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Unified Derivation of the Perturbation Series for the Real and Imaginary Parts of the Energy of Hydrogen in the Stark Effect and of the Negatively Anharmonic Oscillator

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Abstract

The wave function for hydrogen in the Stark effect (or for the negatively anharmonic oscillator) with an outgoing-wave boundary condition, constructed in Langer–Cherry-fJWKB form, is continued back to the origin. The asymptotic expansions for ReE and ImE are determined by the requirement that the wave function be regular at the origin to zeroth and first order in the exponentially small parameter that characterizes ImE. One fJWKB function turns out to be the Rayleigh–Schrödinger perturbation theory wave function.

1. Introduction

The Stark effect in hydrogen is perhaps the simplest physical system displaying resonances. It is well known that Rayleigh–Schrödinger perturbation theory (RSPT) gives a purely real, asymptotic power series for the resonance. Only recently [1]* has the asymptotic series for the imaginary part been calculated—by a technique combining both the Langer–Cherry–JWKB method with RSPT. So different, however, is the technique for calculating the imaginary expansion, that the essential unity of the two series is inapparent. The main purpose of this paper is to develop a single unified technique for calculating both the real and imaginary series together.

The underlying motion is that of "eigenvalue" itself: a value of the "eigenvalue parameter" for which a single solution of the second-order differential (Schrödinger) equation satisfies both boundary conditions. The basic method consists of two steps: (i) construction of a solution that satisfies the boundary condition at infinity for any value of the eigenvalue parameter; and (ii) determination of the eigenvalues by requiring that the solution satisfy the boundary condition at the origin. Step i follows the method of Ref. 1 very closely, except that a key function $S(x)$, which there could be real, is here necessarily complex. Step ii, which turns out to involve a subtlety pathologically typical of the Stark effect, is the main difference.

* See Ref. 1 for an extended bibliography.

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The solution is carried out in parabolic coordinates and holds *a fortiori* for the radially symmetric two-dimensional anharmonic oscillator, which is the separation equation in squared parabolic coordinates.

Somewhat unanticipated, there is a connection with recent treatments of RSPT based on the "logarithm" of the wave function [2–7].

2. Solutions Satisfying the Boundary Condition at Infinity

The Schrödinger equation for the Stark effect in hydrogen

$$(-\tfrac{1}{2}\nabla^2 - 1/r + Fz - E)\psi = 0, \tag{1}$$

conveniently separates in energy-scaled parabolic coordinates

$$\sigma = (-2E)^{1/2}(r+z), \tag{2}$$

$$\rho = (-2E)^{1/2}(r-z), \tag{3}$$

$$\psi = (\sigma\rho)^{-1/2}\Phi_1(\sigma)\Phi_2(\rho)e^{im\phi}, \tag{4}$$

$$\left[-\sigma\left(\frac{d}{d\sigma}\right)^2 + \frac{m^2-1}{4\sigma} + \tfrac{1}{4}\sigma + f\sigma^2 - \beta_1\right]\Phi_1(\sigma) = 0, \tag{5}$$

$$\left[-\rho\left(\frac{d}{d\rho}\right)^2 + \frac{m^2-1}{4\rho} + \tfrac{1}{4}\rho - f\rho^2 - \beta_2\right]\Phi_2(\rho) = 0, \tag{6}$$

$$f = \tfrac{1}{4}(-2E)^{-3/2}F, \tag{7}$$

$$E = -\tfrac{1}{2}(\beta_1+\beta_2)^{-2}. \tag{8}$$

The resonances of E arise via Eq. (8) from the resonances of the separation constant β_2 [Eq. (6)], which in turn are defined by analytic continuation of Eq. (5) in f to $fe^{-\pi i}$ Near infinity it is more convenient to solve Eq. (6) in the variable $x = 4f\rho$ via the equation

$$\left[64f^2\left(\frac{-d^2}{dx^2} + \tfrac{1}{4}(m^2-1)x^{-2}\right) - 16\beta_2 fx^{-1} + (1-x)\right]\Phi_{2,\infty} = 0. \tag{9}$$

The construction of a solution Φ_2 of Eq. (9) that satisfies an outgoing-wave boundary condition, characteristic of a resonance, was discussed in detail in Ref. 1. Important here are the "atomic" and barrier regions, $0 \le x \ll 1$ (for Step ii, one needs $\lim \Phi_2(x)$ as $x \to 0$). We take as our starting point the JWKB-like formulation for Φ_2 in the barrier region ($0 \ll x \ll 1$) in which $8f$ plays the role of $\hbar$ [Eq. (25) of Ref. 1]:

$$\Phi_{2,\infty} = \sqrt{2}\left(\frac{-dS}{dx}\right)^{-1/2}(e^{S/8f} + \tfrac{1}{2}ie^{-S/8f}). \tag{10}$$

The "connection formula" that ensures the outgoing-wave condition for $x \gg 1$ is the $\tfrac{1}{2}i$ and the additional requirement that $(1-x)^{-1/2}S(x)$ be meromorphic at $x = 1$.

The equation that $S(x)$ satisfies follows on substitution of Eq. (10) into Eq. (9):

$$\left(\frac{dS}{dx}\right)^2 = (1-x) - 16\beta_2 f x^{-1} + 64f^2\left[\tfrac{1}{4}(m^2-1)x^{-2} - \left(\frac{-dS}{dx}\right)^{1/2}\left(\frac{d^2}{dx^2}\right)\left(\frac{-dS}{dx}\right)^{-1/2}\right]. \quad (11)$$

Because of the way $\mathrm{Im}\beta_2$ was determined in Ref. 1, for purposes of determining S, the β_2 in Eq. (11) could be taken as real. [Recall that $\mathrm{Im}\beta_2 = O(e^{-1/6f})$.] Here we need S to be complex. To order $O(e^{-1/6f})$, the $\mathrm{Re}S$ is the same as before

$$\mathrm{Re}S = S_0(x) + fS_1(x) + f^2S_2(x) + \cdots + O(e^{-1/6f}), \quad (12)$$

$$S_0(x) = \tfrac{2}{3}(1-x)^{3/2}, \quad (13)$$

$$S_1(x) = 8\beta_2^{(0)} \log\{[1-(1-x)^{1/2}]/[1+(1-x)^{1/2}]\}, \quad (14)$$

$$S_n = (1-x)^{1/2}\{P_n(x^{-1}) + Q_n[(1-x)^{-1}]\} + k_n \log\{1-(1-x)^{1/2}]/[1+(1-x)^{1/2}]\}, \quad (15)$$

where P_n and Q_n are polynomials of degrees $n-1$ and $[\tfrac{3}{2}n]-1$. See Ref. 1 for details.

To $O[(e^{-1/6f})^2]$, the $\mathrm{Im}S$ satisfies an equation obtained directly from Eq. (11):

$$(2\,\mathrm{Re}\dot{S})(\mathrm{Im}\dot{S}) = -16f(\mathrm{Im}\beta_2)x^{-1} - 64f^2\left\{\frac{3}{2}\left(\frac{\mathrm{Re}\ddot{S}}{\mathrm{Re}\dot{S}}\right)^2\left(\frac{\mathrm{Im}\ddot{S}}{\mathrm{Re}\ddot{S}} - \frac{\mathrm{Im}\dot{S}}{\mathrm{Re}\dot{S}}\right) - \frac{1}{2}\frac{\mathrm{Re}\dddot{S}}{\mathrm{Re}\dot{S}}\left(\frac{\mathrm{Im}\dddot{S}}{\mathrm{Re}\dddot{S}} - \frac{\mathrm{Im}\dot{S}}{\mathrm{Re}\dot{S}}\right)\right\} + O[(e^{-1/6f})^2]. \quad (16)$$

Clearly $\mathrm{Im}\dot{S}/(f\,\mathrm{Im}\beta_2)$ satisfies an equation independent of $\mathrm{Im}\beta_2$. We write

$$\mathrm{Im}S(x) = (f\,\mathrm{Im}\beta_2)T(x), \quad (17)$$

$$T(x) = T_0(x) + fT_1(x) + f^2T_2(x) + \cdots. \quad (18)$$

From Eqs. (12)–(16) and (18), one obtains

$$\dot{T}_0(x) = 8x^{-1}(1-x)^{-1/2}, \quad (19)$$

$$\dot{T}_1(x) = -(\dot{S}_1/\dot{S}_0)\dot{T}_0 \quad (20)$$

$$= 64\beta_2^{(0)}x^{-2}(1-x)^{-3/2}, \quad (21)$$

whose integrals are

$$T_0 = 8\log\{[1-(1-x)^{1/2}]/[1+(1-x)^{1/2}]\}, \quad (22)$$

$$T_1 = 64\beta_2^{(0)}\{\tfrac{3}{2}T_0 + (1-x)^{1/2}[-x^{-1} + 2(1-x)^{-1}]\}. \quad (23)$$

Just as is the case for $S_n(x)$, one can show for $T_n(x)$,

$$T_n = (1-x)^{1/2}\{\mathcal{P}_n(x^{-1}) + \mathcal{Q}_n[(1-x)^{-1}]\} \\ + k_n \log\{[1-(1-x)^{1/2}]/[1+(1-x)^{1/2}]\}, \quad (24)$$

where $\mathcal{P}_n$ and $\mathcal{Q}_n$ are polynomals in x^{-1} and $(1-x)^{-1}$, respectively.

In summary, ReS is determined in Ref. 1 as a series in f, (ImS/Imβ_2) is determined here recursively from Eqs. (16)–(24) as a series in f, both to order $O[(e^{-1/6f})^2]$, and then $\Phi_{2,\infty}$ is determined from Eq. (10). In the next section we evaluate both Reβ_2 and Imβ_2 from the requirement $\Phi_2 = O(x^{(m+1)/2})$ as $x \to 0$.

3. Boundary Condition at the Origin and the Determination of the Series for Reβ_2 and Imβ_2

$\Phi_{2,\infty}$ [Eq. (10)] satisfies an outgoing-wave boundary condition at infinity. In this section we see that by appropriate choice of β_2, $\Phi_{2,\infty}$ satisfies a zero boundary condition at $x = 0$. On reflection, such a result seems quite remarkable, because $\Phi_{2,\infty}$ is a JWKB-like function associated with the turning point $x = 1$, extended to $x = 0$ where the potential has a singularity.

We begin by considering $\Phi_{2,\infty}$ for small x, to terms of $O[(e^{-1/6f})^2]$:

$$2^{-1/2}\Phi_{2,\infty} = (-\mathrm{Re}\dot{S})^{-1/2}e^{\mathrm{Re}S/(8f)} \\ + i\{f\,\mathrm{Im}\beta_2[T/8f - \tfrac{1}{2}(\dot{T}/\mathrm{Re}\dot{S})](-\mathrm{Re}\dot{S})^{-1/2}e^{\mathrm{Re}S/(8f)} \\ + \tfrac{1}{2}(-\mathrm{Re}\dot{S})^{-1/2}e^{-\mathrm{Re}S/(8f)}\} + O[(e^{-1/6f})^2]. \quad (25)$$

Consider first the leading term, which is of order 1 (vs. $e^{-1/6f}$). Suppose it is possible to chose Reβ_2 to make this term behave regularly at $x = 0$. The logarithmic term in S_1, for small x, leads to a factor

$$e^{fS_1/8f} = \left(\frac{1-(1-x)^{1/2}}{1+(1-x)^{1/2}}\right)^{\beta_2^{(0)}} \approx (\tfrac{1}{4}x)^{\beta_2^{(0)}} \quad (26)$$

$$\approx (f\rho)^{n_2+(m+1)/2}. \quad (27)$$

If any $S_n(x)$ for $n \geq 2$ were to have a logarithmic contribution [cf. Eq. (15)], then there would be a factor $(f\rho)^{f^{n-1}k_n/8}$, which would be inconsistent with the analytic character of Φ_2 at 0. Thus in the Laurent series for $\dot{S}_n$, the coefficient of x^{-1} must vanish. Since there is an explicit contribution of $8\beta_2^{(n-1)}x^{-1}$ in $\dot{S}_n$ [Eq. (31) of Ref. 1], vanishing of the x^{-1} term in $\dot{S}_n$ is exactly a condition to determine $\beta_2^{(n-1)}$.

Vanishing of k_n ($n \geq 2$) in Eq. (15) does not trivially rule out terms of degrees less than $\tfrac{1}{2}(m+1)$ in $(-\mathrm{Re}\dot{S})^{-1/2}e^{S/(8f)}$, because S_n has terms x^{-n+1}. That the appropriate negative powers in $(-\mathrm{Re}\dot{S})^{-1/2}$ and $e^{\mathrm{Re}S/(8f)}$ cancel is remarkable. It follows from $(-\mathrm{Re}\dot{S})^{-1/2}e^{\mathrm{Re}S/(8f)}$ being a formal solution of the Schrödinger equation with no logarithmic terms at $x = 0$ and with no terms $x^{(m+1)/2-k}$ ($k \geq 1$) in the leading term (in f) as $x \to 0$. The implication is, that except for a relative normalization factor, it is possible to reorder the terms in $(-\mathrm{Re}\dot{S})^{-1/2}\exp[\mathrm{Re}S/(8f)]$ to get the RSPT wave function

$$(-\mathrm{Re}\dot{S})^{-1/2}e^{\mathrm{Re}S/(8f)} = N(f)\Phi_{2,\mathrm{RSPT}}. \quad (28)$$

All of this was already noted or alluded to in Ref. 1.

Next consider the terms in braces in Eq. (25), which are $O(e^{-1/6f})$. Already T_0 [Eq. (22)] has a logarithmic term (note that $\dot{T}_n$ cannot have a logarithmic term). For $\Phi_{2,\infty}$ to behave correctly, the logarithmic term in T_0 must be canceled by a logarithmic term in $e^{-\mathrm{Re}S/4f}$ [cf. Eq. (24)]. But, $e^{-\mathrm{Re}S/4f}$, on the basis of Eq. (15) and $k_n = 0$ for $n \geq 2$, has no logarithmic terms, and the method would appear to fail.

The difficulty is that the expansion for $S(x)$ is apparently asymptotic in x for $x \gg 0$. The induced series for $(-\mathrm{Re}\dot{S})^{-1/2}\exp[\mathrm{Re}S/(8f)]$, however, is also valid for *small* x, while the induced series for the solution irregular at the origin, $(-\mathrm{Re}\dot{S})^{-1/2}\exp[-\mathrm{Re}S/(8f)]$, is not valid for small x.

The resolution of the difficulty for the irregular solution is to note that the ratio $\exp[-\mathrm{Re}S/(4f)]$ can be rewritten

$$\exp[-\mathrm{Re}S/(4f)] = \int dx \frac{d}{dx}\exp\left(\frac{-\mathrm{Re}S}{(4f)}\right) \tag{29}$$

$$= \frac{1}{4f}\int dx \left[(-\mathrm{Re}\dot{S})^{-1/2}\exp\left(\frac{\mathrm{Re}S}{(8f)}\right)\right]^{-2} \tag{30}$$

Term-by-term integration of the expansion of the integrand near $x = 0$ gives an expansion valid for small x.

There is a simple example that clarifies this subtle maneuver: Suppose

$$(-\mathrm{Re}\dot{S})^{-1/2}e^{\mathrm{Re}S/(8f)} = x^{1/2}e^{-x/2}. \tag{31}$$

Then for $\exp[-\mathrm{Re}S/(4f)]$ one easily finds two expansions

$$4fe^{-\mathrm{Re}S/(4f)} = \int x^{-1}e^{x}\,dx$$

$$= \log x + 1 + x/2! + \cdots \qquad \text{(convergent)} \tag{32}$$

$$= x^{-1}e^{x}(1 + x^{-1} + 2!x^{-2} + 3!x^{-3} + \cdots) \qquad \text{(asymptotic).} \tag{33}$$

In such a way, the asymptotic (second) JWKB expansion invalid for small x gets turned to a valid small-x expansion.

The requirement that there be no logarithmic term in braces of Eq. (25) means that there be no x^{-1} term in the derivative. That is,

$$f\,\mathrm{Im}\beta_2 = -\frac{\text{coefficient of } x^{-1} \text{ in } (-\mathrm{Re}\dot{S})e^{-\mathrm{Re}S/(4f)}}{\text{coefficient of } x^{-1} \text{ in } \dot{T}}, \tag{34}$$

which is remarkably similar to the method described above for getting $\mathrm{Re}\beta_2$. That such a choice for $\mathrm{Im}\beta_2$ also leads to cancellation of all powers of x that are too negative has been verified computationally for a few examples and is a consequence of Eq. (25) being a formal solution whose leading term is regular.

To illustrate the use of Eq. (34), consider the ground state: $\beta_2^{(0)} = \frac{1}{2}$, $m = 0$. The coefficient of x^{-1} in $(-\mathrm{Re}\dot{S})\exp[-\mathrm{Re}S/(4f)]$ is $4e^{-1/6f}(1 - \frac{35}{3}f + O(f^2))$. The coefficient of x^{-1} in $\dot{T}$ is $8[1 + 6f + O(f^2)]$. Then $\mathrm{Im}\beta_2$ is given by

$$\mathrm{Im}\beta_2 = -4f^{-1}e^{-1/(6f)}[(1 - \tfrac{35}{3}f)\tfrac{1}{8}(1 + 6f)^{-1} + O(f^2)] \tag{35}$$

$$= -\tfrac{1}{2}f^{-1}e^{-1/(6f)}[1 - \tfrac{53}{3}f + O(f^2)]. \tag{36}$$

Just as ReS can be obtained [1] to high order recursively, so can $\dot{T}$. (Note that T itself is not needed to evaluate Imβ_2: only $\dot{T}$.) From high-order S_n and $\dot{T}_n$, the high-order series for Imβ_2 can be obtained.

4. Remark Concerning RSPT for the Logarithm of the Wavefunction

Several recent articles reformulate RSPT by putting the wave function in exponential form [2–5,7]

$$\Phi = e^{-W} = \exp(-\sum W_N(x)f^N), \tag{37}$$

if Φ has no nodes, or in modified exponential form if Φ has n nodes [6]

$$\Phi = \prod_{k=1}^{n} [x - \xi_k(f)] \exp(-\sum W_N(x)f^N). \tag{38}$$

The modified form clearly becomes more cumbersome as n increases.

In the case of the Stark effect, the fJWKB form $(-\dot{S})^{-1/2} \exp[S/(8f)]$, which by Eq. (28) yields the RSPT wave function, is similar to the exponential forms. It is formally identical to the simple form if one puts $-W = S/(8f) - \frac{1}{2}\log(-\dot{S})$. It has the advantages that nodes are automatically taken care of, and that there is no formal increase in complexity as n increases. Further, the eigenvalue condition, that $\dot{S}_n$ have no x^{-1} term, clearly carries over to $\dot{W}_n$.

5. Discussion

The wave function for the ionizing parabolic coordinate can be represented in the barrier region by a linear combination of JWKB-like terms, where $8f$ plays the role of $\hbar$, and where the "action" $S(x)$ is complex. Since the $S_n(x)$ contain increasingly negative powers of x, it is surprising that (to lowest order in $e^{-1/6f}$) the powers in $\Phi_{2,\infty}$ more negative than $x^{(m+1)/2}$ completely cancel, and the dominant (in the $e^{-1/6f}$ sense) JWKB function is regular at the origin, if, and only if, the eigenvalue β_2 is represented by the usual RSPT series. The terms that are first order in $e^{-1/6f}$ seem at first to resist continuation back to the origin, because the subdominant JWKB function is strictly asymptotic and requires $x \gg 0$. By a fortunate trick, however, the $x \gg 0$ expansion can be turned into a small x expansion, permitting all the $e^{-1/6f}$ terms to be carried back to $x = 0$. These terms are regular if, and only if, Imβ_2 is represented by its appropriate asymptotic series. In such a way the asymptotic series for both Reβ_2 and Imβ_2 have been determined by directly making Φ_2 satisfy both boundary conditions.

Once Imβ_2, Reβ_2, and β_1 have been determined, the expansions for ReE and ImE can be generated from Eqs. (7) and (8) by elementary methods [1].

The JWKB form appears to be a version of the exponential form of RSPT in which excited states require no special treatment.

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