Theory of the ionization of the hydrogen atom by an external electrostatic field*

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The theory of the field ionization of the hydrogen atom is developed analytically. The leading term of an asymptotic expansion for the ionization rate—the reciprocal lifetime—is derived. In the weak-field limit, the formula for the ionization rate reduces to $1/\tau = n^{-3}[n_2!\,(n_2+|m|)!\,]^{-1}\,(n^3F/4)^{-2n_2-|m|-1}\times \exp[3(n_1-n_2)-2/(3n^3F)]$, where n, m, and n_1 and n_2 are the usual principal, magnetic, and parabolic quantum numbers, respectively, and F is the field strength in atomic units. For the ground state, this formula agrees with that of Landau and Lifshitz. For all $m^2=1$ states, the formula agrees asymptotically for large n_2 with that of Lanczos after correction of the latter for an error. It is in disagreement with the result of Oppenheimer and with the low-field result of Rice and Good. Significantly better agreement with numerical calculations of Alexander, of Hehenberger, McIntosh, and Brändas, of Damburg and Kolosov, and of Bailey, Hiskes, and Riviere is obtained with a formula for not quite such small F, $1/\tau = (-2\mathrm{Re}E)^{3/2}[n_2!\,(n_2+|m|)!\,]^{-1}f^{-B}\exp[-1/(6f)]$, where E is the perturbed energy, where $f=[(-2E)^{-3/2}F]/4$, and where $B/2=\beta_{2,n_2}$ is the usual perturbed separation constant $[\beta_2 \to n_2+|m|/2+1/2$, as $F\to 0]$.

I. INTRODUCTION

In a uniform external electrostatic field, the energy levels of atomic hydrogen shift and broaden. The potential in the direction of the anode tends toward $-\infty$, and an electron initially localized near the proton will eventually tunnel through the "barrier" created by the field, and will ionize. There are no true bound states, and the usual Rayleigh-Schrödinger perturbation expansion for the energy[1-6] is an asymptotic expansion for the real part of a pole of the Green's function associated with the perturbed Hamiltonian.[7] The imaginary part gives the reciprocal lifetime of the state.

The theory of the field ionization of hydrogen was first discussed by Oppenheimer,[8] who gave a "golden rule"-type formula for the ionization rate. Lanczos,[9-11] and later, others[12-14] gave a JWKB treatment. More recent theoretical work[15-27] has focused on obtaining to high accuracy, often by numerical methods, the field dependence of the perturbed levels, their widths, and the intensities of the perturbed spectral lines.

The purpose of this paper is to clarify analytically the behavior of hydrogen in the Stark effect. A primary goal is to derive a simple formula for the width at low field strength [Eq. (125)].

The treatment here builds on the theory developed in an earlier paper[28] (hereafter referred to as Paper I) in which (a) the connection of the perturbed real energy levels and ionization rates with the complex energy eigenvalues associated with purely outgoing-wave eigenfunctions was demonstrated via the evolution operator, (b) the problem of calculating the complex energy eigenvalues was developed formally by the techniques of Kapur and Peierls[29] and Bloch;[30] (c) the nature of the Rayleigh-Schrodinger perturbation series as an asymptotic expansion came out in a simple way, and (d) a perturbation theoretic formula for the half-width was derived, which we shall exploit in this paper,

$$\mathrm{Im}E = -g_i(E_{\mathrm{RS}})\Phi_{\mathrm{RS}}(a)^2 \Big/ \int_0^\infty \Phi_{\mathrm{RS}}(x)^2\,dx\,. \qquad (1)$$

Here E_{RS} and Φ_{RS} denote the energy and wave function in Rayleigh-Schrödinger perturbation theory, and $g_i(E_{\mathrm{RS}})$ is the imaginary part of the logarithmic derivative of the outgoing-wave eigenfunction, evaluated at a suitably chosen point a.

In some respects, the hydrogenic problem is more difficult than the one-dimensional finite-range potential problem of paper I.[28] Since the Coulomb field has no cutoff, there is no natural radius a for the atomic potential, nor is the exact wave function known far away from the origin for calculating $g_i(E)$. A less troublesome difference is the higher dimensionality of the hydrogenic problem. These differences must be dealt with before the results of paper I can be applied to hydrogen (Secs. II, III, and V).

In one respect, the specific hydrogenic problem is simpler than the arbitrary general problem in that the solutions of the field-free Schrödinger equation are well known and well characterized. Consequently, it is possible to solve the complex

eigenvalue problem by the elementary "matching method" in the small-field limit (Sec. IV).

In Sec. VI we briefly consider another approach to the complex eigenvalue problem that was suggested to us by Breit's[31] treatment of nuclear disintegration. Rather than divide coordinate space into two distinct regions as in I, we partition (in a loose sense) function space and the Schrödinger equation into two parts, one of which carries the outgoing-wave boundary condition, the other of which carries the behavior near the nucleus. One then solves for the "outer" function in terms of the "inner" function using a Green's function, in order to obtain an effective Schrödinger equation for the "inner" function.

In Sec. VII we compare our formula with those of Oppenheimer,[8] Lanczos,[11] Rice and Good,[12] and Landau and Lisfshitz.[32] It would seem that the field ionization of hydrogen is unsuspectedly insidious, having left a legacy of errors.

In Sec. VIII we give a numerical comparison of our results with ionization rates calculated by other methods.[13,16,19,25]

II. SCHRODINGER EQUATION FOR THE HYDROGEN ATOM IN A UNIFORM FIELD, IN PARABOLIC COORDINATES

In this section we set down the basic equations to be solved and establish notation.

The Schrödinger equation for the hydrogen atom in a uniform electrostatic field separates in parabolic coordinates, as was exploited by Schrödinger[1]:

$$x=(\xi\eta)^{1/2}\cos\phi\,, \tag{2}$$

$$y=(\xi\eta)^{1/2}\sin\phi\,, \tag{3}$$

$$z=\tfrac{1}{2}(\xi-\eta)\,, \tag{4}$$

$$\left(-\frac{\nabla^2}{2}-\frac{1}{r}+Fz-E\right)\psi=0 \tag{5}$$

$$=\left\{-\left[\frac{4}{\xi+\eta}\left(\frac{\partial}{\partial\xi}\xi\frac{\partial}{\partial\xi}+\frac{\partial}{\partial\eta}\eta\frac{\partial}{\partial\eta}\right)+\frac{1}{\xi\eta}\frac{\partial^2}{\partial\phi^2}\right]-\frac{2}{\xi+\eta}+\tfrac{1}{2}F(\xi-\eta)-E\right\}\psi\,, \tag{6}$$

$$\psi=(\xi\eta)^{-1/2}\Phi_1(\xi)\Phi_2(\eta)e^{im\phi}\,, \tag{7}$$

$$\left[-\xi\left(\frac{d}{d\xi}\right)^2+\frac{m^2-1}{4\xi}+\tfrac{1}{4}F\xi^2-\tfrac{1}{2}\xi E-Z_1\right]\Phi_1(\xi)=0\,, \tag{8}$$

$$\left[-\eta\left(\frac{d}{d\eta}\right)^2+\frac{m^2-1}{4\eta}-\tfrac{1}{4}F\eta^2-\tfrac{1}{2}\eta E-Z_2\right]\Phi_2(\eta)=0\,. \tag{9}$$

Z_1 and Z_2 denote separation constants whose sum is unity,

$$Z_1+Z_2=1\,. \tag{10}$$

Throughout this paper we use atomic units, the unit of length being the Bohr radius a_0, and the unit of energy being e^2/a_0. At the origin, Φ_1 and Φ_2 satisfy the boundary conditions

$$\Phi_1(\xi)=O(\xi^{(|m|+1)/2})\,, \tag{11}$$

$$\Phi_2(\eta)=O(\eta^{(|m|+1)/2})\,, \tag{12}$$

while at infinity, both functions must vanish.

When the electric field vanishes, both the ξ and η equations have a partially discrete eigenvalue spectrum for Z_1 and Z_2, characterized by three integers: the parabolic quantum numbers n_1 and n_2, and the magnetic quantum number m. The eigenvalues Z_1 and Z_2, and the energy E are given by the formulas

$$Z_1=(n_1+\tfrac{1}{2}|m|+\tfrac{1}{2})(-2E)^{1/2}\quad(n_1=0,1,2,\ldots)\,, \tag{13}$$

$$Z_2=(n_2+\tfrac{1}{2}|m|+\tfrac{1}{2})(-2E)^{1/2}\quad(n_2=0,1,2,\ldots)\,, \tag{14}$$

$$E=-\tfrac{1}{2}(n_1+n_2+|m|+1)^{-2} \tag{15}$$

$$=-\tfrac{1}{2}n^{-2}\quad(n=n_1+n_2+|m|+1)\,, \tag{16}$$

where n is the principal quantum number.

When the external electric field does not vanish, the spectrum of the ξ equation becomes entirely discrete, while the spectrum of the η equation becomes entirely continuous. The continuum eigenfunctions, however, are not as useful in describing ionization as the discrete set obtained by replacing the finite boundary condition at infinity by a purely outgoing-wave condition, as developed in paper I. With the outgoing-wave boundary conditions on $\Phi_2(\eta)$, and for arbitrary values of E and F, the spectra of Z_1 and Z_2 are both entirely discrete; the set of values of E for which Z_1+Z_2 is unity is then also discrete.

To simplify the solution of Eqs. (8)–(10), it is customary to make a change of scale:

$$\sigma=\xi(-2E)^{1/2}\,, \tag{17}$$

$$\rho=\eta(-2E)^{1/2}\,, \tag{18}$$

$$\beta_1=Z_1(-2E)^{-1/2}\,, \tag{19}$$

$$\beta_2=Z_2(-2E)^{-1/2}\,, \tag{20}$$

$$f=\tfrac{1}{4}F(-2E)^{-3/2}\,. \tag{21}$$

With these quantitites, solution of the Schrödinger equation is reduced to the solution of

$$\left[-\sigma\left(\frac{d}{d\sigma}\right)^2+\frac{m^2-1}{4\sigma}+f\sigma^2+\tfrac{1}{4}\sigma-\beta_1\right]\Phi_1=0\,, \tag{22}$$

$$\left[-\rho\left(\frac{d}{d\rho}\right)^2+\frac{m^2-1}{4\rho}-f\rho^2+\tfrac{1}{4}\rho-\beta_2\right]\Phi_2=0\,, \quad (23)$$

$$\beta_1+\beta_2=(-2E)^{-1/2}\,. \quad (24)$$

The eigenvalues $\beta_1(f)$ and $\beta_2(f)$ are clearly directly functions of f. The energy E is from Eq. (24), an explicit function of f, but because of Eq. (21), an implicit function of F.

The usual textbook treatment of the Stark effect is to expand β_1 and β_2 in power series in f:

$$\beta_j(f)=\beta_j^{(0)}+f\beta_j^{(1)}+f^2\beta_j^{(2)}+\cdots \quad (j=1,2)\,, \quad (25)$$

$$\beta_j^{(0)}=n_j+\tfrac{1}{2}(|m|+1) \quad (j=1,2)\,, \quad (26)$$

$$\beta_j^{(1)}=(-1)^{j+1}(6n_j^2+6n_j|m|+6n_j+m^2+3|m|+2) \quad (j=1,2)\,, \quad (27)$$

$$\beta_j^{(2)}=-(2n_j+|m|+1)\times[17(2n_j^2+2n_j|m|+2n_j+|m|)+4m^2+18] \quad (j=1,2)\,. \quad (28)$$

In the case of β_2, the usual perturbation series is an asymptotic expansion for the real part of the complex outgoing-wave eigenvalue. The imaginary part of β_2 is $O(e^{-1/6f})$, which vanishes faster than any power of f, and is lost in the Rayleigh-Schrödinger approach.

In the sections to follow we will refer to σ, ρ, and f as if they were real, rather than complex. One could at the end use the appropriate complex value of f; the justification would be by analytic continuation.

III. ASYMPTOTIC REPRESENTATION OF THE WAVE FUNCTION IN THE BARRIER AND EXTERIOR REGIONS

The effective potential for the ρ coordinate has three distinct regions: an interior region in which the effect of the external field is small; a classically forbidden barrier region, bounded by the classical turning points $\rho_i\sim 2\beta_2+(4\beta_2^2-m^2+1)^{1/2}$ and $\rho_0\sim(4f)^{-1}$, between which the potential gradually changes from Coulombic to linear; and an exterior region in which the potential is essentially linear. We shall use "atomic region" to mean the entire interior region plus a little bit of the barrier region—that is, that part of space in which the electron has appreciable probability density in the absence of the external field.

To impose an outgoing-wave boundary condition on the eigenvalue equation (23) for β_2, it is essential to have a representation for the wave function, valid from infinity down to the edge of the atomic region, which is well inside the barrier region. To derive and characterize this asymptotic wave function is the immediate task.

It is the nature of the barrier region that makes the hydrogenic problem more difficult than the case treated in paper I. There the atomic potential ended abruptly at a point a (which one may take as the boundary of the atomic region). The analytic character of the wave function changed abruptly at that point, and outside of the atomic region—both inside the barrier and beyond—the wave function was *exactly* given by Airy functions.

In the hydrogenic case, there is no such boundary point. The wave function must change gradually, not abruptly, from $\rho^{\beta_2}e^{-\rho/2}$ in the atomic region to an Airy function in the exterior region. In further contrast with the nonhydrogenic case, there is no convenient exact solution for the wave function outside of the atomic region.

A uniform asymptotic solution, valid for most of the barrier region, for the neighborhood of the outer turning point ρ_0, and for the exterior region, can be obtained via Langer's generalization of the JWKB method.[33] We begin by rewriting Eq. (23), by putting $\Phi(\rho)$ for $\Phi_2(\eta)$, and by dividing by ρ, to obtain

$$\left(\frac{-d^2}{d\rho^2}-f\rho+\tfrac{1}{4}-\frac{\beta_2}{\rho}+\frac{m^2-1}{4\rho^2}\right)\Phi(\rho)=0\,. \quad (29)$$

Langer's method gives

$$\Phi_L(\rho)=\left(\frac{d(\frac{3}{2}\theta)^{2/3}}{d\rho}\right)^{-1/2}\mathrm{Ai}^{(+)}(-(\tfrac{3}{2}\theta)^{2/3})\,, \quad (30)$$

where $\mathrm{Ai}^{(+)}$ is an outgoing-wave Airy function (defined in paper I),

$$\mathrm{Ai}^{(+)}(-z)\equiv \mathrm{Bi}(-z)+i\,\mathrm{Ai}(-z) \quad (31)$$

$$\sim\pi^{-1/2}z^{-1/4}\exp[i(\tfrac{2}{3}z^{3/2}+\tfrac{1}{4}\pi)]\,, \quad \text{as } z\to\infty\,, \quad (32)$$

$$\sim\pi^{-1/2}(-z)^{-1/4}\{\exp[\tfrac{2}{3}(-z)^{3/2}]+\tfrac{1}{2}i\exp[-\tfrac{2}{3}(-z)^{3/2}]\}\,, \quad \text{as } -z\to\infty\,, \quad (33)$$

and where θ is given by

$$\theta\sim\int_{\rho_0}^{\rho}\left(f\rho-\frac{1}{4}+\frac{\beta_2}{\rho}-\frac{m^2-1}{4\rho^2}\right)^{1/2}d\rho\,, \quad \rho\geq\rho_0\,, \quad (34)$$

$$=e^{3\pi i/2}\int_{\rho}^{\rho_0}\left(\tfrac{1}{4}-f\rho-\frac{\beta_2}{\rho}+\frac{m^2-1}{4\rho^2}\right)^{1/2}d\rho\,, \quad \rho\leq\rho_0\,. \quad (35)$$

In the calculations that follow, the asymptotic function $\Phi_L(\rho)$ plays a key role.

We conclude this section with four remarks characterizing the behavior of θ and Φ_L: (i)

We note first that $\theta^{2/3}$ is analytic at $\rho_0 \sim \frac{1}{4}f$:

$$\theta \sim \tfrac{2}{3} f^{-1}(f\rho - \tfrac{1}{4})^{3/2} \quad (\rho \sim \tfrac{1}{4}f)\,, \tag{36}$$

$$(\tfrac{3}{2}\theta)^{2/3} \sim f^{1/3}(\rho - \tfrac{1}{4}f) \quad (\rho \sim \tfrac{1}{4}f)\,. \tag{37}$$

(ii) For large ρ, we compute θ from Eq. (34),

$$\theta \sim \tfrac{2}{3} f^{-1}(f\rho - \tfrac{1}{4})^{3/2} + \beta_2 \pi\,, \quad \text{as } \rho \to \infty\,, \tag{38}$$

$$\frac{d(\frac{3}{2}\theta)^{2/3}}{d\rho} \sim f^{1/3}\,, \quad \text{as } \rho \to \infty\,, \tag{39}$$

so that [from Eqs. (30) and (32)]

$$\Phi_L(\rho) \sim f^{-1/6} e^{\beta_2 \pi}\, \mathrm{Ai}^{(+)}(f^{-2/3}(\tfrac{1}{4} - f\rho))\,, \quad \text{as } \rho \to \infty\,. \tag{40}$$

This simple Airy function behavior is what one would obtain by dropping the $-\beta_2/\rho$ and $(m^2-1)/4\rho^2$ terms from Eq. (29). (iii) For ρ inside the barrier, $\rho_i \ll \rho \ll \rho_0$, we compute for θ (c.f. Landau and Lifshitz[32]),

$$\theta \sim e^{3\pi i/2}[\tfrac{2}{3} f^{-1}(\tfrac{1}{4} - f\rho)^{3/2} + \beta_2 \ln(f\rho)]\,, \quad \rho_i \ll \rho \ll \rho_0\,, \tag{41}$$

and then for $\Phi_L(\rho)$

$$\begin{aligned}\Phi_L(\rho) &\sim \pi^{-1/2}(\tfrac{1}{4} - f\rho)^{-1/4}\{(f\rho)^{\beta_2} \exp[\tfrac{2}{3} f^{-1}(\tfrac{1}{4} - f\rho)^{3/2}] \\ &\qquad + \tfrac{1}{2} i (f\rho)^{\beta_2} \\ &\qquad \times \exp[-\tfrac{2}{3} f^{-1}(\tfrac{1}{4} - f\rho)]^{3/2}\}\,, \end{aligned} \tag{42}$$

$$\begin{aligned} &\sim (2/\pi)^{1/2}\{(f\rho)^{\beta_2} \exp[(12f)^{-1} - \tfrac{1}{2}\rho + \tfrac{1}{2} f\rho^2] \\ &\qquad + \tfrac{1}{2} i (f\rho)^{-\beta_2} \exp[-(12f)^{-1} + \tfrac{1}{2}\rho - \tfrac{1}{2} f\rho^2]\}, \\ &\qquad \rho_i \ll \rho \ll \rho_0\,. \end{aligned} \tag{43}$$

This last equation is quite revealing in that it displays both the $\rho^{\beta_2} e^{\rho/2}$ term that smoothly connects Φ_L with the field-free hydrogenic solution in the atomic region, and the $\rho^{-\beta_2} e^{\rho/2}$ term, with relative weigth $\frac{1}{2} f^{-2\beta_2} e^{-1/6f}$, that represents the contribution of the field-free solution that is irregular at the origin. (iv) Finally, we note that away from ρ_o, Φ_L is essentially just the JWKB approximation. The JWKB "connection formulas," insofar as they are implicit in Eqs. (32) and (33), come out automatically in Langer's method.

IV. ESTIMATION OF IMβ_2 BY THE MATCHING METHOD

Perhaps the simplest way to evaluate Imβ_2, and then ImE through Eq. (24), would be to find a solution Φ_A of Eq. (29) valid in the atomic region, and then to match the two solutions, Φ_A and Φ_L, at some point inside the barrier. Equation (29) is suceptible to such a treatment when the external field is neglected in the atomic region.

For small enough f, $-f\rho$ is negligible in the atomic region, Reβ_2 is essentially the unperturbed value given by Eq. (26), and we may write

$$\beta_2 \sim \beta_2^{(0)} + i\,\mathrm{Im}\beta_2\,, \tag{44}$$

$$\left(\frac{-d^2}{d\rho^2} + \tfrac{1}{4} + \frac{m^2-1}{4\rho^2} - \frac{\beta_2}{\rho}\right)\Phi_A(\rho) = 0\,. \tag{45}$$

The solution involves the (Kummer) confluent hypergeometric function[34] $M(a,b,z)$:

$$\Phi_A(\rho) = \rho^{|m|/2+1/2} e^{-\rho/2} M(\tfrac{1}{2} + \tfrac{1}{2}|m| - \beta_2, 1 + |m|, \rho)\,. \tag{46}$$

For large enough ρ, M has the asymptotic form

$$\begin{aligned}\frac{M(-\beta_2 + \frac{1}{2} + \frac{1}{2}|m|, 1 + |m|, \rho)}{|m|!} &\sim \frac{\exp[i\pi(-\beta_2 + \frac{1}{2} + \frac{1}{2}|m|)]\rho^{\beta_2 - 1/2 - |m|/2}}{\Gamma(\beta_2 + \frac{1}{2} + \frac{1}{2}|m|)} \\ &\quad + \frac{e^{\rho}\rho^{-\beta_2 - 1/2 - |m|/2}}{\Gamma(-\beta_2 + \frac{1}{2} + \frac{1}{2}|m|)}\,, \end{aligned} \tag{47}$$

and, with Eqs. (26), (44) and (46), and the Γ function, we find that

$$\Phi_A(\rho) \sim \frac{(-1)^{n_2}\rho^{\beta_2} e^{-\rho/2}|m|!}{(n_2 + |m|)!} + \frac{\rho^{-\beta_2} e^{\rho/2}|m|!}{\Gamma(-n_2 - i\,\mathrm{Im}\beta_2)}\,. \tag{48}$$

But from the Γ function reflection formula,[34]

$$1/\Gamma(-n_2 - i\,\mathrm{Im}\beta_2) \sim (-1)^{n_2+1} n_2!\, i\,\mathrm{Im}\beta_2\,, \tag{49}$$

so that

$$\begin{aligned}\Phi_A(\rho) &\sim \frac{(-1)^{n_2}\rho^{\beta_2} e^{-\rho/2}|m|!}{(n_2 + |m|)!} \\ &\quad - i\,\mathrm{Im}\beta_2 (-1)^{n_2}|m|!\, n_2!\, \rho^{-\beta_2} e^{\rho/2}\,. \end{aligned} \tag{50}$$

Comparison of Eq. (50) for $\Phi_A(\rho)$ with the expression (43) for $\Phi_L(\rho)$ immediately gives

$$\mathrm{Im}\beta_2 \sim -\tfrac{1}{2} f^{-2\beta_2} e^{-1/6f}/[n_2!(n_2 + |m|)!] \quad \text{as } f \to 0\,. \tag{51}$$

Considering how smoothly Eq. (51) was obtained, one might digress for a moment and ask whether there is an alternative route to the key Eq. (48) when the differential equation is not so well known. The alternative is quickly exhibited via Green's functions: if $\Phi_1(\rho)$ and $\Phi_2(\rho)$ are the regular and irregular eigenfunctions of the operator $-d^2/d\rho^2 + V(\rho)$, with unit Wronskian,

$$\left(\frac{-d^2}{d\rho^2} + V(\rho)\right)\Phi_j(\rho) = \beta^{(0)}\Phi_j(\rho)\,, \quad j = 1, 2\,, \tag{52}$$

$$\Phi_2(\rho)\Phi_1(\rho)' - \Phi_2(\rho)'\Phi_1(\rho) = 1\,, \tag{53}$$

then the asymptotic solution of

$$\left(\frac{-d^2}{d\rho^2}+V(\rho)-\beta^{(0)}\right)\Phi_A(\rho)=i\,\mathrm{Im}\beta\Phi_A(\rho) \tag{54}$$

is given approximately by

$$\Phi_A(\rho)\sim\Phi_1(\rho)+i\,\mathrm{Im}\beta\,\Phi_2(\rho)\int_0^\infty[\Phi_1(\rho)]^2\,d\rho \quad \text{as } \rho\to\infty. \tag{55}$$

Equation (51) gives the leading term in an expansion for $\mathrm{Im}\beta$, valid as $f\to 0$. We now turn to two different methods capable of improving the estimate, one based on paper I, the second inspired by Breit's treatment of the compound nucleus.[31]

V. EXTENSION OF PAPER I

A. Adaptation

The aim of this section is to adapt the method of paper I to hydrogen. The basic method of paper I is to solve the Schrödinger equation on a finite interval, to which we refer here as the atomic region, with the condition that the logarithmic derivative at the boundary be $g^{(+)}$. In paper I, the atomic potential vanishes identically where $g^{(+)}$ is evaluated, so that $g^{(+)}$ is a known function of the energy. If we assume for the moment that we know $g^{(+)}(\beta_2)$, then, with three minor changes, all of paper I is applicable here, except for those formulas that make use of the explicit functional form of $g^{(+)}$. The three minor changes are: (i) $\hbar^2/2m$ in I becomes 1 here, to account for the difference in kinetic energy operators $[-\rho d^2/d\rho^2$ versus $-(\hbar^2/2m)d^2/dx^2]$; (ii) the volume element here is $\rho^{-1}d\rho$, versus dx; (iii) Bloch's boundary condition operator here should be defined by

$$\mathcal{L}=\rho\delta(\rho-\rho_a)\left(\frac{d}{d\rho}-g^{(+)}(\beta_2)\right). \tag{56}$$

Thus one can solve variationally according to Eq. (50) of I, or by perturbation or other methods according to Secs. 3 and 4 of I, for the Kapur-Peierls eigenvalue $\omega_{n_2}(\beta_2)$, from which the n_2th β_2 eigenvalue, β_{2,n_2} is determined by the consistency requirement

$$\omega_{n_2}(\beta_{2,n_2})=\beta_{2,n_2}. \tag{57}$$

What we shall apply here to hydrogen is the perturbation formula referred to in Sec. I [Eq. (101) of I]:

$$\mathrm{Im}\beta_{2,n_2}\sim-[\mathrm{Im}g^{(+)}(\beta_{2,n_2,\mathrm{RS}})]\frac{\Phi_{n_2,\mathrm{RS}}(\rho_a)^2}{\int_0^\infty\Phi_{n_2,\mathrm{RS}}(\rho)^2\rho^{-1}\,d\rho}. \tag{58}$$

Here $\Phi_{n_2,\mathrm{RS}}$ and $\beta_{2,n_2,\mathrm{RS}}$ denote the ordinary Rayleigh-Schrödinger expansions for the wave function and energy (β_{2,n_2}), and ρ_a denotes the boundary of the atomic region, which is to be a point well inside the barrier $\rho_i\ll\rho_a\ll\rho_o$, whose precise location is not crucial.

In the derivation of the above equation in I, use was made of the explicit functional form of $g^{(+)}$ to show (in the present context) that

$$-\frac{d\omega_{n_2}(\beta_{2,n_2,\mathrm{RS}})}{\partial\beta_{2,n_2,\mathrm{RS}}}\int_0^{\rho_a}\Phi_{n_2,\mathrm{RS}}(\rho)^2\rho^{-1}\,d\rho \sim\int_{\rho_a}^\infty\Phi_{n_2,\mathrm{RS}}(\rho)^2\rho^{-1}\,d\rho. \tag{59}$$

We must obtain the same result here without explicit reference to the functional form of $g^{(+)}$, to justify Eq. (58). We note that $g^{(+)}$ is defined by

$$g^{(+)}(\beta_2)\equiv\frac{\partial\Phi(\rho_a)}{\partial\rho_a}\Phi(\rho_a)^{-1}, \tag{60}$$

and that [Eq. (52) of I]

$$-\frac{\partial\omega_{n_2}(\beta_{2,n_2,\mathrm{RS}})}{\partial\beta_{2,n_2,\mathrm{RS}}}=\frac{\partial g^{(+)}(\beta_{2,n_2,\mathrm{RS}})}{\partial\beta_{2,n_2,\mathrm{RS}}}\frac{\Phi_{n_2,\mathrm{RS}}(\rho_a)^2}{\int_0^{\rho_a}\Phi_{n_2,\mathrm{RS}}(\rho)^2\rho^{-1}\,d\rho}, \tag{61}$$

so that

$$-\frac{\partial\omega_{n_2}(\beta_{2,n_2,\mathrm{RS}})}{\partial\beta_{2,n_2,\mathrm{RS}}}\int_0^{\rho_a}\Phi_{n_2,\mathrm{RS}}(\rho)^2\rho^{-1}\,d\rho =\Phi_{n_2,\mathrm{RS}}(\rho_a)^2\Phi(\rho_a)^{-2}\left(\Phi(\rho_a)\frac{\partial}{\partial\beta_{2,n_2,\mathrm{RS}}}\frac{\partial}{\partial\rho_a}\Phi(\rho_a) -\frac{\partial\Phi(\rho_a)}{\partial\beta_{2,n_2,\mathrm{RS}}}\frac{\partial\Phi(\rho_a)}{\partial\rho_a}\right). \tag{62}$$

But since $\Phi(\rho)$ is an "eigenfunction" for $\rho\geq\rho_a$, we have, integrating by parts,

$$0=\frac{\partial}{\partial\beta_2}\int_{\rho_a}^\infty\rho^{-1}\Phi(\rho)\left(\beta_2+\rho\frac{d^2}{d\rho^2}+f\rho^2-\tfrac{1}{4}\rho -\frac{m^2-1}{4\rho}\right)\Phi(\rho)\,d\rho, \tag{63}$$

$$=\int_{\rho_a}^\infty\Phi(\rho)^2\rho^{-1}\,d\rho+\int_{\rho_a}^\infty\rho^{-1}\Phi(\rho)\left(\beta_2+\rho\frac{d^2}{d\rho^2}+f\rho^2-\tfrac{1}{4}\rho -\frac{(m^2-1)}{4\rho}\right)\frac{\partial\Phi(\rho)}{d\beta_2}\,d\rho, \tag{64}$$

$$=\int_{\rho_a}^\infty\Phi(\rho)^2\rho^{-1}\,d\rho-\Phi(\rho_a)\frac{\partial}{\partial\beta_2}\frac{\partial}{\partial\rho_a}\Phi(\rho_a) +\frac{\partial\Phi(\rho_a)}{\partial\rho_a}\frac{\partial\Phi(\rho_a)}{\partial\beta_2}. \tag{65}$$

If one makes the identification

$$\Phi\sim\Phi_{n_2,\mathrm{RS}}, \tag{66}$$

$$\beta_2\sim\beta_{2,n_2,\mathrm{RS}}, \tag{67}$$

then Eq. (59) is clinched. [Note that from Eq. (40), it would appear here that $\int_{\rho_a}^\infty\Phi(\rho)^2\rho^{-1}\,d\rho$ exists (for

real f) in fact, rather than only in the asymptotic sense discussed in I.]

B. Application

We now develop Eq. (58) in more detail. The $\mathrm{Im}g^{(+)}$ can be obtained asymptotically from Eq. (43),

$$\mathrm{Im}g^{(+)}(\beta_2) \sim \mathrm{Im}(\Phi_L'/\Phi_L) \tag{68}$$

$$\sim \tfrac{1}{2} f^{-2\beta_2} e^{-1/6f} \rho^{-2\beta_2} e^{\rho}[1+O(f)] \qquad (\rho_i \ll \rho \ll \rho_o)\,. \tag{69}$$

For $\Phi_{n,\mathrm{RS}}(\rho)$, we take the zeroth-order approximation—the unperturbed eigenfunction

$$\Phi_{n_2,\mathrm{RS}}(\rho) \sim \Phi_{n_2}^{(0)}(\rho)\,, \tag{70}$$

$$\Phi_{n_2}^{(0)}(\rho) = [n_2!/(n_2+m)!^3]^{1/2} \rho^{|m|/2+1/2} e^{-\rho/2} L_{n_2+|m|}^{|m|}(\rho)\,, \tag{71}$$

$$= \left[\frac{n_2!}{(n_2+|m|)!^3}\right]^{1/2} \rho^{|m|/2+1/2} e^{-\rho/2} \times \left(\frac{d}{d\rho}\right)^{|m|} e^{\rho} \left(\frac{d}{d\rho}\right)^{n_2+|m|} \rho^{n_2+|m|} e^{-\rho}\,, \tag{72}$$

$$= (-1)^{n_2+|m|}[n_2!(n_2+|m|)!]^{-1/2} \times \rho^{n_2+|m|/2+1/2} e^{-\rho/2}[1+O(\rho^{-1})]\,. \tag{73}$$

$L_{n+|m|}^{|m|}$ denotes the usual associated Laguerre polynomial, and $\Phi_{n_2}^{(0)}$ is normalized to unity. With Eq. (69) for $\mathrm{Im}g^{(+)}$, with Eq. (73) for $\Phi_{n,\mathrm{RS}}$, and with Eq. (26) for $\beta_{2,n}$ in the limit $f \to 0$, we obtain from Eq. (58) for small f and large ρ (but not too large: $\rho^{-1} \ll 1$, $\rho \ll \rho_o$):

$$\mathrm{Im}\beta_{2,n_2} \sim \frac{-\frac{1}{2} f^{-B} e^{-1/6f}}{n_2!(n_2+|m|)!}\,, \quad B \equiv 2\beta_{2,n_2}\,, \quad \text{as } f \to 0\,. \tag{74}$$

Equation (74) is the same result as Eq. (51).

C. Higher approximations

To improve on Eq. (74), one must estimate both $\mathrm{Im}g^{(+)}$ and $\Phi_{n_2,\mathrm{RS}}$ more accurately. There is no difficulty with the Rayleigh-Schrödinger expansion, $\Phi_{n_2,\mathrm{RS}}$. On the other hand, a better estimate of $g^{(+)}$ requires a better estimate of θ [Eq. (30)], which is not so easy to obtain. We only indicate how it might be done.

The procedure that seems most tractable[35] is the generalization of Langer's method given by Cherry.[36] Instead of $(\frac{3}{2}\theta)^{2/3}$, we write $\lambda^{2/3}\phi$, so that Eq. (30) has the form

$$\Phi(\rho) = \left(\frac{d\phi}{d\rho}\right)^{-1/2} \mathrm{Ai}^{(+)}(-\lambda^{2/3}\phi)\,. \tag{75}$$

The equation satisfied by ϕ, that makes Φ satisfy Eq. (29), is

$$\phi\phi'^2 = \tfrac{1}{4} - f\rho - \lambda^{-2}\frac{\beta_2}{\rho} + \lambda^{-4}\frac{m^2-1}{4\rho^2} - \tfrac{1}{2}\lambda^{-2}(-\phi')^{1/2}\left(\frac{d}{d\rho}\right)^2(-\phi')^{-1/2}\,, \tag{76}$$

where λ is an order parameter set equal to unity at the end. An expansion in λ^{-2} for ϕ is substituted into Eq. (76), and terms of the same order are equated:

$$\phi = \phi_0 + \lambda^{-2}\phi_1 + \lambda^{-4}\phi_2 + \cdots\,, \tag{77}$$

$$\phi_0\phi_0'^2 = (\tfrac{1}{4} - f\rho)\,, \tag{78}$$

$$\phi_1\phi_0'^2 + 2\phi_0'\phi_0'\phi_1' = -\frac{\beta_2}{\rho} - \tfrac{1}{2}(-\phi_0')^{1/2}\left(\frac{d}{d\rho}\right)^2(-\phi_0')^{-1/2}\,, \tag{79}$$

and so forth.

The resulting system of equations is solved so that ϕ is analytic and has a zero at $\rho = (4f)^{-1}$. The results for ϕ_0 and ϕ_1,

$$\phi_0 = f^{-2/3}(\tfrac{1}{4} - f\rho)\,, \tag{80}$$

$$\phi_1 = \beta_2 f^{1/3}(\tfrac{1}{4} - f\rho)^{-1/2} \ln\left(\frac{1-(1-4f\rho)^{1/2}}{1+(1-4f\rho)^{1/2}}\right)\,, \tag{81}$$

$$\sim \beta_2 f^{1/3}(\tfrac{1}{4} - f\rho)^{-1/2}[\ln f\rho + O(f\rho)] \tag{82}$$

lead to Eq. (43). To obtain $\phi_2, \phi_3, \ldots$ is, unfortunately, rather tedious and shall not be pursued further here.

VI. PARTITIONING TECHNIQUE

In this section we develop a third approach, which we were led to by Breit's[31] treatment of nuclear resonances, and which is also related to Löwdin's[37] partitioning technique. The basic idea is to write $\Phi(\rho)$ as a linear combination of two functions, one of which holds the asymptotic behavior for large ρ, the second of which takes care of the atomic region:

$$\Phi(\rho) = \Phi_{\mathrm{inner}}(\rho) + \Phi_{\mathrm{outer}}(\rho)\,, \tag{83}$$

$$\Phi_{\mathrm{outer}}(\rho) \sim \Phi_L(\rho)\,, \quad \text{as } \rho \to \infty\,. \tag{84}$$

The two functions are required to satisfy two coupled inhomogeneous differential equations, chosen so that the homogeneous version of one is just the unperturbed Schrödinger equation, while the *exact* solution of the homogeneous version of the second is an *asymptotic* solution of the (perturbed) Schrödinger equation:

$$\left(\frac{-\rho d^2}{d\rho^2} + \tfrac{1}{4}\rho + \frac{m^2-1}{4\rho} - \beta_2\right)\Phi_{\mathrm{inner}}(\rho) = V_L\Phi_{\mathrm{outer}}(\rho)\,, \tag{85}$$

$$\left(\frac{-\rho d^2}{d\rho^2} + \tfrac{1}{4}\rho + \frac{m^2-1}{4\rho} - \beta_2 + V_L - f\rho^2\right)\Phi_{\mathrm{outer}}(\rho) = f\rho^2\Phi_{\mathrm{inner}}(\rho)\,. \tag{86}$$

The sum of the two equations is just the original Eq. (29). The choice of V_L will be discussed later. One solves the second Eq. (86) for Φ_{outer} in terms of Φ_{inner} with the aid of an appropriate outgoing-wave Green's operator $\hat{G}^{(+)}$,

$$\Phi_{\text{outer}}(\rho)=\hat{G}^{(+)}f\rho\Phi_{\text{inner}}(\rho)\,, \tag{87}$$

and then puts the result in the first Eq. (85) to obtain an effective eigenvalue equation for Φ_{inner},

$$\left(\frac{-\rho d^2}{d\rho^2}+\tfrac{1}{4}\rho+\frac{m^2-1}{4\rho}-V_L\hat{G}^{(+)}f\rho-\beta_2\right)\Phi_{\text{inner}}=0\,. \tag{88}$$

If one then solves Eq. (88) with an appropriate boundary condition at infinity so that $\hat{G}^{(+)}f\rho\Phi_{\text{inner}}$ exists, then one has solved the Schrödinger equation with an outgoing-wave boundary condition.

In the end, we get the same formula as obtained in the two preceding sections. Along the way, however, we get an incorrect result that sheds some light on an earlier, similarly incorrect treatment in the literature.

A. Formal approximate solution

We anticipate that the ratios of the imaginary part to the real part of $\hat{G}^{(+)}$, β_2, and Φ are of the order of $e^{-1/6f}$, and we break up Eq. (88) accordingly:

$$(H^{(0)}-V_L\,\mathrm{Re}\hat{G}^{(+)}f\rho-\mathrm{Re}\beta_2)\,\mathrm{Re}\Phi_{\text{inner}}\sim 0\,, \tag{89}$$

$$(H^{(0)}-V_L\,\mathrm{Re}\hat{G}^{(+)}f\rho-\mathrm{Re}\beta_2)\,\mathrm{Im}\Phi_{\text{inner}}=(V_L\,\mathrm{Im}\hat{G}^{(+)}f\rho+\mathrm{Im}\beta_2)\,\mathrm{Re}\Phi_{\text{inner}}\,, \tag{90}$$

where

$$H^{(0)}=\frac{-\rho d^2}{d\rho^2}+\frac{\rho}{4}+\frac{m^2-1}{4\rho}\,. \tag{91}$$

We regard $-V_L\,\mathrm{Re}\hat{G}^{(+)}f\rho$ as a perturbation, and take the corresponding zeroth-order equations:

$$(H^{(0)}-\mathrm{Re}\beta_2^{(0)})\,\mathrm{Re}\Phi^{(0)}_{\text{inner}}=0 \tag{92}$$

$$(H^{(0)}-\mathrm{Re}\beta_2^{(0)})\,\mathrm{Im}\Phi^{(0)}_{\text{inner}}=(V_L\,\mathrm{Im}\hat{G}^{(+)}f\rho+\mathrm{Im}\beta_2^{(0)})\,\mathrm{Re}\Phi^{(0)}_{\text{inner}}\,. \tag{93}$$

We multiply Eq. (93) by $\mathrm{Re}\Phi^{(0)}_{\text{inner}}$ [which is clearly just the unperturbed eigenfunction given by Eq. (71)] and integrate, using the fact that $\mathrm{Re}\Phi^{(0)}_{\text{inner}}$ satisfies Eq. (92), to obtain

$$\mathrm{Im}\beta_2^{(0)}=-\int d\rho\,\rho^{-1}\,\mathrm{Re}\Phi^{(0)}_{\text{inner}}\,V_L\,\mathrm{Im}\hat{G}^{(+)}f\rho\,\mathrm{Re}\Phi^{(0)}_{\text{inner}}\,. \tag{94}$$

To simplify $V_L\,\mathrm{Im}\hat{G}^{(+)}f\rho$, we use the Green's function property of $\hat{G}^{(+)}$ [cf. Eqs. (86) and (87)],

$$(H^{(0)}+V_L-f\rho^2-\beta_2)\hat{G}^{(+)}=\rho\,, \tag{95}$$

$$V_L\,\mathrm{Im}\hat{G}^{(+)}f\rho=(f\rho^2+\mathrm{Re}\beta_2-H^{(0)})\,\mathrm{Im}\hat{G}^{(+)}f\rho+\mathrm{Im}\beta_2\,\mathrm{Re}\hat{G}^{(+)}f\rho \tag{96}$$

$$\sim(f\rho^2+\mathrm{Re}\beta_2^{(0)}-H^{(0)})\,\mathrm{Im}\hat{G}^{(+)}f\rho\,, \tag{97}$$

where the omitted term $\mathrm{Im}\beta_2\,\mathrm{Re}\hat{G}^{(+)}f\rho$ is $O(f\,\mathrm{Im}\beta_2)$. According, Eq. (94) becomes, again with the aid of Eq. (92),

$$\mathrm{Im}\beta_2^{(0)}\sim-\int d\rho\,(\mathrm{Re}\Phi^{(0)}_{\text{inner}})f\rho(\mathrm{Im}\hat{G}^{(+)})f\rho(\mathrm{Re}\Phi^{(0)}_{\text{inner}})\,. \tag{98}$$

To proceed further, we must specify V_L and $\hat{G}^{(+)}$.

B. Initial choice for $G^{(+)}$ and V_L

As Φ_{outer} must be asymptotically correct as $\rho\to\infty$, we first try [cf. Eq. (40)]

$$\Phi_{\text{outer}}(\rho)\sim f^{-1/6}\,\mathrm{Ai}^{(+)}(f^{-2/3}(\tfrac{1}{4}-f\rho))\,, \tag{99}$$

$$V_L\equiv\beta_2-(m^2-1)/4\rho,\quad\text{(first attempt)}\,. \tag{100}$$

That is, we choose V_L so that the homogeneous part of Eq. (86) is essentially Airy's equation. We take for $\hat{G}^{(+)}$ the Green's (integral) operator for the Airy equation that satisfies a vanishing boundary condition at the origin,

$$\hat{G}^{(+)}=f^{-1/3}\pi\int_0^\infty d\rho'\,\mathrm{Ai}^{(+)}(f^{-2/3}(\tfrac{1}{4}-f\rho_>))\times\mathrm{Ai}_0(f^{-2/3}(\tfrac{1}{4}-f\rho_<))/(1+ic) \tag{101}$$

where $\rho_>$ and $\rho_<$ are the larger and smaller of ρ and ρ', and

$$\mathrm{Ai}_0[f^{-2/3}(\tfrac{1}{4}-f\rho)]=\mathrm{Ai}(f^{-2/3}(\tfrac{1}{4}-f\rho))-c\,\mathrm{Bi}(f^{-2/3}(\tfrac{1}{4}-f\rho))\,, \tag{102}$$

$$c=\mathrm{Ai}(\tfrac{1}{4}f^{-2/3})/\mathrm{Bi}(\tfrac{1}{4}f^{-2/3}) \tag{103}$$

$$\sim\tfrac{1}{2}e^{-(6f)^{-1}},\quad\text{as }\rho\to 0\,. \tag{104}$$

To evaluate $\mathrm{Im}\beta_2^{(0)}$ in the small f limit, we put Eq. (101) into (98), carry out the integrations, and take the leading term as $f\to 0$. From Eq. (101),

$$\mathrm{Im}\hat{G}^{(+)}=f^{-1/3}\pi\,\mathrm{Ai}_0(f^{-2/3}(\tfrac{1}{4}-f\rho))\times\int_0^\infty d\rho'\,\frac{\mathrm{Ai}_0(f^{-2/3}(\tfrac{1}{4}-f\rho'))}{(1+c^2)}\,. \tag{105}$$

From Eqs. (98) and (71),

$$\mathrm{Im}\beta_2^{(0)}=-f^{-1/3}\pi\left(\int_0^\infty\mathrm{Ai}_0(f^{-2/3}(\tfrac{1}{4}-f\rho))\times f\rho\Phi_n^{(0)}(\rho)d\rho\right)^2. \tag{106}$$

After a close examination of the behavior of the

integrand in Eq. (106), one can conclude that the dominant contribution is from the interval $[0,(4f)^{-1}]$, and that the contribution from the $c\mathrm{Bi}$ term in Ai_0 is negligible compared to that from Ai. For the latter, we may use the asymptotic formula,[34] valid for $\rho \ll (4f)^{-1}$, everywhere, as the region $\rho \geq (4f)^{-1}$ contributes negligibly either way. We obtain

$$\mathrm{Im}\beta_2^{(0)} \sim -\tfrac{1}{2}F^2\left(\int_0^\infty \exp[-(12f)^{-1}+\tfrac{1}{2}\rho-\tfrac{1}{2}f\rho^2] \times \rho\Phi_n^{(0)}(\rho)\,d\rho\right)^2 . \tag{107}$$

For $\Phi_n^{(0)}(\rho)$, it sufficies to take the leading term in ρ [Eq. (73)], and we obtain for $\mathrm{Im}\beta_2^{(0)}$ the formula

$$\mathrm{Im}\beta_2^{(0)} \sim -\frac{f^2}{2n_2!(n_2+|m|)!}\left(\int_0^\infty \exp[-(12f)^{-1}+\tfrac{1}{2}\rho-\tfrac{1}{2}f\rho^2]\rho^{n_2+|m|/2+3/2}e^{\rho/2}\,d\rho\right)^2 \tag{108}$$

$$\sim -\tfrac{1}{2}[n_2!(n_2+|m|)!]^{-1}\Gamma(\tfrac{1}{2}n_2+\tfrac{1}{4}|m|+\tfrac{5}{4})^2 2^{n_2+|m|/2+1/2}f^{-(n_2+|m|/2+1/2)}e^{-(6f)^{-1}} . \tag{109}$$

Equation (109) is in clear disagreement with Eqs. (51) and (74). The dominant contribution of the integral in Eq. (98) turns out to be that from the barrier region, but the functions used to construct $\hat{G}^{(+)}$ in Eq. (101) are irrelevant to hydrogen throughout most of the barrier region. If we improve $\hat{G}^{(+)}$, we get the correct result.

C. Second choice for $G^{(+)}$ and V_L

A better asymptotic estimate of Φ is given by Eqs. (30), (34), and (35). Accordingly, we pick V_L so that Φ_L is an exact solution of the homogeneous version of Eq. (86), with one modification: we alter the definition of θ near $\rho=0$ so that the integral in Eq. (35) remains well behaved, real, and positive as $\rho\to 0$. [This nicety is of no numerical consequence here because of the dominance of the barrier region in Eq. (98)]. Following Eqs. (102) and (103), we define Φ_0 by

$$\Phi_0(\rho) = \left(\frac{d(\frac{3}{2}\theta)^{2/3}}{d\rho}\right)^{-1/2}\{\mathrm{Ai}[-(\tfrac{3}{2}\theta)^{2/3}] - c\mathrm{Bi}[-(\tfrac{3}{2}\theta)^{2/3}]\} , \tag{110}$$

where c is chosen so that $\Phi_0(0)$ vanishes. The exact value will depend on how V_L behaves at the origin, which in turn will depend on the behavior of θ. What is clear, however, is that

$$c = O(e^{-(6f)^{-1}}) . \tag{111}$$

With $\hat{G}^{(+)}$ defined by

$$\hat{G}^{(+)} = \pi\int_0^\infty d\rho'\,\frac{\Phi_L(\rho_>)\Phi_0(\rho_<)}{1+ic} , \tag{112}$$

we find

$$\mathrm{Im}\hat{G}^{(+)} = \pi\Phi_0(\rho)\int_0^\infty d\rho'\,\frac{\Phi_0(\rho')}{1+c^2} . \tag{113}$$

Analogously to Eq. (107)–(109), we find [cf. Eq. (43)]

$$\mathrm{Im}\,\beta_2^{(0)} \sim -\tfrac{1}{2}f^2\left(\int_0^\infty (f\rho)^{-\beta_2}\exp[-(12f)^{-1}+\tfrac{1}{2}\rho-\tfrac{1}{2}f\rho^2]\rho\Phi_n^{(0)}(\rho)\,d\rho\right)^2 \tag{114}$$

$$\sim -\tfrac{1}{2}[n_2!(n_2+|m|)!]^{-1}f^2\left(\int_0^\infty \exp[-(12f)^{-1}+\tfrac{1}{2}\rho-\tfrac{1}{2}f\rho^2]f^{-\beta_2}\rho e^{-\rho/2}\,d\rho\right)^2 \tag{115}$$

$$\sim -\tfrac{1}{2}[n_2!(n_2+|m|)!]^{-1}f^{-2\beta_2}e^{-(6f)^{-1}} . \tag{116}$$

This agreement of the partitioning method with the "matching" and perturbation method points out the need for an accurate wave function in the barrier region. We shall return to this point in Sec. VII.

To carry out the partitioning method in a less approximate way, one would need to specify more precisely V_L and $\hat{G}^{(+)}$. By introducing an appropriate basis set, e.g., the unperturbed functions [Eq. (71)], one could then solve Eq. (88) as a matrix eigenvalue problem more in the spirit of Breit.[31] The major computational difficulty in such a scheme would be the evaluation of the matrix elements

$$\int_0^\infty d\rho\,\rho^{-1}\Phi_p^{(0)}V_L\hat{G}^{(+)}f\rho\Phi_q^{(0)} . \tag{117}$$

VII. STARK WIDTHS IN THE SMALL FIELD LIMIT

A. Formula for the ionization rate

In the preceding sections we have derived a formula for $\mathrm{Im}\beta_2$ that is asymptotically valid as $F\to 0$. From Eq. (24), which relates the separation cons-

tants to the energy, we have

$$E = -\tfrac{1}{2}(\beta_1+\beta_2)^{-2}\,, \tag{118}$$

$$\mathrm{Im}E \sim [\mathrm{Re}(\beta_1+\beta_2)]^{-3}\,\mathrm{Im}\beta_2\,. \tag{119}$$

It is straightforward to obtain the asymptotic form of $\mathrm{Im}E$ as $F\to 0$, since

$$\beta_1+\beta_2 \to \beta_1^{(0)}+\beta_2^{(0)} = n\,, \quad \text{as } F\to 0\,, \tag{120}$$

$$f \sim \tfrac{1}{4}n^3F\,, \quad \text{as } F\to 0\,, \tag{121}$$

$$(6f)^{-1} = [\tfrac{3}{2}(-2E)^{-3/2}F]^{-1} \tag{122}$$

$$\sim (2/3F)[(-2E^{(0)})^{3/2} - 3(-2E^{(0)})^{1/2}E^{(1)}F] \tag{123}$$

$$= 2(3n^3F)^{-1} - 3(n_1-n_2)\,, \quad \text{as } F\to 0\,, \tag{124}$$

where we have used the usual formula for $E^{(1)}$: $\frac{3}{2}n(n_1-n_2)$. Putting together Eqs. (118)–(124) with Eqs. (74), (51), and (116), we obtain for the ionization rate, $-2\,\mathrm{Im}E$,

$$-2\,\mathrm{Im}E \sim (-2\,\mathrm{Re}E)^{3/2}[n_2!(n_2+|m|)!\,]^{-1}f^{-2\beta_2}e^{-(6f)^{-1}} \tag{125}$$

$$\sim n^{-3}[n_2!(n_2+|m|)!\,]^{-1}(\tfrac{1}{4}n^3F)^{-2n_2-|m|-1} \times \exp[3(n_1-n_2)-2/(3n^3F)]\,. \tag{126}$$

B. Comparison with other analytic formulas in the literature, and a discussion of errors in some of these formulas

There are a number of analytic formulas for $\mathrm{Im}E$ in (or that may be inferred from) the literature, some of which are listed in Table I. The disagreement is striking.

Oppenheimer's formula,[8] which is the oldest, is the oddest, because of the factor $F^{1/4}$. It would seem that Oppenheimer made a slight computational error, for when we repeated his calculation, we obtained instead, the result listed in Table I under "Oppenheimer (corrected)." But even the "corrected" result disagrees with all the others.

TABLE I. Comparison of analytical formulas for the field-ionization rate of hydrogen in a weak electrostatic field (in a.u.).

Authors	$1/\tau = -2\,\mathrm{Im}E$ (a.u.)
	Ground state
Oppenheimer[a]	$0.1093F^{1/4}e^{-2/3F}$
Oppenheimer (corrected)[b]	$\frac{1}{2}\pi e^{-2/3F}$
Landau and Lifshitz[c]	$(4/F)e^{-2/3F}$
Present work[d]	$(4/F)e^{-2/3F}$
	States with $m^2=1$; $\beta_2^{(0)}=n_2+1$.
Lanczos[e,b]	$(2\pi n^2\beta_2^{(0)})^{-1}\left(\frac{\beta_2^{(0)}}{e}\right)^{-2\beta_2^{(0)}}(\frac{1}{4}n^3F)^{-2\beta_2^{(0)}}\exp\left(3(n_1-n_2)-\frac{2}{3n^3F}\right)$
Lanczos (corrected)[b]	$(2\pi n^3)^{-1}\left(\frac{\beta_2^{(0)}}{e}\right)^{-2\beta_2^{(0)}}(\frac{1}{4}n^3F)^{-2\beta_2^{(0)}}\exp\left(3(n_1-n_2)-\frac{2}{3n^3F}\right)$
Rice and Good[f]	$(nF/\pi)\exp(-2/3n^3F)$
Present work[d]	$[n^3(\beta_2^{(0)}-1)!\beta_2^{(0)}!]^{-1}(\frac{1}{4}n^3F)^{-2\beta_2^{(0)}}\exp\left(3(n_1-n_2)-\frac{2}{3n^3F}\right)$
	States with arbitrary n_1, n_2, and m; $\beta_2^{(0)}=n_2+\frac{1}{2}\lvert m\rvert+\frac{1}{2}$.
Present work[d]	$[n^3n_2!(n_2+\lvert m\rvert)!]^{-1}(\frac{1}{4}n^3F)^{-2\beta_2^{(0)}}\exp\left(3(n_1-n_2)-\frac{2}{3n^3F}\right)$

[a] Reference 8.
[b] See text.
[c] Reference 32.
[d] Equation (126).
[e] Reference 11.
[f] Reference 12.

Apparently there is a more subtle error, which we attribute to an incorrect description of the ionized states: Oppenheimer took as the "final states" in his calculation, an electron in a uniform field, with the Coulomb potential completely neglected. Although physically appealing, we saw in Sec. VI that a similar assumption for the ρ coordinate led to an incorrect final result.

The formula we attribute to Lanczos[11] is actually the $F\to 0$ limit of his more general result. Rice and Good[12] detected an error in Lanczos's formula that they attributed to his "one-dimensional" treatment versus their "full three-dimensional" treatment. Lanczos's error actually occurs in his Eq. (16),[11] where he calculates the "phase shift" of the JWKB wave function in the atomic region at the inner turning point of the barrier. He writes

$$\gamma=\frac{1}{2}\int_0^{x_1}(E-U)^{-1/2}\,dx\,\Delta E \tag{127}$$

to represent

$$\gamma=\Delta\int_0^{x_1}(E-U)^{1/2}\,dx\,. \tag{128}$$

The subtlety is that in hydrogen, U, which is the potential for the η coordinate, depends implicitly on E through the separation constant Z_2,

$$Z_2=Z_2(E,F) \tag{129}$$

$$=1-Z_1(E,F)\,. \tag{130}$$

The correct formula for γ, in the present notation, is

$$\gamma=\Delta\int_0^{\eta_1}\left(\frac{E}{2}+\frac{Z_2}{\eta}+F\eta-\frac{m^2-1}{4\eta^2}\right)^{1/2}d\eta \tag{131}$$

$$=\frac{1}{4}\int_0^{\eta_1}\left(\frac{E}{2}+\frac{Z_2}{\eta}+F\eta-\frac{m^2-1}{4\eta^2}\right)^{-1/2}\times\left(1-\frac{2}{\eta}\frac{\partial Z_1}{\partial E}\right)d\eta\,\Delta E\,. \tag{132}$$

In the limit that $F=0$ and for $m^2=1$, it is straightforward to evaluate γ. The change in Lanczos's formula is in this case simply the factor $\beta_2^{(0)}/n$. Comparing now the "Lanczos (corrected)" result with ours for $m^2=1$, we find their ratio to be

$$2\pi(\beta_2^{(0)}/e)^{2\beta_2^{(0)}}/(\beta_2^{(0)}-1)!\,\beta_2^{(0)}!\sim 1+O(\beta_2^{(0)-1})\,, \tag{133}$$

which by Stirling's approximation is asymptotically unity for large β_2. Thus we have asymptotic agreement with Lanczos's formula and ours for small F, large β_2, and $m^2=1$.

Rice and Good[12] set out to correct Lanczos's treatment in two ways. They treat the origin following Langer,[33] and they correct the oversight discussed above. Nevertheless, their small F formula does not seem to be correct, since it should agree with the Lanczos (corrected) formula, and it does not.

The Landau and Lifshitz[32] treatment, which is related to the "matching method" given here, agrees exactly with ours for the ground state.

TABLE II. Ionization rates for the ground state calculated by Eqs. (125) and (126), compared with accurate numerical calculations by Alexander[a] and by Hehenberger, McIntosh, and Brändas.[b] In Eq. (125), β_2 is calculated by 4th order perturbation theory, while Re(E) is either calculated by 4th order perturbation theory or taken from the numerical calculations, as indicated. The notation N^n is short for $N\times 10^n$.

		$-2\mathrm{Im}(E)$ (a.u.) Eq. (125) with		
F (a.u.)	Eq. (126)	ReE (4th) β_2 (4th)	ReE (num) β_2 (4th)	Accurate numerical calculations[a,b]
0.03	2.98^{-8}	2.24^{-8}	2.24^{-8}	2.25^{-8}
0.04	5.78^{-6}	4.00^{-6}	3.99^{-6}	3.98^{-6}
0.05	1.30^{-4}	8.25^{-5}	8.21^{-5}	7.72^{-5}
0.06	9.96^{-4}	5.83^{-4}	5.77^{-4}	5.15^{-4}
0.07	4.18^{-3}	2.25^{-3}	2.21^{-3}	1.85^{-3}
0.08	1.20^{-2}	5.94^{-3}	5.84^{-3}	4.54^{-3}
0.09	2.70^{-2}	1.22^{-2}	1.21^{-2}	8.80^{-3}
0.10	5.09^{-2}	2.11^{-2}	2.13^{-2}	1.45^{-2}
0.11	8.48^{-2}	3.23^{-2}	3.34^{-2}	2.16^{-2}
0.12	1.29^{-1}	4.49^{-2}	4.79^{-2}	2.99^{-2}
0.13	1.82^{-1}	5.82^{-2}	6.43^{-2}	3.92^{-2}

[a]Reference 16. Professor Alexander kindly provided us with his calculations for $F=0.03$ and 0.04 to three significant figures.

[b]The values for $F=0.05$ through 0.13 are taken from Ref. 19.

TABLE III. Ionization rates for excited states calculated by Eqs. (125) and (126), compared with accurate numerical calculations by Damburg and Kolosov.[a] In Eq. (125), β_2 is calculated by 4th-order perturbation theory, while Re(E) is either calculated by 4th-order perturbation theory or taken from the numerical calculations, as indicated. N^n means $N \times 10^n$.

						$-2\mathrm{Im}(E)$ (a.u.) Eq. (125) with		
n	n_1	n_2	m	F (a.u.)	Eq. (126)	ReE (4th) β_2 (4th)	ReE (num) β_2 (4th)	Accurate numerical calculations[a]
2	0	1	0	4.000^{-3}	1.09^{-5}	4.12^{-6}	4.09^{-6}	4.44^{-6}
				8.000^{-3}	4.55^{-2}	7.97^{-3}	7.88^{-3}	4.16^{-3}
				1.200^{-2}	4.34^{-1}	4.01^{-2}	5.66^{-2}	1.90^{-2}
				1.600^{-2}	1.04	5.65^{-2}	1.01^{-1}	4.41^{-2}
				2.000^{-2}	1.51	3.71^{-2}	5.94^{-2}	8.74^{-2}
2	0	0	1	4.000^{-3}	1.75^{-6}	7.87^{-7}	7.85^{-7}	8.10^{-7}
				8.000^{-3}	1.46^{-2}	3.15^{-3}	3.08^{-3}	2.02^{-3}
				1.200^{-2}	2.09^{-1}	2.20^{-2}	2.59^{-2}	1.17^{-2}
				1.600^{-2}	6.68^{-1}	3.89^{-2}	4.54^{-2}	2.76^{-2}
				2.000^{-2}	1.21	4.26^{-2}	2.15^{-2}	5.19^{-2}
2	1	0	0	4.000^{-3}	2.81^{-7}	1.21^{-7}	1.21^{-7}	1.36^{-7}
				8.000^{-3}	4.70^{-3}	8.77^{-4}	8.74^{-4}	8.51^{-4}
				1.200^{-2}	1.01^{-1}	7.66^{-3}	8.43^{-3}	6.88^{-3}
				1.600^{-2}	4.29^{-1}	1.39^{-2}	1.26^{-2}	1.71^{-2}
				2.000^{-2}	9.73^{-1}	1.73^{-2}	2.41^{-3}	3.04^{-2}
5	0	4	0	1.000^{-4}	2.07^{-11}	7.77^{-13}	7.71^{-13}	4.20^{-12}
				1.500^{-4}	2.83^{-5}	3.10^{-7}	2.95^{-7}	1.92^{-6}
				2.000^{-4}	1.54^{-2}	5.68^{-5}	4.79^{-5}	1.78^{-4}
				2.500^{-4}	4.28^{-1}	6.27^{-4}	6.08^{-4}	8.53^{-4}
				3.000^{-4}	2.90	2.00^{-3}	3.06^{-3}	1.97^{-3}
				3.500^{-4}	9.18	3.49^{-3}	8.41^{-3}	3.64^{-3}
				4.000^{-4}	1.86^{1}	4.32^{-3}	9.72^{-3}	6.35^{-3}
				4.500^{-4}	2.83^{1}	4.15^{-3}	1.16^{-3}	1.27^{-2}
5	4	0	0	1.500^{-4}	1.00^{-10}	1.02^{-11}	1.03^{-11}	2.00^{-11}
				2.000^{-4}	5.46^{-7}	2.58^{-8}	2.67^{-8}	4.03^{-8}
				2.500^{-4}	9.05^{-5}	1.95^{-6}	2.07^{-6}	3.27^{-6}
				3.000^{-4}	2.64^{-3}	2.50^{-5}	2.73^{-5}	4.17^{-5}
				3.500^{-4}	2.87^{-2}	1.14^{-4}	1.29^{-4}	1.79^{-4}
				4.000^{-4}	1.69^{-1}	2.66^{-4}	3.06^{-4}	4.28^{-4}
				4.500^{-4}	6.60^{-1}	3.93^{-4}	3.86^{-4}	7.59^{-4}
				5.000^{-4}	1.94	4.35^{-4}	1.84^{-4}	1.15^{-3}
5	3	0	1	1.556^{-4}	3.57^{-9}	3.10^{-10}	3.13^{-10}	4.20^{-10}
				1.945^{-4}	2.16^{-6}	1.02^{-7}	1.04^{-7}	1.44^{-7}
				2.139^{-4}	2.16^{-5}	7.51^{-7}	7.68^{-7}	1.06^{-6}
				2.528^{-4}	7.16^{-4}	1.32^{-5}	1.36^{-5}	1.76^{-5}
				2.917^{-4}	8.96^{-3}	8.61^{-5}	8.88^{-5}	9.77^{-5}
				3.306^{-4}	5.99^{-2}	2.92^{-4}	3.10^{-4}	2.79^{-4}

[a] Reference 25.

VIII. STARK LEVELS AND WIDTHS IN APPRECIABLE FIELDS

As F increases from zero, so does $-2\,\mathrm{Im}E$. The functions $f^{-2\beta_2}$ and $e^{-1/6f}$ are extremely rapidly varying functions of f. Very quickly $f^{-2\beta_2}e^{-1/6f}$ differs significantly from

$$(\tfrac{1}{4}n^3F)^{-2\beta_2^{(0)}}\exp[3(n_1-n_2)-2/3n^3F]\ ,$$

and Eq. (126) loses its validity. Equation (125), which differs from Eq. (126) in that E, β_2, and $f\,[\equiv \frac{1}{4}(-2E)^{-3/2}F]$ appear explicitly, remains valid to higher values of F, if one has perturbed values to use for E and β_2. At still higher values of F, Eq. (125) is no longer sufficient, and one would need the next term in the expansion of, say Eq. (58). At still higher values of F, Eq. (58) would no longer be valid, and one would have to resort to a more numerical procedure, either along the lines suggested in paper I or as developed by previous workers.

TABLE IV. Ionization rates for excited states calculated by Eqs. (125) and (126), compared with numerical calculations by Damburg and Kolosov,[a] and with JWKB calculations by Bailey, Hiskes, and Riviere.[b] In Eq. (125), both Re(E) and β_2 are calculated by 4th-order perturbation theory. N^n means $N\times 10^n$.

						$-2\mathrm{Im}(E)$ (a.u.)			
						Eq. (125) with ReE (4th) β_2 (4th)	Accurate numerical calculations[a]	JWKB approximation[b] Rice and Good method	Lanczos method
n	n_1	n_2	m	F (a.u.)	Eq. (126)				
10	0	9	0	7.892^{-6}	7.23^{-12}	4.08^{-16}		1.79^{-13}	1.99^{-14}
				8.951^{-6}	1.46^{-8}	3.01^{-13}	1.69^{-10}	1.80^{-10}	1.94^{-11}
				1.007^{-5}	6.08^{-6}	4.59^{-11}	3.17^{-8}	3.36^{-8}	3.45^{-9}
				1.131^{-5}	9.40^{-4}	2.48^{-9}	1.62^{-6}	1.81^{-6}	1.83^{-7}
				1.305^{-5}	1.62^{-1}	1.09^{-7}	3.06^{-5}	3.34^{-5}	4.68^{-6}
10	9	0	0	1.572^{-5}	5.13^{-8}	6.43^{-11}	1.45^{-10}	2.06^{-10}	3.72^{-10}
				1.776^{-5}	6.01^{-6}	3.06^{-9}	7.67^{-9}	1.13^{-8}	2.06^{-8}
				1.986^{-5}	2.81^{-4}	5.57^{-8}	1.59^{-7}	2.39^{-7}	4.36^{-7}
				2.435^{-5}	1.12^{-1}	2.66^{-6}	8.70^{-6}	1.52^{-5}	2.38^{-5}
				3.195^{-5}	5.78^{1}	2.72^{-5}	1.01^{-4}	1.50^{-4}	4.62^{-5}

[a]Reference 25.
[b]Reference 13.

To illustrate the usefulness of Eqs. (125) and (126), we report some calculations for field strengths and states already reported in the literature. Most of the calculations in the literature are at rather high field strengths.

We first tabulate $-2\,\mathrm{Im}E$ for the ground state for various field strengths in Table II, along with accurate values computed by Alexander[16] and by Hehenberger, McIntosh, and Brändas.[19] For orientation, one should note that the natural linewidth of the Balmer series is $\sim 10^{-8}$ a.u., so that even the smallest field (0.03 a.u.) in Table II is not very small. The first column of computed values is based on Eq. (126). The second is based on Eq. (125), in which β_2 and ReE (which also enters in the definition of f) are evaluated by fourth-order perturbation theory.[20] The third differs from the second in that the energy shift is taken from Hehenberger, McIntosh, and Brändas[19] (but β_2 is still taken from fourth-order perturbation theory). The fourth column is by numerical methods. Even at the lowest field strength (0.03 a.u.), Eq. (126) is less accurate than Eq. (125), but the agreement of Eq. (125) with the accurate numerical results at the lower field strengths is remarkable. For more orientation, we remark that at 0.03

TABLE V. Ionization rates for highly excited states, calculated by Eqs. (125) and (126), compared with JWKB calculations by Bailey, Hiskes, and Riviere.[a] In Eq. (125), both Re(E) and β_2 are calculated by 4th-order perturbation theory. N^n means $N\times 10^n$.

						$-2\mathrm{Im}(E)$ (a.u.)		
						Eq. (125) with ReE (4th) β_2 (4th)	JWKB approximation[a] Rice and Good method	Lanczos method
n	n_1	n_2	m	F (a.u.)	Eq. (126)			
25	0	24	0	2.725^{-7}	4.12^{-6}	1.32^{-22}	8.35^{-12}	3.59^{-13}
				2.839^{-7}	3.06^{-4}	3.07^{-21}	2.48^{-10}	1.02^{-11}
				2.960^{-7}	1.81^{-2}	5.58^{-20}	5.44^{-9}	2.10^{-10}
				3.094^{-7}	1.07	9.19^{-19}	8.89^{-8}	3.56^{-9}
				3.351^{-7}	8.36^{2}	6.99^{-17}	2.04^{-6}	1.84^{-7}
25	24	0	0	5.782^{-7}	4.70^{-3}	1.54^{-12}	2.09^{-11}	1.98^{-10}
				6.221^{-7}	8.02^{-1}	4.46^{-11}	8.17^{-10}	8.32^{-9}
				6.674^{-7}	7.87^{1}	6.76^{-10}	1.70^{-8}	1.71^{-7}
				7.147^{-7}	5.03^{3}	5.98^{-9}	2.02^{-7}	1.68^{-6}
				7.524^{-7}	9.54^{4}	2.29^{-8}	9.13^{-7}	3.63^{-6}

[a]Reference 13.

a.u., the perturbed energy shift is 0.4% of the unperturbed energy and is accurately given by fourth-order perturbation theory, but that at 0.13 a.u., the energy shift is 8% and is overestimated by a factor of approximately $\frac{5}{4}$ by fourth-order perturbation theory.

In Tables III–V, similar calculations are compared with numerical calculations by Damburg and Kolosov,[25] and with JWKB calculations by Bailey, Hiskes, and Riviere.[13] For small F and n_2, the results are in reasonable agreement. At high F and high n_2, they are not in such good agreement. It should be noted that in Tables IV–V the field strengths are all so high that the perturbed energy and β_2 are very poorly given by fourth-order perturbation theory. Unfortunately, accurate numerical calculations do not seem to have been published for smaller values of F.

IX. CONCLUDING REMARKS

As an exercise in mathematical analysis, the field ionization of the hydrogen atom has exhibited a peculiar perverseness, with unsuspected pitfalls marring some of the earlier calculations. The barrier region dominates practical calculations, which are surprisingly sensitive to the accuracy of the wave function there. We have obtained a low-field formula for the ionization rate by three unrelated methods. One, the "matching method," is particularly easy to apply to hydrogen. The second, based on perturbation theory, has the promise of greater generality. The third, a partitioning method, brings out the sensitivity to the wave function in the barrier region and one probable difficulty with Oppenheimer's treatment.

Numerical agreement of the analytical low-field formula with accurate numerical calculations is quite good for small F and small n_1, n_2, and m. Agreement is significantly better when perturbed values of ReE and β_2 are used in the formula rather than their unperturbed field-free values. To get better agreement at higher values of F and of n_2, it would be necessary to obtain the next term in the expansion for ImE, and to have methods more accurate than fourth-order perturbation theory for calculating ReE and Reβ_2.

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