)–(F). Equation (4.1) assumes that the nucleus is stationary so that m appearing in the definition (2.2) of η is exactly the electron mass. Wave function ψ satisfies the usual symmetry conditions for spatial exchange (even for singlet states, odd for triplet states).

By introducing parameter ξ into the electron-electron

interaction term of Eq. (4.1), we can take advantage of differing lengths l and ξl for attractions and repulsions, respectively. For the moment ξ will be arbitrary, beyond the requirements that it be positive and independent of η.

By using the previously introduced scale change (3.10) and the λ definition (3.11), Eq. (4.1) transforms into the following:

$$[-\tfrac{1}{2}(\nabla_{s_1}^2 + \nabla_{s_2}^2) + \tfrac{1}{2}(s_1^2 + s_2^2) - (2\xi^3 Z)^{-1}s_{12}^2$$

$$+ V(s_1, s_2, \lambda) - \varepsilon(\lambda)]\phi(s_1, s_2) = 0 . \quad (4.2)$$

Here we have set

$$\varepsilon(\lambda) = \frac{\eta^2 E}{(2f_3 Ze^2)^2\lambda^3} + \frac{(2Z - \xi^{-1})}{2f_3 Z\lambda} , \quad (4.3)$$

or inversely

$$E = 2f_3 Z^2 e^4 \eta^{-2}\lambda^2[2f_3\lambda\varepsilon(\lambda) - 2 + \xi^{-1}Z^{-1}] . \quad (4.4)$$

"Physical" eigenstates require that $\lambda \to +\infty$ at constant η. The perturbation V vanishes when $\lambda = 0$; its form is

$$V(s_1, s_2, \lambda) = -\frac{1}{2f_3\lambda^{3/2}}\left[\frac{f(\lambda^{1/2}s_1)}{s_1} + \frac{f(\lambda^{1/2}s_2)}{s_2} - 2\lambda^{1/2} + f_3\lambda^{3/2}(s_1^2 + s_2^2)\right.$$

$$\left. - \frac{1}{Z}\left[\frac{f(\xi^{-1}\lambda^{1/2}s_{12})}{s_{12}} - \xi^{-1}\lambda^{1/2} + f_3\xi^{-3}\lambda^{3/2}s_{12}^2\right]\right] . \quad (4.5)$$

This has a convergent power series in λ

$$V(s_1, s_2, \lambda) = (2f_3)^{-1}\sum_{n=2}^{\infty}(-1)^{n-1}f_{2n+1}\lambda^{n-1}(s_1^{2n} + s_2^{2n} - Z^{-1}\xi^{-2n-1}s_{12}^{2n}) . \quad (4.6)$$

In the absence of perturbation V, Eq. (4.2) describes a six-dimensional harmonic oscillator. It is natural to introduce sum and difference variables by coordinate rotation:

$$s = 2^{-1/2}(s_2 - s_1), \quad S = 2^{-1/2}(s_2 + s_1) , \quad (4.7)$$

in terms of which the wave equation (4.2) appears thus

$$\left\{-\frac{1}{2}(\nabla_s^2 + \nabla_S^2) + \frac{1}{2}\left[\left[1 - \frac{2}{\xi^3 Z}\right]s^2 + S^2\right]\right.$$

$$\left. + V - \varepsilon\right\}\phi = 0 . \quad (4.8)$$

The unperturbed harmonic-oscillator part of the problem is now diagonal, and in this representation the perturbation V has the form

$$V = (2f_3)^{-1}\sum_{n=2}^{\infty}(-1)^{n-1}2^{-n}f_{2n+1}\lambda^{n-1}$$

$$\times[(S - s)^{2n} + (S + s)^{2n}$$

$$- Z^{-1}\xi^{-2n-1}(s)^{2n}] . \quad (4.9)$$

To carry out any order of perturbation theory, it is necessary only to evaluate matrix elements of positive even powers of coordinates in the harmonic-oscillator basis.

The ground-state normalized eigenfunction and eigenvalue for the unperturbed problem are

$$\phi^0(s, S) = \pi^{-3/2}\left[1 - \frac{2}{\xi^3 Z}\right]^{3/8}$$

$$\times \exp\left[-\frac{1}{2}\left[1 - \frac{2}{\xi^3 Z}\right]^{1/2}s^2 - \tfrac{1}{2}S^2\right] ,$$

$$\varepsilon_0 \equiv \varepsilon(0) = \frac{3}{2}\left[1 + \left[1 - \frac{2}{\xi^3 Z}\right]^{1/2}\right] . \quad (4.10)$$

In order that the harmonic frequency associated with relative position coordinate s be real it is necessary to restrict ξ,

$$\xi > (2/Z)^{1/3} . \quad (4.11)$$

The first-order energy coefficient ε_1 for the ground state is determined by the leading term in expansion (4.9). One finds

$$\varepsilon_1 \equiv \varepsilon'(0)$$

$$= -\frac{15f_5}{32f_3}\left[2 + 4\left[1 - \frac{2}{\xi^3 Z}\right]^{-1/2}\right.$$

$$\left. + \left[2 - \frac{1}{\xi^5 Z}\right]\left[1 - \frac{2}{\xi^3 Z}\right]^{-1}\right] . \quad (4.12)$$

In principle nothing would prevent exact closed-form calculation of the higher-order ε_n's, though in practice this can be expected to become rapidly tedious when done by hand. No doubt the process could be automated with use of symbolic manipulation programs.

The two-electron eigenstates possess asymptotic expansions for large positive λ analogous to that shown in Eq. (3.18) for the modified hydrogen ground state. The

ground state has the following expansion:

$$\epsilon(\lambda) = \frac{C_1}{\lambda} + \frac{C_3}{\lambda^3} + \frac{C_7}{\lambda^7} + \cdots \ ; \tag{4.13}$$

$$C_1 = (2f_3)^{-1}(2 - \xi^{-1}Z^{-1}) \ ,$$

$$C_3 = (4f_3^2)^{-1}\bar{\epsilon}(Z) \ , \tag{4.14}$$

where $\bar{\epsilon}(Z)$ is the ground-state energy of the conventional two-electron problem expressed in Z-reduced atomic units,[14,15] e.g.,

$$\bar{\epsilon}(1) = -0.527\,751,\ldots \ , \quad \bar{\epsilon}(2) = -0.725\,931,\ldots \ ,$$
$$\bar{\epsilon}(3) = -0.808\,879,\ldots \ , \quad \bar{\epsilon}(\infty) = -1 \ . \tag{4.15}$$

Coefficient C_7 is determined by the values of the corresponding Z-reduced wave function at electron-nucleus and at electron-electron confluence. Once again the relevance of Padé approximants is suggested by the perturbation power series in λ coupled with the asymptotic expansion (4.13).

Aside from inequality (4.11), ξ has thus far remained arbitrary. In principle it should not matter what choice is made for ξ, since a precise determination of the resulting $\epsilon(\lambda)$ would produce a ξ-invariant coefficient C_3 [Eqs. (4.13)–(4.14)], which then specifies the "physical" eigenvalue that is the ultimate goal. Nevertheless it may be prudent to select a physically motivated ξ to enhance the accuracy of approximations to $\epsilon(\lambda)$ such as those provided by Padé approximants. In particular it seems reasonable to use the well-known electron-nucleus and electron-electron cusp conditions[16,17] as guides, and thus to require that the spatial correlation lengths exhibited by the wave function in lowest order, ϕ^0 in Eq. (4.10), have the proper Z-dependent ratio. These lengths refer to relative rates of decay of the wave function for (i) simultaneous motion of the two electrons away from one another while their centroid is fixed, and (ii) motion of two coincident electrons away from confluence with the nucleus. The exact cusp conditions require a ratio of $(4Z)^{-1}$, which in conjunction with Eq. (4.10) leads to

$$\left[1 - \frac{2}{\xi^3 Z} \right]^{1/4} = \frac{1}{4Z} \ ,$$

$$\xi = \left[\frac{Z}{2} - \frac{1}{128Z^3} \right]^{-1/3} \ . \tag{4.16}$$

Table I displays some of the calculated ξ values, showing a monotonic decline as Z increases from unity.

TABLE I. Values of range parameter ξ for the two-electron ground state, calculated from Eq. (4.16).

Z	$\xi(Z)$
1	1.266 552
2	1.000 326
3	0.873 637
4	0.793 717
5	0.736 812
6	0.693 364
7	0.658 635
8	0.629 961
9	0.605 707
10	0.584 804

V. MANY-ELECTRON ATOMS

The strategy just employed for the He isoelectronic sequence generalizes straightforwardly to the case of the n-electron atom. In this way we are led to consider the following modification of the Coulomb interactions:

$$W(\mathbf{r}_1, \ldots, \mathbf{r}_n) = -Ze^2 \sum_{j=1}^{n} f(l^{-1}r_j)r_j^{-1}$$

$$+ e^2 \sum_{j<k=1}^{n} f(\xi^{-1}l^{-1}r_{jk})r_{jk}^{-1} \ . \tag{5.1}$$

Once again f is required to obey conditions (A)–(F). The objective is to find solutions to the eigenvalue equation

$$\left[-\tfrac{1}{2}\eta^2 \sum_j \nabla_j^2 + W(\mathbf{r}_1, \ldots, \mathbf{r}_n) - E(\eta) \right]$$

$$\times \psi(\mathbf{r}_1, \ldots, \mathbf{r}_n, \eta) = 0 \tag{5.2}$$

as functions of the scaled Planck constant η. In the strong-coupling or extreme quantum regime ($\eta \to +\infty$), the wave function becomes so extended in space as to be insensitive to the presence of f in W, and $E(\eta)$ becomes asymptotically proportional to η^{-2} with a value that yields the physical energy of ultimate interest. For simplicity we utilize a spin-free formulation; since ψ represents only the spatial part of the wave function it must satisfy antisymmetry and cyclic interchange conditions to correspond to the correct spin state.[18,19]

By using distance scaling (3.10) and the coupling-constant definition (3.11) once again, the wave equation (5.2) adopts the form

$$\left[-\tfrac{1}{2}\sum_j \nabla_{s_j}^2 + \tfrac{1}{2}\sum_j s_j^2 - (2\xi^3 Z)^{-1} \sum_{j<k} s_{jk}^2 + V(\mathbf{s}_1, \ldots, \mathbf{s}_n, \lambda) - \epsilon(\lambda) \right] \phi(\mathbf{s}_1, \ldots, \mathbf{s}_n, \lambda) = 0 \ . \tag{5.3}$$

We now have a perturbation potential,

$$V = (2f_3\lambda^{3/2})^{-1} \left[- \sum_{j=1}^{n} [f(\lambda^{1/2}s_j)s_j^{-1} - \lambda^{1/2} + f_3\lambda^{3/2}s_j^2] \right.$$

$$\left. + Z^{-1} \sum_{j<k=1}^{n} [f(\xi^{-1}\lambda^{1/2}s_{jk})s_{jk}^{-1} - \xi^{-1}\lambda^{1/2} + f_3\xi^{-3}\lambda^{3/2}s_{jk}^2] \right] \ , \tag{5.4}$$

which again possesses a convergent power series in λ. The eigenvalues in Eqs. (5.2) and (5.3) are related by

$$\varepsilon(\lambda) = \frac{\eta^2 E}{(2f_3 Ze^2)^2 \lambda^3} + \frac{n}{2f_3 \lambda} \left[1 - \frac{(n-1)}{2Z\xi} \right] ,$$

$$E = (2f_3 Ze^2)^2 \eta^{-2} \lambda^3$$
$$\times \left[\varepsilon(\lambda) - \frac{n}{2f_3 \lambda} \left[1 - \frac{(n-1)}{2Z\xi} \right] \right] . \qquad (5.5)$$

It is elementary to diagonalize the quadratic unperturbed Hamiltonian appearing in Eq. (5.3). Considering first the x components of electron positions s_j measured relative to the nucleus, define

$$u(k) = n^{-1/2} \sum_{j=1}^{n} \exp(ikj) s_{jx} , \qquad (5.6)$$

where k takes on any of the n values nearest the origin

$$k = 0, \pm 2\pi/n, \pm 4\pi/n, \dots . \qquad (5.7)$$

The inverse transform is

$$s_{jx} = n^{-1/2} \sum_{k} \exp(-ikj) u(k) . \qquad (5.8)$$

Exactly analogous relations can be written down for the y and z components of electron positions, respectively, defining $v(k)$ and $w(k)$. This coordinate rotation leads to the following identity relevant to Eq. (5.3):

$$\tfrac{1}{2} \sum_j s_j^2 - (2\xi^3 Z)^{-1} \sum_{j<l} s_{jl}^2$$
$$\equiv \tfrac{1}{2} [u^2(0) + v^2(0) + w^2(0)]$$
$$+ \frac{1}{2} \left[1 - \frac{n}{\xi^3 Z} \right] \sum_{k \neq 0} [|u(k)|^2 + |v(k)|^2 + |w(k)|^2] .$$
$$(5.9)$$

The absolute values acknowledge that for $k \neq 0$ the u, v, and w variables can be complex; however, linear combinations of those for k and $-k$ can be real. Denoting such linear combinations by carets, for example:

$$\hat{u}(k) = 2^{-1/2} [u(k) + u(-k)] ,$$
$$\hat{u}(-k) = (2^{1/2}i)^{-1} [u(k) - u(-k)] , \qquad (5.10)$$

we have

$$\tfrac{1}{2} \sum_j s_j^2 - (2\xi^3 Z)^{-1} \sum_{j<l} s_{jl}^2$$
$$\equiv \tfrac{1}{2} [u^2(0) + v^2(0) + w^2(0)]$$
$$+ \frac{1}{2} \left[1 - \frac{n}{\xi^3 Z} \right]$$
$$\times \sum_{k \neq 0} [\hat{u}^2(k) + \hat{v}^2(k) + \hat{w}^2(k)] . \qquad (5.11)$$

The diagonalized quadratic form (5.11) obviously is highly degenerate. The three modes describing motion of the centroid of the electron distribution $(k=0)$ have a

common frequency, while the remaining $3(n-1)$ modes $(k \neq 0)$ describing relative motion within the electron distribution are all degenerate at a lower frequency. The last must be real, requiring

$$\xi > (n/Z)^{1/3} , \qquad (5.12)$$

the generalization of the earlier condition (4.11). After transforming the perturbation V in Eq. (5.4) to the collective variables, the generation of the expansion in powers of η can proceed as before, using the collective harmonic-oscillator basis.

As in all cases considered, the leading contribution $E(\eta = 0)$ is equal to the value of the potential energy at its absolute minimum. For the present case this can immediately be extracted from the modified Coulomb form displayed in Eq. (5.1),

$$E(0) = \min W = -\frac{nZe^2}{l} \left[1 - \frac{n-1}{2\xi Z} \right] . \qquad (5.13)$$

The length parameter l has thus far been arbitrary, but results from Thomas-Fermi theory for atoms[20] suggest roughly how it should be chosen in the large-Z neutral atom $(n = Z)$ regime. In particular it is believed that the Thomas-Fermi approach correctly supplies the leading large-Z behavior of the binding energy,

$$E^{TF}(Z) \sim -CZ^{7/3} \quad (C > 0) . \qquad (5.14)$$

It seems logical to require this Z dependence even in the unperturbed energy (5.13), so consequently one should take

$$l \sim l_\infty Z^{-1/3} , \qquad (5.15)$$

where l_∞ is some positive constant. Notice from Eq. (3.11) that this makes the natural coupling constant of the development λ asymptotically proportional to $Z^{-1/3}$ as well. These considerations do not affect the value of ξ, which presumably can be selected to optimize the rate of convergence of the perturbation series. It should be noted in passing that elementary counting arguments show that the total harmonic-oscillator energy for the unperturbed state is also proportional to $Z^{7/3}$ in the large-Z limit.

Once again the strong-coupling regime requires that $\varepsilon(\lambda)$ exhibit an expansion whose leading terms vary as inverse integer powers of λ:

$$\varepsilon(\lambda) = \frac{C_1}{\lambda} + \frac{C_3}{\lambda^3} + \frac{C_7}{\lambda^7} + \cdots , \qquad (5.16)$$

$$C_1 = \frac{n}{2f_3} \left[1 - \frac{(n-1)}{2\xi Z} \right] . \qquad (5.17)$$

The coefficient C_3 carries the desired information about the "physical eigenvalue" for the unmodified Coulomb interaction:

$$E(\text{phys}) = (2f_3 Ze^2)^2 C_3 \eta^{-2} , \qquad (5.18)$$

while C_7 is related to values of the "physical eigenfunction" at particle pair confluence.

It seems to be a reasonable presumption that the family of modification functions f satisfying conditions (A)–(F) of Sec. III cause $\varepsilon(\lambda)$ to be analytic at the origin. The procedure developed above shows in principle how to generate the λ power series from appropriate combinations of harmonic-oscillator matrix elements for arbitrary n and Z. The power series coefficients then could be assembled into a tableau of Padé approximants that are consistent with asymptotic series (5.16), and that should give a reasonable representation of $\varepsilon(\lambda)$ along the positive real axis.

VI. DISCUSSION

The immediate objective of this paper is a modest one, namely to demonstrate the existence of a systematic procedure for generating Planck's-constant expansions for bound states. Application to atomic systems requires short-range modification of the Coulomb interaction to make it bounded below, and "physical" eigenstates then must be extracted from the strong-coupling limit. Padé approximants were suggested as a means to bootstrap from the small-coupling regime to the strong-coupling regime, but this needs stringent testing. In particular it should be possible to carry out accurate variational calculations in the presence of the modified Coulomb interaction to see if the resulting $\varepsilon(\lambda)$ estimate closely tracks those emerging from a Padé analysis along the entire positive λ axis.

One of the primary characteristics of the present approach is that its starting point (the collective harmonic oscillators) already contains electron-correlation effects in a nontrivial manner. In this respect it differs fundamentally from the Hartree-Fock approximation, an intrinsically single-particle approximation. The set of eigenvalue functions $\varepsilon^{(n)}(\lambda)$ for ground and excited states in the present method, when plotted versus real positive λ, produce a kind of correlation diagram between many-body harmonic-oscillator states and "real" atomic states, across the entirety of which electron-correlation effects are present.

The expansion and resummation strategy advocated herein may have significant application to the study of resonance states. Many of these amount to doubly excited atomic states embedded in continua with which they interact and thereby develop widths. The corresponding doubly excited states in our unperturbed harmonic-oscillator limit ($\lambda = 0$) are legitimate eigenstates, and they should remain as such for at least some positive interval of λ values. But as λ increases, an encounter with the continuum eventually ensues, and one expects that $\varepsilon^{DE}(\lambda)$ for the doubly excited state would display a branch point singularity at λ_C, the coupling-constant value at continuum encounter.[15] Analytic continuation beyond λ_C above or below the branch cut extending to $+\infty$ will yield complex values for $\varepsilon^{DE}(\lambda)$ whose real and imaginary parts, respectively, would give resonance position and width.

Extension of the present technique to the polyatomic case in principle is straightforward. Analysis of chemical-bond formation should be quite natural by examining λ series that are the difference between series for the molecular system of interest and those for the component atoms treated separately. If large-Z atoms are involved this would have the beneficial effect of eliminating the large but irrelevant contribution of core (nonbonding) electrons to the eigenvalues. It is also worth noting that the method can include cases where all particles participate as quantum-dynamical entities, as is usually the case in calculations for μ-mesic molecules of the hydrogen isotopes.[21]

ACKNOWLEDGMENTS

[1]D. Ceperley and B. Alder, Science **231**, 555 (1986).

[2]D. M. Ceperley and M. H. Kalos, in *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer, Berlin, 1979), pp. 145–197.

[3]*Density Functional Methods in Physics*, edited by R. M. Dreizler and J. da Providencia (Plenum, New York, 1985).

[4]W. H. Miller, Science **233**, 171 (1986).

[5]D. J. Doren and D. R. Herschbach, Chem. Phys. Lett. **118**, 115 (1985).

[6]L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill, New York, 1935), pp. 67–82.

[7]L. D. Landau and E. M. Lifshitz, *Quantum Mechanics, Non-Relativistic Theory*, translated by J. B. Sykes and J. S. Bell (Addison-Wesley, Reading, MA, 1958), pp. 68 and 69.

[8]R. Courant and F. John, *Introduction to Calculus and Analysis* (Wiley-Interscience, New York, 1974), Vol. 2, p. 221.

[9]C. Domb, in *Critical Phenomena*, edited by M. S. Green and J. V. Sengers, Natl. Bur. Stand. Misc. Publ. No. 273 (U.S. GPO, Washington, D.C., 1966), pp. 29–41.

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

[11]M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (U.S. GPO, Washington, D.C., 1964), Chap. 22.

[12]G. A. Baker, Jr., *Essentials of Padé Approximants* (Academic, New York, 1975).

[13]*Introduction to Quantum Mechanics* (Ref. 6), Chap. V.

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

[15]J. D. Baker, D. E. Freund, R. N. Hill, and J. D. Morgan III, Phys. Rev. A **41**, 1247 (1990).

[16]T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).

[17]R. T. Pack and W. B. Brown, J. Chem. Phys. **45**, 556 (1966).

[18]E. Lieb and D. Mattis, Phys. Rev. **125**, 164 (1962).

[19]R. J. White and F. H. Stillinger, Phys. Rev. A **3**, 1521 (1971).

[20]E. H. Lieb, Rev. Mod. Phys. **53**, 603 (1981).

[21]S. I. Vinitskii, V. I. Korobov, and I. V. Puzynin, Zh. Eksp. Teor. Fiz. **91**, 705 (1986) [Sov. Phys.—JETP **64**, 417 (1986)].