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ABSTRACT

The Stark effect in one-electron atoms is investigated. The reliability of semiclassical approaches as a method to provide the field evolution of the complex resonance parameters is studied in detail. An expression for the asymptotic phase-shift is derived. From a Breit-Wigner parametrization of this phase-shift simple analytical expressions for the resonance parameters are obtained. As a byproduct of this work, we derive a general expression for the phase-shift for problems involving potentials diverging like -r at infinity. We also propose the use of Hadamard's concept of an improper integral as an efficient analytical way of treating the exceedingly complicated high-order semiclassical contributions.

CONTENTS

Introduction

Seventy years ago, in 1913, Stark[1] reported the first observation of the splitting of atomic lines in external static electric fields. Since then, the study of atomic properties under static electric fields, the so-called Stark effect in atoms, has proven to be a valuable source of much useful information. Two quotations might perhaps help us to understand why such a classic problem in atomic physics remains still today a very attractive subject of theoretical and experimental investigation.

The difficulty of the problem and the basic reason for the continued theoretical work on it can easily be recognized in a paper written in 1928 by Oppenheimer[2] where he foresaw, two years before experimentalists observed it, that an electric field would do more than just shift atomic energy levels. He wrote:

> "If one separates the wave equation for the hydrogen atom in an homogeneous electric field in parabolic coordinates, one finds that one of the equations has a potential energy which becomes negatively infinite for infinite values of the coordinate.... There are thus no stable, stationary states possible for a hydrogen atom in such a field. ...We must, therefore, conclude that, under the customary experimental conditions the characteristic functions found by the perturbation method, which yield the Stark effect, are not the stationary solution of the wave equation, and that they do not completely describe the effect of the field."

The nonexistence of stable, stationary states as mentioned by Oppenheimer is common to several physical situations, for which one speaks of "resonant states". Such states can be characterized by a resonant energy and a width. As the resonance energy increases, so does the corresponding width, with the result that an initially narrow resonance becomes more and more diffuse. Perhaps the simplest mathematical description of such resonant states is that they resemble bound stationary states in that they are localized in space [at some initial time, say t=o], and have their time evolution given by

$$\psi(t) = e^{-iEt/h}\ \psi(o).$$

This equation has the usual stationary state time dependence except for the fact that here the energy E, assigned to the resonant state, is complex

$$E = E_r - i\,\frac{\Gamma}{2}, \qquad \Gamma \geqq 0.$$

A traditional definition of resonant states is to identify them with a pole E of the scattering S matrix in the complex energy plane. The boundary conditions for a solution of the radial Schrödinger equation at a resonance pole are that it is regular at the origin and has an outgoing wave only character at infinity[3].

A second quotation shows what type of experimental information may now be obtained, therefore making the experimental investigation of the Stark effect in atoms so attractive. The theory of the Stark effect in hydrogen was revised by Rice and Good[4] in a paper published at about the time that lasers were born. They derived formulas for the complex eigenvalues mentioned above for a region near the autoionizing limit, at that time a region not acessible to experiments. They wrote:

> "The problem [of the Stark effect in hydrogen] is reconsidered below in order to find the position and half-widths of the levels near the peak of the barrier. It is worthwhile to have some information on these levels even though they are not observable by optical spectroscopy. ...Only levels well below the peak of the barrier are observable by optical spectroscopy. It would be interesting if some other type of experiment should turn out to be sensitive to the high levels".

Present day tunable lasers together with field ionization detection techniques are a good example of the probes sought for by Rice and Good. New experimental techniques have allowed one to study highly excited Rydberg states and have reawakened interest in the study of the decay mechanism of Rydberg atoms in static electric fields. Recent experimental investigations brought some unexpected results. A good example is the observation of relatively stable resonances well above the autoionizing limit[5]. All this new experimental work has shown that the complex resonance parameters are not described in enough detail and precision by the available analytical results.

In the present work we reconsider the Stark effect in one-electron atoms, motivated by the various experimental results now being obtained. The Stark effect is a classic subject in atomic physics and, therefore, has a vast amount of bibliography associated with it. Background reading as well as detailed references can be found in the review papers by Kleppner[6], Feneuille and Jaquinot[7], Koch[8], Freeman[9] and Kollath and Standage[10]. There is also a book, by N. Ryde[11], on the Stark effect in atoms and molecules. Here we will study the Stark effect in the light of semiclassical approaches[12,13]. One of our main objectives is to investigate the reliability of semiclassical approaches as a method to provide the field evolution of the complex resonance parameters. As will be seen, contrary to current belief, semiclassical approaches are able to correctly describe spectral properties of atoms in electric fields, even near the autoionization limit. As a byproduct of the present work we generalize semiclassical scattering formulas to include the case of potentials diverging like -r at infinity. We also propose a new approach to analytically treat some complicated pseudo singular integrals which appear in high-order semi-classical theories.

Chapter I Review of the Stark effect in atoms

In this chapter we review the most common theoretical approaches to the problem of atoms in static electric fields. We start by reviewing some well known properties of unperturbed hydrogenic atoms and defining the system of coordinates suitable to treat the DC Stark effect, namely parabolic coordinates. Throughout this work we use atomic units ($e=m_e=\hbar=1$) for all quantities unless otherwise noted.

I-1 Unperturbed Atoms

The Schrödinger equation of a one electron atom of nuclear charge Z is given by

$$(-\frac{1}{2}\Delta - \frac{Z}{r})\psi = E\psi, \qquad \text{I-1}$$

where Δ is the quantum mechanical operator for the kinetic energy. In the above equation spin and relativistic effects have been neglected since we will be concerned with Rydberg states. As is well known, owing to the O(4) symmetry of the fieldless hydrogen problem, Eq. I-1 can be separated in four different systems of coordinates: spheroconical, prolate-spheroidal, parabolic and the usual spherical coordinates. Fortunately for those wishing to study the Stark effect, the separability of I-1 in parabolic coordinates is maintained when the atom is placed in a static electric field. The parabolic coordinates (ξ,η,φ) are connected with the cartesian coordinates (x,y,z) through the relations

$$\begin{aligned} \xi &= r + z \qquad & x &= \sqrt{\xi\eta}\cos\varphi \\ \eta &= r - z \qquad & y &= \sqrt{\xi\eta}\sin\varphi \\ \varphi &= \mathrm{arctg}(y/x) \qquad & z &= (\xi-\eta)/2 \end{aligned} \qquad \text{I-2}$$

where $r = \sqrt{x^2+y^2+z^2} = \frac{1}{2}(\xi+\eta)$. As in the case of spherical coordinates, $0 \leq \varphi < 2\pi$, while ξ and η are defined on the semi-infinite interval $0 \leq \xi,\ \eta < \infty$. In these coordinates the Δ operator is given by

$$\Delta \equiv \frac{4}{\xi+\eta}\left[\frac{\partial}{\partial\xi}\left(\xi\frac{\partial}{\partial\xi}\right)+\frac{\partial}{\partial\eta}\left(\eta\frac{\partial}{\partial\eta}\right)\right] + \frac{1}{\xi\eta}\frac{\partial^2}{\partial\varphi^2} \qquad \text{I-3}$$

Using the product Ansatz

$$\Psi(\xi,\eta,\varphi) = \frac{\Psi_1(\xi)}{\sqrt{\xi}}\,\frac{\Psi_2(\eta)}{\sqrt{\eta}}\,e^{\pm im\varphi} \qquad \text{I-4}$$

for the eigenfunctions, Eq. I-1 can be easily separated and analytically solved. The eigenfunctions of the fieldless problem defined by I-1 are found to be products of exponential functions and generalized Laguerre polynomials in the variables ξ and η. In these coordinates, the principal quantum number is $n = n_1 + n_2 + m + 1$, where n_1 and n_2 are called the parabolic quantum numbers. In general, any of the n-m eigenfunctions in parabolic coordinates for a fixed value of n and m is a linear superposition of the n-m eigenfunctions in spherical coordinates for the same values of n and m. For the (non-degenerate) ground state ($n=1$, i.e. $n_1 = n_2 = m = o$) the eigenfunctions in parabolic and spherical coordinates are identical.

We now proceed by placing the atom described by I-1 in a DC electric field and studying the modifications on its spectrum.

I-2 Atoms in electric fields

If the atom described by Eq. I-1 is placed in a region where a static electric field F, pointing in an arbitrary direction (say z) is present, then I-1 is replaced by

$$(-\frac{1}{2}\Delta - \frac{Z}{r} + Fz)\psi = E\psi. \qquad \text{I-5}$$

As before, the product Ansatz I-4 is used to separate I-5 and to obtain the following set of equations

$$-\frac{d^2\Psi_1}{d\xi^2} + \left(-\frac{Z_1}{\xi} + \frac{m^2-1}{4\xi^2} + \frac{F}{4}\xi\right)\Psi_1 = \frac{E}{2}\Psi_1, \qquad \text{I-6a}$$

$$-\frac{d^2\Psi_2}{d\eta^2} + \left(-\frac{Z_2}{\eta} + \frac{m^2-1}{4\eta^2} - \frac{F}{4}\eta\right)\Psi_2 = \frac{E}{2}\Psi_2, \qquad \text{I-6b}$$

$$Z_1 + Z_2 = Z, \qquad \text{I-6c}$$

Z_1 and Z_2 being separation constants.

This is the set of equations defining the properties of the atom in presence of a static field F. It is easy to recognize that I-6a and I-6b are radial Schrödinger equations for the motions in a ξ- and in a η-potential. Note also that the equations are identical under the replacement of $Z_1 \leftrightarrow Z_2$ and $F \leftrightarrow -F$. Equation I-6a corresponds to a confined motion in the ξ coordinate. Equation I-6b presents a singularity in which the η-potential diverges to $-\infty$ as $\eta \rightarrow \infty$.

Since we are mainly interested in the spectral properties of atoms in electric fields, our attention will be concentrated on the study of the functional dependence of $E = E[F]$. The usual approach to this problem is to solve the differential equations I-6a and I-6b, determining the functional dependence of the parameters Z_1 and Z_2 as functions of E and F. After this has been done, the constraint $Z_1 + Z_2 = Z$ allows one to obtain the energy E as a function of the field strength F.

With regard to the potential in Eq. I-5, $V = - Z/r + Fz$, it is important to realize that it possesses a barrier whose height and width depend on the external electric field. Classicaly one expects that the electron in a particular state would leave the atom if its energy exceeds the maximum of the barrier. Quantum-mechanically one finds that none of the previously bound states (of the fieldless problem) is stationary any more, but all have a finite lifetime since the electron may eventually tunnel through the barrier leaving the atom ionized. The finite ionization probability means that a stationary level of the unperturbed atom is turned into a narrow band of a continuum by the electric field. The problem of calculating the center of this band and its width is quite similar to the problem of quasibound states in scattering theory. These processes are usually described as energy eigenvalue problems with complex eigenvalues. The real part of the eigenvalue gives the center of the band while the imaginary part is connected with its width.

The most common approaches to the Stark problem have been perturbation calculations, semiclassical (WKB) calculations and direct numerical integration of the system of equations I-6. We now proceed by reviewing these three approaches. However, since the Stark problem is

a very old one its literature is enormous. Therefore, rather then trying to summarize everything that was published in this field, we will be more concerned with the mundane but important question of searching for a simple yet reliable way to obtain the spectral evolution as a function of the field. Our motivation is derived from the recent developments in the experimental work with Rydberg states. For more detailed reviews and further references we refer the reader to the works listed as our references [6-13].

I-3 Perturbative approach

The theory of the Stark effect was the first application of perturbation theory in quantum mechanics. This application was done by Schrödinger[14] himself. He was able to reproduce the formula for the linear Stark effect

$$E = - \frac{Z^2}{2n^2} + \frac{3}{2}\frac{Fn}{Z}(n_1 - n_2), \qquad \text{I-7}$$

already known from calculations of Schwarzschild and Epstein based on the old quantum theory. Since then people have been studying the series expansion for the energy whose first two terms are given by I-7. That the calculation of this series is not trivial can be understood when one observes that, despite several attempts, the correct fourth-order term was only found[15] in 1974. In 1978, through intensive use of computers, Silverstone[16] obtained corrections up to the 150th term. More recently the algorithms for computers have been extended and, in principle at least, the whole series can be generated. However, it should be noted that the extension of the perturbative calculations to such high orders is not the same as extending the validity of I-7. Since the middle of the fifties it has been known that the standard summation of the energy series is divergent[17]. Furthermore, perturbation theory in the usual sense is not able to provide a description for the observed width of the energy levels since it does not contain a mechanism to take "tunneling" into account. The resonances are described by a complex eigenvalue and standard perturbation theory only gives the real part of this eigenvalue.

The present interest in evaluating the energy series up to very high orders is connected with discoveries that the standard perturbative series, although being divergent in the usual sense, is Borel summable[18]. Furthermore, a dispersion relation was also found[18]. The fact that the series is Borel summable allows one to use the standard divergent series to still obtain useful information regarding the real part of the eigenvalues. The dispersion relation, on the other hand, allows one to generate the imaginary part of the energy eigenvalue from a knowledge of the real part.

At the moment the results obtained from perturbation theory may be summarized as follows. The standard energy series may be used in applications at weak fields but eventually diverges. The new concepts mentioned above are just in their infancy. The Stark problem has been used as a testing ground for them, but no compact algorithm has emerged yet. The numerical effort needed today to obtain eigenvalues competes with exact numerical treatment of the problem. The problems of perturbation theory at high orders was the subject of a very recent Sanibel Symposium[19].

I-4 Semiclassical approach

Although Sommerfeld and Wentzel had discussed the Stark problem earlier using the semiclassical (or WKB) approach, the 1930-31 work of Lanczos[20] is often quoted more, due perhaps to his more detailed calculations. Lanczos was interested in determining critical fields for the ionization of the hydrogen atom on an electric field in order to explain some spectral features that were being measured by Rausch von Traubenberg. He used the first-order WKB approximation for the problem as defined by I-6. In his calculation the centrifugal term, involving the m^2-1 contribution, was neglected. The numerical values obtained by him were in fairly good agreement with the experimental results then available.

In his investigations Lanczos had been only concerned with states well below the classical autoionizing limit. Later on Rice and Good[4] studied

the region near the peak of the barrier, obtaining an improved formula for the lifetime against ionization. As was done in earlier WKB treatments, the quantization equations were expanded, truncated and integrated. They also took the m^2-1 term into consideration. Although Rice and Good intended to study the region near the peak of the barrier, they treated the problem as a quantization in the well near the core plus a tunneling through the barrier. As we will see in the next chapter, this separation has drastic consequences near the top of the barrier. Their approximated formulas were used by Bailey, Hiskes and Rivière[21] to calculate electric field ionization probabilities for quantum states up to n=25, and since then these have been quoted in the literature as the standard results of WKB calculations.

The last authors to consider the application of the WKB approximation to the Stark Hamiltonian were Beckenstein and Krieger[22]. They also considered the centrifugal term and "replaced" m^2-1 by m^2. As will be discussed in the next chapter, this substitution is of vital importance for WKB calculations. By performing a similar expansion to that previously used by Rice and Good, combined with a different integration technique, they were able to correctly reproduce the three first terms of the perturbation energy series then available. To obtain this result they needed to consider higher order terms of the WKB approximation instead of the usual first-order ones.

Recently, using a first-order WKB approximation, we reinvestigated the Stark effect[23,24]. By using a full scattering approach the problems briefly mentioned above can be overcome. This approach provides one with compact formulas which give resonance parameters in good agreement with experimental values and with results from numerical treatments of the problem. This semiclassical approach will be discussed in more detail in the next chapter.

I-5 Numerical solution of Schrödinger's equation

Of course, the system of equations I-6a-6c can be treated numerically. In practice this treatment is quite elaborate owing to the particular spectral properties of the differential equation I-6b. Damburg and Kolosov[25] and Luc-Koenig and Bachelier[26] have recently numerically studied the Stark effect for some quantum states. Whenever a comparison is possible, both computations are in good agreement at low-to-medium field strengths. As the field increases the agreement is soon lost. However, as argued by Luc-Koenig and Bachelier, these regions would correspond to a regime where the resonances are no longer very well defined. The difficulties in performing a numerical calculation as well as a more detailed discussion of the reasons for the disagreement between numerical results from different groups can be found in the original paper of Luc-Koenig and Bachelier[26].

In spite the above mentioned undesired features, the resonance parameters as calculated by Damburg and Kolosov and by Luc-Koenig are usually regarded in the literature as the "exact" resonance parameters.

In the next chapter we describe a semiclassical alternative to numerical approaches. Since Damburg und Kolosov reported more extensive results we will compare our numerical results with theirs which, for simplicity, we shall refer to as "exact" results.

Chapter II First-order semiclassical approach to the Stark effect

II-0 Introduction

As mentioned before, in the present chapter a full first-order semiclassical (WKB) treatment of the Stark problem for hydrogenlike atoms is presented. We begin by discussing the application of the usual WKB quantization rules to radial equations. This forces us to consider the so-called Langer transformation in detail. Then, we consider semiclassical quantization in the usual sense, assuming effects on the electron due to the well near the core and due to the barrier to be uncorrelated. This approach gives good results for the real part of the complex eigenvalues but very poor ones for the imaginary part (corresponding to the width of the levels). To improve this, a general semiclassical formalism to treat scattering problems in fields such that $V(r) \to -\infty$ for $r \to \infty$ is developed. We conclude the chapter by applying the general scattering formalism to the Stark problem. The scattering treatment gives the desired good complex eigenvalues.

II-1 The Langer transformation

It is well known that when applying the WKB approximation to radial equations (such as Eqs. I-6a, 6c for instance) some care is needed. As pointed out by Langer[27,28], the quantization condition for one-dimensional problems is derived under the assumption that the eigenfunctions [say $u(x)$] go to zero as one approaches $\pm\infty$. For a radial equation, on the other hand, the solutions [say $\psi(r)$] approach zero for $r \to o$ and $r \to \infty$. Therefore, if one wants to apply the one-dimensional WKB quantization rule, derived for $-\infty < x < \infty$, to a radial problem, defined in $o \leqq r < \infty$, one should map the semi-infinte into an infinite interval. To this end Langer used the mapping function $x = \ln r$ [together with the replacement $\psi(r) = e^{x/2}\,u(x)$]. The effect of the mapping is to introduce corrections ΔV in the potential. In this way one easily obtains the celebrated correction $\ell(\ell+1)/r^2 \to \ell(\ell+1)/r^2 + 1/4r^2 = (\ell+\frac{1}{2})^2/r^2$ for the hydrogen atom. However, it is clear that the choice of the mapping function is arbitrary. Unfortunately, as shown by

Adams and Miller[29], different choices of mapping function produce different corrections ΔV. This means that by properly choosing the mapping one could, in principle, introduce any desired "correction" ΔV to the potential. One way out of the dilemma is the Adams-Miller conjecture: the mapping function, and therefore the correction ΔV, should be chosen such that the correct quantum mechanical result is obtained if the potential V is set to zero. For the semi-infinite interval this criterion selects the Langer transformation $x = \ln r$ uniquely.

By Langer-transforming our basic system of equations, namely I-6a, 6b and 6c, we obtain

$$-\frac{d^2\Psi_1}{d\xi^2} + \left(-\frac{Z_1}{\xi} + \frac{m^2}{4\xi^2} + \frac{F}{4}\xi\right)\Psi_1 = \frac{E}{2}\Psi_1 , \qquad \text{II-1a}$$

$$-\frac{d^2\Psi_2}{d\eta^2} + \left(-\frac{Z_2}{\eta} + \frac{m^2}{4\eta^2} - \frac{F}{4}\eta\right)\Psi_2 = \frac{E}{2}\Psi_2 , \qquad \text{II-1b}$$

$$Z_1 + Z_2 = Z . \qquad \text{II-1c}$$

Note that the main effect of the Langer transformation was to replace the m^2-1 by a m^2 term. However, this replacement is of vital importance in order not to violate the WKB approximation[28]. As already mentioned in section I-4, this critical step was not always carefully taken into account in some of the earlier WKB calculations.

II-2 Usual semiclassical quantization

As mentioned before, previous semiclassical studies of the Stark effect treated the problem as a quantization in the well near the ionic core plus a tunneling through the barrier. Furthermore, the quantization rules were usually expanded in a power series involving the centrifugal (m^2) contribution or had this contribution completely neglected. In the present section we explicitly avoid this last approximation and obtain complete quantization rules in the sense that they contain all

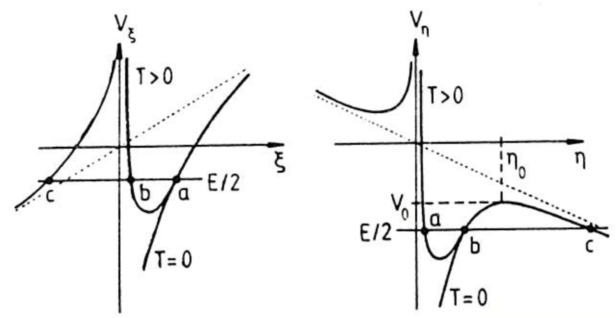
the m^2 contributions neglected in previous works. In the following section we treat the problem avoiding both aforementioned approximations.

The basic set of equations, describing the Stark problem and suitable to WKB calculations, is given by II-1a, 1b and 1c. The first two are Schrödinger equations for motion in the central potentials

$$V_\xi = -\frac{Z_1}{\xi} + \frac{m^2}{4\xi^2} + \frac{F}{4}\xi \qquad \text{II-2}$$

$$V_\eta = -\frac{Z_2}{\eta} + \frac{m^2}{4\eta^2} - \frac{F}{4}\eta \qquad \text{II-3}$$

while II-1c is the constraint on the separation constants Z_1 and Z_2 which couples the system. A schematic view of the potentials is given in Figure II-1. The negative parts of the ξ and η axes have no physical meaning but, as will soon be clear, help the mathematical formulation very much.



(a) (b)

Fig. II-1 Potential for the ξ and η motions as defined in Eqs. II-2 (a) and II-3 (b). In this figure $T = m^2$. The ξ motion is always confined. The η motion is more complicated: the electron may leak through the potential barrier (when $E/2 \leq V_o$) or be autoionizing (when $E/2 > V_o$).

As shown in the figure, the motion along the ξ coordinate, for any field strength, is always confined. The particle is classically bounded to oscillate between the turning points $o \leqq b < a$. The motion in the η coordinate is much more complicated and is the source of all difficulties in studying the Stark effect. For physically meaningful energies lower than V_o, the classical motion near the core is bounded between $o \leqq a < b$ while quantum mechanically the electron may leak through the barrier. In the present section, while quantizing, we neglect the possibility of tunneling. The quantization is then performed in the standard way:

$$I_\xi = (n_1 + \tfrac{1}{2})\pi \qquad \text{II-4}$$

where

$$I_\xi = \int_b^a \sqrt{\frac{E}{2} - V_\xi}\, d\xi$$

$$= \frac{\sqrt{F}}{2} \int_b^a \frac{-\xi^2 + \frac{2E}{F}\xi + \frac{4Z_1}{F} - \frac{m^2}{F}\frac{1}{\xi}}{\sqrt{-\xi^3 + \frac{2E}{F}\xi^2 + \frac{4Z_1}{F}\xi - \frac{m^2}{F}}}\, d\xi \qquad \text{II-5}$$

$$= \frac{\sqrt{F}}{2}\left[\!\left[-I_\xi^{(2)} + \frac{2E}{F} I_\xi^{(1)} + \frac{4Z_1}{F} I_\xi^{(0)} - \frac{m^2}{F} I_\xi^{(-1)} \right]\!\right],$$

where E is the energy and the definition

$$I_\xi^{(j)} \equiv \int_b^a \frac{\xi^j\, d\xi}{\sqrt{-\xi^3 + \frac{2E}{F}\xi^2 + \frac{4Z_1}{F}\xi - \frac{m^2}{F}}} \qquad \text{II-6a}$$

$$\equiv \int_b^a \frac{\xi^j\, d\xi}{\sqrt{(a-\xi)(\xi-b)(\xi-c)}} \qquad \text{II-6b}$$

was introduced. The turning points are the non-negative roots of the cubic

$$-\xi^3 + \frac{2E}{F}\xi^2 + \frac{4Z_1}{F}\xi - \frac{m^2}{F} \equiv (a-\xi)(\xi-b)(\xi-c) = 0, \qquad \text{II-7}$$

and, as shown in Fig. II-1, are ordered as $c < o \leqq b < a$. From II-7 it is trivial to see that

$$\begin{aligned} \frac{2E}{F} &= a + b + c, \\ -(4Z_1)/F &= ab + ac + bc, \\ -\frac{m^2}{F} &= abc. \end{aligned} \qquad \text{II-8}$$

Equation II-5 can be very much simplified if one uses the identity

$$I_\xi = \int_b^a \sqrt{\frac{E}{2} - V_\xi}\, d\xi = \frac{1}{2}\int_b^a \frac{\frac{dV_\xi}{d\xi}}{\sqrt{\frac{E}{2} - V_\xi}}\, \xi\, d\xi \qquad \text{II-9}$$

which is obtained after a trivial integration by parts. From this identity it follows that

$$I_\xi = \frac{\sqrt{F}}{2}\left[\!\left[\frac{1}{2} I_\xi^{(2)} + \frac{2Z_1}{F} I_\xi^{(0)} - \frac{m^2}{F} I_\xi^{(-1)} \right]\!\right]. \qquad \text{II-10}$$

Now, combining II-5, 8 and 10 it is easy to eliminate $I_\xi^{(2)}$ and obtain

$$I_\xi = \frac{\sqrt{F}}{2}\left[\!\left[\frac{a+b+c}{3} I_\xi^{(1)} - \frac{2}{3}(ab+ac+bc) I_\xi^{(0)} + abc\, I_\xi^{(-1)} \right]\!\right]. \qquad \text{II-11}$$

The utility of eliminating $I_\xi^{(2)}$ [i.e. of expressing it as a function of $I_\xi^{(1)}$, $I_\xi^{(0)}$ and $I_\xi^{(-1)}$] will be transparent to anyone that explicitely evaluates $I_\xi^{(2)}$ without using the identity II-9: it takes about half a page to write it down explicitely [plus the boring effort to derive it!].

The integrals $I_\xi^{(j)}$ can be analytically evaluated:

$$\left.\begin{aligned} I_\xi^{(0)} &= g\, \mathbb{K}(k), \qquad I_\xi^{(-1)} = \frac{g}{a}\, \Pi\left(\frac{a-b}{a}, k\right), \\ I_\xi^{(1)} &= g\left[\!\left[c\, \mathbb{K}(k) + (a-c)\, \mathbb{E}(k) \right]\!\right], \end{aligned}\right\} \qquad \text{II-12}$$

where $g^2 = 4/(a-c)$, $k^2 = \frac{a-b}{a-c}$ and $\mathbb{E}$, $\mathbb{K}$ and Π are standard complete elliptic integrals of the first, second and third kinds, respectively.

For states below the autoionizing limit ($V_o \leqq E/2$ in figure II-1b) the analytical expression for the η quantization can easily be obtained. With the η-roots $o \leqq a < b < c$ obtained now from the equation

$$\eta^3 + \frac{2E}{F}\eta^2 + \frac{4Z_2}{F}\eta - \frac{m^2}{F} \equiv (\eta-a)(b-\eta)(c-\eta) = o, \qquad \text{II-13}$$

the quantization reads

$$I_\eta = (n_2 + \tfrac{1}{2})\pi$$

$$= -\frac{\sqrt{F}}{2}\left[\frac{a+b+c}{3} I_\eta^{(1)} - \frac{2}{3}(ab+ac+bc) I_\eta^{(0)} + abc\, I_\eta^{(-1)}\right], \qquad \text{II-14}$$

where the integrals $I_\eta^{(j)}$ are defined by

$$I_\eta^{(j)} \equiv \int_a^b \frac{\eta^j d\eta}{\sqrt{(\eta-a)(b-\eta)(c-\eta)}} \; . \qquad \text{II-15}$$

The particular values $j = -1, 0$ and 1 needed in Eq. II-14 can be obtained directly from II-12 by replacing ξ by η. This symmetry owes much to the equivalence of V_ξ and V_η under the replacements $Z_1 \leftrightarrow Z_2$ and $F \leftrightarrow -F$. Note, however, that although the analytical expressions for these integrals are identical, the numerical values of a, b and c are different for the ξ an η quantizations as clearly defined by Eqs. II-7 and II-13.

It is interesting to stress the highly symmetrical form of the two quantization rules as provided by the WKB approximation. Furthermore, observe that the quantization has been reduced to the evaluation of two families of integrals, namely $I_\xi^{(j)}$ and $I_\eta^{(j)}$. These in turn may be reduced to standard elliptic integrals which can be easily evaluated even on programmable pocket calculators.

For energies above the autoionizing limit, i.e. for $E/2 > V_o$, the extension of the semiclassical calculation is not trivial. However, we observed that if one replaced b (the upper limit of integration of the

η-motion in II-14 and 15) by η_o (the location of the peak of the barrier; see figure II-1b), then a good approximation could be obtained for the position of the classically autoionizing lines. In some sense this is not surprising since the "classical well" continues to be responsible for the amplitude of the eigenfunctions near the ionic core, i.e. the origin. In this case the two turning points become complex conjugate numbers and the quantization reads

$$I_\eta = \frac{\sqrt{F}}{2}\int_a^{\eta_o} \frac{d\eta}{\eta} \sqrt{(\eta-a)[(\eta-b_1)^2 + a_1^2]}$$

$$= (n_2 + \tfrac{1}{2})\pi . \qquad \text{II-16}$$

Although this integral can still be evaluated in terms of (now incomplete) elliptic integrals of the three kinds, the final expression is so complicated that numerical integration is more convenient.

In connection with the semiclassical quantization of the Stark problem it is interesting to point out that very compact expressions for I_ξ and I_η may be obtained by using Appell's double hypergeometric series F_1, namely[30]

$$F_1(\alpha,\beta,\beta';\gamma;x,y) \equiv \frac{\Gamma(\gamma)}{\Gamma(\alpha)\Gamma(\gamma-\alpha)}\int_0^1 t^{\alpha-1}(1-t)^{\gamma-\alpha-1}(1-xt)^{-\beta}(1-yt)^{-\beta'}dt$$

$$\equiv \sum_{i=0}^{\infty}\sum_{j=0}^{\infty} \frac{(\alpha,i+j)(\beta,i)(\beta',j)}{(\gamma,i+j)\; i!\; j!} x^i y^j ,$$

where $(a,n) \equiv \Gamma(a+n)/\Gamma(a)$. Using $\xi = a-(a-b)t$ it follows that

$$I_\xi = \frac{\pi\alpha^2}{16}(a-b)\sqrt{F(a-c)}\; F_1\left(\tfrac{3}{2}, 1, -\tfrac{1}{2}; 3; \alpha^2, k^2\right), \qquad \text{II-17}$$

where $\alpha^2 = (a-b)/a$ and $k^2 = (a-b)/(a-c)$ as before. A similar result can be easily obtained for I_η. However, although more compact, the numerical evaluation of Appell's series F_1 involves a doubly infinite sum of products of transcendental functions. For restricted ranges of α^2 and k^2 summation of this series should work well since the coefficients satisfy rather simple recurrence relations. For other ranges one can use the series obtained by analytic continuation of F_1 (see

Olsson[31]). However, the use of elliptic integrals seems to be preferable since it is not at all sensitive to the magnitude of α^2 and k^2.

To conclude this section we present a brief comparison between the numerical results as obtained from the formulas derived in this chapter and the ones from exact numerical calculations and from perturbation theory. In Figure II-2 we present the field dependence of the energy for the particular quantum state $n_1 = 0$, $n_2 = 4$, and $m = 0$ for which accurate numerical calculations were reported by Damburg and Kolosov[25]. The dashed lines are their results: the line in the middle gives the center of the resonance, while the other two give the corresponding width. The dashed curves are based on the numbers given in Table III of reference[25] which were interpolated by a cubic polynomial. The crosses represent results obtained from the fourth-order perturbation equation[15]. The solid line shows our WKB results. The arrow indicates the threshold field F_o above which the state is autoionizing. As is easy to see, the WKB approximation gives resonable results even well above the top of the barrier where the spectral lines are, in fact, broad bands.

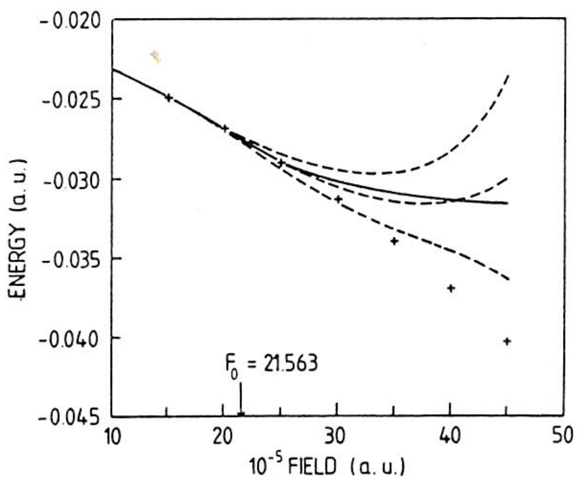


Fig. II-2 Evolution of the $n_1 = 0$, $n_2 = 4$, and $m = 0$ level for increasing field strength. For fields larger than $F_o = 21.563 \times 10^{-5}$ a.u. the state is autoionizing. The central dashed line gives the numerical results of Damburg and Kolosov[25]. The outermost dashed lines show the broadening (width) of the level. The solid line shows the present WKB results, while crosses are the values predicted by fourth-order perturbative calculations.

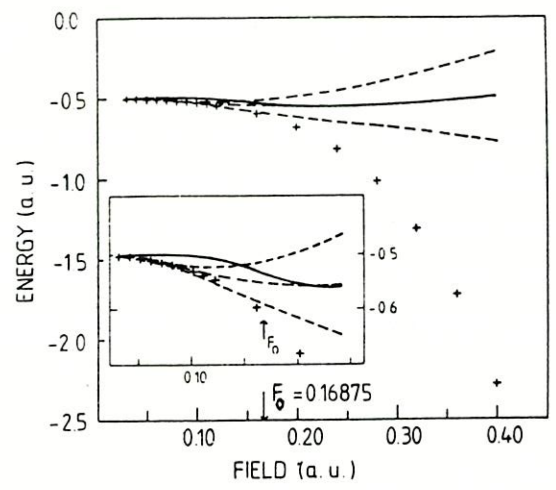


Fig. II-3 Same as in Fig. II-2 but for the ground state ($n_1 = n_2 = m = 0$). Here $F_o = 0.16875$ a.u..

Although we know that the ground state is not the best place to test WKB calculations, we present in Figure II-3 a comparison similar to the one in Fig. II-2. It is motivated by the fact that the ground state has been extensively studied by several workers, and that results at several different field values are available for it. In this figure we present in more detail the region near F_o where the WKB result may be expected to be less reliable, since the two turning points a and b (in Eq. II-14) are very close to each other. The agreement found well above F_o is striking. This supports the approximation introduced in Eq. II-16.

From the comparison above it is clear that the equations derived in this section provide reliable results for the real part of the Stark resonances. The next step is to use these energies to obtain the width of the resonances. Using the standard WKB formulas, involving a simple exponential tunneling, the widths for Rydberg states turn out to be about one order of magnitude too small. To improve this one has to consider the full three turning-point scattering problem instead of the simple approach used in this section. In the next section we develop such a general formalism and in the following section we apply it to the Stark problem.

II-3 General scattering approach

We now wish to consider the scattering problem, defined on the half-line $0 \leqq r < \infty$, in a potential of the type represented in Figure II-4.

For $E/2 < V_0$ this potential has three classical turning points, i.e. there are two classicaly allowed regions separated by a potential barrier. The semiclassical treatment of three-turning-point problems for potentials which go to zero at infinity is well-known[32]. Here we want to discuss a more complicated case, namely one in which $\lim_{r\to\infty} V(r) \to -r$.

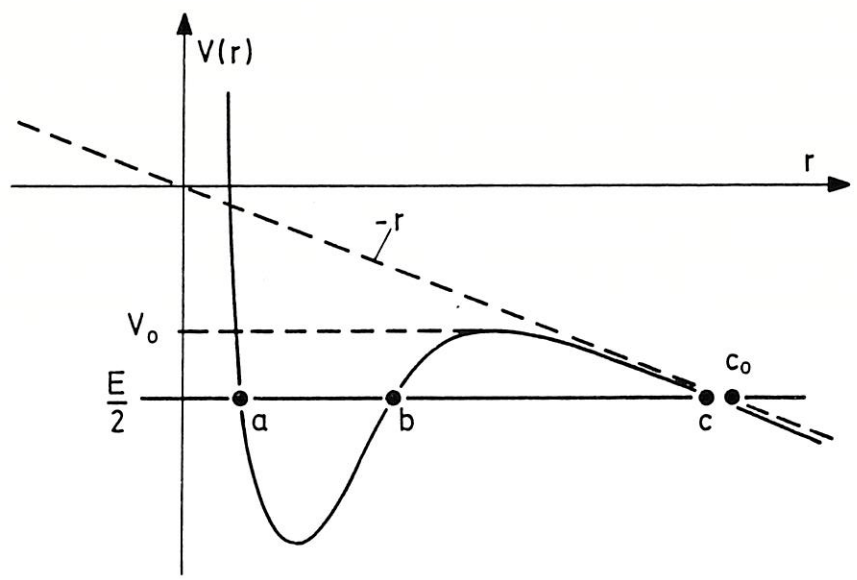


Fig. II-4 Schematic representation of the divergent potential V(r). For convenience we call region II the range $a \leqq r \leqq b$ and region I the range $r \geqq c$. The turning point c_o is obtained from Eq. II-32.

This means that our problem is not bounded from below and diverges as -r at infinity, as schematically shown in Fig. II-4. With no loss of generality we will think of V(r) as being given by the potential in Eq. II-3 and, for convenience, will replace the symbol η by r.

As typical in scattering studies, the problem consists in obtaining an expression for the phase shift from which one is able to learn all the scattering information. The phase shift is obtained from a comparison very far from the scattering center between the eigenfunction describing the physical problem with that of a free wave. In the present problem a free wave is not given by the usual sin(kr) eigenfunction since the -r background term in the potential is always present. Instead, the asymptotic free eigenfunction is given by the Airy function,

$$\lim_{z\to\infty} \psi_I(z) = \lim_{z\to\infty} Ai(-z) = z^{-1/4} \sin\left(\frac{2}{3} z^{3/2} + \frac{\pi}{4}\right), \qquad \text{II-18}$$

corresponding to the exact scattering solution in a potential V(r) = -r. The relationship between r and z depends on the specific form of the potential and will be given below.

The requirement that the eigenfunction be exponentially decaying for r << a yields the usual WKB solution in region II:

$$\psi_{II}(r) = \frac{N}{\sqrt{k(r)}} \sin\left(\int_a^r k(r')dr' + \frac{\pi}{4}\right) \qquad \text{II-19}$$

$$= \frac{N}{\sqrt{k(r)}} \sin\left(\int_b^r k(r')dr' + \varphi + \frac{\pi}{4}\right)$$

$$= \frac{N}{\sqrt{k(r)}} \left[A e^{i\int_b^r k(r')dr'} + B e^{-i\int_b^r k(r')dr'} \right],$$

where

$$k(r) = \sqrt{\frac{E}{2} - V(r)} = \sqrt{\frac{E}{2} - \frac{Z_2}{r} - \frac{m^2}{4r^2} + \frac{F}{4} r}, \qquad \text{II-20}$$

$$\varphi \equiv I_\psi = \int_a^b k(r)\,dr \qquad \text{II-21}$$

$$A = \frac{1}{2i}\, e^{i(\varphi+\pi/4)}, \qquad B = A^* = \frac{-1}{2i}\, e^{-i(\varphi+\pi/4)}, \qquad \text{II-22}$$

and where N is a normalization constant. Now, if we write the eigenfunctions to the left and to the right of the barrier as

$$[k(r)]^{1/2}\,\psi_{II}(r) = A\, e^{i\int_b^r k(r')dr'} + B\, e^{-i\int_b^r k(r')dr'},$$

$$[k(r)]^{1/2}\,\psi_{I}(r) = C\, e^{i\int_c^r k(r')dr'} + D\, e^{-i\int_c^r k(r')dr'}, \qquad \text{II-23}$$

respectively, then the connection formula relating the constants A and B to C and D is given by [33]

$$\begin{pmatrix} C \\ D \end{pmatrix} = e^{\theta} \begin{pmatrix} \sqrt{1+e^{-2\theta}} & -i \\ i & \sqrt{1+e^{-2\theta}} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} \qquad \text{II-24}$$

where θ is the tunneling integral defined by

$$\theta = \int_b^c \sqrt{V(r) - \frac{E}{2}}\; dr$$

$$= \int_b^c \sqrt{-\frac{Z_2}{r} + \frac{m^2}{4r^2} - \frac{F}{4}r - \frac{E}{2}}\; dr. \qquad \text{II-25}$$

Equation II-24 is also valid if the energy is above the top of barrier. In this case the turning points are complex conjugate numbers. The branches for the integral II-25 are chosen such that $\theta>0$ for energies below the top of the barrier and $\theta<0$ for energies above it.

From Eqs. II-22 and 24, and defining $R^2 = 1+e^{-2\theta}$, it follows that

$$C = e^{\theta}\left[RA - iB\right]$$

$$= \tfrac{1}{2} e^{\theta}\left[R\, e^{i(\varphi+\frac{\pi}{4}-\frac{\pi}{2})} + e^{-i(\varphi+\frac{\pi}{4})}\right]$$

$$= \tfrac{1}{2} e^{\theta}\left[R\, e^{i\varphi} + e^{-i\varphi}\right] e^{-i\pi/4}$$

$$= \tfrac{1}{2} e^{\theta}\left[(R+1)\cos\varphi + i(R-1)\sin\varphi\right] e^{-i\pi/4} \qquad \text{II-27}$$

$$= \tfrac{1}{2} e^{\theta}\left[\alpha\, e^{i\delta_r}\right] e^{-i\pi/4},$$

where $\alpha^2 = R^2 + 1 + 2R(2\cos^2\varphi - 1)$ and

$$tg\,\delta_r = \frac{R-1}{R+1}\,\frac{\sin\varphi}{\cos\varphi} = w(\theta)\, tg\,\varphi, \qquad \text{II-28}$$

$$W(\theta) = \frac{R-1}{R+1} = \frac{\sqrt{1+e^{-2\theta}} - 1}{\sqrt{1+e^{-2\theta}} + 1}. \qquad \text{II-29}$$

Now, it is not difficult to see that

$$D = C^* = \frac{\alpha}{2}\, e^{\theta}\, e^{-i\delta_r}\, e^{i\pi/4}. \qquad \text{II-30}$$

From Eqs. II-23, 27 and 30 one sees that the eigenfunction in region I is given by

$$\psi_I(r) = \frac{N\alpha e^{\theta}}{2\sqrt{k(r)}}\left[e^{i(\delta_r - \pi/4)}\, e^{i\int_c^r k(r')dr'} + \text{complex conj.}\right] \qquad \text{II-31}$$

$$= \frac{N\alpha e^{\theta}}{\sqrt{k(r)}}\; {\cos \atop \sin}\left[\int_c^r k(r')dr' + \delta_r \pm \frac{\pi}{4}\right].$$

To finally obtain the phase shift we now study the argument of the trigonometric function in II-31 very far from the scattering center i.e.

at infinity. The background "momentum" is given by

$$k_o(r) = \lim_{r\to\infty} k(r) = \left(\frac{E}{2} + \frac{F}{4}\, r\right)^{1/2} \qquad \text{II-32}$$

The corresponding turning point is given by $k_o(c_o) = 0$, i.e. $c_o = -2E/F$. From Figure II-4 it is clear that $c < c_o$. The integral in II-31 can be rewritten as

$$\begin{aligned}\int_c^r K &= \int_c^r k + \int_r^\infty k - \int_r^\infty k = \int_c^\infty k - \int_r^\infty k \\ &= \int_c^{c_o} k + \int_{c_o}^r k_o + \int_r^\infty k_o + \int_{c_o}^\infty (k-k_o) - \int_r^\infty k \\ &= \int_c^{c_o} k + \int_{c_o}^r k_o + \int_{c_o}^\infty (k-k_o) - \int_r^\infty (k-k_o),\end{aligned} \qquad \text{II-33}$$

where $k(r)$ is defined in Eq. II-20 and $k_o(r)$ in II-32. It is not difficult to find that

$$\int_{c_o}^r k_o(r')\,dr' = \frac{8}{3F}\left(\frac{E}{2} + \frac{F}{4} r'\right)^{3/2}\Bigg|_{c_o}^r = \frac{8}{3F}\left(\frac{E}{2} + \frac{F}{4} r\right)^{3/2}. \qquad \text{II-34}$$

Since

$$\lim_{r\to\infty} \int_r^\infty (k-k_o) = 0, \qquad \text{II-35}$$

the eigenfunction II-31, at infinity, can be written as

$$\psi_I(r) = \frac{N\alpha e^\theta}{\sqrt{k_o(r)}} \sin\left[\!\left[\frac{8}{3F}\left(\frac{E}{2} + \frac{F}{4} r\right)^{3/2} + \frac{\pi}{4} + \delta\right]\!\right], \qquad \text{II-36}$$

where the phase shift δ is given by [compare with II-18]

$$\delta = \delta_o + \delta_r \qquad \text{II-37}$$

$$\delta_r = \operatorname{arctg}\{w(\theta)\, \operatorname{tg}\varphi\}, \qquad \text{II-38}$$

$$\left.\begin{aligned}\delta_o &= \int_c^{c_o} k(r)\,dr + \int_{c_o}^\infty [k(r) - k_o(r)]\,dr \\ &= \int_c^\infty k(r)\,dr - \int_{c_o}^\infty k_o(r)\,dr.\end{aligned}\right\} \qquad \text{II-39}$$

Note that although each of the integrals in II-39 is infinite, their difference is finite and easy to evaluate [we actually did this numerically, using Simpson's rule]. The above formula for the phase shift contains all the physically relevant information regarding the scattering process. The phase shift is given by two terms, whose generic variations with energy are schematically indicated in Fig. II-5.

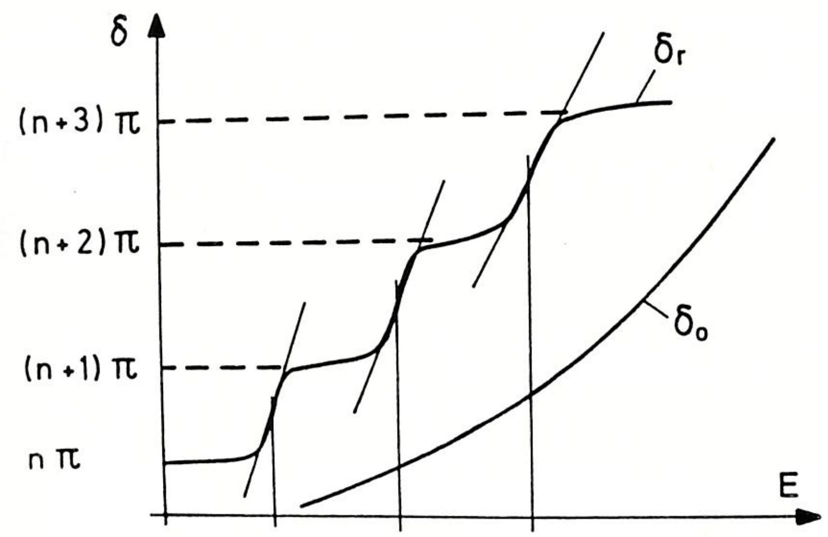


Fig. II-5 Schematic representation of δ_o and δ_r as functions of the energy.

The first term δ_o is the usual semiclassical phase shift, obtained by simply ignoring the inner region. The second term δ_r, the resonant part, is the modification produced by the ionic core and the barrier. For most values of the energy the $w(\theta)$ factor [see figure II-6, below] ensures that δ_r is almost an integral multiple of π. Therefore the scattering eigenfunction, which depends on $\sin(\frac{2}{3}z^{3/2} + \frac{\pi}{4} + \delta_r + \delta_o)$ and not on the absolute value of δ_r, is not affected by the inner region. It is clear that resonances of tg δ_r occur when E passes through one of the energy levels E_n of the well. If the usual Breit-Wigner parametrization of the resonant phase shift

$$\operatorname{tg}\delta_r(E) \simeq \frac{\Gamma_n}{2(E-E_n)} \qquad \text{II-40}$$

for E near E_n is used, then the condition for resonance is

$$\varphi(E_n) = (n+\tfrac{1}{2})\pi \qquad \text{II-41}$$

with the width of the resonance being given by

$$\Gamma_n = \frac{2\,w(\theta)}{(\partial\varphi/\partial E)|_{E_n}} . \qquad \text{II-42}$$

To conclude, we evaluate the tunneling integral θ, as defined in II-25, and study the behaviour of the function w(θ), defined by II-29. The tunneling integral can be evaluated in the same way as I_ξ [section II-2]. The final result is

$$\theta = \frac{\sqrt{F}}{2}\left[\!\left[\frac{a+b+c}{3}\,\theta^{(1)} - \frac{2}{3}(ab+ac+bc)\,\theta^{(0)} + abc\,\theta^{(-1)}\right]\!\right] \qquad \text{II-43}$$

with

$$\left.\begin{aligned} &\theta^{(0)} = g\,\mathbb{K}(k), \qquad \theta^{(-1)} = \frac{g}{c}\,\Pi\left(\frac{c-b}{c}, k\right), \\ &\theta^{(1)} = g\left[a\,\mathbb{K}(k) + (c-a)\,\mathbb{E}(k)\right], \end{aligned}\right\} \qquad \text{II-44}$$

where now $g^2 = 4/(c-a)$ and $k^2 = (c-b)/(c-a)$. Of course, the roots a, b and c are the same as defined in Eq. II-13. One of the particularities of the scattering treatment is that the usual "exponential decay", given by $e^{-2\theta}$, is replaced by a more complicated function of $e^{-2\theta}$, namely by w(θ) [see Eq. II-29]. In the limit of energies well below the top of the barrier $w(\theta) \cong e^{-2\theta}/4$. These two functions are compared in Figure II-6. The tunneling integral θ is positive for energies below the top of the barrier, which is caracterized by having θ=0. Note that the top [θ ≅ 0] is the region were w(θ) and $e^{-2\theta}/4$ are most different.

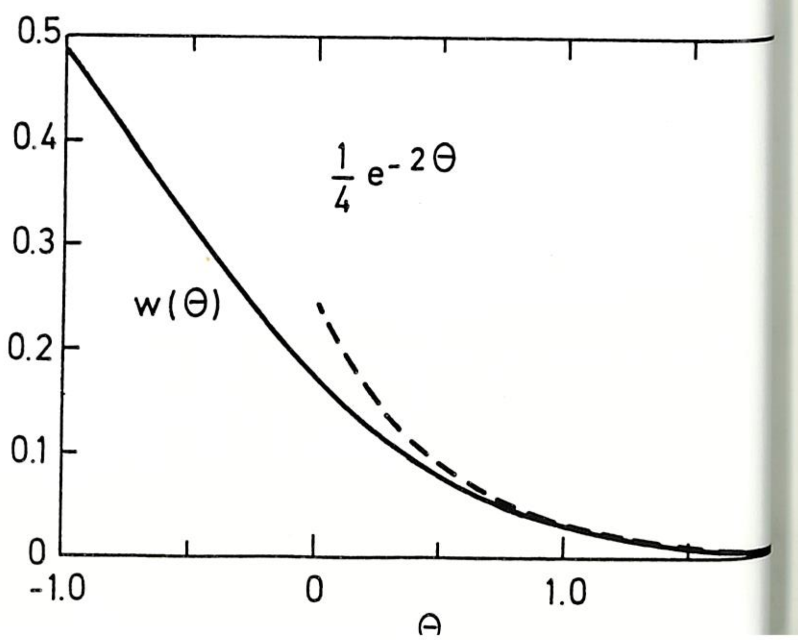


Fig. II-6
The functions w(θ) and 0.25 $e^{2\theta}$.

II-4 Application to the Stark effect

In section II-2 we studied the Stark effect ignoring the effects of the outer region in the quantization of the motion along the η coordinate. As already mentioned, this approximation produces good results for the position of the lines but very poor ones for the widths. We now want to treat the problem in a more rigorous semiclassical approximation, namely we want to apply the scattering formalism developed in the previous section to the electronic motion along the η coordinate. To this end the quantization as given by Eq. II-14 is replaced by the study of the phase shift

$$\delta = \delta_0 + \delta_r , \qquad \text{II-37}$$

$$\delta_r = \operatorname{arctg}\{ w(\theta)\, \operatorname{tg} I_\eta \} , \qquad \text{II-38}$$

$$\delta_0 = \int_c^{c_0} k(r)\,dr + \int_{c_0}^{\infty} [k(r) - k_0(r)]\,dr , \qquad \text{II-39}$$

where all symbols were defined in the previous two sections. In particular, note that $\varphi \equiv I_\eta$, I_η being defined in II-14. Figure II-7 shows a plot of δ versus E, for fixed F,m and n_1. For comparison we also plot $n_2 = I_\eta/\pi - 1/2$, [which corresponds to the simplified quantization discussed in section II-2]. It is easy to see that the phase δ jumps by π every time that the energy is such that $\delta/\pi = 2n_2 + 1 + m/2$.

The corresponding width of the resonances is given by Eq. II-42, namely

$$\Gamma = 2\,w(\theta)\left(\frac{\partial I_\eta}{\partial E}\right)^{-1} . \qquad \text{II-42}$$

It is not difficult to see that

$$\frac{\partial I_\eta}{\partial E} = \frac{1}{\sqrt{F}}\left(\frac{1}{2}\, I_\eta^{(1)} + \frac{\partial Z_2}{\partial E}\, I_\eta^{(0)}\right) . \qquad \text{II-45}$$

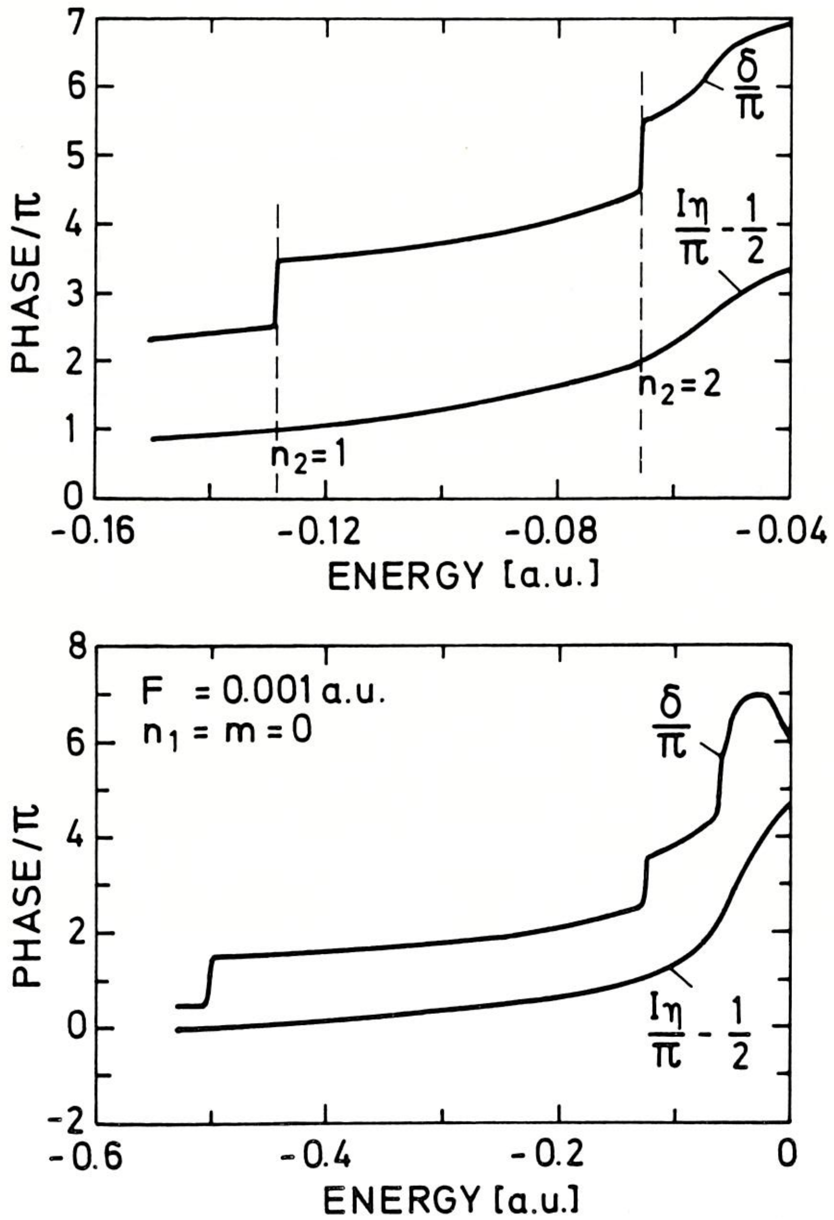


Fig. II-7

This figure shows the semiclassical solution of the Stark effect [defined by Eq. II-1] in two different approximations: (a) $n_2 = I_\eta/\pi - 1/2$, from Eq. II-4, and (b) δ/π, from Eq. II-37. A solution $E = E_r - i\,\Gamma/2$ is obtained every time (a) $n_2 = 0, 1, 2, \ldots$ or, in the other approximation, (b) whenever $\delta = (2n_2 + 1 + m/2)\pi$. The upper part is an enlarged view of the region close to the autoionization threshold. Solutions corresponding to $n_2 = 1$ and $n_2 = 2$ are indicated by dashed vertical lines. The effect of vertical jumps in δ is due to the scale being used. The curve is in fact smooth.

Since at resonance $\partial I_\xi/\partial E = 0$, it follows that

$$\frac{\partial Z_2}{\partial E} = -\frac{\partial Z_1}{\partial E} = \frac{I_\xi^{(1)}}{2 I_\xi^{(0)}}, \qquad \text{II-46}$$

and, therefore,

$$\Gamma = \frac{4\,w(\theta)\,\sqrt{F}\,I_\xi^{(0)}}{I_\xi^{(0)} I_\eta^{(1)} + I_\xi^{(1)} I_\eta^{(0)}} \qquad \text{II-47}$$

Table II-1 Comparison of present WKB results with exact numerical calculations of Damburg and Kolosov[35]. Ratio means exact/WKB. The principal quantum number is given by $n = n_1 + n_2 + m + 1$. Ionization rate is defined as $-2\,\mathrm{Im}(E)$. Here 1.54+6 means 1.54×10^6.

n	n_1	n_2	m	Field (kV/cm)	-Energy (cm^{-1})	Ionization rate (s^{-1})	Energy ratio	Ionization rate ratio
12	6	3	2	30	716.60	1.54 + 6	1.0000	1.01
				33	715.06	1.21 + 8	1.0000	1.01
				35	714.47	1.25 + 9	1.0000	1.00
				37	714.30	8.82 + 9	1.0000	0.99
12	7	2	2	33	662.15	8.22 + 6	0.9994	1.10
				35	657.99	1.03 + 8	1.0000	1.01
				37	654.13	8.91 + 8	1.0000	1.01
				40	649.01	1.24 + 10	1.0002	0.99
12	8	1	2	35	601.42	4.55 + 6	1.0003	1.03
				37	593.94	4.74 + 7	1.0001	1.03
				40	583.16	8.88 + 8	1.0001	1.02
				43	573.90	9.30 + 9	1.0004	1.00
13	2	8	2	19	761.98	6.15 + 6	1.0000	1.00
				20	769.26	8.61 + 7	1.0000	1.00
				22	784.56	5.66 + 9	1.0000	0.99
				25	810.17	2.69 + 11	1.0001	0.92
13	3	7	2	19	729.98	9.08 + 5	1.0000	1.00
				20	735.47	1.45 + 7	1.0000	1.00
				22	747.08	1.27 + 9	1.0000	1.00
				25	766.67	1.07 + 11	1.0000	0.93
13	4	6	2	20	701.58	1.97 + 6	0.9997	1.03
				22	709.52	2.27 + 8	0.9998	1.02
				25	723.14	3.20 + 10	0.9999	0.97
				27	733.81	2.45 + 11	1.0001	0.91
14	0	11	2	13.5	707.03	6.34 + 6	1.0000	1.00
				14	713.28	4.78 + 7	1.0000	1.00
				15	726.10	1.45 + 9	1.0000	1.00
				16	739.47	2.01 + 10	1.0000	0.96
				17	753.57	1.33 + 11	1.0000	0.92
14	1	10	2	14	688.08	1.01 + 7	1.0004	1.00
				15	698.96	3.68 + 8	1.0000	1.00
				16	710.31	6.42 + 9	1.0000	0.98
				17	722.28	5.58 + 10	1.0000	0.94
				18	734.92	2.49 + 11	1.0000	0.92

It is interesting to observe that this expression is given in terms of the same phase integrals of the simple quantization discussed in section II-2. Therefore, numerical evaluation of Γ just requires determination of θ [Eq. II-43] since all $I_{\xi}^{(j)}$ and $I_{\eta}^{(j)}$ are automatically obtained during calculation of the eigenvalue E. For energies well below the autoionization limit [when $w(\theta) \cong e^{-2\theta}/4$], Eq. II-47 reduces to the approximation obtained by Rice and Good[4]. In this same energy range, by further doing the crude approximation $\partial Z_2/\partial E = 0$, we obtain $\Gamma = 8\Gamma_{BS}$, where Γ_{BS} refers to the width as obtained from Eq. 54.6 of Bethe and Salpeter[12]. This give some hint of why the results from the simple WKB-formula for the width are usually found to be about one order of magnitude too small.

In table II-1 we compare our WKB results with exact numerical work of Damburg and Kolosov[35]. As mentioned by them, certain sublevels in this table cannot be correctly described by perturbation theory. As seen from our table, the WKB resonance parameters, obtained from a full three-turning-point treatment, are excellent approximations to the exact numerical parameters.

Chapter III High-order contributions in semiclassical calculations.

III-0 Introduction

From a theoretical point of view it might be somewhat surprising that, although the standard perturbative Stark energy series is known to be divergent, so much work is still being done to evaluate it as well as to resum it. In this particular point [the effect of high-order contributions], the effort spent in semiclassical and perturbative approaches differs very much: the investigation of the effect of high-order semiclassical contributions is practically non-existing.

As we divided it, there are basically two levels of approximation to the semiclassical treatment of the Stark effect: (i) the simpler quantization, described in section II-2, and (ii) the scattering approach, described in section II-4. In the present chapter we want to study the effect of high-order contributions in the simpler quantization. It is clear that this will be also part of the more complicated scattering approach although this problem is not touched here. A very interesting open question is the convergency of high-order semiclassical contributions. In the present chapter we investigate Stark states with m = o [states with m ≠ o are discussed in the next chapter]. In addition, we will show that Hadaward's concept of an improper integral may be conveniently applied to simplify the evaluation of high-order pseudo-singular WKB integrals. As far as we know, the application of Hadamard's finite part concept of an integral to evaluate high-order semiclassical corrections is original and constitutes an alternative method of treating such increasingly complicated integrals.

III-1 High-order contributions

For convenience we now briefly sketch the derivation of the well known high-order contributions to the semiclassical eigenfunction. For further details and references we refer the reader to a recent review by N. Fröman[36], which we follow here.

Consider the Schrödinger equation

$$\psi'' + Q^2(x)\,\psi = 0, \qquad \text{III-1}$$

where we define

$$Q^2(x) \equiv \frac{2m}{\hbar^2}\left[E - V(x)\right] \equiv \frac{q(x)}{\hbar^2}. \qquad \text{III-2}$$

The semiclassical Ansatz assumes the eigenfunction to be given by

$$\psi = A\, e^{\frac{i}{\hbar}S(x)}, \qquad A \to \text{constant} \qquad \text{III-3}$$

where

$$S(x) = \sum_{k=0}^{\infty} \hbar^k S_k(x)$$

$$= S_0 + \hbar S_1 + \hbar^2 S_2 + \ldots \; . \qquad \text{III-4}$$

Replacing III-3 in III-1 one obtains a non-linear differential equation for S(x), namely

$$i\hbar S'' - (S')^2 + q = 0. \qquad \text{III-5}$$

From this equation, using III-4 to construct S'', S' and $(S')^2$, and equating powers of $\hbar$ of the same degree it is easy to obtain

$$-(S_0')^2 + q = 0, \qquad \text{III-6a}$$

$$i S_0'' - 2 S_0' S_1' = 0, \qquad \text{III-6b}$$

$$i S_1'' - (S_1')^2 - 2 S_0' S_2' = 0, \qquad \text{etc} \ldots \qquad \text{III-6c}$$

Hence

$$S_0 = \pm \int \sqrt{2m(E - V(x))}\, dx, \qquad \text{III-7a}$$

$$S_1 = \frac{i}{4} \ln\left[2m(E - V(x))\right], \qquad \text{III-7b}$$

$$S_2 = \pm \frac{1}{32} \int \left(\frac{5(q')^2}{q^{5/2}} - \frac{4q''}{q^{3/2}} \right) dx, \qquad \text{III-7c}$$

$$S_3 = i\left(-\frac{q''}{16q^2} + \frac{5(q')^2}{64q^3} \right), \qquad \text{etc} \ldots \qquad \text{III-7d}$$

It turns out that the terms S_k of even order k appear with the double sign $\pm$, whereas no sign ambiguity occurs for the terms S_k of odd order k. Thus one obtains two formal solutions of the differential equation corresponding to the plus and minus signs. It also turns out that every function S_k with odd index k can be written as the derivative with respect to x of an expression containing only functions S_k with even indices. By truncating this series at different terms one obtains WKB approximations of different orders. Formulas up to the sixth-order have been recently reported by Kesarwani and Varshni[37]. Looking at their results it is not difficult to convince oneself that high-order WKB approximations are rather complicated. The WKB eigenfunction can then be written

$$\psi = A\, e^{\frac{i}{\hbar}\left(S_0 + \hbar S_1 + \hbar^2 S_2 + \ldots\right)}$$

$$= \frac{A\, e^{\pm i\left\{ \int \sqrt{q}\, dx + \frac{\hbar}{32} \int \left(\frac{5(q')^2}{q^{5/2}} - \frac{4q''}{q^{3/2}} \right) dx + \ldots \right\}}}{\sqrt{\sqrt{q}\; e^{-\left(\frac{q''}{8q^2} + \frac{5(q')^2}{32q^3} - \ldots \right)}}} \qquad \text{III-8}$$

As seen from this equation, the second-order term to the semiclassical quantization is given by

$$I_2 = \frac{\hbar}{32} \int \left\{ \frac{5(q')^2}{q^{5/2}} - \frac{4q''}{q^{3/2}} \right\} dx. \qquad \text{III-9a}$$

This integral, as well as all other high-order corrections, has non-integrable singularities at the turning points. The standard analytical way to treat it[38] is to write these expressions as a parametric derivative with respect to the energy. For example

$$I_2 = -\left(\frac{\hbar^2}{2m}\right)^{1/2} \frac{1}{24} \frac{\partial}{\partial E} \int_{x_1}^{x_2} \frac{V''(x)}{\sqrt{E-V(x)}}\, dx \,. \qquad \text{III-9b}$$

In general, the quantization rule is then written as

$$\left(n+\tfrac{1}{2}\right)\pi = I_1 + I_2 + I_3 + I_4 + \ldots \qquad \text{III-10}$$

The expressions for I_3, I_4, ... are very complicated and, as mentioned before, can be obtained from the literature[37]. It is interesting to observe that the same integrals I_2, ... can be used to obtain high-order corrections to the phase shift discussed in section II-3.

III-2 Some applications

If instead of starting our semiclassical treatment by studying the quantization integral II-5, namely

$$I_\xi = \int_b^a \sqrt{\frac{E}{2} + \frac{Z_1}{\xi} - \frac{m^2}{4\xi^2} - \frac{F}{4}\xi}\; d\xi \,, \qquad \text{III-11}$$

had we first chosen to change variable according to $\xi = u^2$, then the quantization integral would have been given by

$$I_\xi = 2\int_{\sqrt{b}}^{\sqrt{a}} \sqrt{Z_1 + \frac{E}{2}u^2 - \frac{m^2}{4u^2} - \frac{F}{4}u^4}\; du \,. \qquad \text{III-12}$$

This equation shows perhaps more clearly that we are dealing with an eigenvalue problem for the separation constant Z_1. It also shows that the Stark problem can be represented by a perturbed harmonic oscillator. This fact is closely connected with the possibility of separating the Stark Hamiltonian in the so-called "squared" parabolic coordinates[39]. Therefore we will now discuss some applications of high-order quantization to the particular polynomial terms which appear in III-12.

It is a trivial and cumbersome job to show that the second-order WKB

term III-9a, 9b can be rewritten in the following identical forms:

$$-\left(\frac{2m}{\hbar^2}\right)^{1/2} I_2 = \frac{1}{64} \oint \frac{(V')^2}{(E-V)^{5/2}} \qquad \text{III-13a}$$

$$= \frac{1}{32} \fint_{x_1}^{x_2} \frac{V'}{(E-V)^{5/2}}\, dx \qquad \text{III-13b}$$

$$= -\frac{1}{48} \fint_{x_1}^{x_2} \frac{V''}{(E-V)^{3/2}}\, dx \qquad \text{III-13c}$$

$$= \frac{1}{24} \frac{\partial}{\partial E} \int_{x_1}^{x_2} \frac{V''}{\sqrt{E-V}}\, dx \qquad \text{III-13d}$$

$$= \frac{1}{24} \fint_{x_1}^{x_2} \left[\frac{V'''}{V'} - \left(\frac{V''}{V'}\right)^2 \right] \frac{dx}{\sqrt{E-V}} \qquad \text{III-13e}$$

$$= \frac{1}{12} \fint_{x_1}^{x_2} \left[\frac{V^{IV}}{(V')^2} - \frac{4V''V'''}{(V')^3} + \frac{3(V'')^3}{(V')^4} \right] \sqrt{E-V}\, dx \qquad \text{III-13f}$$

$$= \frac{1}{18} \fint_{x_1}^{x_2} \left[\frac{V^{V}}{(V')^3} - \frac{7V^{IV}V'' + 4(V''')^2}{(V')^4} + \frac{25V'''(V'')^2}{(V')^5} - \frac{15(V'')^4}{(V')^6} \right] (E-V)^{3/2}\, dx \,. \qquad \text{III-13g}$$

The symbol $\fint$ means that the integral is interpreted as Hadamard's finite part (see Appendix). The possibility of writing I_2 in so many different forms helps very much in its evaluation. As mentioned before, the usual approach to evaluate high-order integrals is to use the parametric derivative form given by III-13d. However, we want to make the point that III-13e, by avoiding the need for parametric differentiation, may be more convenient. The form 13-e is especially suited for computer programs able to do algebraic manipulations. It is also convenient for use with standard quadrature formulas[40,41]. Of course all high-order WKB integrals may be written in terms of the finite part concept.

We now use the interaction $V(x) = x^4$ to show how the identity

$$\frac{\partial}{\partial E}\int_{x_1}^{x_2}\frac{V''}{\sqrt{E-V}}\,dx = \fint_{x_1}^{x_2}\left[\frac{V'''}{V'}-\left(\frac{V''}{V'}\right)^2\right]\frac{dx}{\sqrt{E-V}} \qquad \text{III-14}$$

indeed holds. As in II-9, identities between integrals involving the potential $V(x)$ are extremely useful to show symmetries of the semi-classical solution of the relevant physical problem. Taking $x = E^{1/4}\,y$, Eq. III-14 may be rewritten as

$$\frac{\partial}{\partial E}\left\{12\,E^{1/4}\int_{-1}^{1}\frac{y^2dy}{\sqrt{1-y^4}}\right\} = -3\,E^{-3/4}\fint_{-1}^{1}\frac{dy}{y^2\sqrt{1-y^2}}\;. \qquad \text{III-15}$$

Therefore

$$\int_0^1\frac{y^2dy}{\sqrt{1-y^4}} = -\fint_0^1\frac{dy}{y^2\sqrt{1-y^4}}\;. \qquad \text{III-16}$$

In general the parametric derivative is not so simple to evaluate since the energy does not always exactly factor. The identity of III-16 is easy to verify:

$$\int_0^1\frac{y^2dy}{\sqrt{1-y^4}} = \frac{1}{\sqrt2}\int_0^{\mathbb{K}} cn^2u\;du$$

$$= \frac{1}{\sqrt2}\left[2\mathbb{E}\left(\tfrac{\sqrt2}{2}\right)-\mathbb{K}\left(\tfrac{\sqrt2}{2}\right)\right], \qquad \text{III-17}$$

where cnu is the cosine amplitude jacobian elliptic function[42]. The finite part can be evaluated in a similar way

$$-\fint_0^1\frac{dy}{y^2\sqrt{1-y^4}} = -\frac{1}{\sqrt2}\fint_0^{\mathbb{K}} nc^2u\;du \qquad \text{III-18a}$$

$$= -\frac{1}{\sqrt2}\left\{u-2\mathbb{E}(u)-2\,dn\,u\;tn\,u\right\}\fint_0^{\mathbb{K}},$$

where, as before, ncu, dnu and tnu are jacobian elliptic functions.

Considering only the finite part it follows that

$$-\fint_0^1\frac{dy}{y^2\sqrt{1-y^4}} = -\frac{1}{\sqrt2}\left[\mathbb{K}\left(\tfrac{\sqrt2}{2}\right)-2\mathbb{E}\left(\tfrac{\sqrt2}{2}\right)\right], \qquad \text{III-18b}$$

and, therefore, Eq. III-16 is verified. It is straighforward and tedious to verify that the same results are obtained from any of Eqs. III-13a-g. For the particular modulus of the elliptic integrals in III-17-18 it is possible to show, using properties of hypergeometric functions that,

$$2\mathbb{E}\left(\tfrac{\sqrt2}{2}\right)-\mathbb{K}\left(\tfrac{\sqrt2}{2}\right) = \frac{\pi}{2\mathbb{K}\left(\tfrac{\sqrt2}{2}\right)} = \frac{2\pi\sqrt{\pi}}{\{\Gamma(1/4)\}^2}\,, \qquad \text{III-19}$$

where $\Gamma(x)$ is the gamma function. Noting that $R = \Gamma(1/4)\,/\,\Gamma(3/4) = \{\Gamma(1/4)\}^2\,/\,(\pi\sqrt2)$, it is easy to see that the above results perfectly agree with the large order WKB analysis of Bender et al.[43]). It turns out that all high-order corrections are given by simple functions of R, i.e. of the constant defined in III-19. For applications, it is interesting to know that Bender et al.[43] determined R to 26 significant digits.

We now consider quartic oscillators with quadratic perturbations, as is the case for the m=0 Stark problem defined by Eq. III-12. Before proceeding, a very useful remark concerning the Hamiltonian

$$H(A,B) = \tfrac12 p^2 + Ax^2 + Bx^4, \qquad B>0 \qquad \text{III-20}$$

is in order. Through the trivial rescaling $x \to sx$ $(p \to p/s)$ it follows that $H(A,B)$ and $s^{-2}\,H(s^4A,\,s^6B)$ are equivalent and therefore have the same eigenvalues. Hence

$$E(A,B) = B^{1/3}\,E(C,1), \qquad C = B^{-2/3}A, \qquad \text{III-21}$$

and, therefore, the problem reduces to the study of the spectrum of

$$H(C,1) = \tfrac12 p^2 + Cx^2 + x^4,$$

which contain only one free parameter, namely C.

Introducing the abbreviations

$$y = C/\sqrt{C^2+4E} = 1-2k^2 , \qquad \text{III-22a}$$

$$k^2 = \tfrac{1}{2}(1-y) , \qquad \text{III-22b}$$

$$z = k^2(1-k^2) = \tfrac{1}{4}(1-y^2) , \qquad \text{III-22c}$$

$$\beta = 4\left(\frac{2m}{\hbar^2}\right)^{1/2} \{4E+C^2\}^{3/4} \qquad \text{III-22d}$$

one can show, after an extremely tedious calculation, that the first five high-order contributions to the quantization rule [see section III-1]

$$(n+\tfrac{1}{2})\pi = I_1 + I_2 + I_3 + \ldots \qquad \text{III-23}$$

are given by

$$I_1 = \frac{\beta}{6}\{2zP - yQ\} , \qquad \text{III-24a}$$

$$I_2 = \frac{1}{3\beta}\{-4yP - (\tfrac{1}{z}+8)Q\} , \qquad \text{III-24b}$$

$$I_3 = \frac{4}{45\beta^3}\Big\{\Big(-\frac{28}{z^2}+\frac{66}{z}-5664+28672z\Big)P$$

$$+\Big(\frac{56}{z^3}-\frac{69}{z^2}+\frac{144}{z}-14336\Big)yQ\Big\} , \qquad \text{III-24c}$$

$$I_4 = \frac{2^5}{315\beta^5}\Big\{\Big(\frac{124}{z^4}-\frac{441}{4z^3}+\frac{587}{4z^2}+\frac{1108}{z}-551424+4063232z\Big)yP$$

$$-\Big(\frac{248}{z^5}-\frac{1867}{2z^4}+\frac{10189}{16z^3}+\frac{2135}{2z^2}-\frac{11624}{z}+1610752-8126464z\Big)Q\Big\} , \qquad \text{III-24d}$$

$$I_5 = \frac{2^7}{315\beta^7}\Big\{\Big(-\frac{1524}{z^6}+\frac{5883}{z^5}-\frac{55079}{16z^4}-\frac{7253}{64z^3}+\frac{32591}{2z^2}+\frac{83596}{z}$$

$$-149719040+2128740352z-6392119296z^2\Big)P$$

$$+\Big(\frac{3048}{z^7}-\frac{8337}{z^6}+\frac{15169}{4z^5}+\frac{316085}{128z^4}-\frac{87275}{4z^3}-\frac{158246}{z^2}$$

$$+\frac{1696768}{z}-465108992+3196059648z\Big)yQ\Big\} , \qquad \text{III-24e}$$

where

$$P = \mathbb{K}(k) , \qquad \text{III-25}$$

$$Q = \mathbb{E}(k) - (1-k^2)\mathbb{K}(k) . \qquad \text{III-26}$$

As it is obvious from the above equations, the evaluation of $I_1+I_2+I_3+I_4+I_5$ amounts basically to the evaluation of P and Q, i.e. of the complete elliptic integrals and , since the remaining operations in Eqs. III-24a-e are all trivial. For C = 0 one finds $k^2 = 1/2$ and all the I_j above reduce to known results[43], which we had previously mentioned [compare III-26 and III-194]. Recently[44], using what they call phase-integral method, Lakshmanan, Karlsson and Fröman derived for C ≠ 0 quantization integrals, up to the 4th order, which agree with ours III-24a-d. It is important to realize that the quantization equation III-23 remains valid as long as E > 0 [i.e. as long as the problem remains a two-turning-point problem]. Therefore, the parameter C may be negative. The lower limit of C depends on the quantum state being investigated as well as on the order of the quantization being used. This is illustrated in Figure III-1. The fact that C may be negative has not been appreciated in the literature [see ref. 44 and references therein].

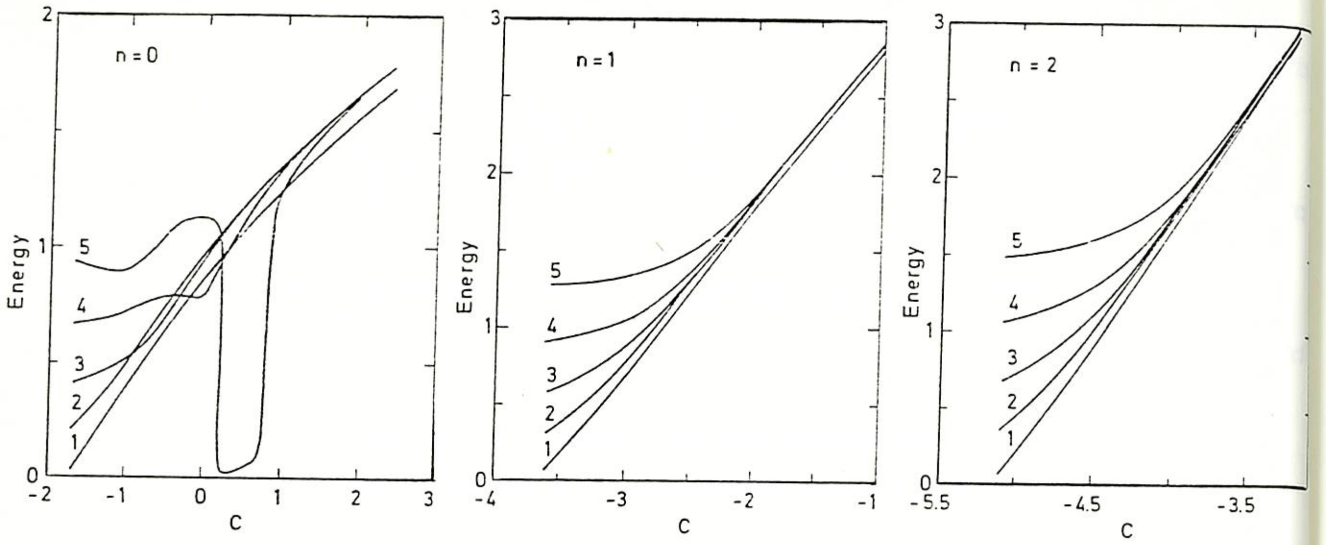


Fig. III-1 The three lowest eigenvalues of $V(x) = Cx^2 + x^4$ as a function of C. The semiclassical solution is valid for $C < 0$ as long as $E_n > 0$. Here units are such that $2m = \hbar^2$.

One striking feature in Figure III-1 is the behaviour of the fifth-order WKB approximation to the ground state eigenvalue in the region $0 \lesssim C \lesssim 1$. We have no explanation for this behaviour. [We do not believe our I_j to be incorrect. For the particular case $C = 0$ Bender et al.[43] derived formulas up to the seventh-order and our five equations perfectly reduce to theirs. For $C \neq 0$, the same behaviour (with less intensity) is already present in the third- and fourth-order approximations. Lakshmanan et al.[44], in their fourth-order investigation, missed this behaviour because they did not go to low enough C. Up to fourth-order, their formulas are identical to ours]. Another striking feature of Figure III-1 is that, independently of the quantum number, one can always find a region of C where the eigenvalues seem to diverge. Since for $C < 0$ the potential contains two wells separated by a barrier whose energy maximum is at $E = 0$, it seems that every quantum level "knows" when it is going to "hit the top" [i.e. to change from $E_n > 0$ to $E_n < 0$].

To show the effect of the high-order terms as the quantum number increases and C is maintained fixed, we present in Table III-1 some numbers for $C = 0$ for which case exact results are available[43]. This table corroborates the common knowledge that the accuracy of WKB eigenvalues increases as the quantum number increases. However, as shown in Figure III-1, this does not precludes the possibility of, for any given n, finding a region of C such that the eigenvalues become quickly inaccurate.

n	order	eigenvalue	I_1	I_2	I_3	I_4	I_5
0	1	0.867	1.5708				
	2	0.980	1.7228	-0.1520			
	3	0.951	1.6842	-0.1554	0.0420		
	4	0.787	1.4614	-0.1791	0.0643	0.2243	
	5	1.129	1.9151	-0.1367	0.0286	0.0580	-0.2942
	exact	1.06036209048418					
2	1	7.41398	7.8540				
	2	7.45579	7.8872	-0.0332			
	3	7.45528	7.8868	-0.0332	0.0004		
	4	7.45522	7.8867	-0.0332	0.0004	0.0000	
	5	7.45523	7.8867	-0.0332	0.0004	0.0000	-0.0000
	exact	7.45569793798673					
4	1	16.23361469	14.1372				
	2	16.26193674	14.1557	-0.0185			
	3	16.26182856	14.1556	-0.0185	0.0001		
	4	16.26182453	14.1556	-0.0185	0.0001	0.0000	
	5	16.26182491	14.1556	-0.0185	0.0001	0.0000	-0.0000
	exact	16.26182601885022					
6	1	26.5063355109	20.4204				
	2	26.5285125517	20.4332	-0.0128			
	3	26.5284718732	20.4331	-0.0128	0.0000		
	4	26.5284711471	20.4331	-0.0128	0.0000	0.0000	
	5	26.5284711794	20.4331	-0.0128	0.0000	0.0000	-0.0000
	exact	26.52847188368251					
8	1	37.90447184506	26.7035				
	2	37.92302114052	26.7133	-0.0098			
	3	37.92300122935	26.7133	-0.0098	0.0000		
	4	37.92300102141	26.7133	-0.0098	0.0000	0.0000	
	5	37.92300102683	26.7133	-0.0098	0.0000	0.0000	-0.0000
	exact	37.92300102703395					
10	1	50.2401523191725	32.9867				
	2	50.2562659320022	32.9947	-0.0079			
	3	50.2562545929486	32.9947	-0.0079	0.0000		
	4	50.2562545153248	32.9947	-0.0079	0.0000	0.0000	
	5	50.2562545166505	32.9947	-0.0079	0.0000	0.0000	-0.0000
	exact	50.25625451668291					

Table III-1. Comparison of the exact eigenvalues[43] of the x^4 interaction with the 1,2,3,4 and 5th order WKB approximations to them. Observe how rapidly the maximal accuracy increases with n. Observe also that the eigenvalue for the ground-state seems to diverge. The several I_j in this table show the relative contribution from the high orders.

To conclude we observe that Eqs. III-28a-e above generalizes to fifth-order the ξ-quantization rule discussed in chapter II. Note that, as shown in chapter II, once the ξ-quantization is known, the η-quantization follows from symmetry considerations. As they stand, these generalizations are valid only for m = 0 states. In the next chapter we discuss an alternative semiclassical quantization which extends the fifth-order formula for arbitrary m states.

Chapter IV A different semiclassical quantization

IV-1 Alternative quantization

We now want to show how the high-order results of the previous chapter, valid for m = 0, can be used for states with arbitrary m values.

Up to this point we have been discussing the quantization of the Stark problem using the WKB semiclassical approximation. The simplest version of this quantization is given by the equations [see III-12].

$$2\int \sqrt{Z_1 + \frac{E}{2}\xi^2 - \frac{m^2}{4\xi^2} - \frac{F}{4}\xi^4}\, d\xi = \left(n_1 + \tfrac{1}{2}\right)\pi, \qquad \text{IV-1a}$$

$$2\int \sqrt{Z_2 + \frac{E}{2}\eta^2 - \frac{m^2}{4\eta^2} + \frac{F}{4}\eta^4}\, d\eta = \left(n_2 + \tfrac{1}{2}\right)\pi, \qquad \text{IV-1b}$$

subjected to the condition $Z_1 + Z_2 = Z$, and where, as already discussed, the integrals are to be evaluated between turning points defined from their respective integrands. In this section we want to investigate a very interesting alternative semiclassical quantization which was recently discussed by Hioe and Yoo[45]. When applied to the Stark problem, this alternative quantization reads

$$2\int \sqrt{Z_1 + \frac{E}{2}u^2 - \frac{F}{4}u^4}\, du = \left(n_1 + \frac{m}{2} + \frac{1}{2}\right)\pi \qquad \text{IV-2a}$$

$$2\int \sqrt{Z_2 + \frac{E}{2}v^2 + \frac{F}{4}v^4}\, dv = \left(n_2 + \frac{m}{2} + \frac{1}{2}\right)\pi \qquad \text{IV-2b}$$

This quantization is particularly interesting owing to the simplicity with which the centrifugal contribution (the m^2 term) is treated. It clearly shows that the results for $m = 0$ derived in the previous chapter can be extended to states with $m \neq 0$. Equations 1a-b involve elliptic integrals of <u>three kinds</u> while, as shown in the previous chapter, equations 2a-b involve only integrals of <u>two kinds.</u> Besides this simplification, high-order contributions to the quantization defined by 2a-b can all be reduced to simple functions of the <u>same</u> two integrals needed for the first-order quantization [see formulas III-24a-e]. It is important to observe that one could think of calculating high-order corrections for the potentials in 1a-b. However, owing to the presence of the centrifugal term, the resulting integrals are just intractable.

The original derivation of the quantization rules IV-2 is due to Titchmarsh[17]. Titchmarsh obtained these equations while studying approximations to poles of Green's function corresponding to the Stark problem. For a detailed derivation of the equations see Titchmarsh[17].

The integrals appearing in the quantization rule defined in IV-2 were extensively discussed in previous chapters. From IV-1 and IV-2 it is obvious that WKB and Titchmarsh's quantizations give exactly the same results for $m = 0$ states. We want to investigate how they compare when $m \neq 0$. In the following, a brief comparison of results from first-order WKB and Titchmarsh's rules with exact numerical results is presented.

IV-2 <u>Comparison</u>

As mentioned before, IV-2 reduces to standard WKB quantization when $m = 0$. It is a simple calculation to use the identity

$$\int_{r_1}^{r_2} \frac{dr}{r} \sqrt{-r^2 + (r_1+r_2)r - r_1 r_2} = \frac{\pi}{2}\left(r_1 + r_2 - \sqrt{r_1 r_2}\right) \qquad \text{IV-3}$$

to show that IV-1 and IV-2 give the same result when $F = 0$ and $m \neq 0$. For $F \neq 0$ and $m \neq 0$ the identity between both quantization rules

<u>Table IV-1</u> Comparison between Exact[25], WKB and Titchmarsh resonance energies.

n_1	n_2	m	10^4F	$-E_{exact}$	WKB/Exact	Titchmarsh/Exact
0	0	1	40	0.126316885	0.9972	0.9984
0	0	1	80	0.13118859	0.9845	0.9895
3	0	1	1.556	0.0168552372	0.9988	0.9994
3	0	1	1.9448	0.0161793885	0.9982	0.9993
3	0	1	2.1393	0.015860468	0.9972	0.9985
3	0	1	2.5282	0.015269204	0.9947	0.9968
3	0	1	2.9172	0.014740243	0.9913	0.9946

does not hold anymore. The lowest quantum state satisfying these conditions is $n = 2$ [$n_1 = n_2 = 0$, $m = 1$]. In Table IV-1 we compare WKB and Titchmarsh's quantization with exact numerical calculations of Damburg and Kolosov[25]. The majority of the numerical results reported by these authors are for states with $m = 0$ and, therefore, cannot be used for the present purpose.

The values of the field strengths for the quantum states given in Table IV-1 are such that the states lie very close to the autoionization limit. It is important to realize that the numbers given in Table IV-1 were obtained from the simplest possible semiclassical calculation, namely neglecting the possibility of tunneling. It is also important to note that, in principle, semiclassical calculations should not be expected to give accurate results for low n_1 and n_2 quantum numbers. Therefore we see that the numbers being compared in Table IV-1 correspond to the <u>most unfavorable</u> situations for semiclassical calculations, namely low quantum numbers and energy region close to the autoionization limit (where two of the turning points coalesce). Even so the semiclassical results are close to the exact ones. It is easy to recognize that values from Titchmarsh's quantization are slightly better then the ones from standard WKB quantization.

Summary

Motivated by recent very interesting experimental results we investigated spectral properties of one-electron atoms in the presence of static electric fields. Of particular interest is the behaviour of Rydberg states near the classical autoionization threshold. Using a semiclassical WKB approach we first reconsidered the standard first-order treatment of this problem. For the first time, the complete analytical semiclassical quantization rules for this problem was obtained. This analytical quantization is complete in the sense of including all effects of the magnetic quantum number of the electron and is exact, within first-order theory, in the standard approximation of treating as uncorrelated the motions near the atomic core and in the asymptotic region. By comparing predictions of this quantization with experimental results and with results from alternative calculations one sees that, although such quantization is capable of reproducing the center of the Stark resonances well, it predicts far too small values for the widths of Rydberg states. In other words, thinking of the resonance parameters as complex eigenvalues, the above quantization predicts reasonable results for the real part of the eigenvalues but gives too small values (of about one order of magnitude) for their imaginary part. To improve upon this result one may either try to obtain high-order quantization rules or treat the first-order problem as a scattering problem. This Stark scattering problem is difficult to treat since the relevant potential [see Eq. II-3 and section II-3] is not bounded from below, in contrast with usual situations where the potential goes to zero far from the scattering center. In section II-3 we developed a general semiclassical formalism to treat scattering from potentials which behave as r very far from the scattering center. When applied to the Stark problem this scattering formalism produces resonance parameters (i.e. complex eigenvalues) which are excellent approximations to the measured ones. Furthermore, the general semiclassical solution is very compact and can be expressed as very simple functions of the three usual phase integrals [our $I_\xi^{(j)}$, $I_\eta^{(j)}$ and $\theta^{(j)}$].

We have also considered high-order semiclassical quantization. Since the direct high-order quantization in parabolic coordinates is an

extremelly difficult problem, we considered the analogy between the spectrum of the Stark Hamiltonian and of some anharmonic oscillators. For m = 0 states, after some very tedious work, the high-order quantization rules can all be expressed as simple functions of the same phase integrals used in the first-order quantization [see Eq. III-24]. This implies that practically the same effort used to obtain first-order resonance parameters is needed to generate highly accurate Stark eigenvalues. For arbitary m states an alternative semiclassical quantization rule, due to Titchmarsh, may be efficiently used.

Our study indicates that, for any physical problem, it is always possible to express first-order semiclassical quantization rules as simple functions of some (usually 2 or 3) basic phase integrals. It also indicates that all high-order corrections can be reduced to simple functions of the same basic phase integrals. To reduce high-order semiclassical contributions to this basic set of phase integrals, we proposed in section III-2 a new approach based on Hadamard's concept of improper integrals. This new approach can be implemented in computers able to manipulate algebraic expressions. Such computer manipulations are realizable nowadays[46]. The observations above allow one to hope for, in the near future, a fully automated semiclassical quantization. Upon definition of a potential a computer would be able to perform the algebraic reduction and, of course, the numerical work.

In conclusion, we have revised the semiclassical treatment of the Stark effect. Using first-order theory we obtained analytical formulas for the quantization rule. By studying scattering problems from potentials which diverge as -r far from the scattering center we obtained the correct imaginary part of the Stark complex eigenvalues, giving the ionization rate as a function of the field strength. The semiclassical formulation is very compact [it is based in three phase integrals] and, contrary to current belief, produces excellent approximations to experimental resonance parameters. Semiclassical quantization in higher orders was also investigated. We proposed Hadamard's concept of an improper integral as a useful device to compute pseudo

singular WKB integrals. By exploring the symmetries of the Stark and anharmonic oscillator problems, a quantization rule up to the fifth-order was given. Using Titchmarsh's alternative semi-classical quantization, which we considered in chapter IV, the fifth-order quantization rule mentioned above can be directly used to obtain Stark eigenvalues. It is also important to note that the scattering formalism developed in chapter II as well as the new approach to treat pseudo singular semiclassical integrals, besides being original, are of general use in semiclassical theory. In particular, we have also been able to use them to investigate Zeeman diamagnetism in hydrogen[28,47].

Appendix

Hadamard's concept of an integral.

In 1923, while studying properties of hyperbolic differential equations Hadamard[48] introduced what he called the "rather paradoxical notion" of a "new kind of improper integral". We now present the arguments originally used by Hadamard to introduce his improper integral.

Let us start from the integral

$$\int_a^b \frac{A(x)}{\sqrt{b-x}}\, dx \,. \qquad \text{A-1}$$

A direct differentiation of this integral with respect to b appears impossible: indeed this would consist in writing the absurd expression

$$-\frac{1}{2}\int_a^b \frac{A(x)\,dx}{(b-x)^{3/2}} + \left[\frac{A(x)}{\sqrt{b-x}}\right]_{x=b} \qquad \text{A-2}$$

a sum of two terms, the first of which has no meaning as it contains an infinity of order 3/2 in the integrand and the second being evidently meaningless.

There is, however, an immediate means of performing directly (i.e., without any transformation) this differentiation. It would consist in replacing the real integral A-1 by the half of the complex integral taken along a path constituted by two lines along ab, connected by a small circle around b as shown in Figure A-1: for such a path differentiation presents no difficulty. Of course one must have somehow a means of doing this without introducing complex quantities. Indeed, as noticed by Hadamard, one has only to observe that (replacing b by x in the upper limit), not the integral

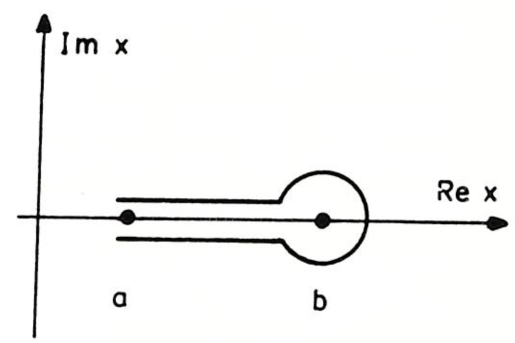


Fig. A-1

$$\int_a^x \frac{A(x)}{(b-x)^{3/2}}\,dx \qquad \text{A-3}$$

but the algebraic sum

$$\int_a^x \frac{A(x)}{(b-x)^{3/2}}\,dx - \frac{2A(x)}{\sqrt{b-x}} \qquad \text{A-4}$$

approaches a perfectly definite limit when x approaches b. Moreover, the same remains valid for

$$\int_a^x \frac{A(x)}{(b-x)^{3/2}}\,dx - \frac{B(x)}{\sqrt{b-x}} \qquad \text{A-5}$$

if B be any differentiable function of x such that B(b) = - 2A(b). Furthermore, the result obtained is independent of the choice of the function B. This is due to the fact that the denominator is of a fractional order, while a change of the function B (under the above hypothesis) would alter it by terms containing at least b-x in the first power as factor, so that the corresponding terms in the fraction would necessarily vanish for x = b. Therefore, to calculate the limit A-5 we do not even need to indicate what special function B we choose. This limit was called by Hadamard "the finite part" of the integral A-2. Instead of using Hadamard's original notation we will denote this improper integral by

$$\ne\!\!\!\!\int_a^b \frac{A(x)}{(b-x)^{3/2}}\,dx\,, \qquad \text{A-6}$$

the = sign in the integral being read "finite part of". If A is analytic, besides the limit as defined by A-5, the finite part A-6 can just as well be defined as half of the corresponding integral taken along the aforementioned path. No difficulties arise in defining the same symbol for higher orders of infinity, provided they always are fractional. Further details can be found in the original book by Hadamard[48]. Hadamard's finite part turns out to be a distribution function. Therefore more recent literature is found in this particular area of mathematical analysis[49/50].

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