Role of electron correlation in determining the binding limit for two-electron atoms

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(Received 22 May 1974)

Using two trial wave functions for a nonlinear variational study, the ground state of the two-electron isoelectronic sequence has been investigated for a continuously variable electron-electron coupling constant λ. These calculations extend the analogous study of the preceding paper by including explicit angular correlation on the one hand, and extra orbital flexibility on the other hand. The results confirm the earlier conclusion that for sufficiently large positive λ (corresponding to nuclear charge $Z < 1$) the ground-state energy penetrates into the continuum as a localized "bound" state, before terminating at a branch-point singularity.

I. INTRODUCTION

A convenient mathematical setting, in which to assess the influence of electron correlation on atomic eigenstates, is provided by "$1/Z$ perturbation theory." This format measures energy in terms of the unit

$$m_e Z^2 e^4 / \hbar^2 , \tag{1.1}$$

and lengths in terms of the unit

$$\hbar^2 / m_e Z e^2 , \tag{1.2}$$

where Z is the atomic number, m_e is the electron mass, and $\hbar$ and e have conventional meanings. Consequently, the spin-independent, nonrelativistic Hamiltonian for n electrons moving in the presence of an infinitely massive point nucleus has the following reduced form:

$$H(\lambda) = -\sum_{j=1}^{n} \left(\frac{1}{2} \nabla_j^2 + \frac{1}{r_j} \right) + \lambda \sum_{j<k=1}^{n} \frac{1}{r_{jk}} , \quad \lambda = 1/Z . \tag{1.3}$$

For large atomic numbers, λ is small, so it makes good physical sense when $Z \geq n$ to consider the last terms in the Hamiltonian to be a perturbation of modest influence.

Kato has proved[1] that all eigenvalues $\epsilon^{(\nu)}(\lambda)$ of Hamiltonian $H(\lambda)$, which are isolated when $\lambda = 0$, are analytic functions of the coupling constant λ in the neighborhood of the origin. This implies that power series for those eigenvalues,

$$\epsilon^{(\nu)}(\lambda) = \sum_{j=0}^{\infty} \epsilon_j^{(\nu)} \lambda^j , \tag{1.4}$$

are convergent.

As λ increases from zero along the positive real axis, the magnitude of electron repulsion likewise increases until the nucleus is no longer able to bind all n electrons simultaneously in a localized eigenstate. Since the value of λ at the critical binding limit may equal or exceed the convergence limit

for the relevant power series (1.4), it becomes important to be able to effect analytic continuation of $\epsilon^{(\nu)}(\lambda)$ beyond the power-series convergence circle. Equivalently, one seeks to specify the positions and types of the singularities of the $\epsilon^{(\nu)}(\lambda)$ throughout the complex λ plane.

As a result of concentrated numerical effort, an extensive set of precisely determined power-series coefficients is available for the two-electron ($n = 2$) ground state.[2,3] These coefficients present a systematic pattern from which it is tempting to infer the behavior of the underlying analytic function $\epsilon^{(0)}(\lambda)$. By using ratio-test methods that were developed to analyze power series in phase-transition theory,[4] it has been concluded that a branch-point singularity on the positive real λ axis (at $\lambda^* = 1.1184$) defines the radius of convergence of the power series.[5] By extrapolating the established coefficient trend to infinite order, one obtains[5]

$$\epsilon^{(0)}(\lambda) = -0.20563(\lambda^* - \lambda)^{1.2057} + \zeta(\lambda) . \tag{1.5}$$

The function $\zeta(\lambda)$ is regular at λ^* (or at worst very weakly singular), and is accurately determined by known coefficients. The form shown in Eq. (1.5) effectively sums the λ power series to infinite order, and permits analytic continuation past the singularity at λ^*.

The result (1.5) exhibits a particularly interesting feature. As λ increases from 0 toward λ^*, $\epsilon^{(0)}(\lambda)$ rises toward and penetrates into the continuum that begins at energy equal to $-\frac{1}{2}$.[6] This penetration occurs at[5]

$$\lambda_c = 1.0975 , \tag{1.6}$$

and when $\lambda_c \leq \lambda \leq \lambda^*$ the eigenstate consists of a bound (localized and normalizable) state in the continuum.

The notion of a stable bound state embedded in the continuum is sufficiently at variance with orthodox intuition that independent verification is important. After all, the finite set of coefficients

upon which Eq. (1.5) is based conceivably could be atypical and therefore misleading. However, qualitatively, the same behavior as exhibited by Eq. (1.5) has been shown to follow from a nonlinear variational approximation for the two-electron ground state.[7] That variational study was based on the Hylleraas-Eckart-Chandrasekhar (HEC) wave function

$$\psi(\vec{r}_1, \vec{r}_2) = e^{-\alpha r_1 - \beta r_2} + e^{-\beta r_1 - \alpha r_2}, \qquad (1.7)$$

for which orbital exponents α and β were optimized for each value of the coupling constant λ. The resulting variational energy crosses into the continuum (at $\lambda_c = 1.048\,486$) before terminating at a branch point [when $\lambda = \lambda*(\text{HEC}) = 1.078\,0113$].

Though the case for stable bound atomic states in the continuum is strengthened by the cited variational result, it is still not definitive. Wave function (1.7) contains radial correlation between the electrons but no angular correlation, and it is possible that inclusion of the latter might inhibit penetration of the continuum. It is the specific aim of this paper to establish numerically the effect of improving wave function (1.7) on the continuum penetration and critical binding phenomena for the two-electron ground state.

Two specific improvements have been studied. One (Sec. III) introduces angular correlation by multiplying form (1.7) by an explicit function of the interelectron distance r_{12}. The other (Sec. IV) provides extra orbital flexibility by replacing each Slater orbital in (1.7) by a function of the Hulthén type.[8]

Before launching into a description of our specific calculations, we dispose of an important matter of principle in Sec. II. "Conventional wisdom" in atomic quantum mechanics is normally based on independent electron arguments. Among other conclusions, this type of reasoning implies that approach to a continuum edge from below (i.e., the ionization potential going to zero) is accompanied by an orbital exponent going to zero.[9] As a result an eigenstate could never penetrate the continuum as a localized bound state. The analysis in Sec. II demonstrates the inapplicability of the independent-electron viewpoint, and thus stresses that stable bound states in the continuum can only owe their existence to explicit correlation effects.

Our detailed numerical procedures and results are discussed in Sec. V. The major impact of those results is further support for the presumption that $\epsilon^{(0)}(\lambda)$ for two electrons penetrates into the continuum.

Section VI attempts to point the way toward future contributions to understanding the mathematical nature of the exact eigenfunctions and their analyt-

ic eigenvalues $\epsilon^{(\nu)}(\lambda)$.

Although the emphasis in this paper is primarily mathematical, physical consequences of our general n-electron perturbation theory have been stressed previously.[5,7] Included among them are scattering resonances for states that have been forced to penetrate the continuum ($O^- + e$ provides a particularly interesting ten-electron example[7]). Furthermore, potential energy curves (such as $H + H^-$) involving anions develop anomalies, related to analytic singularities discussed here, that affect the collision dynamics and electron ejection probabilities.[7] Finally, efficient high-accuracy calculations of anion structures and properties can best be designed with knowledge of nearest singularities in the coupling constant (λ) plane, and indeed that knowledge permits summation of perturbation theory to infinite order.[5] The present paper represents a small contribution to elucidation of these phenomena.

II. COUNTERARGUMENT

The Schrödinger equation for the ground state of the two-electron system is the following:

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{\lambda}{r_{12}}\right)\psi(\vec{r}_1, \vec{r}_2) = \epsilon^{(0)}(\lambda)\psi(\vec{r}_1, \vec{r}_2).$$

(2.1)

When $\lambda = 0$, the equation is separable and may be solved exactly to yield

$$\psi = e^{-r_1 - r_2}, \qquad (2.2)$$

$$\epsilon^{(0)}(0) = -1.$$

As λ moves along the positive real axis toward λ_c, $\epsilon^{(0)}(\lambda)$ rises monotonically to $-\frac{1}{2}$.

Choose λ to be slightly less than λ_c, so that the ionization energy

$$-\Delta\epsilon = -\epsilon^{(0)}(\lambda) - \frac{1}{2} \qquad (2.3)$$

is small but positive. Under this circumstance, we ask how ψ behaves in that specific asymptotic region of configuration space where an electron, say the one at $\vec{r}_1$, is far from the nucleus. It is tempting then tentatively to write the asymptotic form

$$\psi(\vec{r}_1, \vec{r}_2) \sim \varphi(r_1)\chi(r_2), \qquad (2.4)$$

where φ describes the spatial distribution in the large-distance "fringe region" of the atom. The inner electron 2 experiences the full nuclear charge, without the perturbing influence of a nearby partner electron, so χ should resemble a hydrogenic $1s$ orbital.

After substituting expression (2.4) into Schrö-

dinger equation (2.1), and rearranging, one obtains

$$\chi(r_2)\left(-\frac{1}{2}\nabla_1^2 + \frac{\lambda-1}{r_1} - \Delta\epsilon\right)\varphi(r_1)$$

$$= \varphi(r_1)\left[\frac{1}{2}\nabla_2^2 + \frac{1}{r_2} + \lambda\left(\frac{1}{r_1} - \frac{1}{r_{12}}\right) - \frac{1}{2}\right]\chi(r_2). \quad (2.5)$$

In the asymptotic region under consideration, where $r_1 \gg r_2$, the difference

$$\frac{1}{r_1} - \frac{1}{r_{12}} \quad (2.6)$$

is of order r_1^{-2}, and should be negligible. Consequently, the right member of Eq. (2.5) collapses to zero, since for the hydrogenic $1s$ orbital χ

$$\left(\frac{1}{2}\nabla_2^2 + \frac{1}{r_2} - \frac{1}{2}\right)\chi(r_2) = 0. \quad (2.7)$$

Thus Eq. (2.5) reduces to a differential equation for φ alone:

$$\left(-\frac{1}{2}\nabla_1^2 + \frac{\lambda-1}{r_1} - \Delta\epsilon\right)\varphi(r_1) = 0, \quad (2.8)$$

which according to the conventional view being purposely followed should determine the "fringe region" electron density.

Equation (2.8) is a standard form, and has the following solution:

$$\varphi(r_1) = \varphi_0 \kappa^a e^{-\kappa r_1} U(a, 2, 2\kappa r_1),$$
$$\kappa = (-2\Delta\epsilon)^{1/2}, \quad a = 1 + (\lambda-1)/\kappa, \quad (2.9)$$

where U is the confluent hypergeometric function which approaches zero at infinity,[10]

$$U(a, b, z) = [\Gamma(a)]^{-1}\int_0^\infty e^{-zt}t^{a-1}(1+t)^{b-a-1}dt, \quad (2.10)$$

and where φ_0 is a suitable constant. From the asymptotic behavior of U as $z \to \infty$,[10]

$$U(a, b, z) \sim z^{-a}, \quad (2.11)$$

one can infer that $\varphi(r_1)$ behaves thus at large r_1:

$$\varphi(r_1) \sim \varphi_0 e^{-\kappa r_1}/r^a. \quad (2.12)$$

If the vanishing of $\Delta\epsilon$ as $\lambda \to \lambda_c$ is accompanied by a weakening tendency for the outer electron to remain locally bound to the atom, then $\varphi(r)$ should become more and more extended in space. Indeed in the limit $\lambda = \lambda_c$, φ^2 should then not be integrable. An obvious corollary is that the expectation value of r_{12}^{-1} should approach zero in this limit. Since

$$\frac{\partial\epsilon^{(0)}(\lambda)}{\partial\lambda} = \frac{\langle\psi|r_{12}^{-1}|\psi\rangle}{\langle\psi|\psi\rangle}, \quad (2.13)$$

one would be forced to conclude that the energy function $\epsilon^{(0)}(\lambda)$ is tangent to the continuum edge at $-\frac{1}{2}$, when $\lambda = \lambda_c$.

Since the hydride anion ($\lambda = 1$) lies lower in energy than the continuum, we know that $\lambda_c > 1$. Therefore $\lambda - 1$ in differential equation (2.8), and in definition (2.9) for a, can be taken to be positive. The exponential decay constant κ appearing in the asymptotic expression (2.12) for $\varphi(r_1)$ vanishes as λ increases to λ_c, and that fact alone would be consistent with a diverging mean distance for the outer electron. But at the same time the positivity of $\lambda - 1$ requires

$$a \to +\infty, \quad (2.14)$$

so that in spite of loss of the exponential factor in Eq. (2.12), $\varphi(r_1)$ still rapidly approaches zero with increasing r_1, even when $\lambda = \lambda_c$.

We are therefore forced to admit that the outer electron does *not* develop an infinite mean distance from its partner and the nucleus. Also we must have

$$\left(\frac{\partial\epsilon^{(0)}(\lambda)}{\partial\lambda}\right)_{\lambda=\lambda_c} > 0. \quad (2.15)$$

These conclusions undermine logical consistency of the the initial asymptotic factorization (2.4), for in order that it be relevant to the problem at hand, it is necessary that the electrons be sufficiently far from one another in the mean that explicit angular correlation not arise. Our counterargument therefore consists in showing that existence of binding for the anion leads inevitably to a compact ψ at λ_c and hence to an important role for electron spatial correlation; it thus invalidates any attempt to invoke a single-particle description for the exact wave function.

In order to complete the picture, we should also adapt this line of reasoning to states for which the hydride anion is *not* bound. An example would be the $(1s)(2s)^3S$ excited state for two electrons, for which $-\frac{1}{2}$ again serves as the energy of the continuum edge.[7]

First, note that whenever λ is less than 1, however small the negative difference $\lambda - 1$, the nucleus plus core electron 2 present a net positive charge for the outer electron 1, which therefore essentially moves in the potential

$$(\lambda - 1)/r_1. \quad (2.16)$$

It is a property of such an attractive Coulomb potential that it permits an infinite set of bound Rydberg states, including the specific excited state of interest. Hence λ_c cannot be less than 1; it must be identically 1.

The task then reduces to finding a consistent behavior for $\Delta\epsilon$, κ, a, and $\langle\psi|r_{12}^{-1}|\psi\rangle$ as functions of λ near 1. We remark that the only possibility entails quadratic behavior for $\Delta\epsilon$,

$$\Delta\epsilon = -A(1-\lambda)^2 + O((1-\lambda)^3) , \qquad (2.17)$$

where A is a positive constant. This in turn requires

$$\kappa = (2A)^{1/2}(1-\lambda) + O((1-\lambda)^2) \qquad (2.18)$$

and

$$a = 1 - (2A)^{-1/2} + O((1-\lambda)^{+1}) . \qquad (2.19)$$

Unlike the preceding case for which the anion was bound, a does not diverge as $\lambda \to \lambda_c$, but instead it remains bounded. In fact it is clear that at λ_c,

$$\varphi(r_1) \sim \varphi_0/r_1^{1-(2A)^{1/2}} , \qquad (2.20)$$

so that φ^2 is not integrable. But this is precisely what is required by Eq. (2.17), since now the eigenvalue derivative

$$\frac{\partial\epsilon^{(\nu)}}{\partial\lambda} = \frac{\langle\psi_\nu|r_{12}^{-1}|\psi_\nu\rangle}{\langle\psi_\nu|\psi_\nu\rangle} \qquad (2.21)$$

must vanish at $\lambda = \lambda_c = 1$.

This second case therefore *does* admit the consistency of asymptotic wave-function factorization, as shown in Eq. (2.4). It is thus clear that a dichotomy exists in the behavior of discrete eigenvalues as increased electron coupling forces them upward to the continuum.

It should be noted in passing that the quadratic energy behavior displayed in Eq. (2.17) for $\lambda = 1$ conforms to Lekner's analysis of potentials that lead to weakly bound states.[11]

These considerations emphasize that general specification of the asymptotic electron density far from an atom or molecule remains a deep and unsolved problem.

III. BONHAM-KOHL WAVE FUNCTION

The major defect from which the Hylleraas-Eckart-Chandrasekhar wave function (1.7) suffers is its total lack of angular correlation. In order to rectify that weakness it is possible to incorporate an explicit function of r_{12} as a correlation factor multiplying the function shown in Eq. (1.7). The specific correlated trial function with which we have worked is the following:

$$\psi(\vec{r}_1, \vec{r}_2) = (e^{-\alpha r_1 - \beta r_2} + e^{-\beta r_1 - \alpha r_2})(1 + ke^{-cr_{12}}) . \quad (3.1)$$

All four parameters α, β, k, and c were treated as variables with respect to which the energy should be optimized. This variational function was one of several that were examined by Bonham and Kohl[12] for $Z = 1, 2$, and 3 ($\lambda = 1$, $\frac{1}{2}$, and $\frac{1}{3}$, respectively).

The correlation factor appearing in expression (3.1) permits ψ to develop a cusp at $r_{12} = 0$, as one knows to be the case for the exact eigenfunction.[13,14]

In particular,

$$\psi(\vec{r}_1, \vec{r}_2) = \psi(r_{12}=0) \left(1 - \frac{kc}{1+k}r_{12}\right) + O(r_{12}^2). \quad (3.2)$$

The strict cusp condition requires[13, 14]

$$-kc/(1+k) = \tfrac{1}{2}\lambda , \qquad (3.3)$$

though variationally determined parameters k and c may fail to satisfy this condition. The extent to which equality is approached in Eq. (3.3) provides one convenient way of assessing the quality of trial function (3.1).

It may be worth pointing out that wave function (3.1) is capable of giving an exact description of the two-electron ground state in the asymptotic limit that λ approaches $-\infty$. In this limit the two electrons bind together tightly to form a compact "dielectron,"[5] with

$$c \sim \tfrac{1}{2}|\lambda|, \quad \alpha, \beta \sim 2, \quad k \to +\infty, \qquad (3.4)$$
$$\epsilon^{(0)} \sim -\tfrac{1}{4}\lambda^2 - 4 .$$

By contrast, the simpler wave function (1.7) cannot describe an orbiting "dielectron" structure, and would predict a relatively inaccurate eigenvalue in this limit.

Since all distance coordinates in (3.1) appear in combination with multiplying variational parameters, the optimized wave function will satisfy the quantum-mechanical virial theorem.[15]

IV. HULTHÉN ORBITALS

A secondary defect in the Hylleraas-Eckardt-Chandrasekhar function (1.7) is its orbital inflexibility. In place of the simple exponential factors, it is desirable to use orbitals which can separately adjust their shapes near the nucleus, and at large distance from the nucleus. We have chosen to employ Hulthén orbitals:

$$u(r, \alpha, \beta) = (e^{-\alpha r} - e^{-\beta r})/(\alpha - \beta)r . \qquad (4.1)$$

They can be combined to provide an improved version of function (1.7), namely

$$\psi(\vec{r}_1, \vec{r}_2) = u(r_1, \alpha, \beta)u(r_2, \gamma, \delta)$$
$$+ u(r_1, \gamma, \delta)u(r_2, \alpha, \beta) . \qquad (4.2)$$

On account of the fact that

$$\lim_{\beta \to \alpha} u(r, \alpha, \beta) = e^{-\alpha r} , \qquad (4.3)$$

Eq. (4.2) may be regarded as including Eq. (1.7) as a special case for which $\beta \to \alpha$, $\delta \to \gamma$. However, the general capacity for all four nonlinear parameters α, β, γ, δ to be unequal has been the subject of prior analysis,[8] and proves to be important.

Once again, all distances are multiplied by

variational parameters, so that the fully optimized result should obey the virial relation.[15]

V. NUMERICAL PROCEDURE AND RESULTS

The variational energy

$$\epsilon_{var} = \int \psi H(\lambda) \psi \, d\vec{r}_1 \, d\vec{r}_2 \Big/ \int \psi^2 \, d\vec{r}_1 \, d\vec{r}_2 , \qquad (5.1)$$

for both trial functions (3.1) and (4.2), contains only terms that may be generated from the basic integral

$$I(a, b, c) = \int (e^{-ar_1}/r_1)(e^{-br_{12}}/r_{12})(e^{-cr_2}/r_2) d\vec{r}_1 \, d\vec{r}_2 ,$$

$$= 16\pi^2 \left(-\frac{a}{(b^2 - a^2)(c^2 - a^2)} - \frac{b}{(a^2 - b^2)(c^2 - b^2)} \right.$$

$$\left. - \frac{c}{(a^2 - c^2)(b^2 - c^2)} \right) \qquad (5.2)$$

by applying suitable differentiations and limits. As a result, ϵ_{var} is a rational combination of λ, and the variational parameters contained in ψ.

For each value of λ selected, ϵ_{var} was minimized directly in a multidimensional parameter space by a pattern-search computer program.[16] Experience has shown[7] that simultaneous local minima often occur at different locations in the parameter space. However, we have had no difficulty in identifying that minimum which corresponds to the physical solution of interest, since the wave function reduction in the $\lambda = 0$ limit is known.

In order to improve the convergence rate for the minimization in the case of the Bonham-Kohl wave function, α was treated as a common scale factor which could easily be removed from the computation so as to assure compliance with the virial theorem.[15] Furthermore, it was possible to minimize ϵ_{var} with respect to k by solving a quartic polynomial[17] in this parameter by standard formulas.[18] Consequently the pattern-search operation for the Bonham-Kohl wave function was carried out only on the two-dimensional space of the reduced parameters β/α and c/α, though with running evaluation of k. By contrast, the full four-dimensional space of parameters α, β, γ, and δ was pattern-searched for the Hulthén orbital (HO) ψ.

Table I provides some energies computed for the two wave functions, for selected values of λ. In both cases the hydride ion is stable against ionization, and further increase carries the energy up into the continuum. The relevant local energy minimum ceases to exist beyond a critical value of the coupling constant λ, which we find to be larger for the Bonham-Kohl (BK) wave function. Our estimates of the critical binding values for λ are the following:

$$\lambda^*(BK) = 1.1517 , \qquad (5.3)$$

$$\lambda^*(HO) = 1.0589 ,$$

and at these binding limits the energies are equal to

$$\epsilon^{(0)}(BK, \lambda^*) = -0.483\,969 , \qquad (5.4)$$

$$\epsilon^{(0)}(HO, \lambda^*) = -0.498\,092 .$$

The respective coupling-constant values at the crossings into the continuum were found to be

$$\lambda_c(BK) = 1.087\,602 , \qquad (5.5)$$

$$\lambda_c(HO) = 1.049\,789 .$$

The computed energy curves versus λ are shown in Fig. 1, for the region around $\lambda = 1$. For comparison, the corresponding curve for the Hylleraas-Eckart-Chandrasekhar (HEC) function (1.7), taken from Ref. 7, has been included in Fig. 1. The curve labeled "exact" is a plot of the function (1.5) as specified in Ref. 5.

Presuming that the "exact" curve lives up to its name, we see that the elaborations of simple wave function (1.7) which are respectively represented by BK and by HO produce opposing errors in λ^* and $\epsilon^{(0)}(\lambda^*)$. Evidently the inclusion of explicit spatial correlation in BK, by permitting the electrons to avoid each other more effectively, reduces the influence of the electron repulsion which eventually must destroy the stable localized state. On the other hand, extra orbital flexibility brought to the

TABLE I. Ground-state energy for the two-electron system, with variable coupling constant λ. The results refer to the Bonham-Kohl (BK) wave function in Eq. (3.1), and the Hulthén-orbital (HO) wave function in Eq. (4.2).

λ	$\epsilon^{(0)}$ (BK)	$\epsilon^{(0)}$ (HO)
0.20	−0.881 163 071	−0.882 222 042
0.40	−0.774 413 359	−0.765 090 652
0.60	−0.679 490 048	−0.667 718 644
0.80	−0.596 410 064	−0.583 516 226
1.00	−0.526 001 995	−0.513 374 025
1.01	−0.522 860 069	−0.510 453 742
1.02	−0.519 759 432	−0.507 630 251
1.03	−0.516 701 307	−0.504 918 990
1.04	−0.513 687 105	−0.502 344 275
1.05	−0.510 718 447	−0.499 952 049
1.06	−0.507 797 207	
1.07	−0.504 925 612	
1.08	−0.502 106 310	
1.09	−0.499 342 550	
1.10	−0.496 638 406	
1.11	−0.493 999 155	
1.12	−0.491 432 015	
1.13	−0.488 947 613	
1.14	−0.486 563 913	
1.15	−0.484 323 976	

problem by Hulthén functions makes it easier to develop an extended tail on the electron density far from the nucleus, which is likely a necessary precursor to the critical binding state at λ^*. It seems probable that a wave function combining Hulthén orbitals with the Bonham-Kohl correlation factor would give an excellent approximation to the λ^* for the exact problem, thought to be about 1.1184. In any further elaborate calculation of the critical binding phenomenon, it is obvious that care must be exercised to include a balance between spatial correlation and orbital flexibility.

Table II lists the variational parameters calculated for the Bonham-Kohl wave function. These results indicate that the rate of change with λ of each of the parameters becomes infinite as λ approaches λ^*(BK), though the parameters themselves remain bounded.

That the correlation-factor exponential decay constant c is small, and declining with λ, confirms the earlier argument that correlation is extremely important. Evidently the spatial range of angular correlation is very large, for even when one electron is moderately far from the nucleus it still polarizes the inner-core electron.

The last column in Table II checks the extent to which electron-electron cusp condition (3.3) is satisfied. Ideally the entries should be all precisely $\frac{1}{2}$. Since they are smaller than $\frac{1}{2}$ it is clear that greater correlation-factor flexibility could be used to good advantage in a more elaborate calculation.

Table III contains the HO parameters. Once again they display diverging rates of change as λ increases to the relevant λ^*(HO), while remaining
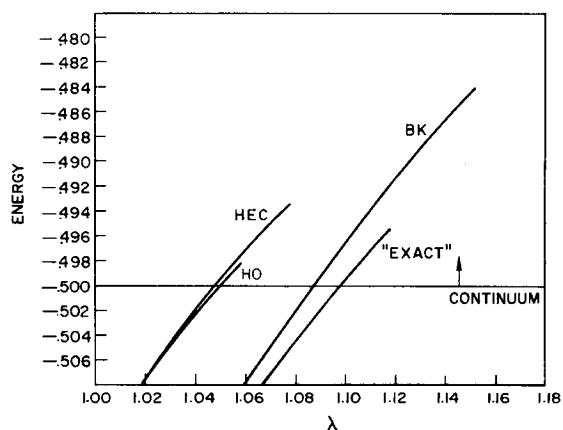

FIG. 1. Energy curves for the two-electron ground state. The "exact" result is a plot of Eq. (1.5), taken from Ref. 5. Curve HEC refers to results from Ref. 7 for the Hylleraas-Eckart-Chandrasekhar function (1.7); curve BK is the energy for wave function (3.1); curve HO refers to wave function (4.2). The energy unit is specified by Eq. (1.1).

TABLE II. Variationally determined parameters for the Bonham-Kohl wave function, Eq. (3.1). The last column gives the electron-electron cusp magnitude, whose exact value is $\frac{1}{2}$.

λ	α	β	k	c	$\dfrac{-kc}{(1+k)\lambda}$
0.20	1.089 14	0.839 42	−0.302 25	0.168 48	0.365
0.40	1.102 59	0.748 61	−0.532 54	0.128 51	0.366
0.60	1.101 65	0.663 99	−0.699 77	0.094 69	0.368
0.80	1.091 58	0.575 12	−0.811 62	0.068 49	0.369
1.00	1.072 08	0.466 29	−0.873 66	0.051 96	0.359
1.01	1.070 72	0.459 60	−0.875 45	0.051 41	0.358
1.02	1.069 32	0.452 71	−0.877 19	0.050 86	0.356
1.03	1.067 84	0.445 57	−0.878 62	0.050 41	0.354
1.04	1.066 30	0.438 16	−0.879 98	0.049 94	0.352
1.05	1.064 68	0.430 44	−0.881 14	0.049 52	0.350
1.06	1.062 98	0.422 37	−0.882 12	0.049 12	0.347
1.07	1.061 16	0.413 86	−0.882 89	0.048 75	0.343
1.08	1.059 23	0.404 87	−0.883 54	0.048 34	0.340
1.09	1.057 15	0.395 24	−0.883 80	0.048 01	0.335
1.10	1.054 89	0.384 88	−0.884 08	0.047 51	0.329
1.11	1.052 39	0.373 49	−0.883 91	0.047 04	0.323
1.12	1.049 57	0.360 68	−0.883 31	0.046 47	0.314
1.13	1.046 27	0.345 72	−0.882 40	0.045 58	0.303
1.14	1.042 09	0.326 80	−0.880 99	0.044 01	0.286
1.15	1.035 10	0.294 88	−0.879 58	0.039 50	0.251
1.151	1.033 62	0.287 97	−0.880 18	0.037 92	0.242
1.1516	1.032 01	0.280 36	−0.882 65	0.035 38	0.231

bounded. The fact that γ, the smallest of the orbital parameters, gets so close to zero at the critical binding limit provides evidence that the exact wave function is likely not exponentially decaying with increasing distance, when $\lambda = \lambda^*$.

Our calculations show that γ and δ are distinct real numbers only when λ exceeds 0.995. At this point they become confluent, and in principle would become complex conjugates upon further reduction in λ:

$$\gamma, \delta = \xi \pm i\zeta. \tag{5.6}$$

TABLE III. Variationally determined parameters for the Hulthén-orbital wave function, Eq. (4.2).

λ	α	β	γ	δ
0.20	0.915 03	1.296 98	0.786 83	0.786 83
0.40	0.844 53	1.412 53	0.661 15	0.661 15
0.60	0.803 63	1.459 86	0.545 28	0.545 28
0.80	0.794 74	1.432 93	0.427 64	0.427 64
1.00	0.843 48	1.284 80	0.246 36	0.329 67
1.01	0.847 27	1.272 75	0.209 79	0.358 77
1.02	0.851 70	1.259 31	0.180 99	0.380 96
1.03	0.856 92	1.244 08	0.154 24	0.402 55
1.04	0.863 44	1.225 91	0.127 18	0.427 07
1.05	0.872 41	1.202 05	0.096 77	0.461 28
1.058	0.886 54	1.166 71	0.059 95	0.522 87
1.0588	0.891 25	1.155 54	0.0518	0.546 34

The corresponding Hulthén orbital would then effectively become

$$e^{-\xi r}\sin(\zeta r)/\zeta r. \tag{5.7}$$

The HO results listed in Tables I and III for λ <0.995, however, were calculated under the restraint that γ and δ be real, i.e., $\zeta = 0$. We believe that the effect of this artificial restraint on the calculated energy is very small, and so its removal would be pointless in the present context. One should note though that in the unrestrained situation, the inherent permutation symmetry of γ and δ will not permit the confluence and drift off the real axis to generate a singularity in $\epsilon^{(0)}(\lambda,\text{HO})$ at $\lambda = 0.995$.

VI. DISCUSSION

(i) The results reported in this paper strongly support the hypothesis that the exact eigenvalue $\epsilon^{(0)}(\lambda)$ penetrates the continuum. Presuming that this has been established for the two-electron ground state, it seems hard to avoid similar occurrences in some excited states, and in atomic and molecular systems with more than two electrons. Some years ago von Neumann and Wigner constructed an example of a potential which for a single particle led to a bound normalizable state in the continuum.[19] At first sight, the connection between their synthetic example and atomic physics might seem remote. However, it now appears that a widespread and general phenomenon may be involved, so a motivation exists to generalize the von Neumann-Wigner method to the widest possible scope.

(ii) The singularity at λ^* for the Hylleraas-Eckart-Chandrasekhar approximation arises from the confluence of the minimum in ϵ_{var} with a neighboring maximum. It is easy to show that this simple event causes the variational parameters to behave (in leading order) as $(\lambda^* - \lambda)^{1/2}$ near λ^*, thereby explaining their divergent rates of change with λ.[7] At the same time $\epsilon^{(0)}(\lambda)$ in that approximation exhibits a singularity of the type $(\lambda^* - \lambda)^{3/2}$. Our present studies show that these same singular behaviors obtain for the more accurate BK and HO wave functions, taking due account of the greater dimensionality of the underlying parameter space.

To extend that former analysis to cover the present more general context, let $a_0, \cdots, a_n$ denote the full set of variational parameters included in a given trial wave function. The variational minimum in the corresponding energy function

$$\epsilon_{\text{var}}(a_0, \cdots, a_n; \lambda), \tag{6.1}$$

is a point in the $(n+1)$-dimensional parameter space at which

$$\frac{\partial \epsilon_{\text{var}}}{\partial a_j} = 0 \quad (j = 0, \ldots, n), \tag{6.2}$$

while the matrix of second derivatives

$$(\underline{M})_{jk} = \frac{\partial^2 \epsilon_{\text{var}}}{\partial a_j \partial a_k} \tag{6.3}$$

is positive definite. Thus ϵ_{var} increases quadratically in leading order along any ray in the space leading away from the position of the minimum.

It is characteristic of the critical binding phenomenon that as λ increases toward λ^* one of the eigenvalues of $\underline{M}$ declines to zero. The principal direction for $\underline{M}$ corresponding to this vanishing eigenvalue is one for which the local quadratic nature of ϵ_{var} degenerates at $\lambda = \lambda^*$ to cubic behavior. In other words, ϵ_{var} becomes anomalously flat along the distinguished direction.

Let $a_0^*, \ldots, a_n^*$ represent the limit as $\lambda \to \lambda^*$ of the set of parameter values which minimize ϵ_{var}. An orthogonal transformation $\underline{T}$, which diagonalizes $\underline{M}$ at $\lambda = \lambda^*$, introduces new coordinates $b_0, \ldots, b_n$ in the parameter space:

$$b_j = \sum_{k=0}^{n} T_{jk}(a_k - a_k^*). \tag{6.4}$$

For convenience we shall suppose that b_0 is the coordinate along which $\epsilon_{\text{var}}(\lambda^*)$ displays cubic variation, so that the local behavior of ϵ_{var} may be represented in terms of the new coordinates thus:

$$\epsilon_{\text{var}}(b_0, \ldots, b_n; \lambda^*) \cong \epsilon_{\text{var}}(0, \ldots, 0; \lambda^*)$$
$$+ B_0 b_0^3 + \sum_{j=1}^{n} A_j b_j^2, \tag{6.5}$$

with suppression of higher-order terms in the b's. Here B_0 and the A_j are suitable nonvanishing coefficients. Expression (6.5) represents the leading portion of a multiple Taylor series which for other purposes might have to include more terms.

When λ differs from λ^*, the multiple Taylor series for ϵ_{var} must be extended to include powers of $\lambda - \lambda^*$. For the present it suffices to expand Eq. (6.6) to the following form:

$$\epsilon_{\text{var}}(b_0, \ldots, b_n; \lambda) \cong \epsilon_{\text{var}}(0, \ldots, 0; \lambda^*) + K(\lambda - \lambda^*)$$
$$+ L(\lambda - \lambda^*)b_0 + B_0 b_0^3 + \sum_{j=1}^{n} A_j b_j^2, \tag{6.6}$$

where K and L are constants. In order to restore the existence of a stable minimum when $\lambda < \lambda^*$, K and L must have the same sign. By setting $\partial \epsilon_{\text{var}}/\partial b_0$ equal to zero, one finds that expression (6.6) is stationary at the two positions

$$b_0 = \pm [L(\lambda^* - \lambda)/3B_0]^{1/2} ,$$

$$b_j = 0 \quad (j > 0) .$$

(6.7)

The upper sign corresponds to the stable minimum, while the lower sign corresponds to a multidimensional "saddle point."

Upon inserting (6.7) into (6.6), we find that the extremal values for the energy depend on λ in the following way:

$$\epsilon^{(0)}(\lambda) = \epsilon_{\text{var}}(0, \ldots, 0; \lambda^*) + L(\lambda - \lambda^*)$$

$$\mp (2L^{3/2}/3^{3/2}B_0^{1/2})(\lambda^* - \lambda)^{3/2} + O((\lambda^* - \lambda)^2) .$$

(6.8)

This explicitly demonstrates the branch-point character of the energy at λ^*, and shows how it arises from the confluence of extremal positions on the variational energy hypersurface.

The coordinate transformation inverse to the one exhibited in Eq. (6.4),

$$a_j = a_j^* + \sum_{k=0}^{n} (\underline{T}^{-1})_{jk} b_k ,$$

(6.9)

would have coefficients $(\underline{T}^{-1})_{j0}$ differing from zero except in accidental (and hence unlikely) circumstances. Therefore on account of the square-root behavior cited for b_0 in Eq. (6.7), each of the original variational parameters $a_0 \ldots a_n$ would normally also include $(\lambda^* - \lambda)^{1/2}$ contributions. This explains their diverging rates of change near λ^*.

(iii) The characteristic parameter and energy fractional-power behaviors near λ^* just adduced relate only to approximate variational calculations in which a finite number of variational parameters occur. However, an exact description of the quantum-mechanical problem can be achieved only in the limit that an infinite number of variational parameters be simultaneously considered. Equation (1.5) raises the possibility that the $\frac{3}{2}$-power branch point, which invariably arises for $\epsilon^{(0)}(\lambda)$ in a finite-parameter basis, should undergo a shift to a somewhat different fractional power.

Such a shift could occur in several ways. One possibility would be a clustering together of more and more ϵ_{var} extrema as the parameter space dimensionality increases. Another might be associated with the existence at λ^* of zero as a limit point for the eigenvalues of an infinite-order matrix $\underline{M}$. For the future, it would be very informative to carry out a systematic series of variational calculations, with increasing numbers of parameters, to investigate trends in the differential geometry of the respective ϵ_{var} hypersurfaces near λ^*.

(iv) Associated with the $\epsilon^{(0)}$ branch point at λ^* must be a branch cut, which conventionally would run along the positive real axis. Analytic continuation of $\epsilon^{(0)}$ around λ^* to the branch cut will lead to complex energies:

$$\epsilon^{(0)}(\lambda) = \epsilon_r \pm i\epsilon_i \quad (\lambda > \lambda^*) ,$$

(6.10)

where the sign of the imaginary part should be positive or negative if the cut is approached respectively from above or below. Since the time-dependent wave function is

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \psi(\vec{r}_1, \vec{r}_2)e^{-i\epsilon^{(0)}t/\hbar} ,$$

(6.11)

the complex energies (6.10) correspond to exponentially growing or decaying states.

Consider the decaying case, for which the imaginary part of $\epsilon^{(0)}$ is negative. The two-electron complex may be regarded as a "radioactive" entity, whose half-life requires and determines a diverging particle current. From this point of view, one would expect the wave function ψ at large distance from the nucleus to show the outward current flow explicitly. The specific asymptotic form for ψ therefore should be

$$\sum_{j=1,2} r_j^{-1} \exp\left\{\frac{\epsilon_i r_j}{k} + i\left[kr_j + \left(\frac{1-\lambda}{k}\right) \ln(kr_j)\right]\right\} .$$

(6.12)

In this expression k is the final momentum of the ejected particle, which is determined by the amount to which ϵ_r exceeds the bottom of the continuum:

$$\tfrac{1}{2}k^2 = \epsilon_r + \tfrac{1}{2} .$$

(6.13)

The logarithmic term in (6.12) represents the standard wave distortion expected for a Coulomb field,[20] in this case due to the nucleus plus remaining electron.

Changing the sign of ϵ_i and k in Eq. (6.12) produces the exponentially growing case, with inwardly converging current.

The point of displaying Eq. (6.12) is to aid in selection of variational functions for future detailed investigation of the critical binding phenomenon. It is desirable that they be able automatically to yield radial current flow upon analytic continuation past λ^*. Furthermore, Eq. (6.12) shows that a self-consistency is required between the quantities ϵ_i and k which appear in the asymptotic part of ψ, and the real and imaginary parts of the corresponding variationally determined energy for that ψ.

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