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THE SPONTANEOUS IONIZATION OF A HYDROGEN ATOM IN AN ELECTRIC FIELD, I *

by

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ABSTRACT

The time independent Schrodinger equation expressed in parabolic coordinates for a hydrogen atom in an electric field was numerically integrated for the state n=5, n_1=3, n_2=0, and m=1 to obtain the resonance energy E_r and the rate of ionization τ^{-1} for field intensities ranging from 8×10^5 to 11×10^5 volts/cm. It is found that near the resonance energy, τ^{-1} varies quadratically with $(E-E_r)^2$ in accordance with the well known Weisskopf-Wigner treatment of metastable states. When E is nearly equal to E_r, the wave function has a node at the outer turning point - no explanation is offered. At the very high field intensities considered, there was considerable difference between E_r and the energy calculated by Rayleigh-Schrodinger perturbation theory.

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The spontaneous ionization of a hydrogen atom in an electric field is an old problem, but it still remains interesting. The Schrodinger equation separates in parabolic coordinates and the separated one dimensional equations can be integrated numerically. The flux I_o corresponding to the outward component of the wave function and N_o, the number of systems inside of the outer turning point, can then be calculated for various values of the energy, E. The lifetime of the hydrogen atom is then taken to be $\tau(E) = N_o(E)/I_o(E)$. The resonance energy, E_r, is then the value of E for which $\tau(E)$ has a maximum value.

We find that near the resonance energy, the rate of ionization varies quadratically with $(E-E_r)$ in accordance with the Weisskopf-Wigner treatment of metastable energy states. We were surprised to find that the wave function has a node at the outer turning point when the energy is almost equal to E_r. At the very high field intensities where the lifetimes are less than 10^{-9} sec, there is a considerable difference between the energy calculated by Rayleigh-Schrodinger perturbation theory and E_r. In a subsequent paper, we will make accurate calculations for a large number of states of both the H and the D atomic species. We also will consider the related problem of the scattering and capture of an electron by a proton.

The potential energy of a hydrogen-like atom or ion of nuclear charge Z placed in a uniform electric field (in the z-direction) of strength F is $V = - Z r^{-1} + F z$. This potential has a saddle point at $z_o = - (Z/F)^{\frac{1}{2}}$, $x_o = 0 = y_o$. The value of the potential at the saddle point is $V_o = - 2(ZF)^{\frac{1}{2}}$. Thus, on the basis of classical mechanics,

we might expect that the hydrogen atom would spontaneously ionize if E, the energy of the atom, were greater than V_o; or, equivalently, the atom would ionize if the electric field strength is greater than $F_o = E^2/(4Z)$. If we approximate E by the energy of the atomic state in the absence of the external field, $E^{(0)} = -Z^2\mu^2/(2n^2)$ where n is the principal quantum number and μ is the effective mass of the atom, then the classical ionizing field F_o becomes $F_o' = Z^3\mu^2/(16n^4)$. Because of quantum mechanical leakage through the potential barrier, some spontaneous ionization can occur even when the external field is very weak and an appreciable rate of ionization might occur when the field strength is considerably less than F_o. On the other hand, the quantum mechanical problem is separable in parabolic coordinates and only a fraction of the energy of the atom is involved with the motion across the potential barrier. This argument indicates that the field corresponding to appreciable ionization might be larger than F_o. There is also the possibility (which we do not consider in the present paper) that the rate of spontaneous ionization may vary with pressure when z_o becomes comparable with the mean distance between the hydrogen atoms in the gas.[1]

There may be some good experimental data, but the authors are only familiar with a few rather old references which do not provide accurate information regarding the rate of spontaneous ionization as a function of field strength for each of the quantum states. From studies of field

emission[2,3], hydrogen gas is observed to be highly ionized at field strengths ranging from 1.08 F_o' for n = 1 to 2.2 F_o' for n = 7. On the other hand, the Stark Effect spectral lines of atomic hydrogen cease to exist when the field strength is considerably smaller than the F_o' corresponding to the emitting state.[4] As Bethe and Salpeter explain, such spectral lines cease to exist when the rate of spontaneous ionization of the emitting state becomes greater than the rate of its radiative transitions (usually of the order of 10^8 per second).

Bethe and Salpeter[4] have reviewed the early theoretical work on this problem. Already in 1926, Schrodinger[5] and Epstein[6] used perturbation theory and Wentzel[7] used the WKB approximation to estimate the energy shift of a hydrogen atom in an electric field. In 1930, Lanczos[8] used the WKB approximation to calculate the rate of spontaneous ionization. There have been many other calculations since that time. Alexander[9] has carried out the most rigorous treatment for the mean-lifetime of the ground state and his method could be extended to higher quantum states of the hydrogen atom. In the present paper, we determine the rate of ionization in a simpler and more direct fashion by numerically integrating the Schrodinger equation. In principle, our procedure has the advantage that one can determine the rate of ionization (for a fixed external field) as a function of energy and obtain the deviations from the familiar Weisskopf-Wigner quadratic relationship as $E_r - E$ becomes large. Here E_r is the resonance energy which plays the role of the energy level of the pseudo-stationary atomic state.

In the presence of the electric field, all of the discrete atomic energy levels become narrow bands of dense continuum which become wider and more diffuse as the electric field becomes more intense. A resonance energy E_r is the centroid of a band. Kato has shown[10] that the Rayleigh-Schrodinger perturbation series for the Stark Effect energy provides an asymptotic approximation to E_r. The WKB formulation (including higher order terms in powers of h^2 and corrected for the 0 to ∞ range of the parabolic coordinates, but ignoring the region of space where the electron is free) provides another type of asymptotic approximation to E_r. Beckenstein and Krieger[3] have found that such a WKB treatment including all of the integrals of $O(h^4)$ agrees <u>exactly</u> with the Rayleigh-Schrodinger perturbation energies through terms of $O(F^4)$. They also point out that for the ground state of hydrogen, Mendelsohn's[11] calculation of the Rayleigh-Schrodinger energy through terms of $O(F^{10})$ agrees within one percent with Alexander's[9] accurate calculation of E_r up to field strengths comparable with F_o. From these results we conclude that the Stark Effect energy shift is almost unaffected by the part of the potential energy beyond the outer turning point where the electron is free.

In order to calculate the rate of spontaneous ionization of a particular quantum state in the presence of an electric field of specified strength, it is necessary to solve the Schrodinger equation corresponding to a number of values of the energy lying close to E_r.

The Schrodinger equation, $(H-E)\Psi = 0$, for the hydrogen-like atom in the uniform electric field (in the z-direction) is separable in the

parabolic coordinates $\zeta = r + z$, $\eta = r - z$, and ϕ into the equations[4]

$$-\frac{\hbar^2}{2\mu}\frac{d^2\Phi_{n_1,m}}{d\zeta^2} + (V_\zeta - \frac{E}{4})\Phi_{n_1,m} = 0 \qquad (1)$$

and

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi_{n_2,m}}{d\eta^2} + (V_\eta - \frac{E}{4})\chi_{n_2,m} = 0 \qquad (2)$$

where

$$V_\zeta = -\frac{(1 - m^2)\hbar^2}{8\zeta^2\mu} - \frac{Z_1}{2\zeta} + \frac{F\zeta}{8} \qquad (3)$$

and

$$V_\eta = -\frac{(1 - m^2)\hbar^2}{8\eta^2\mu} - \frac{Z - Z_1}{2\eta} - \frac{F\eta}{8} \qquad (4)$$

Here Z_1 is the separation constant; m is the absolute value of the magnetic quantum number; and n_1 and n_2 are the parabolic quantum numbers. The principle quantum number of the state is $n = n_1 + n_2 + m + 1$. The complete unnormalized wave function for the atom is

$$\Psi_{n_1,n_2,\pm m} = (\zeta\eta)^{-1/2}\Phi_{n_1,m}(\zeta)\chi_{n_2,m}(\eta)\exp(\pm i\, m\, \phi) \qquad (5)$$

It is convenient to normalize $\Phi_{n_1,m}(\zeta)$ so that

$$\int_0^\infty \Phi^*_{n_1,m}\,\Phi_{n_1,m}\, d\zeta/\zeta = 1 \qquad (6)$$

Figure 1 shows a schematic drawing of V_ζ and V_η for different values of m. As far as the rate of spontaneous ionization is concerned, the behaviour near the origin is relatively unimportant. The classical turning points correspond to values of η for which $V_\eta = E/4$. There is always an outer turning point η_{ot} for a very large value of η and an index turning point η_{it} for an intermediate value of η. In addition, for $m > 1$, there is a turning point η_{ct} for a very small value of η. The number of systems which lie within the outer turning point is

$$N_o = \frac{1}{4} \int_0^{2\pi} d\phi \int_0^{\infty} d\zeta \int_0^{\eta_{ot}} (\zeta + \eta)\, \Psi^* \Psi \, d\eta \tag{7}$$

The flux of systems passing through a surface of constant η is

$$I = \int_s \underline{j} \cdot d\underline{A}_\eta \tag{8}$$

Here $\underline{j}$ is the current density

$$\underline{j} = \left(\frac{i\hbar}{2\mu}\right)[\Psi \nabla \Psi^* - \Psi^* \nabla \Psi] \tag{9}$$

and $d\underline{A}_\eta = [\frac{1}{2}\eta^{1/2}(\zeta + \eta)^{1/2}\, d\zeta d\phi]\hat{\eta}$. The η component of ∇ is $2\eta^{1/2}(\zeta + \eta)^{-1/2} \frac{\delta}{\delta\eta}$. Thus,

$$I = \frac{i\hbar}{2\mu} \int_0^{\infty} d\zeta \int_0^{2\pi} d\phi\, \eta[\Psi \frac{\delta\Psi^*}{\delta\eta} - \Psi^* \frac{\delta\Psi}{\delta\eta}] \tag{10}$$

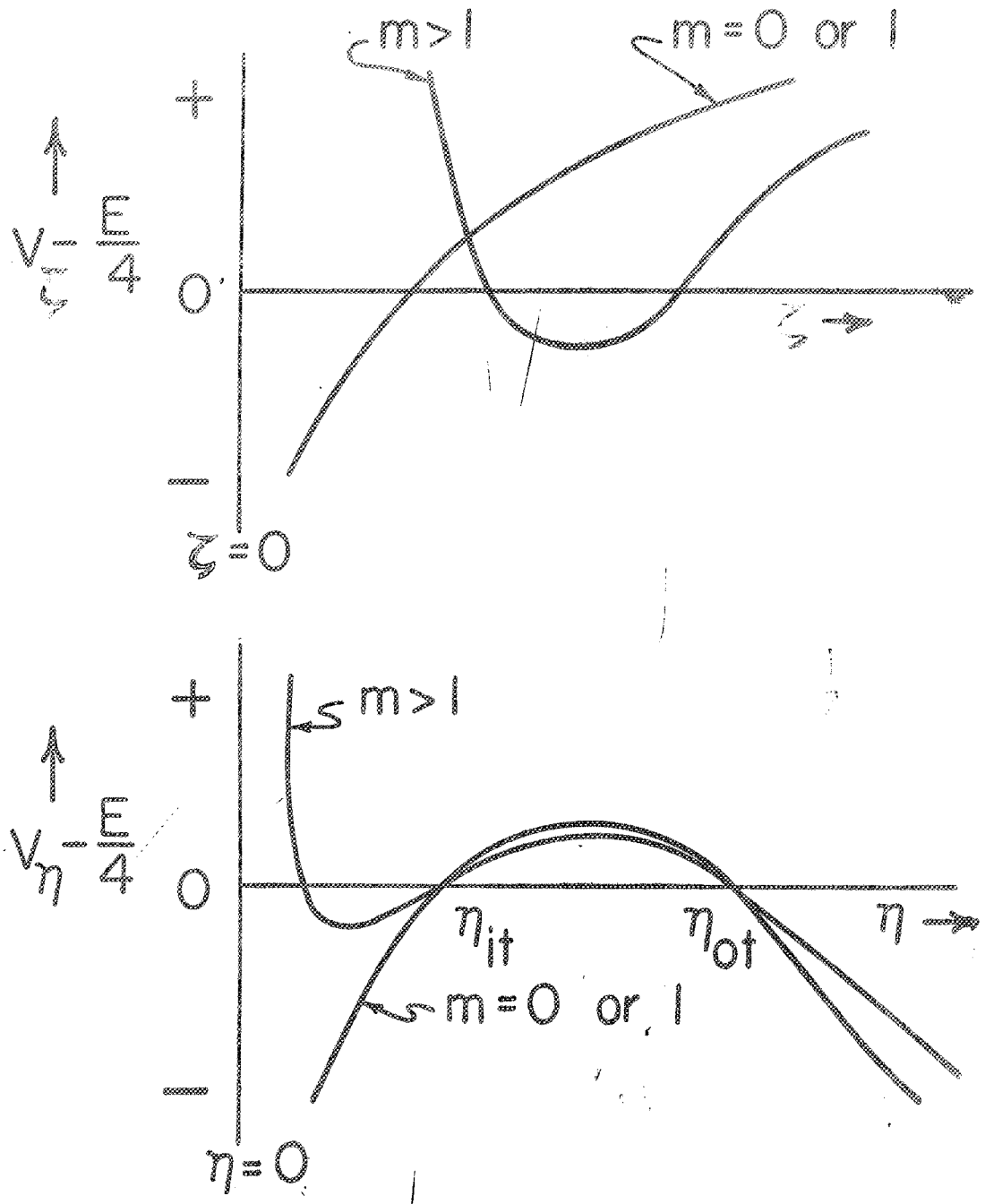

Figure 1. Schematic Drawings of the Potential Energy Functions V_ζ and V_η for Different Values of m, the absolute value of the magnetic quantum number.

Or making use of Eqs. (5) and (6),

$$I = \frac{ih}{2\mu} \left[\chi_{n_2,m} \frac{\delta\chi^*_{n_2,m}}{\delta\eta} - \chi^*_{n_2,m} \frac{\delta\chi_{n_2,m}}{\delta\eta}\right] \tag{11}$$

I. THE SCHRODINGER EQUATION FOR ζ

Equation (1) in the variable ζ behaves like a one-dimensional Schrodinger equation for a system with bound states. At $\zeta = 0$ and $\zeta = \infty$, the value of $\Phi_{n_1,m}$ is zero. Between $\zeta = 0$ and $\zeta = \infty$, the $\Phi_{n_1,m}$ has n_1 nodes. Since values of E and F are assigned, Z_1 serves as the eigenvalue. There are a number of ways in which this equation can be solved:

1) From perturbation theory, through the third order of the field strength

$$
\begin{aligned}
Z_1 = {} & (\varepsilon/\mu)[n_1 + \tfrac{1}{2}(m+1)] + (F/4\varepsilon^2)[6n_1(n_1+m+1) + (m+1)(m+2)] \\
& - (F^2\mu/32\varepsilon^5)[2n_1+m+1][8m^2+34m(2n_1+1) + 4(17n_1^2+17n_1+9)] \\
& + (F^3\mu^2/64\varepsilon^8)\left[\begin{array}{l} 1500n_1^4 + 3000n_1^3 + 3168n_1^2 + 1668n_1 + 356 \\ + m[3000n_1^3 + 4500n_1^2 + 3168n_1 + 834] \\ + m^2[1992n_1^2 + 1992n_1 + 692] \\ + m^3[492n_1 + 246] + 32m^4 \end{array}\right]
\end{aligned}
\tag{12}
$$

Here $\varepsilon = (-2\mu E)^{1/2}$. Basu[12] calculated the energy through the fourth order. However, he expanded the secular equation and therefore he never calculated Z_1. Presumably Doi, Ishida and Hiyama,[13] who calculated the energy through the third order, obtained the third order term of Z_1 but we have not been able to obtain a copy of their paper,

However, Bethe and Salpeter[4] only give Z_1 through the second order.

2) Probably the best method of obtaining Z_1 to high precision is the power-series boundary-condition method[14,15] which Alexander[9] adapted to the solution of this problem. Alexander assumed that $\Phi_{n_1,m}$ can be expressed in terms of a power series*. Then

$$\Phi_{n_1,m} = \zeta^{(m+1)/2} \exp(-Z\mu\zeta/2n)[a_o + a_1\zeta + a_2\zeta^2 + \ldots] \quad (13)$$

---

* Unfortunately, Alexander[9] omitted the factor $\zeta^{m/2}$ from his power series. Since this factor is required in order to satisfy the indicial equations, his recursion relation Eq. (12) is wrong except for cases where m = 0. This does not affect the remainder of Alexander's paper since numerical results are only given for the ground state of hydrogen. The correct recursion relations are given by our Eqs. (8) - (10).

Substituting this power series into Eq. (10) leads to the four-term recursion relations,

$$a_1/a_o = (Z\mu/2n) - Z_1\mu(m+1)^{-1} \quad (14)$$

$$2(m+2)(a_2/a_o) = [(m+3)(Z\mu/2n) - Z_1\mu](a_1/a_o) - [(Z\mu/2n)^2 + \frac{1}{2}\mu E] \quad (15)$$

$$k(m+k)(a_k/a_o) = [(m+2k-1)(Z\mu/2n)-Z_1\mu](a_{k-1}/a_o)$$

$$- [(Z\mu/2n)^2 + \frac{1}{2}\mu E](a_{k-2}/a_o) + (F\mu/4)(a_{k-3}/a_o) \quad (16)$$

For large values of ζ, the value of $\Phi_{n_1,m}$ approaches zero. However, it is found that if the correct value of Z_1 lies between two trial

values, for one trial value the series diverges so as to make $\Phi_{n_1,m}$ approach $+\infty$ as ζ becomes large; for the other trial value $\Phi_{n_1,m}$ approaches $-\infty$. Alexander proves this by showing that only the first few a_k's alternate in sign so that beyond a critical value of k all of the a_k's are either positive or negative. Furthermore, beyond a critical value of k, the absolute value of a_k is greater than $b_k = (Z\mu/2n)^k/k!$ where the b_k are the coefficients in the power series expansion of $\exp(Z\mu\zeta/2n)$. Thus, the power-series boundary-condition technique can be used to obtain Z_1 to a high degree of precision. Eq. (12) provides an excellent initial trial value of Z_1.

3) The WKB procedure is the oldest method for determining Z_1. It was first used by Wentzel[7]; later by Rice and Good[16] and Bailey, Hiskes, and Riviere;[17] and recently by Bekenstein and Krieger[3]. Eq. (1) is a "two-turning-point" Schrodinger equation similar to the equation for the vibrational motion of a diatomic molecule. Before applying the quantization rules, Bekenstein and Krieger made the Langer transformation from ζ to $x = \log_e(\zeta)$ so that the range of the independent variable becomes $-\infty < x < \infty$. They also included Dunham's correction terms so as to make $\Phi_{n_1,m}$ accurate through terms in $\hbar^4$. The expressions for Z_1 which they obtained (but unfortunately did not publish) are accurate through the fourth power in the field strength, or one order better than the best current results from perturbation theory [Eq. (12)].*

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* Treating both Eq. (1) and Eq. (2) by this sort of corrected WKB procedure, Bekenstein and Krieger[3] obtained expressions for the weak field limit of the energy levels which agree through terms of the order of F^4 with the perturbation calculations. The WKB treatment is particularly accurate when applied to perturbations of either hydrogen atoms or simple harmonic oscillators, since the formulation without the Dunham corrections gives the exact energy of the unperturbed system.

From perturbation theory, through the first order of the field strength,

$$\Phi_{n_1,m}(\zeta) = \Phi^{(0)}_{n_1,m} + \left(\frac{F\mu}{4\varepsilon^3}\right) \Phi^{(1)}_{n_1,m} + \ldots \qquad (17)$$

where $\varepsilon = (-2\mu E)^{1/2}$. Letting $s = \varepsilon\zeta$ and

$$L^m_{k+m}(s) = \frac{d^m}{ds^m}\left[e^s \frac{d^{k+m}}{ds^{k+m}} (s^{k+m} e^{-s})\right] , \qquad (18)$$

then

$$\Phi^{(0)}_{n_1,m}(\zeta) = \left[\frac{n_1!}{(n_1+m)!^3}\right]^{1/2} s^{(m+1)/2} L^m_{n_1+m}(s) \exp(-s/2) \qquad (19)$$

and

$$\Phi^{(1)}_{n_1,m}(\zeta) = -\frac{1}{2}[n_1+1)(n_1+2)(n_1+m+1)(n_1+m+2)]^{1/2}\Phi^{(0)}_{n_1+2,m}(\zeta)$$

$$+ 2(2n_1+m+2)[(n_1+1)(n_1+m+1)]^{1/2}\Phi^{(0)}_{n_1+1,m}(\zeta)$$

$$- 2(2n_1+m)[n_1(n_1+m)]^{1/2}\Phi^{(0)}_{n_1-1,m}(\zeta) \tag{20}$$

$$+ \frac{1}{2}[(n_1-1)n_1(n_1+m-1)(n_1+m)]^{1/2}\ \Phi^{(0)}_{n_1-2,m}(\zeta)$$

Then since

$$\int_0^\infty e^{-s}\ s^{m+1}\ L^m_{k+m}(s)\ L^m_{\ell+m}(s)\ ds$$

$$= (m+2k+1)(m+k)!^3(k!)^{-1} \quad , \quad \ell = k$$

$$= -\ (m+k)!(m+k+1)!^2(k!)^{-1} \quad , \quad \ell = k+1 \tag{21}$$

$$= -\ (m+k-1)!(m+k)!^2[(k-1)!]^{-1}, \quad \ell = k-1$$

$$= 0 \text{ for all other values of } \ell \ ,$$

it follows that through the first order of the field strength,

$$\int_0^\infty \Phi^*_{n_1,m}(\zeta)\Phi_{n_1,m}(\zeta)d\zeta = \varepsilon^{-1}[2n_1+m+1] \tag{22}$$

$$- F\mu\,\varepsilon^{-4}[6n_1(n_1+m+1) + (m+1)(m+2)]$$

$$+ \ldots.$$

Eq. (22) is useful in the evaluation of N_o from Eq. (7).

II. THE SCHRODINGER EQUATION FOR η

The Schrodinger equation in the η variable, Eq. (2), has no discrete energy states since V approaches $-\infty$ as $-F\eta/8$ when η becomes large. At some intermediate value η_o, the effective potential has a maximum value $(V_\eta)_o$. If $m = 1$, then $\eta_o = 2[(Z-Z_1)/F]^{1/2}$, $(V_\eta)_o = -\frac{1}{2}[(Z-Z_1)F]^{1/2}$, and the classical ionizing field [where $(V_\eta)_o = E/4$] is $F''_o = E^2/[4(Z-Z_1)]$. If m is not equal to unity, in order to determine η_o it is necessary to solve a cubic equation. Note that because of the partitioning of the energy into the ζ, η, and ϕ degrees of freedom, F''_o is greater than F_o.

Alexander[9] expressed $\chi_{n_2,m}(\eta)$ as a power series having the same functional form as Eq. (13). The coefficients a_k are then given by Eqs. (14)-(16) which are modified so that $(Z-Z_1)$ replaces Z_1 and $-F$ replaces F. For weak fields, Alexander found a significantly large range $k_o < k < k_1$ in which all of the a_k's have the same sign and where $|a_k| > b_k$. If k_1 were infinite, then the series would diverge to either $+\infty$ or $-\infty$ depending upon the sign of the a_k's in the range $k_o < k < k_1$. The weaker the field, the larger is k_1. Thus, for weak fields the sign of the a_k's in this region provides upper and lower bounds to the "energy" of the atom. This criterion is no longer applicable to strong fields where the range $k_o < k < k_1$ becomes small and indistinguishable. For values of $k > k_1$, the signs of the a_k oscillate corresponding to the oscillations of the wave function values of η beyond the outer turning point, η_{ot}.

Beyond the outer turning point, it is convenient to express $\chi_{n_2,m}(\eta)$ in the WKB-type functional form

$$\chi_{n_2,m}(\eta) = CW^{-1/2} \cos[\frac{1}{\hbar} \int W d\eta + \alpha] \tag{23}$$

Here α is the phase shift (a function of the energy), C is the normalization constant, and W is a function of η . Substituting the $\chi_{n_2,m}$ of Eq. (23) into the Schrodinger equation (2) and letting

$$G = 2\mu[\frac{E}{4} - V_\eta] \tag{24}$$

it follows that

$$W^2 + \hbar^2[\frac{1}{2W}\frac{d^2W}{d\eta^2} - \frac{3}{4W^2}(\frac{dW}{d\eta})^2] = G \tag{25}$$

The WKB series corresponds to expanding W in powers of $i\hbar$,

$$W = W_o - \hbar^2 W_2 + \hbar^4 W_4 - \ldots\ldots \tag{26}$$

where

$$W_o = G^{1/2} \tag{27}$$

$$W_2 = \frac{d}{d\eta}[\frac{5}{48} G^{-3/2} \frac{dG}{d\eta}] + \frac{1}{48} G^{-3/2} \frac{d^2G}{d\eta^2} \tag{28}$$

$$W_4 = \frac{d}{d\eta}[\frac{G^{-5/2}}{32} \frac{d^3G}{d\eta^3} - \frac{19G^{-7/2}}{128} \frac{dG}{d\eta} \frac{d^2G}{d\eta^2} + \frac{11G^{-9/2}}{96} (\frac{dG}{d\eta})^3]$$

$$+ \frac{G^{-7/2}}{128} \frac{dG}{d\eta} \frac{d^3G}{d\eta^3} - \frac{49G^{-11/2}}{2048} (\frac{dG}{d\eta})^4 \tag{29}$$

Here W_2, W_4, ... are the Dunham[18] correction terms to the usual WKB treatment (in Dunham's notation our W_n is his y_n). Eqs. (23) and (26) provide an asymptotic approximation to $\chi_{n_2,m}$ which converges rapidly for values of η slightly larger than η_{ot}.

For strong fields, Alexander[9] used the power series solution for $\chi_{n_2,m}$ for values of η less than some point η_1 (where η_1 is slightly greater than η_{ot}) and the WKB-type solution for η greater than η_1. The values of C and α are chosen by requiring that at η_1 the functions $\chi_{n_2,m}$ and $d\chi_{n_2,m}/d\eta$ are continuous. Alexander truncated the series for W after the first Dunham correction term, W_2. Other research workers[8,16,17] who have used the WKB technique* for η greater than η_{ot} have considered $W = W_o$.

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* Bechenstein and Krieger[3] used the WKB technique for η less than η_{ot} with W truncated after W_4. Before applying the WKB treatment, however, they made the Langer transformation from η to $y = \log_e(\eta)$. This improved the accuracy of their quantization condition for the energy.

III. DIRECT INTEGRATION OF THE SCHRODINGER EQUATION FOR η

The Schrodinger equation for η can also be directly integrated. At $\eta = 0$, the value of $\chi_{n_2,m}$ must be zero. For small values of η, the terms $-E/4$ and $-F\eta/8$ in Eq.(2) can be neglected and $\chi_{n_2,m}$ approaches $\eta^{1/2}$ times an m-th order Bessel function of argument $2[\mu(1-Z_1)\eta]^{1/2}$ which can be expanded in the form

$$\chi_{n_2,m} \approx \eta^{1/2}[\mu(1-Z_1)\eta]^{m/2}\left[\frac{1}{m!} - \frac{\mu(1-Z_1)\eta}{(m+1)!} + \ldots \right] \qquad (30)$$

Numerov's method[19] can then be used to integrate Eq. (2) from $\eta = 0$ to large values of η and obtain $\chi_{n_2,m}(\eta)$ for given values of E and F. If we take the interval size of η to be d, then the Numerov difference equation corresponding to Eq. (2) is

$$\chi_{n_2,m}((k+1)d) = \left\{\frac{2 - (5d^2/3)[\frac{E}{4} - V_\eta(kd)]}{1 + (d^2/6)[\frac{E}{4} - V_\eta(kd)]}\right\}\chi_{n_2,m}(kd) - \chi_{n_2,m}((k-1)d) \qquad (31)$$

If $\chi_{n_2,m}(kd)$ and $\chi_{n_2,m}((k-1)d)$ were accurate, the error in $\chi_{n_2,m}((k+1)d)$ might be expected to be of the order of $(d^6/240)d^6\chi_{n_2,m}/d\eta^6$. The two initial values, $\chi_{n_2,m}(d)$ and $\chi_{n_2,m}(2d)$, are taken from Eq. (30). However, since Eq. (30) is only valid for very small values of η (of the order of $10^{-7}a_o$), the initial value of d must be taken to be extremely small. As η becomes larger, the value of d can be rapidly increased without any appreciable loss of accuracy.

Calculations were made for the state $n = 5$, $m = 1$, $n_1 = 3$, and $n_2 = 0$ (which is a hybridized mixture of 5p, 5d, 5f, and 5g spherical wave functions). A rough estimate of the resonance energy for various values of the field strength was obtained from perturbation theory. In the Numerov integration of the η equation, d was varied from $10^{-7} a_o$ near $\eta = 0$ to $0.01\ a_o$ at η_{ot}. Beyond η_{ot}, the value of d was taken to lie between $1\ a_o$ and $3\ a_o$. Simpson's Rule[20] (with an error of around $(d^5/180) d^6 \chi_{n_2,m}/d\eta^6$ per interval) was then used together with Eq. (7) to determine N_o.

In comparing our numerically determined $\chi_{n_2,m}$ with the functional form given by Eq. (23), it is convenient to define C_ℓ as the ℓ-th maximum (beyond the outer turning point) of $(\mu F/4)^{1/4} \chi_{n_2,m} \eta^{1/4}$. In the limit as ℓ becomes large, W^2 approaches G which in turn approaches $(\mu F/4)\eta$ and C_ℓ approaches C. Thus, when $\ell = 30$ we found that C_ℓ had converged to within one percent of its final value. However, our procedure for numerical integration was not sufficiently accurate to enable us to obtain accurate values of the phase shift α. That is, the values of α which we obtained did not vary smoothly with energy in the vicinity of a resonance.

IV. THE RATE OF SPONTANEOUS IONIZATION

Now let us consider the lifetime of a quasi-stationary state from the Weisskopf-Wigner[21,22] standpoint. Beyond the outer turning point we can express $\chi_{n_2,m}(\eta)$ as a linear combination of an outgoing wave χ_o and an incoming wave χ_i,

$$\chi_{n_2,m}(\eta) = A(E)\chi_o + B(E)\chi_i \tag{32}$$

According to Eq. (23), if E is <u>real</u>, then

$$A(E) = \frac{1}{2} C \exp(i\alpha(E)) = B(E)^* \tag{33}$$

and

$$\chi_o = W^{-1/2} \exp((i/\hbar)\int W \, d\eta) = \chi_i^* \tag{34}$$

Since $\chi_{n_2,m}$ is necessarily <u>real</u> for <u>real</u> values of E, it follows from Eq. (11) that the net flux I is zero; or, the outward flux I_o (calculated with $A(E)\chi_o$) is equal to minus the inward flux I_i (calculated with $B(E)\chi_i$).

However, if E is complex, then it is possible for $A(E)$ to remain finite while $B(E) = 0$. Indeed, this situation occurs when the energy is equal to $E_c = E_r - i\,\Gamma$ where E_r is the resonance energy and Γ is the half-width of the energy wave packet. Thus, for $E = E_c$, the wave function contains only the outgoing component and represents a hydrogen atom dissociating into a proton plus an electron. The time factor for this wave function is $\exp(-i(E_c/\hbar)t) = \exp(-(\Gamma/\hbar)t)\exp(-i(E_r/\hbar)t)$.

Thus in a time $\tau_o = \hbar/(2\Gamma)$, the absolute square of the wave function has been reduced in value by a factor of exp(-1). In this sense, τ_o is the lifetime of the hydrogen atom corresponding to the complex energy E_c. If there are $N_o(E_c)$ hydrogen atoms (with their electron inside of the outer turning point) and each one has a rate of ionization $1/\tau_o$, then the outward flux $I_o(E_c)$ is given by

$$I_o(E_c) = N_o(E_c)/\tau_o = 2\ \Gamma N_o(E_c)/\hbar \tag{35}$$

In the vicinity of the resonance energy, the phase shift changes rapidly with the energy. It is convenient to express the phase shift as the sum of a slowly varying component $\alpha_o(E)$ which is analytic in the complex energy, and a rapidly varying component $\alpha_r(E)$ which is not analytic. Thus,

$$\alpha(E) = \alpha_o(E) + \alpha_r(E) \quad . \tag{36}$$

It is easy to show from arguments with respect to the analyticity of the wave function with respect to the energy that (except when the resonance energy is degenerate) B(E) has a simple zero[23] when $E = E_c$. Thus,

$$B(E) = \frac{1}{2}\ (E - E_r + i\Gamma)\ \exp(-\ i\ \alpha_o(E))C' \tag{37}$$

Similarly, it must be possible to expand A(E) in a Taylor's series in $E - E_c$ for energies close to E_c. Thus, we can express A(E) in the form

$$A(E) = \frac{1}{2}[(a+ib) + (c+if)(E - E_r + i\Gamma)]\ \exp(i\ \alpha_o(E))C' \tag{38}$$

The constants a,b,c, and f are uniquely determined by the requirement that for <u>real</u> values of E, we must have $A(E) = B(E)^*$. With these values for the constants, for complex (as well as real) energies,

$$A(E) = \frac{1}{2}(E - E_r - i\Gamma)\exp(i\,\alpha_o(E))C' \tag{39}$$

Now for <u>real</u> energies, Eqs. (36) and (38) agree with Eq. (33) if

$$C' = -C[(E - E_r)^2 + \Gamma^2]^{-\frac{1}{2}} \tag{40}$$

and

$$\alpha_r = \tan^{-1}[\Gamma/(E_r - E)] \tag{41}$$

In passing through the entire resonance region (going from energies less than, to energies greater than E_r), α_r increases by π. Also,

$$(d\alpha_r/dE)^{-1} = \Gamma[1 + \left\{(E_r - E)/\Gamma\right\}^2] \tag{42}$$

<u>When $E = E_c$</u>, it follows from Eqs. (32), (34), and (39) that the wave function is

$$\chi_{n_2,m} = -i\,\Gamma C'\exp(i\alpha_o(E))\,W^{-1/2}\exp((i/\hbar)\int W\,d\eta) \tag{43}$$

Thus, according to Eq. (11), the corresponding flux is

$$I_o(E_c) = 2\pi\,\Gamma^2(C')^2\mu^{-1} \tag{44}$$

However, in order for Eqs. (35) and (44) to be consistent,

$$N_o(E_c) = \frac{1}{2}\hbar\,\Gamma\,(C')^2\mu^{-1} \tag{45}$$

Now let us return to <u>real values of the energy</u> close to E_r. According to Eqs. (34), (39), and (11), the flux corresponding to the outgoing component of the wave function is

$$I_o(E) = \frac{1}{2}\pi\, \Gamma^2 (C')^2 \mu^{-1}\, [1 + \left\{(E-E_r)/\Gamma\right\}^2] \tag{46}$$

Since there is no interference between I_o and the flux of the incoming component of the wave function, the lifetime of the state is

$$\tau(E) = N_o(E)/I_o(E) \tag{47}$$

If we adjust the normalization so that $N_o(E) = N_o(E_c)$, then

$$\tau(E)/\tau_o = I_o(E_c)/I_o(E) = 4\, [1 + ((E-E_r)/\Gamma)^2]^{-1} \tag{48}$$

Note that $\tau(E_r) = 4\tau_o$. Furthermore, since $\tau_o = \hbar/(2\Gamma)$,

$$\hbar/\tau(E) = (\Gamma/2)[1 + \left\{(E-E_r)/\Gamma\right\}^2] \tag{49}$$

V. NUMERICAL RESULTS

For the case $n = 5$, $n_1 = 3$, $n_2 = 0$, $m = 1$, we have numerically calculated $N_o(E)$ (according to Eq. (7)) and $I_o = \frac{1}{2}\pi\mu^{-1}C^2$. This gives $1/\tau(E) = I_o(E)/N_o(E)$. Fig. 2 shows a plot of $1/\tau(E)$ versus E for a field strength of 10^6 volts/cm (1.9448×10^{-4} a.u.). The minimum value of $1/\tau = \Gamma/2$. We define E_r as the energy at which this minimum occurs. It appears from Fig. 2 that the parabola corresponding to Eq. (48) is indeed an excellent approximation to $1/\tau(E)$ for values of $|E-E_r|$ as large as 3Γ.

Table I gives the values of E_r, Γ, τ, η_{it}, η_{ot}, and Z_1 which we calculated for very strong electric fields ranging in intensity from 8×10^5 to 11×10^5 volts/cm.

The lifetime τ is compared with the calculations of Bailey, Hiskes, and Riviere[17] who used the method of Rice and Good[16] which is essentially a first-order WKB approximation to both the ζ and η equations. However, they made a number of corrections to the standard WKB treatment while making a number of additional approximations such as omitting the (m^2-1) terms in V_ζ and V_η. Bekenstein and Krieger[3] point out that at weak fields, the Rice and Good treatment only gives the energy to a precision comparable to Rayleigh-Schrodinger perturbation through the first order. Thus, the disagreement at $F = 11\times10^5$ volt/cm is not surprising.

Fig. 3 shows the variation of $\log_{10}(\tau)$ with F. When the field strength is equal to $F_o'' = 11.73\times10^5$ volts/cm, the effective energy

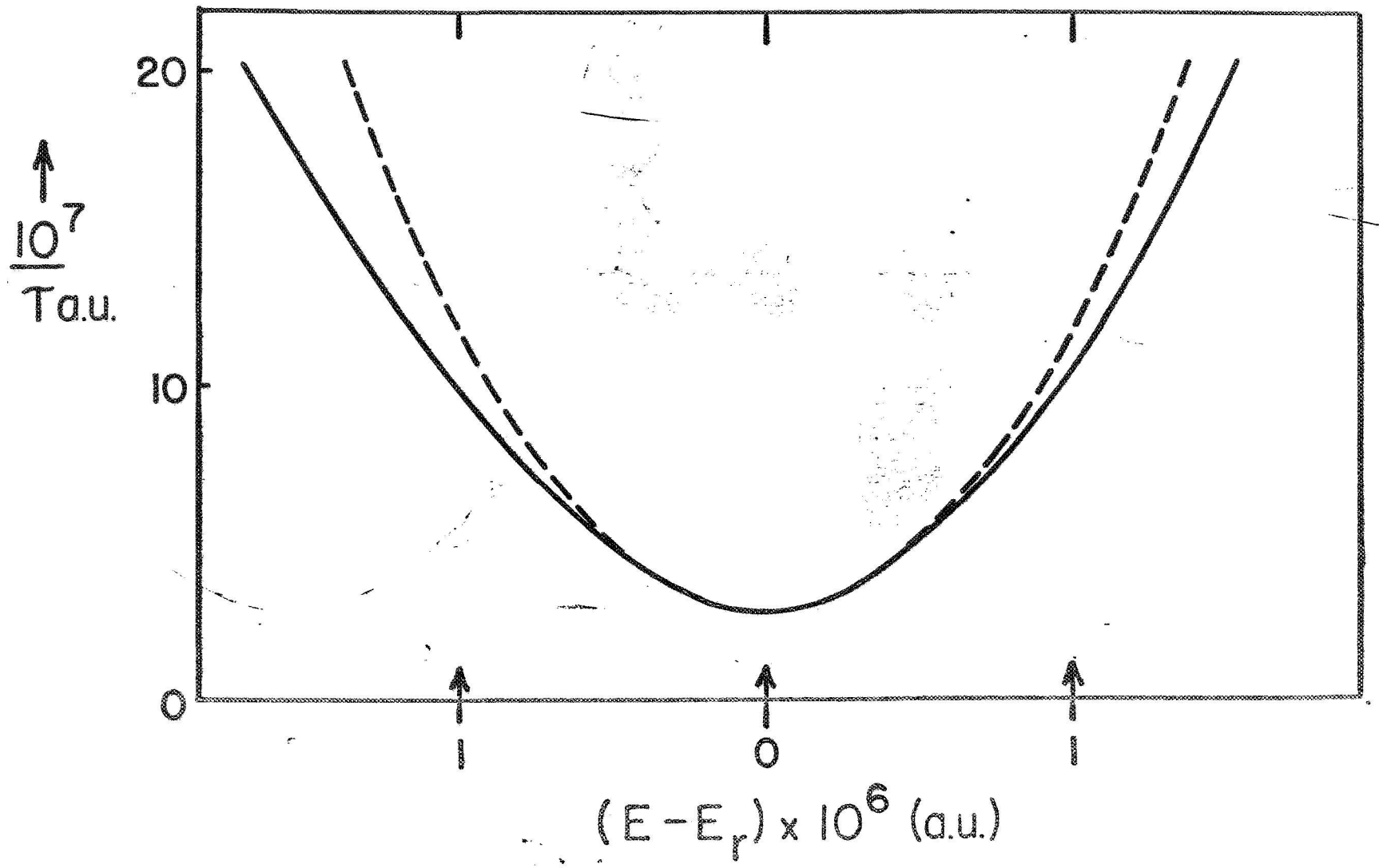

Figure 2. The rate of ionization $1/\tau$ versus E for the case of n=5, n_1=3, n_2=0, and m=1 in a field of 10^6 volts/cm. Here $E_r = -0.01502415$ a.u. and $\Gamma = 0.552 \times 10^{-6}$ a.u. The solid line represents the calculated values. The dotted line corresponds to the Weisskopf-Wigner parabola as given by Eq. (48).

TABLE I. Numerical Results Calculated for a Hydrogen Atom in the State n=5, n_1=3, n_2=0, and m=1. Here $E_{pert}(4)$ is the Rayleigh-Schrodinger perturbation energy calculated through the fourth power in the field strength; $Z_1(3)$ is the value of Z_1 calculated through the third power of F making use of E_r. Also, τ(BHR) is the lifetime as calculated by Bailey, Hiskes, and Riviere[17]; the ± corresponds to the error in reading their graphs. The τ , η_{it}, η_{ot}, and Z_1 correspond to E_r. The values in parenthesis are given in atomic units.*

F	$-E_{pert}(4)$	$-E_r$	Γ	τ	τ(BHR)	η_{it}	η_{ot}	$Z_1(3)$
volts/cm	cm^{-1}	cm^{-1}	cm^{-1}	sec	sec	A	A	
8.0×10^5	3700.03	3624.395	.000152	6.97×10^{-8}	$6\pm1\times10^{-8}$	12.5	99	.826005
(1.5560×10^{-4})	(.0168586)	(.01651396)	(6.92×10^{-10})	(2.88×10^{9})	$(2.3\pm5\times10^{9})$	(23.7)	(188)	
9.5×10^5	3587.69	3400.989	.0244	4.11×10^{-10}	$4\pm1\times10^{-10}$	13.3	75	.834196
(1.8500×10^{-4})	(.0163467)	(.01549605)	(1.11×10^{-7})	(1.70×10^{7})	$(1.5\pm5\times10^{7})$	(25.2)	(142)	
10.0×10^5	3552.81	3297.419	.121	8.78×10^{-11}	$11\pm1\times10^{-11}$	13.7	68	.838000
(1.9448×10^{-4})	(.0161878)	(.01502415)	(5.52×10^{-7})	(3.63×10^{6})	$(4.4\pm5\times10^{6})$	(25.9)	(129)	
10.5×10^5	3517.78	3144.35	6.67	1.65×10^{-11}	$5\pm1\times10^{-11}$	14.3	60	.843645
(2.0420×10^{-4})	(.0160282)	(.0143267)	(3.04×10^{-5})	(6.82×10^{5})	$(1.9\pm5\times10^{6})$	(27.1)	(113)	
11.0×10^5	3483.48	2820.2	419.	2.54×10^{-14}	$2\pm1\times10^{-11}$	15.0	49	.860743
(2.1393×10^{-4})	(.0158719)	(.012850)	(1.91×10^{-3})	(1.05×10^{3})	$(7.6\pm5\times10^{5})$	(28.3)	(93)	

* The atomic unit of field strength is $e/a_o^2 = 5.142\times10^9$ volt/cm, of energy is $e^2/a_o = 219474.6\ cm^{-1}$, of time is $\hbar^3/(me^4) = 2.4189\times10^{-17}$ sec, and of distance is $a_o = 0.52917$ A[see Ref. (4), p. 2].

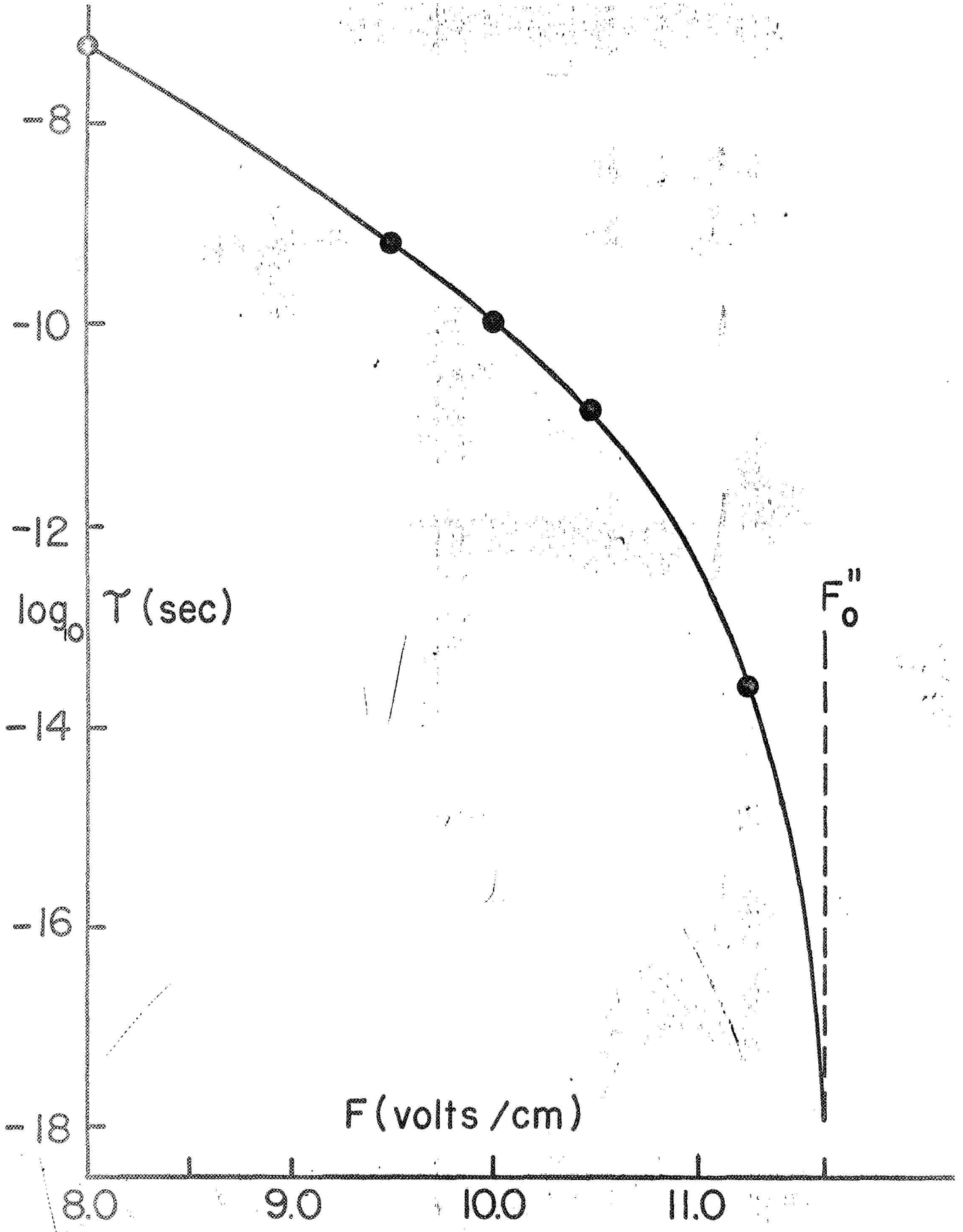

Figure 3. The variation of $\log_{10}(\tau)$ with F. Note that when the field strength is equal to $F_o'' = E_r^2/[4(Z-Z_1)]$ and the atom can ionize classically, the lifetime is very small.

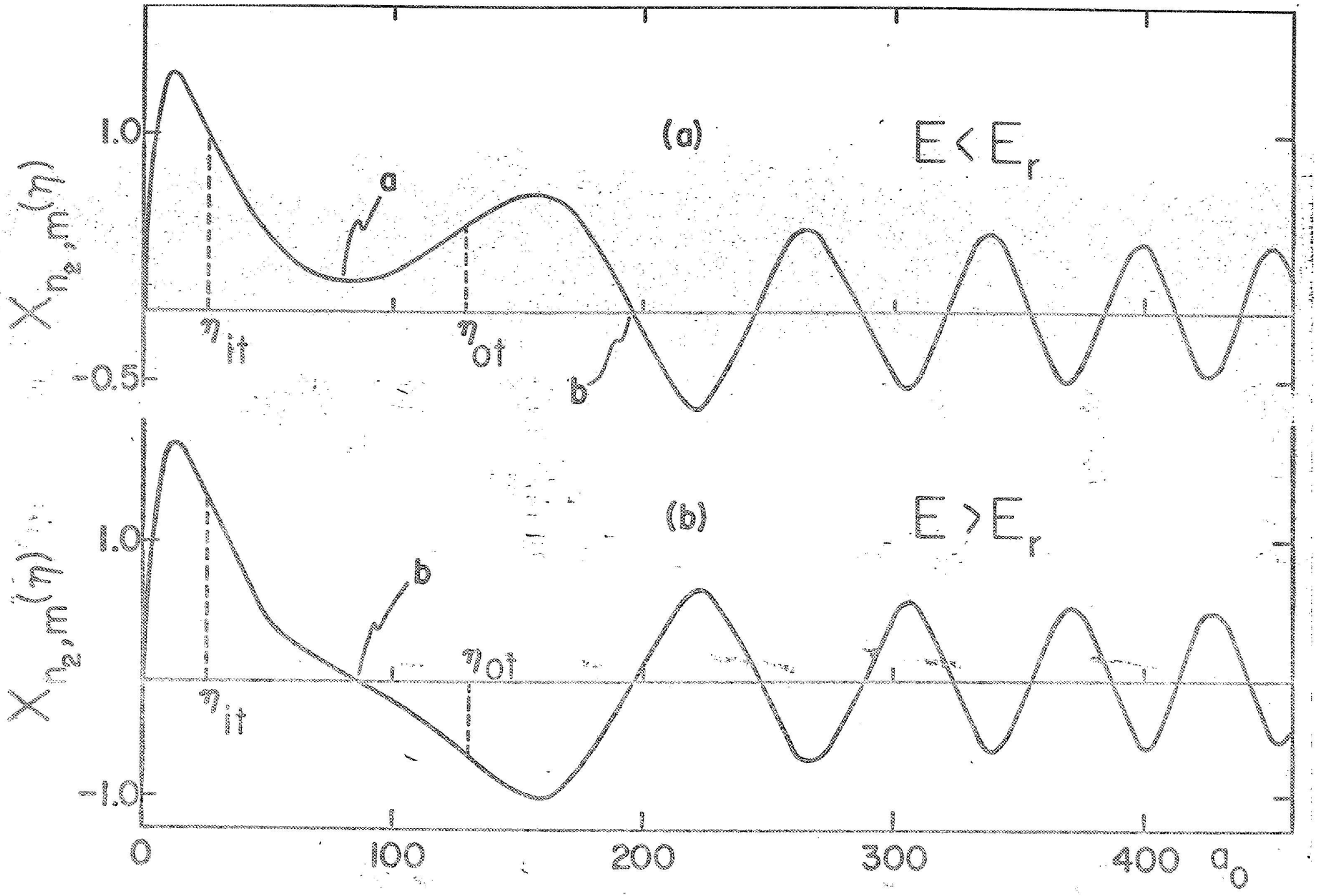

Figure 4. The Wave Function $\chi_{n_2,m}(\eta)$ for the case n=5, n_1=3, n_2=0, and m=1 in a field of 10^6 volts/cm. In (a), where E=-.015037 a.u. is <u>less</u> than E_r, the first node [point b] occurs when $\eta > \eta_{ot}$. In (b), where E=-.015010 a.u. is <u>greater</u> than E_r, the first node [point b] occurs when $\eta < \eta_{ot}$.

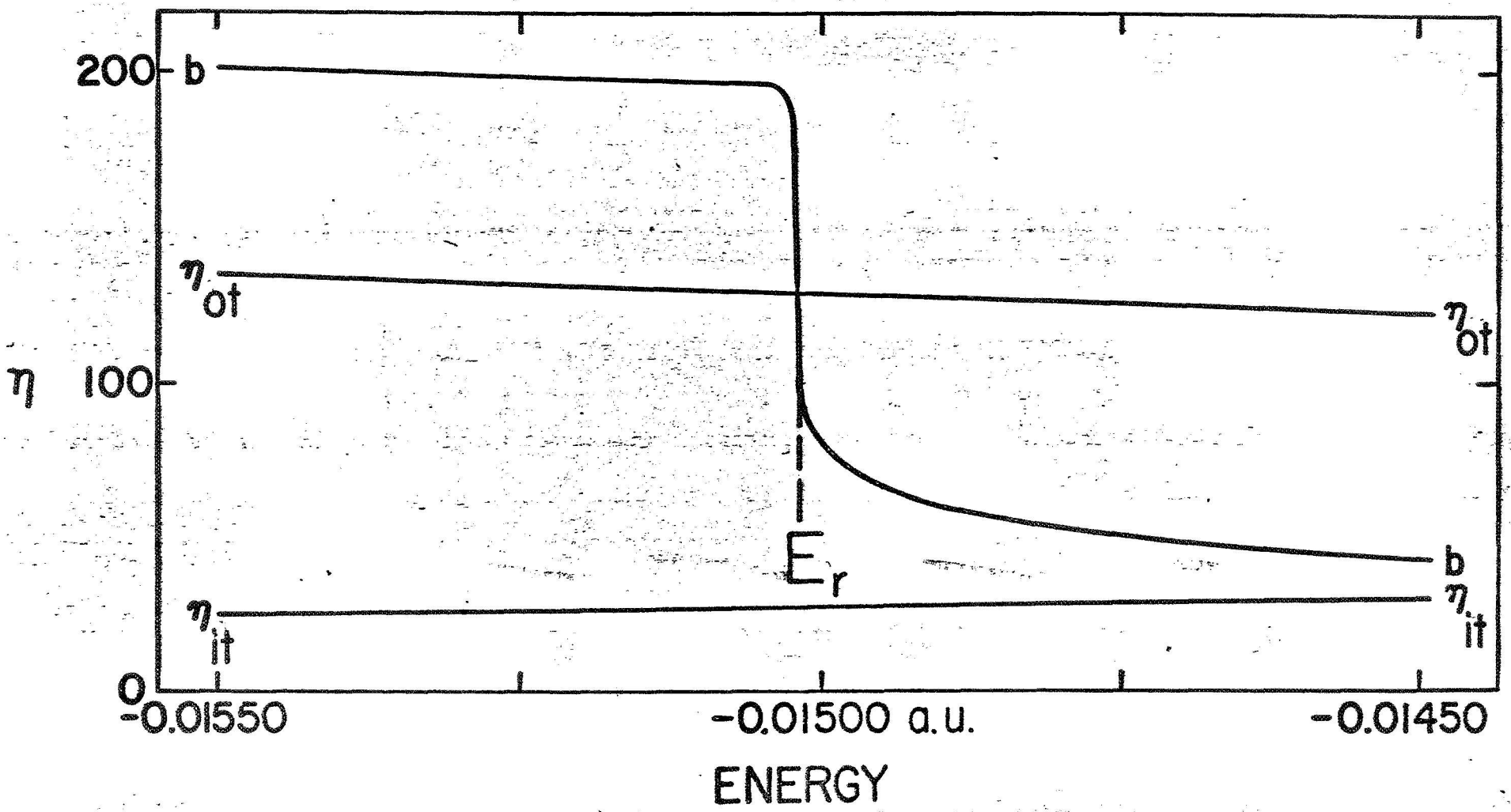

Figure 5. The Position $\eta = b$ of the First Node in $\chi_{n_2,m}(\eta)$ as a function of E for the case n=5, n_1=3, n_2=0, and m=1 in a field of 10^6 volts/cm. Note that $b = \eta_{ot}$ when $E = E_r$.

of the system is equal to the maximum value of V_η and from the standpoint of classical mechanics the atom can spontaneously ionize. Thus, as shown in the figure, the lifetime of an atom would be extremely small if F were greater than F_o'' .

It is not surprising that at the very high field strengths of more than twice $F_o = 4.27\text{x}10^4$ volts/cm or $F_o' = 5.14\text{x}10^5$ volts/cm. which we consider, the agreement between the resonance energy and the energy calculated by the Rayleigh-Schrodinger perturbation series is fair to poor. In calculating $E_{pert}(4) = E^{(0)} + F\,E^{(1)} + \ldots + F^4E^{(4)}$, the zero through third order energies are given in Ref. (4). The fourth order energy is[3]

$$E^{(4)}_{n_1,n_2,m} = -\frac{n^{10}}{1024\mu^7 Z^{10}}\left[\begin{array}{l} 5487n^4+35182n^2-1134m^2(n_1-n_2)^2+1806n^2(n_1-n_2)^2 \\ -\ 3402n^2m^2-3093(n_1-n_2)^4-549m^4+5754(n_1-n_2)^2 \\ -\ 8622m^2+16211 \end{array}\right] \tag{50}$$

One of the most curious features of the numerical calculations was the observation that the first node in $\chi_{n_2,m}(\eta)$ is located at the outer turning point when the energy is very nearly equal to the resonant energy. This is shown by Figs. 4 and 5. For cases where n_2 is different from zero we would expect that it would be the (n_2+1)-st node which would occur at η_{ot} when $E = E_r$.

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FIGURE CAPTIONS

Figure 1. Schematic Drawings of the Potential Energy Functions V_ζ and V_η for Different Values of m, the absolute value of the magnetic quantum number.

Figure 2. The rate of ionization $1/\tau$ versus E for the case n=5, n_1=3, n_2=0, and m=1 in a field of 10^6 volts/cm. Here $E_r = -0.01502415$ a.u. and $\Gamma = 0.552\times10^{-6}$ a.u. The solid line represents the calculated values. The dotted line corresponds to the Weisskopf-Wigner parabola as given by Eq. (48).

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