

## WKB solution of the Stark effect in hydrogen

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We present an analytical solution for the nonrelativistic Stark effect in hydrogen separated in parabolic coordinates. The solution is given in terms of elliptic integrals and is obtained in a first-order WKB approximation. In addition, by a suitable approximation, we extend the WKB results to autoionizing states, above the threshold barrier. A short comparison of the present results with exact numerical calculations is also presented.

The problem of a hydrogen atom placed in a uniform electric field has in recent years attracted a great deal of attention due to the impressive experimental developments of the physics of Rydberg states. As is well known, the application of an electric field breaks the degeneracy of the pure Coulombic problem and broadens the energy levels. The basic problem then consists in calculating the new positions as well as the widths of the energy levels (more correctly, bands) in the presence of the static field.

Literature concerning this problem exists since the early days of quantum mechanics and can be divided into three main categories: perturbative calculations,<sup>1-3</sup> WKB calculations,<sup>4-6</sup> and numerical approaches.<sup>7-9</sup> Our list of references is by no means complete. Further references can be found in the quoted articles. The perturbative energy series, although giving good results at low field, is known to be only asymptotically convergent,<sup>10</sup> being, however, Borel summable.<sup>11</sup> Also, a useful definition of low field is hard to give.

It is well known that the Hamiltonian corresponding to the nonrelativistic Stark effect in hydrogen can be separated in parabolic coordinates.<sup>12</sup> The electronic motion is ruled by two Schrödinger radial-like equations (we use atomic units):

$$\frac{d^2}{d\xi^2}\psi_1 + \left( \frac{E}{2} + \frac{Z_1}{\xi} - \frac{T}{4\xi^2} - \frac{F}{4}\xi \right)\psi_1 = 0, \quad (1)$$

and

$$\frac{d^2}{d\eta^2}\psi_2 + \left( \frac{E}{2} + \frac{Z_2}{\eta} - \frac{T}{4\eta^2} + \frac{F}{4}\eta \right)\psi_2 = 0, \quad (2)$$

where  $F$  is the field,  $E$  the energy,  $Z_1$  and  $Z_2$  ( $Z_1 + Z_2 = 1$ ) are the separation constants, and  $T = m^2$ , where  $m$  is the magnetic quantum number of the electron. In obtaining Eqs. (1) and (2) the term  $m^2 - 1$  was replaced by  $m^2$  on account of the applicability of the WKB approximation.<sup>13</sup>

Although it was long ago recognized by Lanczos<sup>4</sup> that the WKB quantization rules following from (1) and (2) could be analytically solved in terms of elliptic integrals, no such solution was ever given. Lanczos himself neglected the  $m^2$  term and solved the simplified problem. Later, Rice and Good<sup>5</sup> also studied the Stark effect in hydrogen: They expanded the WKB quantization rule in terms of the  $m^2 - 1$  variable and considered only first-order contributions. In this approximation they were able to obtain results very close to the perturbative ones. The difference may be traced to their use of  $m^2 - 1$  instead of  $m^2$ . The last authors to consider the application of the WKB approximation to the Stark Hamiltonian were Bekenstein and Krieger.<sup>6</sup> They used the correct  $m^2$  term. By performing a similar expansion as previously used by Rice and Good, combined with a different integration technique, they were able to correctly reproduce the three first perturbation terms then available. To obtain this results they needed to consider higher-order terms of the WKB approximation instead of the usual first-order ones.

In this Report we solve analytically the first-order WKB quantization rules in terms of elliptic integrals. These solutions are complete in the sense that they contain *all* the contributions in  $m^2$ , including the ones neglected in previous works.<sup>4-6</sup> By a suitable approximation we also extend the WKB calculations to states above the classical ionization limit.

We begin by considering the motion of the electron in the potential  $V_\xi = -Z_1/\xi + T/(4\xi^2) + F\xi/4$ . A schematic view of this potential is given in Fig. 1(a). The quantization rule corresponding to this potential is

$$I_\xi = \frac{\sqrt{F}}{2} \int_b^a \frac{d\xi}{\xi} \left( -\xi^3 + \frac{2E}{F}\xi^2 + \frac{4Z_1}{F}\xi - \frac{T}{F} \right)^{1/2} \\ = (n_1 + \frac{1}{2})\pi, \quad (3)$$

where the turning points  $a$  and  $b$  are the two non-

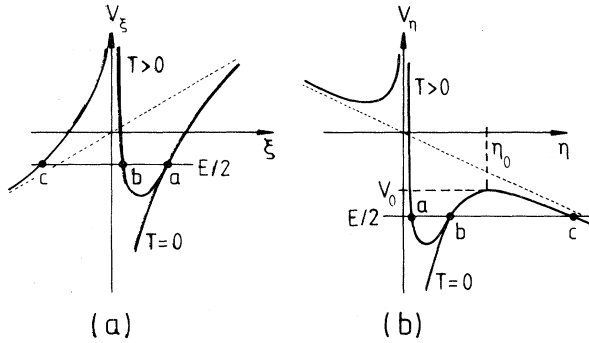


FIG. 1. Potentials for the  $\xi$  and  $\eta$  motions as defined in Eqs. (1) and (2): (a)  $V_\xi = -Z_1/\xi + T/(4\xi^2) + F\xi/4$ ; (b)  $V_\eta = -Z_2/\eta + T/(4\eta^2) - F\eta/4$ . The  $\xi$  motion is always confined. The  $\eta$  motion is more complicated: the electron may leak through the potential barrier (when  $E/2 \leq V_0$ ) or be autoionizing (when  $E/2 > V_0$ ).

negative roots of the equation

$$-\xi^3 + \frac{2E}{F}\xi^2 + \frac{4Z_1}{F}\xi - \frac{T}{F} \equiv (a - \xi)(\xi - b)(\xi - c) = 0, \quad (4)$$

ordered as  $c < 0 \leq b < a$ .

It is a straightforward but tedious task to show that the integral in Eq. (3) is

$$I_\xi = \left[ \frac{F}{a - c} \right]^{1/2} [-xK(k) + yE(k) + bc\Pi(\alpha^2, k)], \quad (5)$$

where  $x = [b(c + 2a) + c(a - c)]/3$ ,  $y = -(c - a) \times (a + b + c)/3$ ,  $k^2 = (a - b)/(a - c)$ , and  $\alpha^2 = (a - b)/a$ . In Eq. (5),  $K(k)$ ,  $E(k)$ , and  $\Pi(\alpha^2, k)$  are the complete elliptic integrals of the

$$F_1(\alpha, \beta, \beta'; \gamma; x, y) = \frac{\Gamma(\gamma)}{\Gamma(\alpha)\Gamma(\gamma - \alpha)} \int_0^1 t^{\alpha-1}(1-t)^{\gamma-\alpha-1}(1-xt)^{-\beta}(1-yt)^{-\beta'} dt = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \frac{(\alpha, i+j)(\beta, i)(\beta', j)}{(\gamma, i+j)! i! j!} x^i y^j,$$

where  $(a, n) \equiv \Gamma(a+n)/\Gamma(a)$ ,  $\Gamma(x)$  being the gamma function,  $I_\xi$  can be more compactly written as  $[ \xi = a - (a - b) t ]$ ,

$$I_\xi = \frac{\pi}{16} \alpha^2 (a - b) [F(a - c)]^{1/2} F_1\left(\frac{3}{2}, 1, -\frac{1}{2}; 3; \alpha^2, k^2\right).$$

A similar result can be easily obtained for  $I_\eta$ . However, although more elegant, the numerical evaluation of this last expression for  $I_\xi$  involves a doubly infinite sum of products of transcendental functions. The connection of Appell's series with elliptic integrals, as well as their classification and evaluation, is discussed by Carlson.<sup>15</sup> Carlson<sup>16</sup> also developed efficient and accurate algorithms to evaluate complete as well as incomplete elliptic integrals which may be easily implemented in programmable pocket calculators.

first, second, and third kind, respectively.<sup>14</sup>

The quantization rule corresponding to the  $\eta$  motion is slightly more complicated due to the presence of the relative maximum  $V_0$  at  $\eta_0$  [see Fig. 1(b)]. It is given by

$$I_\eta = \frac{\sqrt{F}}{2} \int_a^b \frac{d\eta}{\eta} \left( \eta^3 + \frac{2E}{F}\eta^2 + \frac{4Z_2}{F}\eta - \frac{T}{F} \right)^{1/2} = \left( n_2 + \frac{1}{2} \right) \pi. \quad (6)$$

For all classically allowed energies such that  $E/2 < V_0$ , the turning points obtained by solving the cubic equation

$$\eta^3 + \frac{2E}{F}\eta^2 + \frac{4Z_2}{F}\eta - \frac{T}{F} \equiv (\eta - a)(b - \eta)(c - \eta) = 0 \quad (7)$$

are non-negative numbers that can be ordered as  $0 \leq a < b < c$  [see Fig. 1(b)]. In this case the integral in Eq. (6) can be shown to be

$$I_\eta = \left[ \frac{F}{c - a} \right]^{1/2} [xK(k) - yE(k) - bc\Pi(\alpha^2, k)], \quad (8)$$

where  $x, y, k$ , and  $\alpha$  are defined as above. The similarity of Eqs. (5) and (8) reflects the fact that Eqs. (1) and (2) are formally identical under the replacement  $Z_1 \leftrightarrow Z_2$  and  $F \leftrightarrow -F$ . For  $T=0$  we have  $b=0$  in Eq. (4) and the term involving the elliptic integral of the third kind vanishes in Eq. (5). Similarly,  $a=0$  in Eq. (7) implies  $\alpha^2 \rightarrow \infty$  and  $\Pi(\alpha^2, k) \rightarrow 0$  in Eq. (8). Therefore, for  $T=0$ , the term involving the elliptic integral of the third kind is absent in both Eqs. (5) and (8). We also point out that by using Appell's double hypergeometric series  $F_1$ , namely,<sup>15</sup>

For  $E/2 \geq V_0$  we replace  $b$  in Eq. (6) by  $\eta_0$ . This proves to be a good approximation since the "classical well" continues to be responsible for the amplitude of the eigenfunction near the origin. In this case the polynomial in Eq. (7) has two complex conjugate roots:

$$\eta^3 + \frac{2E}{F}\eta^2 + \frac{4Z_2}{F}\eta - \frac{T}{F} \equiv (\eta - a)[(\eta - b_1)^2 + a_1^2] = 0. \quad (9)$$

In our approximation the center of the resonances is then obtained from

$$I_\eta = \frac{\sqrt{F}}{2} \int_a^{\eta_0} \frac{d\eta}{\eta} \{ (\eta - a)[(\eta - b_1)^2 + a_1^2] \}^{1/2} = \left( n_2 + \frac{1}{2} \right) \pi. \quad (10)$$

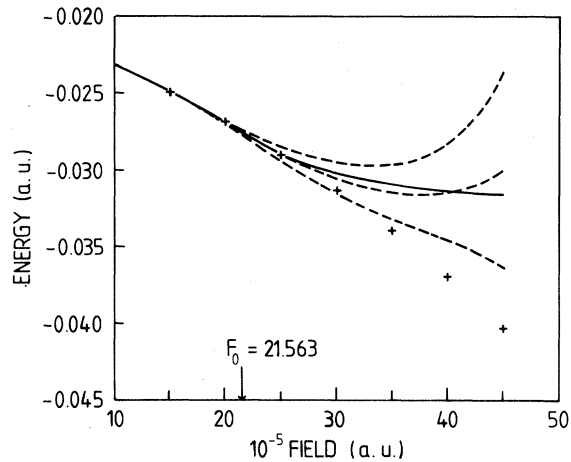


FIG. 2. Evolution of the  $n_1=0$ ,  $n_2=4$ , and  $m=0$  level for increasing field strength. For fields larger than  $F_0=21.563 \times 10^{-5}$  a.u. the state is autoionizing [in Fig. 1(b),  $E/2 > V_0$ ]. The central dashed line gives the numerical results of Damburg and Kolosov (Ref. 8). The outermost 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 (see text).

Although this integral can be evaluated in terms of incomplete elliptic integrals of the three kinds, the final expression is so complicated that numerical integration is more convenient. As before, one may represent the integral in Eq. (10) by generalized hypergeometric series. However, for Eq. (10) such representation requires Lauricella's function  $F_D$ , which is nothing but an extension of  $F_1$  to three variables. For more details we refer the reader, once again, to Carlson.<sup>17</sup>

For any given combination of quantum numbers  $n_1$ ,  $n_2$ , and  $m$  and field  $F$ , the system of equations  $I_\xi = (n_1 + \frac{1}{2})\pi$ ,  $I_\eta = (n_2 + \frac{1}{2})\pi$  can be easily solved for the eigenvalue  $E$ .

In Fig. 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.<sup>8</sup> The dashed lines are their<sup>8</sup> 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 Ref. 8, which were interpolated by a cubic polynomial. The crosses represent the results obtained from the fourth-order perturbation equation.<sup>1</sup> The solid line shows our WKB results. The arrow indicates the threshold field  $F_0$  above which the state is autoioniz-

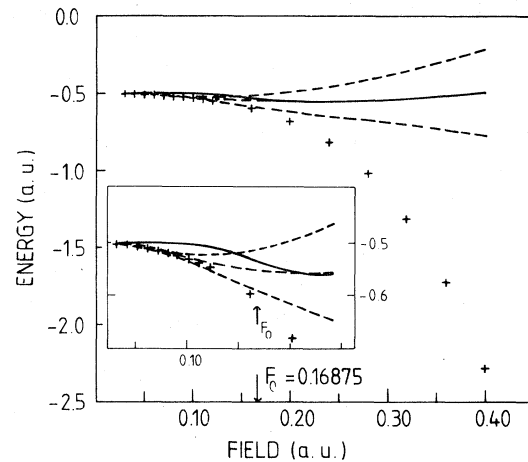


FIG. 3. Same as in Fig. 2 but for the ground state ( $n_1=n_2=m=0$ ). Here  $F_0=0.16875$  a.u..

ing. As is easy to see, the WKB approximation gives reliable results even *well above the top of the barrier* where the spectra lines are, in fact, broad bands.

Though we know that the ground state is not the best place to test WKB calculations, we present in Fig. 3 a comparison similar to the one in Fig. 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  $F_0$  where the WKB result may be expected to be less reliable, since the two turning points  $a$  and  $b$  in Eq. (6) are very close to each other. The agreement found well above  $F_0$  is striking. This supports the approximation introduced in Eq. (10).

In this Report we presented analytical solutions to the first-order WKB quantization rules for the problem of the Stark effect in hydrogen. We also extended the calculations well above the top of the  $\eta$ -potential barrier by considering the electronic motion as still trapped between the leftmost turning point and the position of the top of the barrier. The width, as well as contributions to the resonances coming from high-order terms in the WKB approximation, will be discussed elsewhere.

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