

Ground-State Energy of Two-Electron Atoms

FRANK H. STILLINGER, JR.

Bell Telephone Laboratories, Inc., Murray Hill, New Jersey

(Received 29 June 1966)

We examine the ground-state energy $\epsilon(\lambda)$ for two electrons bound to an infinite-mass point nucleus regarded as a function of the complex coupling constant λ for the interelectron interaction. In the units used, the ground states of the homologous series H^- , He, Li^+ , Be^{++} , \dots , correspond, respectively, to $\lambda=1, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \dots$, so the λ power-series expansion of $\epsilon(\lambda)$ is equivalent to the familiar expansion in inverse nuclear charge Z^{-1} . It is argued that the power series has a finite radius of convergence imposed by the existence of a branch point on the positive real axis at $\lambda=\lambda^*\cong 1.1184$ with exponent approximately $6/5$. Furthermore, $\epsilon(\lambda^*)$ apparently lies *above* the continuum limit, but still corresponds to a localized wavefunction.

I. INTRODUCTION

SINGLE-electron quantum-mechanical descriptions of atoms and molecules have been developed and successfully exploited over the past several decades in elucidation of a wide variety of physical and chemical phenomena. The primary remaining problem appears to be concerned with understanding the nature of electron correlation, and with practical techniques for taking electron correlation into account in large-molecule computations.

A necessary prerequisite for resolving the nature of correlation in systems of large numbers of electrons obviously is the ability to understand the simpler cases. With this emphasis in mind, we have undertaken to elucidate certain aspects of the simplest nontrivial (and physically important) case exhibiting electron correlation: the sequence of two-electron atoms, H^- , He, Li^+ , Be^{++} , \dots , in their ground states.

In the next section we write the Hamiltonian for the sequence in a common form in which only a variation in coupling strength λ between the electrons is necessary to pass from one member of the sequence to the next. We then have the option of a global enquiry into the analytic nature of the ground-state energy $\epsilon(\lambda)$ in the complex λ plane, of which the perturbation series in λ comprises only one aspect. In particular we may easily investigate the process of allowing $\lambda \rightarrow -\infty$, and thereby establish the asymptotics of $\epsilon(\lambda)$ in the neighborhood of infinity (Sec. III).

The impressively accurate and extensive information currently available for the λ perturbation series (more commonly known as energy expansions in inverse nuclear charge for the homologous sequence) provides the basis for the analysis in Sec. IV. By means of the ratio test, the nearest singularity of $\epsilon(\lambda)$ to the origin is tentatively located on the positive real axis, and identified as a branch point. Subsequently, it is possible to rewrite $\epsilon(\lambda)$ as a contribution from this nearest singularity, plus a manageable correction. Re-expansion then permits easy quantitative prediction of perturbation coefficients of arbitrarily high order.

The final section V is devoted to a discussion of results and their implications for variational calculations on two-electron systems, and to conjectures concerning many-electron systems and excited states. Also, an Appendix is included giving details of two relevant elementary variational calculations.

II. ELEMENTARY CONSIDERATIONS

The Schrödinger equation for the ground-state energy E and wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2)$ for two electrons bound to an infinite mass nucleus with atomic number Z is

$$\mathbf{H}(\lambda')\psi(\mathbf{r}_1, \mathbf{r}_2, \lambda') = E(\lambda')\psi(\mathbf{r}_1, \mathbf{r}_2, \lambda'), \quad (1)$$

$$\mathbf{H}(\lambda') = -(\hbar^2/2m_e)(\nabla_1^2 + \nabla_2^2) - Ze^2(r_1^{-1} + r_2^{-1}) + (\lambda'e^2/r_{12}), \quad (2)$$

where in anticipation of subsequent development we have formally included an electron-electron coupling constant λ' . We note in passing that spin may be suppressed since ψ represents a singlet-state symmetric with respect to interchange of electron positions \mathbf{r}_1 and \mathbf{r}_2 . Introduce the following reductions:

$$\begin{aligned} \boldsymbol{\rho} &= \mathbf{r}/l, \\ l &= \hbar^2/m_e Z e^2, \end{aligned} \quad (3)$$

$$\begin{aligned} \epsilon(\lambda) &= \hbar^2 E(\lambda')/m_e Z^2 e^4, \\ \lambda &= \lambda'/Z, \end{aligned} \quad (4)$$

so that the eigenvalue equation (1) adopts the simpler form in terms of $\boldsymbol{\rho}_1, \boldsymbol{\rho}_2$:

$$\left[\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + \rho_1^{-1} + \rho_2^{-1} - (\lambda/\rho_{12}) + \epsilon(\lambda)\right] \times \phi(\boldsymbol{\rho}_1, \boldsymbol{\rho}_2, \lambda) = 0. \quad (5)$$

The interelectron repulsion may of course be removed by setting $\lambda=0$, and in this limit

$$\begin{aligned} \epsilon(0) &= -1, \\ \phi(\boldsymbol{\rho}_1, \boldsymbol{\rho}_2, \lambda=0) &= (1/\pi) \exp(-\rho_1 - \rho_2). \end{aligned} \quad (6)$$

From the second Eq. (4) it is clear that the real systems H^- , He, Li^+ , Be^{++} , \dots , in their ground states correspond to $\lambda = 1, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \dots$.

If $\epsilon(\lambda)$ is regarded as a power-series expansion in λ ,

$$\epsilon(\lambda) = \sum_{n=0}^{\infty} \epsilon_n \lambda^n. \quad (7)$$

The coefficient ϵ_n is then equivalent to the n th-order perturbation energy to the state described by Eq. (6), where the interelectron repulsion is treated as the perturbation. It is known that Expansion (7) has a finite radius of convergence,^{1,2} with the immediate consequence that the ϵ_n cannot increase in magnitude with n any faster than exponentially. Besides the value $\epsilon_0 = -1$, it is easy to carry out the first-order perturbation calculation³ with the result $\epsilon_1 = \frac{5}{8}$. Although the coefficient ϵ_2 is necessarily negative (as any second-order energy to a nondegenerate ground state must be), its precise value is unknown, and it has not even been established whether ϵ_2 is a rational number.⁴ However, in spite of the lack of rigorously exact information concerning the ϵ_n , the Hylleraas⁵-Scherr-Knight⁶ variational perturbation approach to the two-electron problem has succeeded in providing undoubtedly very accurate numerical estimates for the first few coefficients, whose values provide the basis for the analysis in Sec. IV.

Two final elementary properties of $\epsilon(\lambda)$ may next be noted. First, if λ is varied by a sufficiently small amount $\delta\lambda$ such that the linear estimate

$$\epsilon(\lambda + \delta\lambda) = \epsilon(\lambda) + \epsilon'(\lambda) \delta\lambda \quad (8)$$

suffices, then formal treatment of the extra Coulomb repulsion between the electrons, $(\delta\lambda)/\rho_{12}$, as a perturbation obviously identifies $\epsilon'(\lambda)$ in the form

$$\epsilon'(\lambda) = \langle \lambda | 1/\rho_{12} | \lambda \rangle, \quad (9)$$

a matrix element of ρ_{12}^{-1} in the ground state for degree of coupling λ . Now, Expression (9) is clearly a positive number, so we trivially establish that $\epsilon(\lambda)$ is a monotonically increasing function of coupling strength λ . But additionally the fact that slope $\epsilon'(\lambda)$ is the expectation value of ρ_{12}^{-1} allows identification of $[\epsilon'(\lambda)]^{-1}$ as a measure of spatial extension of the ground-state wavefunction $\phi(\boldsymbol{\rho}_1, \boldsymbol{\rho}_2, \lambda)$. In similar fashion $\epsilon''(\lambda)$ may be regarded as essentially the second-order perturbation energy for perturbation $\delta\lambda/\rho_{12}$ when the coupling

is initially degree λ . Since this second-order perturbation to the nondegenerate ground state is necessarily negative, $\epsilon''(\lambda)$ is negative, so we conclude the second property of $\epsilon(\lambda)$: it has downward curvature. Therefore, the positive quantity $\epsilon'(\lambda)$ decreases with λ , and we have then systematically verified the intuitively clear notion that the ground-state wavefunction should increase in spatial extension as λ increases.

III. BEHAVIOR AS $\lambda \rightarrow -\infty$

One of the advantages of using the interelectronic coupling λ as variable in investigating the ground-state energy, as compared with inverse nuclear charge Z^{-1} , is that negative real values of the parameter have a clear meaning. As λ passes through zero from positive to negative values, the electron-electron repulsion converts to an attraction. Although $\phi(\boldsymbol{\rho}_1, \boldsymbol{\rho}_2, \lambda)$ exhibits the tendency for electrons to avoid one another when $\lambda > 0$, it must likewise reflect their tendency to stay close together for $\lambda < 0$, which is another manifestation of electron correlation.

The situation is especially simple in the limit as $\lambda \rightarrow -\infty$. The very strong attraction between the electrons in this asymptotic regime will bind these two particles together to form a "di-electron," i.e., substantially a point particle with twice the mass and charge of a single electron, and then this di-electron will be bound to the positively charged nucleus in a suitably scaled hydrogenic ($1s$) orbital.

It is easy to arrive at the behavior of $\epsilon(\lambda)$ as $\lambda \rightarrow -\infty$, an extreme limit of electron correlation. The Hamiltonian in Eq. (2) may be rewritten as follows:

$$\mathbf{H}(\lambda) = \mathbf{H}^{(0)}(\lambda) + \mathbf{H}^{(1)},$$

$$\mathbf{H}^{(0)}(\lambda) = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + (\lambda/\rho_{12}) - (2/\rho),$$

$$\mathbf{H}^{(1)} = (2/\rho) - (1/\rho_1) - (1/\rho_2),$$

$$\boldsymbol{\rho} = \frac{1}{2}(\boldsymbol{\rho}_1 + \boldsymbol{\rho}_2). \quad (10)$$

Retention of just $\mathbf{H}^{(0)}(\lambda)$ is equivalent to treatment of the di-electron strictly as a point particle insofar as its binding to the nucleus is concerned, and the corresponding eigenvalue problem,

$$\mathbf{H}^{(0)}(\lambda) \phi^{(0)}(\boldsymbol{\rho}_1, \boldsymbol{\rho}_2, \lambda) = \epsilon^{(0)}(\lambda) \phi^{(0)}(\boldsymbol{\rho}_1, \boldsymbol{\rho}_2, \lambda), \quad (11)$$

can be readily solved since transformation to di-electron center of mass ($\boldsymbol{\rho}$) and relative ($\boldsymbol{\rho}_{12}$) coordinates effects separation of variables. One finds ($\lambda < 0$)

$$\phi^{(0)}(\boldsymbol{\rho}_1, \boldsymbol{\rho}_2, \lambda) = (8/\pi^{\frac{1}{2}}) \exp(-4\rho) [(-\lambda)^{\frac{1}{2}}/2(2\pi)^{\frac{1}{2}}] \times \exp(\frac{1}{2}\lambda\rho_{12}); \quad (12)$$

$$\epsilon^{(0)}(\lambda) = -\frac{1}{4}\lambda^2 - 4. \quad (13)$$

The two terms in $\epsilon^{(0)}(\lambda)$ may be identified, respectively, as the internal binding energy of the di-electron and the binding energy between the di-electron and the nucleus.

¹ T. Kato, J. Fac. Sci. Univ. Tokyo Sec. I **6**, 145 (1951).

² A. Fröman and G. G. Hall, J. Mol. Spectry. **7**, 410 (1961).

³ L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Co., Inc., New York, 1935), pp. 446-447.

⁴ Since closed-form expressions have recently become available for single-particle Green's functions in Coulomb fields [e.g., J. Schwinger, J. Math. Phys. **5**, 1606 (1964)], it seems probable that ϵ_2 likewise could be written in closed form (i.e., not involving infinite series).

⁵ E. A. Hylleraas, Z. Physik **65**, 209 (1930).

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

When λ is negative and very large in magnitude, but not infinite, the finite extension of the di-electron will manifest itself as an energy increase above $\epsilon^{(0)}(\lambda)$, which may to leading order be taken into account by treating $\mathbf{H}^{(1)}$ as a small perturbation. We are thus led to examine the integral

$$\begin{aligned} \epsilon^{(1)}(\lambda) &= \int d\boldsymbol{\varrho}_1 d\boldsymbol{\varrho}_2 [\phi^{(0)}(\boldsymbol{\varrho}_1, \boldsymbol{\varrho}_2, \lambda)]^2 \mathbf{H}^{(1)} \\ &= \int d\boldsymbol{\varrho} d\boldsymbol{\varrho}_{12} [\phi^{(0)}(\boldsymbol{\rho}_1, \boldsymbol{\rho}_2, \lambda)]^2 \left[\frac{2}{\rho} - \frac{2}{\rho_2} \right]. \end{aligned} \quad (14)$$

The first contribution is trivial:

$$\int d\boldsymbol{\varrho} d\boldsymbol{\varrho}_{12} [\phi^{(0)}(\boldsymbol{\varrho}, \boldsymbol{\varrho}_{12})]^2 \frac{2}{\rho} = 512 \int_0^\infty \rho \exp(-8\rho) d\rho = 8. \quad (15)$$

The second contribution to the right member of (14) is

$$-\frac{16 |\lambda|^3}{\pi^2} \int d\boldsymbol{\varrho} d\boldsymbol{\varrho}_{12} \rho_2^{-1} \exp(-8\rho - |\lambda| \rho_{12}).$$

Transform from vector variable $\boldsymbol{\varrho}_{12}$ to $\mathbf{s} = \frac{1}{2}\boldsymbol{\varrho}_{12}$ (remembering $d\boldsymbol{\varrho} d\boldsymbol{\varrho}_{12} = 8d\boldsymbol{\varrho} ds$) to obtain a form in which the \mathbf{s} integration may be explicitly carried out:

$$\begin{aligned} &-\frac{128 |\lambda|^3}{\pi^2} \int d\boldsymbol{\varrho} ds \frac{\exp(-8\rho - 2|\lambda|s)}{|\boldsymbol{\varrho} + \mathbf{s}|} \\ &= -512 \int_0^\infty d\rho \rho [1 - (|\lambda| \rho + 1)] \\ &\quad \times \exp(-2|\lambda| \rho) \rho \exp(-8\rho). \end{aligned} \quad (16)$$

In combination with Eq. (15) we obtain

$$\begin{aligned} \epsilon^{(1)}(\lambda) &= 512 \int_0^\infty d\rho \rho (|\lambda| \rho + 1) \exp[-(8+2|\lambda|)\rho] \\ &= \frac{128}{|\lambda|^2} \left\{ \frac{1}{[1+(4/|\lambda|)]^3} + \frac{1}{[1+(4/|\lambda|)]^2} \right\} \\ &= (256/|\lambda|^2) - (2560/|\lambda|^3) + O(|\lambda|^{-4}). \end{aligned} \quad (17)$$

The leading term in Eq. (17) is the asymptotically exact di-electron structure energy shift.⁷ Although the numerical coefficient of the leading term is given correctly by this first-order calculation, coefficients of succeeding powers of $|\lambda|^{-1}$ are not, and in particular a second-order calculation should lower the coefficient of $|\lambda|^{-3}$. The number 2560 shown in Eq. (17) thus

⁷ The leading power of λ is easy to rationalize insofar as the exponent is concerned. The di-electron has spatial extent $\sim |\lambda|^{-1}$, requiring a cutoff on its Coulomb interaction with the nucleus at roughly the same distance. The change in mean potential (and hence total energy by the virial theorem) varies thus as

$$\epsilon^{(1)} \sim \int_0^{|\lambda|^{-1}} \rho^{-1} d\rho \sim |\lambda|^{-2}.$$

should be regarded as a lower limit on the true value of $|c_3|$ in the series

$$\epsilon(\lambda) = -\frac{\lambda^2}{4} - 4 + \frac{256}{\lambda^2} + \frac{c_3}{\lambda^3} + \frac{c_4}{\lambda^4} + \dots, \quad (18)$$

appropriate in the neighborhood of minus infinity.

The unperturbed wavefunction $\phi^{(0)}$ and energy $\epsilon^{(0)}$ shown in Eqs. (12) and (13) are actually correct for all complex λ with negative real parts, and the perturbation calculation leading to Result (18) applies in this extended region. Thus for any ray extending from $\lambda=0$ toward infinity within the left half-space of the entire complex λ plane, the energy diverges only as a second-order pole at infinity. It is incidentally clear from Eq. (12) that, for complex λ , $\phi^{(0)}$ is itself complex and oscillatory.

It is next natural to enquire whether Expression (18) is an appropriate energy asymptote as $\lambda = \infty$ is approached along *any* ray from the origin. One must proceed with caution since $\phi^{(0)}$ in Eq. (12) is not normalizable when the real part of λ is greater than or equal to zero. Nevertheless it is formally possible to construct the analytic continuation of $\epsilon(\lambda)$ from the left half-plane across the imaginary axis. That no fractional powers are encountered at least among the first few terms of Expansion (18) (as indeed they are, for example, in the ground-state energy for the single-particle square-well problem as a function of well depth) suggests strongly that the point at infinity is more likely only a second-order pole, rather than a fractional power branch point. Unfortunately we cannot with present considerations exclude an essentially singular contribution at infinity of the type $\exp(c\lambda)$ which could not show up in a left half-plane asymptotic expansion of Type (18), though it is conceivable that an analysis patterned after that of Ref. 1 could effect such an exclusion. It would in the future also be desirable to extend the set of known coefficients in (18) by accurate variational perturbation calculations. For the moment, it seems most reasonable tentatively to suppose that the point at infinity is nothing but a second-order pole, and that Form (18) is indeed proper for all radial approaches to infinity.

IV. POWER-SERIES ANALYSIS

We return now to examination of the λ power series in Eq. (7), with the point of view that the variationally determined numerical estimates to the first few ϵ_n may harbor valuable information about the complex-variable function $\epsilon(\lambda)$. The best values to date have been computed by Midtdal,⁸ and are entered into Table I.

The principal question of interest concerns the position in the complex λ plane and nature of the singularity of $\epsilon(\lambda)$ nearest the origin. The physical relevance

⁸ J. Midtdal, Phys. Rev. **138**, A1010 (1965). Because of different choice of units, we are compelled to divide perturbation coefficients appearing in this paper by 2.

of such a question rests upon the fact that the radius of convergence of perturbation series (7) is by definition determined by the distance from the origin to this nearest singularity, and the large- n behavior of coefficients ϵ_n will be entirely determined by the analytic character of this singularity (i.e., simple pole, multiple pole, branch point, etc.). A glance at the numerical values for the ϵ_n in Table I shows that for $n > 3$ the ϵ_n apparently remain uniform in sign. This strongly suggests that the singularity of interest lies on the positive real axis. Since increase of λ through positive real values amounts to increasing the electron-electron repulsion, it might well be anticipated that a certain value of λ would be reached such that the nucleus could no longer bind both electrons simultaneously, and at this point $\epsilon(\lambda)$ should suffer an anomaly. It is the major object in this section to support this physical identification of the convergence-limiting singularity by quantitative means.

Let λ^* denote the position in the complex plane of the $\epsilon(\lambda)$ singularity nearest the origin. Furthermore, suppose tentatively that the singularity has the character of a fractional power, so that it is possible to write

$$\epsilon(\lambda) = A(\lambda^* - \lambda)^\theta + \zeta(\lambda), \tag{19}$$

where A is a suitable multiplicative coefficient and the remainder function $\zeta(\lambda)$ is analytic at λ^* or at worst has a singularity dominated by the leading term in Eq. (19).⁹ If $\zeta(\lambda)$ has the power-series expansion

$$\zeta(\lambda) = \sum_{n=0}^{\infty} \zeta_n \lambda^n, \tag{20}$$

then as n increases toward infinity, the corresponding coefficients of λ^n from expansion of the term $A(\lambda^* - \lambda)^\theta$ in Eq. (19) will dominate the ζ_n strongly.¹⁰

The ratio test constitutes a useful diagnostic tool in the present context. The sequence of numbers

$$r_n = \epsilon_n / \epsilon_{n-1} \tag{21}$$

will of course approach the limit $(\lambda^*)^{-1}$,¹¹ but of equal importance is the precise manner in which this limit is approached. For large n it is entirely sufficient to calculate r_n using just the numerical coefficients from the θ -power term in Eq. (19), which one readily obtains from the binomial expansion formula, and consequently it is found that in the large- n regime

$$r_n \sim (1/\lambda^*) \{1 - [(1+\theta)/n]\} \tag{22}$$

⁹The case of simple or multiple poles is included here by selecting θ to be a negative integer and also a logarithmic singularity may be regarded as the limiting case of vanishing θ , since

$$\lim_{\theta \rightarrow 0} [\theta(\lambda^*)^\theta]^{-1} [(\lambda^* - \lambda)^\theta - (\lambda^*)^\theta] = \ln[1 - (\lambda/\lambda^*)].$$

¹⁰In fact the ratio of coefficients should behave exponentially with n if $\zeta(\lambda^*)$ has a convergent series.

¹¹K. Knopp, *Infinite Sequences and Series*, transl. by F. Bagemihl (Dover Publications, Inc., New York, 1956), p. 59.

(this would actually be an equality if the ζ_n were zero). It now follows that, if the r_n are plotted versus n^{-1} , the resulting points would approach a straight line whose intercept would give λ^* , and whose slope would give the exponent θ .

Table I also displays r_n 's computed from the available numerical estimates to the ϵ_n . It hardly needs to be pointed out that knowledge of the first few coefficients cannot uniquely specify the remaining coefficients; even if the leading coefficients appear to display complete regularity they may be atypical. In the following, however, we take the point of view that if the r_n all the way to twenty-first order (as shown in Table I) do actually show a consistent trend, then this fact is valuable circumstantial evidence for the behavior of the remainder of the series.

Figure 1 exhibits the r_n -vs- n^{-1} plot on a rather expanded scale. It is very obvious that well before twenty-first order the linearity indicated by Eq. (22) obtains. Although there is no objective criterion available for construction of the best limiting line, we have arbitrarily chosen the least-squares linear fit to the last eight r_n 's in the sequence, with results as follows:

$$\lambda^* = 1.1184, \quad \theta = 1.2057. \tag{23}$$

Explicit error estimates are difficult to assign here because:

- (a) It is unknown how "typical" the first 21 ϵ_n are.
- (b) No absolute error estimates are available on the variationally determined ϵ_n .

TABLE I. Coupling-constant power-series coefficients and their ratios. The ϵ_n are adapted from Ref. 8.

n	ϵ_n	r_n	ζ_n
0	-1.000 000 000	...	-0.764 672 126
1	+0.625 000 000	-0.62500	+0.371 302 916
2	-0.157 666 428	-0.25227	-0.134 336 005
3	+0.008 699 029	-0.05517	0.014 222 203
4	-0.000 888 705	-0.10216	0.001 326 565
5	-0.001 036 374	+1.16616	0.000 070 588
6	-0.000 612 932	0.59142	0.000 012 984
7	-0.000 372 184	0.60722	0.000 011 122
8	-0.000 242 874	0.65256	0.000 005 359
9	-0.000 165 662	0.68209	0.000 001 896
10	-0.000 116 179	0.70130	0.000 000 595
11	-0.000 083 302	0.71701	0.000 000 173
12	-0.000 060 881	0.73085	0.000 000 038
13	-0.000 045 232	0.74296	-0.000 000 004
14	-0.000 034 080	0.75345	-0.000 000 012
15	-0.000 025 993	0.76271	-0.000 000 011
16	-0.000 020 034	0.77073	-0.000 000 005
17	-0.000 015 586	0.77797	-0.000 000 001
18	-0.000 012 226	0.78442	0.000 000 001
19	-0.000 009 661	0.79024	0.000 000 003
20	-0.000 007 686	0.79557	0.000 000 002
21	-0.000 006 152	0.80042	0.000 000 000

(c) It is uncertain how the r_n approach the limiting linear behavior shown in Eq. (22) (whether from above or below, for example).

On the basis of several alternative linear fittings, it informally seems safe to conclude that values (23) are accurate to within ± 0.003 for λ^* and ± 0.03 for θ . It is probably impossible at this stage to try to distinguish the θ value from the rational number $\frac{8}{9}$.

In spite of the various uncertainties, it appears reasonable to conclude that $\epsilon(\lambda)$ possesses a branch point with index about $\frac{8}{9}$, on the positive real axis, and it is this singularity which limits the radius of convergence of the $\epsilon(\lambda)$ power series. We may incidentally exclude from consideration the possibility of two or more singularities lying at the $\epsilon(\lambda)$ series convergence circle boundary, since this case yields an oscillating sequence of r_n 's which is not observed.

In view of the impressive extent of linearity in Fig. 1 for the larger n 's, it seems that the ϵ_n have become "saturated" by the contributions from $A(\lambda^*-\lambda)^\theta$ for $n \cong 21$. We may therefore evaluate A by assuming ζ_{21} is negligible. The requisite calculation gives

$$A = -0.20563. \quad (24)$$

Therefore, we write

$$\epsilon(\lambda) = -0.20563(1.1184-\lambda)^{1.2057} + \zeta(\lambda). \quad (25)$$

Next, comparison of power-series coefficients of both members of this last expression permits evaluation of the remainder function coefficients ζ_n . The results have been entered in the third column of Table I. Although by construction ζ_{21} has been forced to vanish identically, it is interesting to note the dramatic reduction in magnitude that has occurred for smaller n in passing from ϵ_n 's to ζ_n 's.

The expression (25), with neglect of ζ_n 's for $n > 20$, represents effectively an attempt to sum the perturbation series to infinite order. Inversely, it may be utilized to predict the values that should be obtained for ϵ_n 's of higher order than currently available numerically, presuming that the variation-perturbation

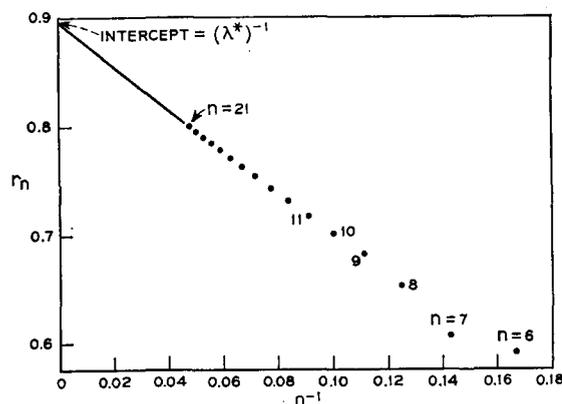


FIG. 1. Plot of $\epsilon(\lambda)$ power-series coefficient ratios r_n vs n^{-1} .

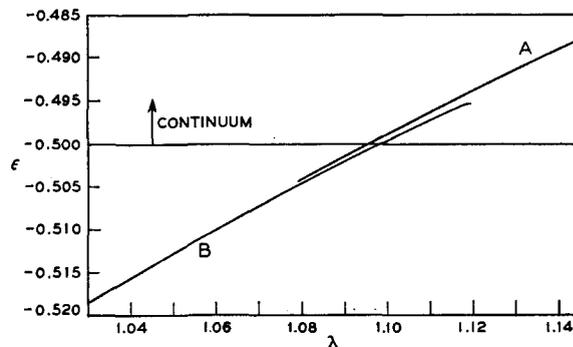


FIG. 2. (A) The 21st-degree-polynomial approximation to $\epsilon(\lambda)$, with the variationally determined coefficients in Table I; (B) the "infinite-order" expression (25) for $\epsilon(\lambda)$ possessing a fractional-power branch point at $\lambda^* = 1.1184$. The two curves asymptotically approach one another as λ decreases.

scheme can eventually be pushed to higher order. Without much effort one calculates, for instance,

$$\begin{aligned} \epsilon_{100} &= -2.7064 \times 10^{-11}, \\ \epsilon_{1000} &= -3.4559 \times 10^{-48}. \end{aligned} \quad (26)$$

Figure 2 displays for real positive λ in the neighborhood of λ^* , both the 21st-degree polynomial for $\epsilon(\lambda)$ assuming all ϵ_n beyond those shown in Table I vanish, and Expression (25) with the fractional power term. The curve for the latter naturally terminates at λ^* , unlike the polynomial, because ϵ for larger λ becomes complex. For $\lambda < \lambda^*$, the principal quantitative effect of "carrying the perturbation series to infinite order" is to induce a relatively small downward shift in energy, whose magnitude increases as the coupling constant is increased to λ^* . There are several important points to notice:

(1) Both curves unflinchingly pass upward through $-\frac{1}{2}$, the energy corresponding to the continuum limit [one electron bound in a (1s) orbital, the other ionized], even accounting for the quoted λ^* and θ uncertainties. Presuming that function (25) gives an accurate assessment of the physical situation, the nodeless localized bound state strictly speaking ceases to be the true ground state of the two-electron system for $\lambda > \lambda_c = 1.0975$. Beyond λ_c one apparently has an autoionizing state, which ends at $\epsilon(\lambda^*) = -0.49527 \dots$, according to Eq. (25).

(2) Although it may not be obvious from a plot such as Fig. 2, the expression (25) nevertheless has infinite downward curvature at λ^* . The slope, however, is still positive and is evaluated as follows:

$$\left[\frac{d\epsilon(\lambda)}{d\lambda} \right]_{\lambda^*-0} = \left[\frac{d\zeta(\lambda)}{d\lambda} \right]_{\lambda^*-0} = 0.13261 \dots \quad (27)$$

By virtue of the comments in the previous section, this number's inverse, 7.5409, \dots , measures spatial extension of the wavefunction at the binding limit λ^* , and may be compared with the corresponding value $\frac{8}{9} = 1.6000 \dots$ at $\lambda = 0$.

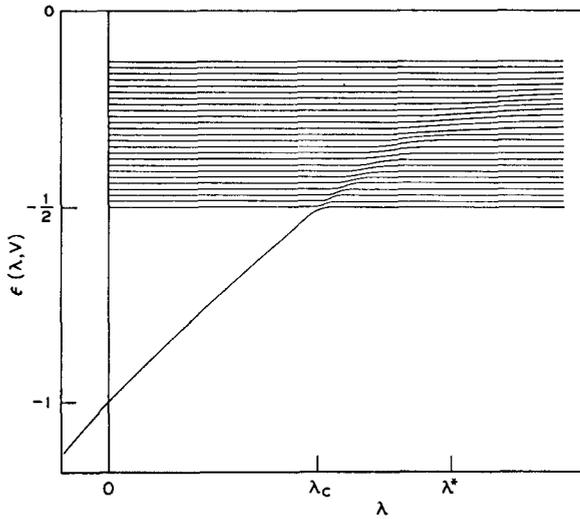


FIG. 3. Schematic diagram of energy levels in a box with large finite volume V . The true ground-state energy bends over sharply at λ_c to become essentially the lowest "continuum" level. Only the subset of states mixing with the ground state under the electron-electron repulsion are shown.

V. COMMENTARY

No obvious rationale for the existence of a fractional power branch point with index approximately $\frac{2}{3}$ seems to suggest itself. However, the results of the variational calculation carried out in the Appendix, based on Wavefunction (A14), have a certain heuristic value. As shown in the Appendix, the variational result qualitatively shares with $\epsilon(\lambda)$ the existence of a branch point above the continuum limit (with finite slope and infinite downward curvature), but with characteristic index $\frac{2}{3}$, rather than $\frac{5}{6}$. It seems likely that any *finite* generalization of the variational function (A14) to include more parameters [e.g., (A21)] will lead to basically the same result with index $\frac{2}{3}$. But in the infinite-parameter limit, there is no reason to exclude the possibility that the limiting variational energy [which then becomes $\epsilon(\lambda)$ itself] should not exhibit a somewhat different index. The situation here is strongly analogous to that surrounding critical phenomena in the statistical mechanical theory of phase change: Systematic theories carried to finite order yield "classical" values of critical point exponents (for magnetization, susceptibility, etc.) differing from exact ("infinite-order") values.¹²

It is necessary to realize that the fact that $\epsilon(\lambda)$ actually enters the continuum as λ increases beyond some $\lambda_c > 1$ is a result of considering the two-electron problem in infinite space. If the related problem were considered in which the nucleus sat at the center of a very large, but finite, box at whose walls the wavefunction vanished, the situation would be drastically altered. Although the new ground-state energy would be substantially equal to $\epsilon(\lambda)$ for $\lambda < \lambda_c$, there would be a sharp bend at λ_c , after which the energy would remain

¹² M. E. Fisher, *J. Math Phys.* **4**, 278 (1963).

equal to nearly $-\frac{1}{2}$. The situation is illustrated in rough schematic form in Fig. 3. For $\lambda_c < \lambda < \lambda^*$ in the very large box, our localized bound state really amounts to a wavepacket formed from a set of closely spaced states near in energy to $\epsilon(\lambda)$, rather than a true stationary state.

Associated with the fractional-power singularity of the infinite volume $\epsilon(\lambda)$ at λ^* is a branch cut. Because we tentatively found in Sec. III that in the neighborhood of infinity $\epsilon(\lambda)$ has only a double pole [i.e., no fractional powers occur in expansion of $\epsilon(\lambda)$ in powers of λ^{-1} , at least as far as we were able to carry it], this branch cut is apparently forced to terminate somewhere in the finite plane. The simplest possibility reasonably consistent with facts that we have been able to establish about $\epsilon(\lambda)$ is the existence of another branch point at real positive $\lambda^{**} > \lambda^*$, with index equal to an integer n minus the previous index θ . Thus for example $\epsilon(\lambda)$ might conceivably be a closed-form expression of the type

$$\epsilon(\lambda) = D(\lambda^* - \lambda)^\theta (\lambda^{**} - \lambda)^{n-\theta} + M(\lambda), \quad (28)$$

where D is a negative real number, and $M(\lambda)$ is a meromorphic function,¹³ hence possessing, at worst, multiple poles. Figure 4 illustrates this simplest possible branch cut. Of course, it is also possible that $\epsilon(\lambda)$ has more than two branch points requiring a more elaborate branch cut structure, but unfortunately these ambiguities cannot be resolved at present.

The Hamilton operators in Eqs. (2) and (5) are not Hermitian when the coupling constant λ is complex, and as a result the eigenvalue $\epsilon(\lambda)$ (as well as the wavefunction) will necessarily be complex. But since $\epsilon(\lambda)$ is real on at least a portion of the real λ axis, we know that ϵ evaluated, respectively, at any λ and at its complex conjugate $\bar{\lambda}$, will give complex conjugate values ϵ and $\bar{\epsilon}$. In addition the quantum mechanical virial theorem remains valid throughout the complex λ plane, with the consequence that if $\epsilon(\lambda)$ were to be unbounded at any finite point it would be necessary to have an infinite expectation value for the Coulomb interactions. Since this latter demands either that the

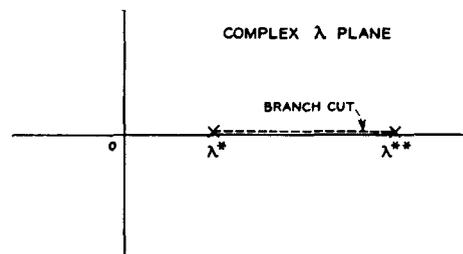


FIG. 4. Simplest possible branch-cut structure for $\epsilon(\lambda)$ in the complex λ plane, as generated for example by Eq. (28). $\epsilon(\lambda)$ is real on the horizontal real axis to either side of the dotted branch cut.

¹³ K. Knopp, *Theory of Functions*, transl. by F. Bagemihl (Dover Publications, Inc., New York, 1947), Part 2, Chap. 2.

electrons in the mean get arbitrarily close to one another or to the nucleus with but finite-strength Coulomb forces, we must conclude that $\epsilon(\lambda)$ is bounded in absolute value in any finite region of the complex λ plane. In terms of the provisional expression (28) for $\epsilon(\lambda)$, this requires that integer n be no less than 2, and that $M(\lambda)$ have no poles except at infinity (i.e., a polynomial).

If, as in Fig. 4, one proceeds along the positive real λ axis from the origin toward branch point λ^* , the energy is initially a real quantity. At λ^* one has the option of passing either above or below the singularity in order to proceed further to the right. However, by virtue of the branch cut two different values of $\epsilon(\lambda)$ will be obtained subsequent to passing λ^* , depending on whether the real axis is approached from above or below. From Eq. (19) we find that only the imaginary part of $\epsilon(\lambda)$ is discontinuous across the branch cut:

$$\begin{aligned}\epsilon(\lambda+0i) &= A(\lambda-\lambda^*)^\theta \exp(\pi\theta i) + \zeta(\lambda+0i), \\ \epsilon(\lambda-0i) &= A(\lambda-\lambda^*)^\theta \exp(-\pi\theta i) + \zeta(\lambda-0i),\end{aligned}\quad (29)$$

so that in fact the leading behavior of the discontinuity for λ slightly larger than λ^* is

$$\begin{aligned}\epsilon(\lambda+0) - \epsilon(\lambda-0) &= 2i \operatorname{Im}[\epsilon(\lambda+0)] \\ &\sim 2Ai(\lambda-\lambda^*)^\theta \sin(\pi\theta).\end{aligned}\quad (30)$$

Therefore, the discontinuity grows in magnitude from zero at the singularity as λ increases. The imaginary part of the energy beyond λ^* , and therefore the discontinuity across the cut, is inversely proportional to the lifetime of the localized "bound state,"¹⁴ which is now forced to dissociate by the strong electron-electron repulsion.

Many of the ideas applied in this paper to the ground state of the two-electron system are also applicable to excited states. By means of the ratio test approach in Sec. IV, for example, the $(2p)^2\ ^3P$ excited state, for which lengthy perturbation-variation series are also available in Ref. 8 (and which has already been known to lie in the continuum for H^-), also appears to exhibit a branch point singularity on the positive real axis.¹⁵ Very likely similar considerations and results apply as well to many-electron atoms and polynuclear systems, but these possibilities must await future investigation for detailed elucidation. It is our hope that in this broad class of atomic and molecular quantum-mechanical problems eventually one might establish the universality of complex energy function branch points as a

¹⁴L. D. Landau and E. M. Lifshitz, *Quantum Mechanics, Non-Relativistic Theory*, transl. by J. B. Sykes and J. S. Bell (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1958), p. 440.

¹⁵For this case however one finds $\lambda^* \cong 1.0128$, $\theta \cong 1.0730$. Unlike the $(1s)^2\ ^1S$ ground state considered at length in this paper, however, this excited state cannot autoionize due to its different symmetry. Some other excited closed (i.e., localized) states which for $\lambda=1$ lie in the continuum and are autoionizing are listed in: J. Midtdal, Phys. Math. Univ. Oslo. No. 21 (1964), Table 1.

principal manifestation of electron correlation, for this would result in the ability generally to infer from finite-order variation-perturbation calculations the quantitative nature of the infinite-order result.

ACKNOWLEDGMENT

The author is indebted to Robert L. Kornegay for carrying out the various computational facets of the investigation reported in this paper.

APPENDIX

We present here two simple variational calculations for $\epsilon(\lambda)$. In the first, consider the variational form

$$\phi_{\text{var}}(\rho_1, \rho_2) = C^{-1}(\alpha, \beta) \exp[-\alpha(\rho_1 + \rho_2) - \beta\rho_{12}], \quad (A1)$$

where α and β are the variational parameters, and $C(\alpha, \beta)$ is the normalization constant ensuring

$$\int \phi_{\text{var}}^2(\rho_1, \rho_2) d\rho_1 d\rho_2 = 1. \quad (A2)$$

The variational energy is equal to

$$\begin{aligned}\epsilon_{\text{var}}(\alpha, \beta, \lambda) &= \int \phi_{\text{var}} \left[-\frac{1}{2}(\nabla_1^2 + \nabla_2^2) \right. \\ &\quad \left. - \rho_1^{-1} - \rho_2^{-1} + \frac{\lambda}{\rho_{12}} \right] \phi_{\text{var}} d\rho_1 d\rho_2.\end{aligned}\quad (A3)$$

All of the separate integrals occurring after substitution of (A1) into (A2) and (A3) have similar convolution character, and may therefore each be expressed as quadratures of Fourier transform products for the separate convolution links. We do not reproduce tedious details here. One ultimately finds, after setting $\beta = \theta\alpha$,

$$\begin{aligned}\epsilon_{\text{var}} &= [(1+\theta)/(8+5\theta+\theta^2)] \{ (8+7\theta+4\theta^2+\theta^3)\alpha^2 \\ &\quad - [(16+4\theta) - \lambda(5+4\theta+\theta^2)]\alpha \},\end{aligned}\quad (A4)$$

which is required to be a minimum with respect to both α and θ variations.

Elimination of α from Expression (A4) is trivial because this parameter appears only quadratically. Therefore set the α derivative of ϵ_{var} at constant θ equal to zero to obtain

$$\alpha = \frac{16+4\theta - \lambda(5+4\theta+\theta^2)}{2(8+7\theta+4\theta^2+\theta^3)}, \quad (A5)$$

which thereupon allows ϵ_{var} in Eq. (A4) to be expressed solely as a function of θ :

$$\epsilon_{\text{var}} = \frac{(1+\theta)[16+4\theta - \lambda(5+4\theta+\theta^2)]^2}{4(8+5\theta+\theta^2)(8+7\theta+4\theta+\theta^3)}. \quad (A6)$$

Next set the θ derivative of this last expression equal to zero to obtain the following equation for the de-

termination of θ :

$$0 = 624\theta + 1056\theta^2 + 768\theta^3 + 292\theta^4 + 56\theta^5 + 4\theta^6 + \lambda(176 + 329\theta + 238\theta^2 + 82\theta^3 + 14\theta^4 + \theta^5). \quad (A7)$$

It is now a relatively simple matter to compare the structure of the variationally determined ground-state energy, $\epsilon_{\text{var}}(\lambda)$, with the exact $\epsilon(\lambda)$ in various regions of the complex λ plane. Since our intuition tells us that θ should be small when λ is small, it is convenient to rewrite Eq. (A7) in a form lending itself to easy iteration in powers of λ :

$$\theta = -\frac{1}{3}\lambda - \frac{1}{6}\lambda^2 [1056\theta^2 + 768\theta^3 + 292\theta^4 + 56\theta^5 + 4\theta^6 + \lambda(329\theta + 238\theta^2 + 82\theta^3 + 14\theta^4 + \theta^5)]. \quad (A8)$$

Therefore, near the origin we have

$$\theta(\lambda) = -\frac{1}{3}\lambda + O(\lambda^2), \quad (A9)$$

and consequently $\epsilon_{\text{var}}(\lambda)$ may be evaluated to one higher order from (A6):

$$\epsilon_{\text{var}}(\lambda) = -1 + \frac{5}{8}\lambda - \frac{1}{9}\frac{45}{8}\lambda^2 + O(\lambda^3). \quad (A10)$$

The rational-number coefficient of λ^2 (decimal equivalent: 0.14613...) constitutes a rigorous upper bound to ϵ_2 .

In similar fashion, the iterable form of condition Eq. (A7) for large magnitudes of λ ,

$$\theta = -\frac{\lambda}{4} \left[1 + \frac{(9/\theta^2) + (46/\theta^3) + (65/\theta^4) + (20/\theta^5)}{1 + (14/\theta) + (73/\theta^2) + (192/\theta^3) + (264/\theta^4) + (156/\theta^5)} \right], \quad (A11)$$

yields

$$\theta(\lambda) = -\frac{\lambda}{4} - \frac{36}{\lambda} - \frac{1280}{\lambda^2} - \frac{23424}{\lambda^3} + \frac{87040}{\lambda^4} + O(\lambda^{-5}). \quad (A12)$$

The resulting variational energy in this large $-\lambda$ regime thereupon is calculated to be

$$\epsilon_{\text{var}}(\lambda) = -\frac{\lambda^2}{4} - 4 + \frac{448}{\lambda^2} + \frac{10240}{\lambda^3} + O(\lambda^{-4}). \quad (A13)$$

Although the first two terms agree with Eq. (18), the coefficient shown here for λ^{-2} is obviously at variance with the correct value 256 in Eq. (18), as a result of the failure of ϕ_{var} to factor as shown in Eq. (12).

In a rough way, then, variational wavefunction (A1) successfully accounts for the behavior of the two-electron atom ground-state energy both for small λ , and

for large (negative) λ . So far as the interesting neighborhood of λ^* is concerned, a detailed numerical investigation is required. We remark that such an investigation first shows that although the predicted energy for $\lambda = 1$ is still below the continuum [$\epsilon_{\text{var}}(1) \cong -0.508$], its value is rather high compared to the "exact" value [$\epsilon(1) \cong -0.528^8$] for this hydride ion. As λ increases beyond about 1.01, though, the predicted variational energy moves above the continuum limit, in qualitative accord with the behavior inferred in Sec. IV for the exact function $\epsilon(\lambda)$, but the predicted energy continues to rise smoothly to very large λ values with no hint of a singularity near λ^* .

The evidence therefore suggests that variational wavefunction (A1) cannot give an adequate account of electron-electron correlation near the threshold λ^* . Some years ago, Chandrasekhar¹⁶ suggested that at least for the hydride ion a more suitable choice would be the Eckart-Hylleraas function

$$\tilde{\phi}_{\text{var}}(\rho_1, \rho_2) = \tilde{C}^{-1}(a, b) [\exp(-a\rho_1 - b\rho_2) + \exp(-b\rho_1 - a\rho_2)]. \quad (A14)$$

By means of manipulations very similar to the previous case, we find (setting $b = \eta a$)

$$a(\lambda) = \frac{(1+\eta) \{ \lambda [\eta(1+\eta)^2(1+3\eta+\eta^2) + 20\eta^3] - (1+\eta)^6 - 64\eta^3 \}}{(1+\eta)^6(1+\eta^2) + 128\eta^4}, \quad (A15)$$

and then η is to be obtained by finding the minimum in the variational energy

$$\tilde{\epsilon}_{\text{var}} = \frac{(1+\eta)^2 \{ \lambda [\eta(1+\eta)^2(1+3\eta+\eta^2) + 20\eta^3] - (1+\eta)^6 - 64\eta^3 \}^2}{2[(1+\eta)^6(1+\eta^2) + 128\eta^4][(1+\eta)^6 + 64\eta^3]}. \quad (A16)$$

Both expressions (A15) and (A16) are invariant with respect to replacement of η by η^{-1} , reflecting the symmetry of $\tilde{\phi}_{\text{var}}$ with respect to a and b .

Numerical analysis now shows $\tilde{\epsilon}_{\text{var}}(1) \cong -0.513$, demonstrating the better accounting of electron correlation at this coupling strength. Again, increase of λ beyond 1 has the effect of increasing the predicted

energy until it passes upward through the continuum limit $-\frac{1}{2}$; now, however, this passage does not occur until $\lambda \cong 1.05$.¹⁷

¹⁶ S. Chandrasekhar, *Astrophys. J.* **100**, 176 (1944).

¹⁷ Since variationally obtained energies always lie above the true $\epsilon(\lambda)$, continuum-limit crossing estimates for λ such as this one will be lower bounds on λ_c .

Qualitative details of the computations for λ in the neighborhood of 1 are outlined schematically in Fig. 5. The relevant minimum, as λ increases, moves up and toward smaller η , and the curvature at the minimum decreases in magnitude. Eventually the curve ceases to possess a minimum at all, so the variational solution suffers a singularity. This vanishing is found to occur at $\lambda = \tilde{\lambda} \cong 1.07$ (at which point the η value at the minimum has declined to $\tilde{\eta} \cong 0.12$), and the curve $\tilde{\epsilon}_{\text{var}}(\eta, \tilde{\lambda})$ is substantially a cubic for η near $\tilde{\eta}$.

These few observations permit us next to establish the analytic nature of the singularity in the variational energy for $\tilde{\phi}_{\text{var}}$. Defining

$$\begin{aligned} \delta\lambda &= \lambda - \tilde{\lambda}, \\ \delta\eta &= \eta - \tilde{\eta}, \end{aligned} \tag{A17}$$

we represent $\tilde{\epsilon}_{\text{var}}(\eta, \lambda)$ by means of a truncated multiple Taylor's series

$$\tilde{\epsilon}_{\text{var}}(\eta, \lambda) \cong \tilde{\epsilon}_{\text{var}}(\tilde{\eta}, \tilde{\lambda}) + A_1(\delta\lambda) + A_2(\delta\lambda)(\delta\eta) + A_3(\delta\eta)^3, \tag{A18}$$

valid for small $\delta\lambda$ and $\delta\eta$, where A_1 , A_2 , and A_3 are positive constants.¹⁸ The minimum then occurs at

$$(\delta\eta)_{\text{min}} = [-A_2(\delta\lambda)/3A_3]^{\frac{1}{2}} \tag{A19}$$

for negative $\delta\lambda$. If this result is substituted into (A18), we find

$$\begin{aligned} (\tilde{\epsilon}_{\text{var}})_{\text{min}} &= \tilde{\epsilon}_{\text{var}}(\tilde{\eta}, \tilde{\lambda}) + A_1(\delta\lambda) \\ &\quad - [2(A_2)^{\frac{1}{2}}/3^{\frac{1}{2}}(A_3)^{\frac{1}{2}}](-\delta\lambda)^{\frac{3}{2}}. \end{aligned} \tag{A20}$$

Therefore one predicts a branch point in the energy at $\tilde{\lambda}$, at which the first derivative (A_1) is finite and positive, but with infinite downward curvature.

¹⁸ The A_1 term gives the upward drift to the family of curves in Fig. 5, the A_2 term the "tipping" as λ varies, and the A_3 term the cubic shape when $\lambda = \tilde{\lambda}$.

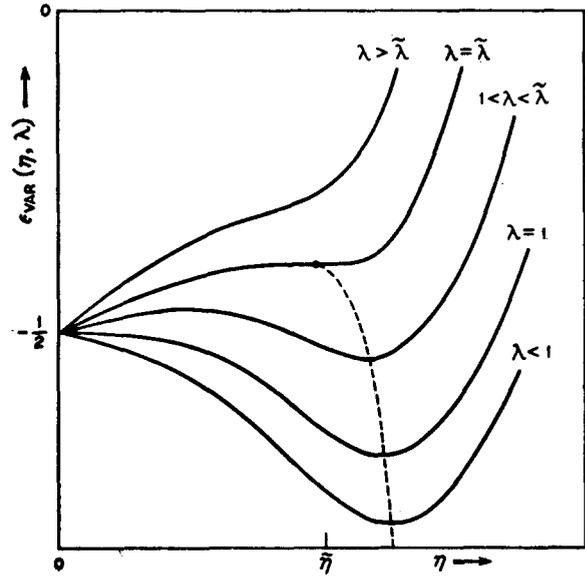


FIG. 5. Family of variational energy curves, for λ in the neighborhood of 1, for the Chandrasekhar variational wavefunction (A14). The dotted curve represents the locus of minima, which disappears when $\lambda > \tilde{\lambda}$.

In order to perform a variational calculation with assurance that good results would be obtained in the vicinities of all three of 0, 1, and ∞ , it would be desirable to combine the features of both ϕ_{var} and $\tilde{\phi}_{\text{var}}$. One possibility would be consideration of a wavefunction of the type

$$\begin{aligned} &[\exp(-a\rho_1 - b\rho_2) + \exp(-b\rho_1 - a\rho_2)] \\ &\quad \times [1 + B \exp(-\beta\rho_{12})], \end{aligned} \tag{A21}$$

yet to be normalized, containing four variational parameters a , b , B , and β . Although this form is again tractable by means of the techniques already utilized for (A1) and (A14), the resulting labor is far larger.