Bound states in the continuum

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Quantum-mechanical examples have been constructed of local potentials with bound eigenstates embedded in the dense continuum of scattering states. The method employed corrects and extends a procedure invented by von Neumann and Wigner. Cases are cited whereby deformation of the local potential causes the continuum bound state to move downward through the bottom of the continuum, and to connect analytically to a nodeless ground state. A doubly excited model atom is also displayed, with interactions between its two "electrons," having an infinite lifetime (in the Schrödinger equation regime). In the light of these examples, attention is focused on quantitative interpretation of real tunneling phenomena, and on the existence of continuum bound states in atoms and molecules.

I. INTRODUCTION

In 1929, von Neumann and Wigner[1] claimed that the single-particle Schrödinger equation could possess isolated eigenvalues embedded in the continuum of positive energy states. They offered a constructive method, based upon amplitude modulation of a free-particle wave function, leading to a localized (i.e., integrable) eigenfunction and a local potential which produces it. The potential was bounded and could be made to vanish at infinity. Diffractive interference was cited as the reason such localized positive-energy states could exist.

The von Neumann-Wigner states have gained importance recently with the growing suspicion that some atomic and molecular systems might also exhibit bound states in the relevant continua.[2-4] For that reason, we have reexamined the von Neumann-Wigner analysis with a view to exposing those directions in which it could fruitfully be generalized. The results obtained thus far raise interesting questions about the validity of conventional theory for tunneling phenomena, and for certain resonance processes in atomic and molecular spectroscopy.

The original von Neumann-Wigner paper contains a superficial algebraic error which affects its results in a significant way. However, that lapse in no way compromises the cleverness of those authors's underlying strategy. We provide the corrected version in the following Sec. II, for completeness.

Section III demonstrates by concrete example how localized states can be adiabatically manipulated so that their energy drops below the bottom of the continuum. This process can occur formally as the result of continuous change in a parameter in the potential. It is noteworthy that the energy eigenvalue, the potential, and the localized wave function can all be analytic functions of that parameter in the neighborhood of its value corresponding to the crossing.

Several generalizations are examined in Sec. IV. Included are cases involving higher angular momentum, dimensionality differing from three, Coulomb interactions, and external electric fields. In each of these categories, families of localized steady-state solutions to the Schrödinger equation can be constructed, with energies embedded in the continuum.

In order to pave the way for eventual consideration of many-electron systems, we have devised a model involving a doubly excited atomic state. The specific two-electron realization appears in Sec. V. Despite interactions between the "electrons" which one might expect to cause autoionization, the state lives forever (in the Schrödinger description).

We terminate this exploratory paper with discussion of a wide variety of chemical and physical phenomena whose quantitative interpretation may require careful accounting for the possible existence of bound states in the continuum.

II. VON NEUMANN-WIGNER METHOD

Using suitable reduced units, we consider the single-particle wave equation

$$(-\tfrac{1}{2}\nabla^2 + V)\Psi = E\Psi \tag{2.1}$$

to be solved in infinite three-space. We restrict attention initially to potentials V which are bounded, and which are local operators in position representation. Since an equivalent form of (2.1) is

$$V = E + \tfrac{1}{2}[(\nabla^2\Psi)/\Psi], \tag{2.2}$$

it is obvious that nodes of the wave function Ψ must be matched by vanishing of its Laplacian.

The free-particle S wave

$$\Psi_0(\vec{r}) = (\sin kr)/kr \tag{2.3}$$

satisfies Eq. (2.2) with energy eigenvalue

$$E = \tfrac{1}{2}k^2, \tag{2.4}$$

and V identically zero. Although Ψ_0^2 is not integrable, von Neumann and Wigner suggested that it would be possible to generate an integrable wave function by modulating the amplitude of Ψ_0 in an appropriate way. If one writes

$$\Psi(\vec{r}) = \Psi_0(\vec{r})f(r), \tag{2.5}$$

then Ψ^2 integrability only requires that $f(r)$ drop to zero as r^{-p}, $p > \tfrac{1}{2}$, for diverging r.

Substituting expression (2.5) into Eq. (2.2), one obtains

$$V(r) = E - \tfrac{1}{2}k^2 + k(\cot kr)f'(r)/f(r)$$
$$+ \tfrac{1}{2}f''(r)/f(r). \tag{2.6}$$

We note in passing that von Neumann and Wigner erroneously obtained "tan" in place of "cot" for their version of this last equation.[1]

In order that $V(r)$ remain bounded, it is clear from Eq. (2.6) that f'/f must vanish at the poles of $\cot(kr)$, i.e., at the zeros of $\sin(kr)$. This can be achieved by selecting $f(r)$ to be a differentiable function of the variable

$$k \int_0^r \sin^2(kr')\,dr' = \tfrac{1}{2}kr - \tfrac{1}{4}\sin(2kr). \tag{2.7}$$

The specific choice suggested by Ref. 1 is

$$f(r) = \{A^2 + [2kr - \sin(2kr)]^2\}^{-1}, \tag{2.8}$$

where A is an arbitrary nonzero constant. Because $f(r)$ decreases as r^{-2} in the limit $r \to \infty$, it is obvious that Ψ^2 is integrable.

Having made assumption (2.8) about the form of f, one can verify by substitution that the terms containing f in Eq. (2.6) vanish as $r \to \infty$. Therefore $V(r)$ itself will vanish in this limit provided that E continues to be identified with $\tfrac{1}{2}k^2$. The potential then can be readily derived:

$$V(r) = -\frac{64k^2 A^2 \sin^4 kr}{[A^2 + (2kr - \sin 2kr)^2]^2}$$
$$+ \frac{48k^2 \sin^4 kr - 8k^2(2kr - \sin 2kr)\sin 2kr}{A^2 + (2kr - \sin 2kr)^2}. \tag{2.9}$$

Near the origin, the function behaves thusly:

$$V(r) = (80/3A^2 - 64)k^2(kr)^4 + O((kr)^6), \tag{2.10}$$

while its large-r character is[5]

$$V(r) \sim -8k^2(\sin 2kr)/2kr. \tag{2.11}$$

We have established that the local potential (2.9) possesses a bound (that is, normalizable) eigenstate with positive energy $\tfrac{1}{2}k^2$. Unfortunately, the

approach cannot supply any other exact wave functions and their energies for that same potential. But since $V(r)$ vanishes at infinity, scattering states for all energies $E > 0$ will exist with wave functions that could numerically be approximated by standard techniques. The existence of the bound state in this continuum requires a discontinuous increase by π in the S-wave scattering phase shift as the incident energy rises through the fixed value $\tfrac{1}{2}k^2$. In other words, the bound state amounts to an infinitely narrow resonance.[6]

A far wider class of modulating functions f can be considered, such as

$$f(r) = \{A^2 + [2kr - \sin(2kr)]^m\}^{-n},$$
$$m \geq \tfrac{2}{3}, \quad mn > \tfrac{1}{2}, \tag{2.12}$$

for which a corresponding $V(r)$ can be derived. Note, however, that a choice which decays exponentially to zero as $r \to \infty$ is not consistent with vanishing of $V(r)$ in the same limit. It should also be stressed that no $f(r)$ seems to exist, producing a bound state in the continuum, whose $V(r)$ decays more rapidly with increasing r than the type of modulated r^{-1} shown in Eq. (2.11).

III. ANALYTIC CONTINUATION ACROSS THE CONTINUUM EDGE

The eigenvalue for the preceding positive-energy bound state can be moved up or down within the continuum merely by varying k. Equation (2.9) specifies the way in which $V(r)$ must deform to continue supporting its bound state. We shall now see that it is possible analytically to carry such a bound state downward, through the bottom of the continuum, into the negative energy regime.

This feature can easily be demonstrated for the corrected von Neumann-Wigner example. However, it turns out that after the crossing the potential $V(r)$ approaches an infinite-r limit that begins to rise above zero. The continuum edge would of course have to rise as well. Fortunately, we can circumvent this peculiarity by examining instead any of several slightly modified examples for which $V(r \to \infty)$ remains zero after the crossing.

One possible modification consists first in replacing the variable shown in Eq. (2.7) by the equally acceptable choice

$$s(r) = 8k^2 \int_0^r r' \sin^2(kr')\,dr'$$
$$= \tfrac{1}{2}(2kr)^2 - 2kr\sin(2kr) - \cos(2kr) + 1. \tag{3.1}$$

If the modulating factor f is now taken to be a function of s, the poles of $\cot(kr)$ in Eq. (2.6) will continue to be cancelled. For simplicity we use

$$f(r) = [A^2 + s(r)]^{-1}, \tag{3.2}$$

where again A is nominally an arbitrary parameter. Since s rises quadratically with r in the large-r regime, wave-function normalizability is assured. By using expression (3.2) in Eq. (2.6), the potential which produces the bound S state, $\Psi_0 f$, is found to be

$$V(r) = \frac{64k^4r^2\sin^4 kr}{[A^2+s(r)]^2} - \frac{4k^2(\sin^2 kr + 2kr\sin 2kr)}{A^2+s(r)}.$$

(3.3)

This modified potential displays the same asymptotic form shown in Eq. (2.11) for the prior case. However, near the origin

$$V(r) = -(20k^2/A^2)(kr)^2 + O((kr)^4),$$

(3.4)

in place of expression (2.10).

In general, $V(r)$ could be deformed by separate and independent variations in A and k. For present purposes it suffices to consider just a single degree of parametric freedom; so A and k will be varied together in a special way. In particular, we shall set

$$A^2 = a^2 k^4,$$

(3.5)

where a is fixed. It is important that the resulting expressions for Ψ and V, when expanded in power series, contain only even powers of k.

As a result of condition (3.5), the wave function and potential undergo simplification to algebraic forms as k approaches zero:

$$\lim_{k\to 0} k^4 \Psi(r) = (a^2 + 2r^4)^{-1};$$

(3.6)

$$\lim_{k\to 0} V(r) = 4r^2(6r^4 - 5a^2)/(a^2 + 2r^4)^2.$$

(3.7)

Note that in this limit Ψ is uniform in sign; its zeros have all receded to infinity.

As a matter of notational convenience, we use a "coupling parameter" λ to follow the variation:

$$\lambda = \lambda_c + \tfrac{1}{2}k^2 \equiv \lambda_c + E,$$

(3.8)

where λ_c is the (arbitrary) coupling strength at which the continuum edge is encountered. The extension of both $V(r, \lambda)$ and $\Psi(r, \lambda)$ to negative E (or equivalently $\lambda < \lambda_c$), both as real functions, is permitted by occurrence in each of only even powers of k. Writing for this case $(\kappa > 0)$

$$E = -\tfrac{1}{2}\kappa^2, \quad \kappa = \pm ik, \quad \lambda = \lambda_c - \tfrac{1}{2}\kappa^2,$$

(3.9)

the extension of $s(r)$ has the form

$$s(r) = -\tfrac{1}{2}(2\kappa r)^2 + 2\kappa r\sinh(2\kappa r) - \cosh(2\kappa r) + 1.$$

(3.10)

This expression rises exponentially with increasing r at such a rate that the wave function is exponentially damped as follows:

$$\Psi(r, \lambda < \lambda_c) = (\sinh\kappa r)/\kappa r[a^2\kappa^4 + s(r)]$$

$$\sim (2\kappa^2 r^2 e^{\kappa r})^{-1}.$$

(3.11)

The potential becomes

$$V(r, \lambda < \lambda_c) = \frac{64\kappa^4 r^2\sinh^4\kappa r}{[a^2\kappa^4 + s(r)]^2}$$

$$- \frac{4\kappa^2(\sinh^2\kappa r + 2\kappa r\sinh 2\kappa r)}{a^2\kappa^4 + s(r)};$$

(3.12)

somewhat surprisingly, the long-range behavior of V has become Coulombic:

$$V(r, \lambda < \lambda_c) \sim \kappa/r, \quad \kappa > 0.$$

(3.13)

The energy E is trivially analytic in λ at λ_c, by definition. For any r, both $V(r, \lambda)$ and $\Psi(r, \lambda)$ are also analytic in λ at λ_c since they possess power series in $k^2 = -\kappa^2$ that are convergent is some non-vanishing neighborhood of the origin. Note, however, that the convergence is not uniform in r since zeros of the denominator factors

$$a^2 k^4 + s(r, k)$$

(3.14)

in the complex k^2 plane move inward toward the origin as r increases.

The variations of $V(r, \lambda)$ and $\Psi(r, \lambda)$ as λ sweeps through λ_c are illustrated in Figs. 1–5 for $a = 1$. When $\lambda < \lambda_c$, the negative-energy state continues to have a nodeless wave function, as Eq. (3.6) has shown to occur at the continuum edge. Consequently, this state must be the ground state for the given potential $V(r, \lambda)$ when $\lambda < \lambda_c$.[7] The continuation effected by increasing λ beyond λ_c causes the state to lose this distinction as it rises above an infinite number of continuum states. It is interesting that this situation superficially might appear to violate the "noncrossing rule" for energy levels of the same symmetry type,[8] but in fact this rule is
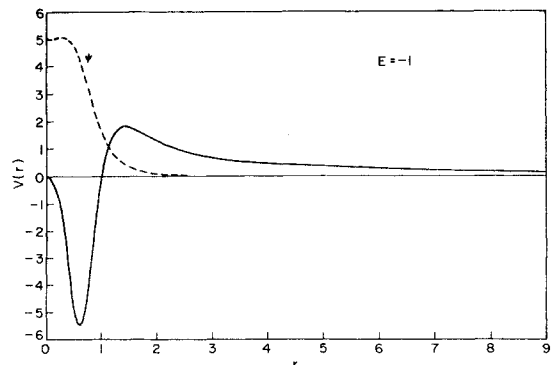

FIG. 1. Potential-energy function constructed in Sec. III. The specific form shown follows from Eq. (3.12) upon setting $a = 1$ and $\kappa = 2^{1/2}$. The wave function Ψ (dashed line) has energy -1 and is the nodeless ground-state function.
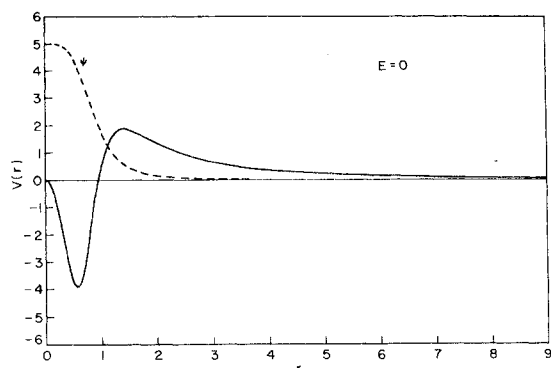
FIG. 2. Potential (3.7), with $a=1$. The nodeless ground-state wave function Ψ is the dashed curve; it has moved up to zero energy (the continuum edge).

FIG. 4. Potential-energy function from Sec. III for energy 1.

not applicable where dense continua are involved.

With the present example, eigenvalue E is unlimited both above and below. The continuation process can carry E to infinity in either direction. For very large negative E, the potential develops a deep single minimum, while for large positive E it is rapidly oscillating. Figure 5 shows that E can rise above the maximum of V; so even classical mechanics would not permit trapping of the particle in the neighborhood of the origin.

The ascent of ground-state energy E for increasing λ, eventually through the continuum edge, is analogous to the behavior that appears to apply to the two-electron isoelectronic sequence. The reduced Hamiltonian for this sequence is

$$H(\lambda) = -\tfrac{1}{2}(\nabla_1^2 + \nabla_2^2) - 1/r - 1/r_2 + \lambda/r_{12}, \qquad (3.15)$$

where λ represents the inverse of the atomic number. Numerical study[2,9] of this physically important system suggests that its ground-state energy penetrates the $(1s)(ks)$ continuum (at reduced energy $-\tfrac{1}{2}$) when λ increases through

$$\lambda_c = 1.0975. \qquad (3.16)$$

IV. SOME EXTENSIONS

A. Higher angular momentum

The non-normalizable free-particle state with total-angular-momentum quantum number l,

$$\Psi_0^{(l)}(\vec{r}) = j_l(kr)Y_{lm}(\theta, \varphi), \qquad (4.1)$$

has energy $E = \tfrac{1}{2}k^2$. It may be converted to a localized normalizable state with a suitable radial modulating function f_l:

$$\Psi^{(l)}(\vec{r}) = f_l(r)j_l(kr)Y_{lm}(\theta, \varphi). \qquad (4.2)$$

One must still require that f_l drop to zero as r^{-p}, $p > \tfrac{1}{2}$, in the limit $r \to \infty$.

This new class of states may be supported by central potentials. The analog of Eq. (2.6) is

$$V(r) = E - \tfrac{1}{2}k^2 + \left(\frac{k j_l'(kr)}{j_l(kr)} + \frac{1}{r}\right)\frac{f_l'(r)}{f_l(r)} + \frac{f_l''(r)}{2f_l(r)}. \qquad (4.3)$$

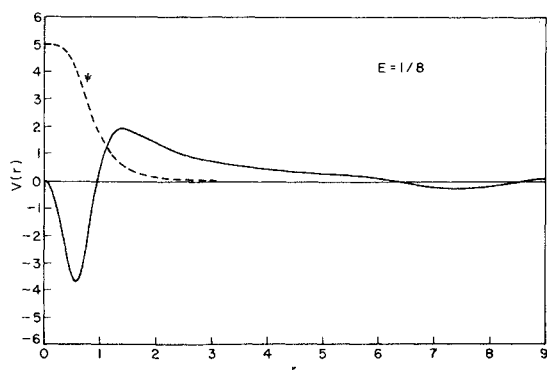To keep $V(r)$ bounded it is obvious that f_l'/f_l must

FIG. 3. Potential-energy function (Sec. III) for energy $\tfrac{1}{8}$. Equations (3.1), (3.3), and (3.5) provide the functional form, with $a=1$ and $k=\tfrac{1}{2}$.
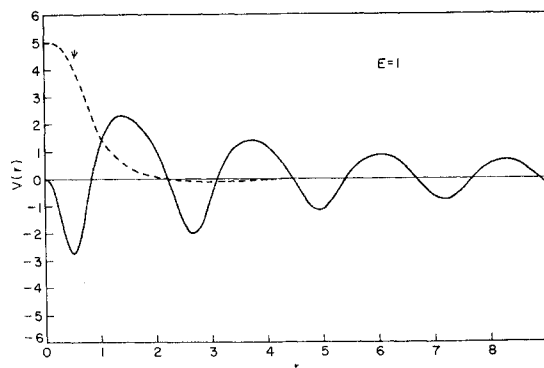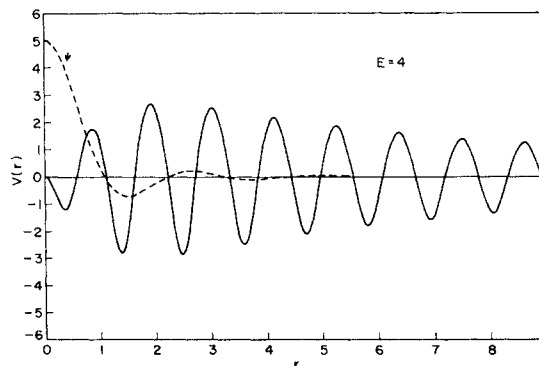

FIG. 5. Potential-energy function from Sec. III for energy 4. This energy exceeds the maximum value ≈ 2.7 for the potential, so the particle could not be trapped by classical mechanics.

vanish when $j_l(kr)$ does. This can be accomplished with

$$f_l(r) = [A^2 + s_l(r)]^{-1},$$ (4.4)

where

$$s_l(r) = k \int_0^r (kr')^{2l+3} j_l^2(kr') \, dr'$$

$$= \frac{(kr)^{2l+4}}{4(l+1)} [j_l^2(kr) + j_{l+1}^2(kr)].$$ (4.5)

This quantity always rises fast enough with increasing r to render Ψ^2 integrable.

The central potential $V(r)$ implied by Eqs. (4.3) and (4.4), subject to vanishing at infinity, may be easily computed:

$$V(r) = k^2 \left(\frac{(kr)^{4l+6} j_l^4(kr)}{[A^2 + s_l(r)]^2} \right.$$

$$\left. - \frac{2(kr)^{2l+3} j_l(kr) j_l'(kr) + (l + \frac{5}{2})(kr)^{2l+2} j_l^2(kr)}{A^2 + s_l(r)} \right).$$

(4.6)

Its long-range behavior follows the previously established pattern:

$$V(r) \sim (-1)^{l+1} 8(l+1) k^2 [(\sin 2kr)/2kr].$$ (4.7)

No new difficulties arise in causing these states to continue analytically across the continuum edge at $E = 0$.

B. Variable dimensionality

The ground state of the helium isoelectronic sequence has recently been studied for variable dimensionality.[10] In this generalization the Hamiltonian (3.15) continued formally to apply, but the arbitrary number D of spatial dimensions for each particle required that the Laplacian have the obvious form (for particle j)

$$\nabla_j^2 = \sum_{\alpha=1}^D \frac{\partial^2}{\partial x_{j\alpha}^2}.$$ (4.8)

An important part of that study concerned the con-

tinuing penetration of the continuum, for some $D \neq 3$, when λ became sufficiently large. We now outline construction of model states in the D-dimensional continuum, along the lines of the preceding sections.

The D-dimensional free-particle state Ψ_0 with energy $\frac{1}{2} k^2$ satisfies the equation

$$(\nabla^2 + k^2) \Psi_0(\vec{r}) = 0.$$ (4.9)

The solution corresponding to no angular momentum is

$$\Psi_0(\vec{r}) = (kr)^{-\nu} J_\nu(kr), \quad \nu = \frac{1}{2}(D - 2),$$ (4.10)

where we have used standard notation for the Bessel function. Ψ_0 is not normalizable, of course, but can be made so by amplitude modulation:

$$\Psi(\vec{r}) = \Psi_0(\vec{r}) f(r, D).$$ (4.11)

It must still be required that

$$f(r, D) \sim \text{const} \times r^{-p} \quad (p > \frac{1}{2}),$$ (4.12)

for arbitrary D.

The potential-energy expression for the present case is

$$V(r, D) = E - \frac{1}{2} k^2 + \left(\frac{(2\nu + 1) J_\nu(kr) - 2kr J_{\nu+1}(kr)}{2r J_\nu(kr)} \right)$$

$$\times \frac{f'(r, D)}{f(r, D)} + \frac{1}{2} \frac{f''(r, D)}{f(r, D)}.$$ (4.13)

Choose

$$f(r, D) = [A^2 + s(r, D)]^{-1},$$ (4.14)

where

$$s(r, D) = k \int_0^r (kr')^{2\nu+1} [J_\nu(kr')]^2 \, dr'$$

$$= \frac{(kr)^{2\nu+2}}{2(2\nu+1)} \{ [J_\nu(kr)]^2 + [J_{\nu+1}(kr)]^2 \}.$$

(4.15)

The requirement of normalizability demands that $D > \frac{2}{3}$. One calculates the potential corresponding to expressions (4.14) and (4.15) to be

$$V(r, D) = k^2 \left(\frac{2(kr)^{2\nu+1} J_\nu(kr) J_{\nu+1}(kr) - (3\nu+1)(kr)^{2\nu} [J_\nu(kr)]^2}{A^2 + s(r, D)} + \frac{(kr)^{4\nu+2} [J_\nu(kr)]^4}{[A^2 + s(r, D)]^2} \right).$$ (4.16)

This result leads to asymptotic behavior similar to the preceding cases:

$$V(r, D) \sim [4(D - 1) k^2 / 2kr] \sin[2kr - \frac{1}{2}(D - 1)\pi].$$

(4.17)

Once again these positive-energy bound states can by analytically continued downward across $E = 0$, provided A^2 varies properly with k.

It is no coincidence that the variable-D generalization resembles the preceding variable-l case. The radial wave equation encompassing both cases is invariant to replacement of l, D by $l + \delta, D - 2\delta$ for any δ.[10]

C. Coulomb interactions

The pattern of wave-function nodes displayed by each of the continuum bound states constructed

thus far has been the same as the pattern in the initial free-particle Ψ_0. However, a displaced pattern of nodes can also appear in the final bound state provided they were initially present as such. For this purpose one is obliged to replace the free-particle Ψ_0 with an analogous continuum state in the presence of a stationary force center. We now examine the case of a repulsive Coulombic force center.

The unbound Coulomb wave function satisfies the equation $(Z \geq 0)$

$$(\nabla^2 - 2Z/r + k^2)\Psi_0(\vec{r}) = 0. \qquad (4.18)$$

The solution in three dimensions, with vanishing angular momentum, which is regular at the origin has the form[11]

$$\Psi_0(\vec{r}) = \varphi_0(r)/r,$$
$$\varphi_0(r) = C_0(\eta)\rho e^{-i\rho}M(1 - i\eta, 2, 2i\rho),$$
$$C_0(\eta) = e^{-\pi\eta/2}|\Gamma(1 + i\eta)|, \qquad (4.19)$$
$$\rho = kr, \quad \eta = Z/k, \quad E = \tfrac{1}{2}k^2,$$

where $M(a, b, z)$ is Kummer's function. In the form shown, Ψ_0 is real; however, it is not normalizable.

Following the usual procedure, we utilize an amplitude-modulating factor f to induce normalizability,

$$f(r) = [A^2 + s(r)]^{-1}; \qquad (4.20)$$

$$s(r) = k \int_0^r (kr')^q [\varphi_0(r')]^2 dr'. \qquad (4.21)$$

Exponent q will remain arbitrary for the moment, subject only to the requirement

$$q > -\tfrac{1}{2}. \qquad (4.22)$$

The potential for which $\Psi = \Psi_0 f$ is an exact eigenstate will be

$$V(r) = \frac{Z}{r} - \frac{\tfrac{1}{2}qk^2(kr)^{q-1}[\varphi_0(r)]^2 + 2k(kr)^q\varphi_0(r)\varphi_0'(r)}{A^2 + s(r)}$$
$$+ \frac{k^2(kr)^{2q}[\varphi_0(r)]^4}{[A^2 + s(r)]^2}. \qquad (4.23)$$

In the large-r limit, the asymptotic form of φ_0 is well known to be

$$\varphi_0(r) \sim \sin[kr - (Z/k)\ln(2kr) + \sigma_0],$$
$$\sigma_0 = \arg\Gamma(1 + iZ/k). \qquad (4.24)$$

This permits one to conclude that

$$s(r) \sim (kr)^{q+1}/2(q+1), \qquad (4.25)$$

and that

$$V(r) \sim (Z/r)\{1 - [2k(q+1)/Z]$$
$$\times \sin[2kr - (2Z/k)\ln(2kr) + 2\sigma_0]\}. \qquad (4.26)$$

Although the potential possesses an oscillatory component, it can differ from the preceding cases by having only a finite number of zeros for $r > 0$ provided that

$$Z > 2k(q+1). \qquad (4.27)$$

Analytic continuation from positive E to negative E is possible if one first requires A^2 to vary with k in the manner

$$A^2 = a^2 k^{q+3} C_0^2(Z/k), \qquad (4.28)$$

where $a^2 > 0$ is independent of k. This condition plays the same role as that in Eq. (3.5) did earlier for the simpler non-Coulombic case.

Just at the continuum edge $(E = 0)$, it is necessary to appeal to a Bessel-Clifford function expansion[11] of φ_0 to extract the behavior of Ψ and V. One finds

$$\Psi(r, E = 0) \sim \text{const} \times r^{-q-3/4} \exp[-(8Zr)^{1/2}], \qquad (4.29)$$

and V manifests *only* the Coulomb interaction at long range:

$$V(r, E = 0) \sim Z/r. \qquad (4.30)$$

At negative energy, $\Psi(r)$ becomes nodeless and exponentially damped with increasing r. The asymptotic form (4.30) for V continues to hold.

The analysis just provided applies only to the case $Z > 0$, that is, a repulsive Coulombic interaction. The situation for $Z < 0$ is drastically different, for even as the bottom of the continuum is approached from above the wave function will retain an infinite number of nodes. It is doubtful that useful analytic continuation for $Z < 0$ can be produced to connect to bound states below the continuum edge.

D. Constant electric field

Von Neumann and Wigner hinted[1] that localized eigenstates could be constructed for the Schrödinger equation in the presence of a static, uniform electric field. However they did not display explicit results of this kind. We now adapt their method to supply an example.

In the presence *only* of an electric field (i.e., potential linear in displacement along the field) we begin with the corresponding one-dimensional wave equation

$$\left(\frac{d^2}{dx^2} + Fx\right)\Psi_0(x) = 0, \qquad (4.31)$$

where we can assume $F > 0$. The coordinate origin has been chosen to annihilate the constant term. The solution of interest over $-\infty < x < +\infty$ is the Airy function,[12]

$$\Psi_0(x) = A i (-F^{1/3}x). \tag{4.32}$$

The following asymptotic formulas apply:

$$\Psi_0(x) \sim \{2\pi^{1/2}F^{1/12}|x|^{1/4}\}^{-1} \exp\{-\tfrac{2}{3}F^{1/2}|x|^{3/2}\}$$

$$(x \to -\infty); \tag{4.33}$$

and

$$\Psi_0(x) \sim (\pi^{1/2}F^{1/12}x^{1/4})^{-1} \sin(\tfrac{2}{3}F^{1/2}x^{3/2} + \tfrac{1}{4}\pi)$$

$$(x \to +\infty). \tag{4.34}$$

In order to convert Ψ_0 to a normalizable function, we introduce the quantity

$$s(x) = \int_{-\infty}^{x} [\Psi_0(x')]^2 \, dx'. \tag{4.35}$$

Since

$$s(x) \sim (\pi F^{1/6})^{-1} x^{1/2} \tag{4.36}$$

as $x \to +\infty$, it suffices to use the amplitude-modulating factor f for Ψ_0:

$$f(x) = [A^2 + s(x)]^{-1}. \tag{4.37}$$

The model potential-energy function for which $\Psi_0 f$ is an exact eigenfunction can easily be found:

$$V(x) = -\tfrac{1}{2}Fx - \frac{2\Psi_0(x)\Psi_0'(x)}{A^2 + s(x)} + \frac{[\Psi_0(x)]^4}{[A^2 + s(x)]^2}. \tag{4.38}$$

For large negative x only the constant-field term $-\tfrac{1}{2}Fx$ survives in V, but in the large positive x limit

$$V(x) \sim -\tfrac{1}{2}Fx - (F/x)^{1/2} \sin(\tfrac{4}{3}F^{1/2}x^{3/2} + \tfrac{1}{2}\pi). \tag{4.39}$$

The oscillatory component of $V(x)$ is confined largely to the neighborhood of $x = 0$; it suffices to prevent the particle from being permanently removed to $+\infty$ by the constant field.

V. DOUBLY EXCITED ATOM

All of the bound states in the continuum constructed thus far have had wave functions with an infinite number of nodes and associated potentials with comparable oscillatory character. However, these examples have each involved just single particles, and, furthermore, have each reduced to one-dimensional form by virtue of separability. Under these conditions the occurrence of an infinite number of nodes in Ψ may be a general requirement. We shall now demonstrate that this feature is not universal. To do so we introduce a model "two-electron" atom which, with suitable interaction between the electrons, will have a doubly excited state with infinite lifetime (within the Schrödinger description).

Warning should be posted that this doubly excited state may be misleading in regard to the nature of doubly excited states in real atoms. Most, if not all, of the latter should be expected to possess finite lifetimes in the Schrödinger description.[13] The present case nevertheless serves an illustrative purpose in the larger mathematical context of general Schrödinger operator spectra.

The general class of two-particle Hamiltonians of interest includes the one shown earlier in Eq. (3.15) as a special case:

$$H = -\tfrac{1}{2}(\nabla_1^2 + \nabla_2^2) + V(\vec{r}_1, \vec{r}_2). \tag{5.1}$$

If the electrons were attracted only to a fixed nucleus and did not interact with each other,

$$V(\vec{r}_1, \vec{r}_2) \to -1/r_1 - 1/r_2 \equiv V_0(r_1, r_2). \tag{5.2}$$

With V_0 the problem is separable; one solution is the doubly excited $(2s^2)$ ^1S state

$$\Psi_0(r_1, r_2) = (2 - r_1)(2 - r_2)\exp[-\tfrac{1}{2}(r_1 + r_2)], \tag{5.3}$$

for which the energy is

$$E_0 = -\tfrac{1}{4}. \tag{5.4}$$

This state formally lies in the $(1s)(ks)$ continuum beginning at energy $-\tfrac{1}{2}$, but that fact has little significance while the electrons move independently.

To induce interaction between the electrons, Ψ_0 can be modified to include spatial correlation between those electrons. Specifically, we examine the wave-function family

$$\Psi(\vec{r}_1, \vec{r}_2) = \Psi_0(r_1, r_2)C(\vec{r}_1, \vec{r}_2), \tag{5.5}$$

where C represents a positive correlation factor with interchange symmetry,

$$C(\vec{r}_2, \vec{r}_1) = C(\vec{r}_1, \vec{r}_2), \tag{5.6}$$

and with the usual rotational invariance required for S states. The potential to which Ψ belongs as an exact eigenstate will be

$$V = E + \tfrac{1}{4} + (\Psi_0 C)^{-1}(\nabla_1\Psi_0 \cdot \nabla_1 C + \nabla_2\Psi_0 \cdot \nabla_2 C)$$

$$+ (2C)^{-1}(\nabla_1^2 C + \nabla_2^2 C). \tag{5.7}$$

Since Ψ_0 vanishes on the surfaces $r_1 = 2$ and $r_2 = 2$, divergence of V can be avoided there only if $\nabla_1 C$ and $\nabla_2 C$ vanish, respectively, on those surfaces.[14]

For the sake of concreteness we assume

$$C = 1 - \frac{g(2 - r_1)^2(2 - r_2)^2 e^{-br_{12}}}{[a + (2 - r_1)^2][a + (2 - r_2)^2]}, \tag{5.8}$$

where a, $b \geq 0$, and $g < 1$. This correlation factor serves to keep the electrons apart in a fashion qualitatively similar to that for the purely Coulombic problem (3.15). It also renders the present model inherently unseparable.

Straightforward but tedious calculation leads to an explicit expression for V:

$$V = V_0 + \frac{age^{-br_{12}}}{C(\vec{r}_1,\vec{r}_2)w(r_1)w(r_2)}\left(-\frac{(5-r_1)(2-r_2)^2}{w(r_1)} - \frac{(2-r_1)^2(5-r_2)}{w(r_2)}\right)$$

$$+ \frac{g(2-r_1)(2-r_2)e^{-br_{12}}}{C(\vec{r}_1,\vec{r}_2)w(r_1)w(r_2)}\left[-\tfrac{1}{2}b(2-r_2)\left(4-r_1+\frac{4a}{w(r_1)}\right)\vec{u}_1\cdot\vec{u}_{21} - \tfrac{1}{2}b(2-r_1)\left(4-r_2+\frac{4a}{w(r_2)}\right)\vec{u}_2\cdot\vec{u}_{12}\right.$$

$$\left.+ \frac{2a(2-r_2)}{r_1 w(r_1)} + \frac{2a(2-r_1)}{r_2 w(r_2)} + (2-r_1)(2-r_2)\left(-b^2 + \frac{4a}{w^2(r_1)} + \frac{4a}{w^2(r_2)} + \frac{2b}{r_{12}}\right)\right].$$

$$(5.9)$$

Here we have introduced the abbreviations

$$w(r_i) = a + (2-r_i)^2,$$

$$\vec{u}_i = \vec{r}_i/r_i,$$

$$\vec{u}_{ij} = (\vec{r}_j - \vec{r}_i)/|\vec{r}_j - \vec{r}_i|.$$

$$(5.10)$$

The energy E remains equal to $-\tfrac{1}{4}$ as V replaces V_0. In the event that one of the electrons, say electron 2, recedes to infinity, V reduces to the nuclear attraction for the remaining electron:

$$\lim_{r_2 \to \infty} V(\vec{r}_1,\vec{r}_2) = -1/r_1.$$

$$(5.11)$$

If both electrons recede from the nucleus, but at fixed interelectron separation, those electrons experience a nontrivial central interaction:

$$\lim_{r_1,r_2 \to \infty} V(\vec{r}_1,\vec{r}_2) = \frac{gb(2/r_{12}-b)e^{-br_{12}}}{1 - ge^{-br_{12}}}.$$

$$(5.12)$$

On account of the interelectron coupling present in V, it is kinematically possible for autoionization to occur. However, it does not; the perturbed doubly excited state lives forever. The significant point to notice is that Ψ has only the two nodal surfaces that occur in Ψ_0, not an infinite number. Furthermore, no characteristic energy shows up as an oscillatory-component wavelength in either Ψ or V. Apparently, nonseparability in multiple-particle systems permits bound states to exist in the relevant continua for reasons somewhat different from the simple diffractive interference applicable to the elementary examples in Secs. II–IV. It must be these less obvious considerations to which one must appeal in arguing for the existence of continuum bound states for realistic atomic and molecular Hamiltonians, such as $H(\lambda)$ in Eq. (3.15).

VI. DISCUSSION

Quantum-mechanical tunneling appears in a wide variety of physical phenomena. Cold emission of electrons from metals, under the influence of strong electric fields, supplies a prominent example whose explanation has often been based on the venerable Fowler-Nordheim formula.[15] Alpha decay rates of radioactive nuclei are also controlled by tunneling.[16] In addition, it has been proposed[17] that some cases of molecular predissociation require tunneling. Finally, tunneling through films between adjacent solid phases ("tunnel junctions") has become an important research tool and a source of solid-state electronic devices.[18-20]

The examples of continuum bound states constructed in this paper should sound a warning against quantitative over-interpretation of the cited tunneling phenomena. These modelistic examples each have characteristics for which orthodox opinion (and the WKB approximation) would predict finite transition rates for tunneling into the continuum. Yet their lifetimes are infinite. If a given physical system were to possess a potential close (in some suitable sense) to the subspace of potentials with continuum bound states, then its tunneling rate would be anomalously small. Uncritical use of the WKB approximation in such an instance would mislead one with respect to barrier height or width.

A similar situation obtains in understanding autoionizing states and resonances for atoms and molecules. The usual theoretical methods for describing these states are ill suited to identification of infinite-lifetime positive-energy bound states; included among the methods are the "stabilization method" devised by Taylor,[21] Feshbach's projection-operator technique,[22] and the close-coupling approach.[23] It would be interesting to see numerically how each would come to grips with the model doubly excited state offered here in Sec. V. More to the point, there may exist real atomic and molecular states (specifically for doubly charged anions[24]) in the continuum with infinite lifetimes in the Schrödinger description. Exceptional computational care would have to be exercised to avoid assigning spurious widths to these states.

On account of the requirements of wavelength matching of oscillatory components in Ψ and V, for those examples which are separable (Secs. II–IV), an arbitrary small change in V would, with probability one, destroy the continuum bound

state. Only if the variation in the potential (a) maintained a long-range oscillatory character in V and (b) were consistent with an eigenvalue whose associated wave-vector magnitude k appeared in V would it then be possible to retain the continuum bound state. In this sense, positive-energy bound states are an unstable feature of separable Hamiltonians. However, the situation may well be different for *nonseparable* problems, as indeed real atoms and molecules are with two or more electrons. The doubly excited "atom" provided in Sec. V clearly shows the irrelevance of oscillatory-component wavelength matching. Thus positive-energy bound states in atoms and molecules may not be zero-probability occurrences at all, but physically realizable phenomena.[2-4] It seems obvious that serious effort should be devoted to developing more realistic atomic and molecular models with bound states in the continuum.

Finally, we remark that conditions on potentials have been identified which eliminate the possibility of bound states in the continuum.[25] However, they do not include the cases of interest in real atomic and molecular systems.

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