Rate of field ionization from S states with a quantum defect

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The WKB approximation in parabolic coordinates is used to calculate electric-field-ionization rates from $L = 0$ states with quantum defects. The range of applied electric field and principal quantum number have been given for which the rate formula is valid. Previous studies of field ionization of shallow impurity levels with quantum defects in solid-state systems have shown this formula to be in agreement with experiments.

Recently, there has been considerable activity,[1,2] both experimental and theoretical in the study of field-ionization processes in atoms. In their paper, Yamabe *et al.*[3] have developed the theory of field ionization of hydrogenic atoms and summarized work in that field. More recently Harrell and Simon[4] have given an algorithmic solution of the hydrogen-atom Stark problem. However, these results are only for the case of a purely Coulombic potential in which the principal quantum number is an integer, i.e., the quantum defect is zero. It is therefore interesting to consider the case of more complex atoms in which the wave function of the outermost electron may be approximated, at large distances from the core, by a hydrogenic wave function with a nonintegral quantum number n^*, and to obtain corresponding expressions for field-ionization rates applicable to such cases. Our approach is to consider fields which are of insufficient strength to cause classical field ionization and to obtain approximate expressions for the rate of field ionization via quantum-mechanical tunneling. While "classical" considerations lead one to expect an n^{*4} dependence of the field for appreciable ionization, quantum-mechanical-tunneling ionization rates are characterized by a more complicated field dependence. For simplicity, we consider only states in which the angular momentum L is zero. Generally, quantum defects are most significant for $L=0$ states, which are most sensitive to short-distance effects and therefore show the strongest splitting from the degeneracy exhibited by excited states for Coulombic potentials. The splitting is due to core effects and, in the case of impurity atoms in solids, to intervalley mixing as well. These are both short-distance effects.

One area of interest to the authors is that of localized wave functions for charge carriers which are weakly bound to impurities in semiconductors. It is well known[5] that the weakly bound levels of impurity atoms can be fairly well described by considering the Kohn-Luttinger envelope wave functions to be hydrogenic with a quantum defect. We have recently reported the observation of ground-state field ionization of shallow impurity levels in semiconductors in conjunction with a charge-storage effect[6] in Si p-i-n diodes at cryogenic temperatures. The storage of charge and its subsequent release were attributed, respectively, to the deionization of localized impurity levels by electron capture and subsequent field ionization of these levels. We are currently developing direct and precise experimental impurity atom field-ionization-rate measurement techniques. Because of weak binding, experimentally convenient rates of field ionization for ground states can be achieved with fields of the order of 10^4 V/cm. For comparison, we estimate that the fields required for ground-state field ionization of isolated alkali atoms are of the order of 10^7 V/cm. Thus, solid-state systems offer a convenient laboratory to study effects such as ground-state field ionization in electric fields which are easily accessible experimentally.

We begin with the hydrogenic wave functions[7] for $L=0$ and integral principal quantum number n:

$$\psi_n = [2/\sqrt{4\pi}(na)^{3/2}]\, e^{-r/na}\, {}_1F_1(1-n;2;2r/na)\,, \tag{1}$$

where $a = 4\pi\epsilon\hbar^2/me^2$ is the Bohr radius and ${}_1F_1$ is the confluent hypergeometric function. Reexpressing the wave function in terms of the ${}_2F_0$ hypergeometric function[8] yields

$$\psi_n = [2(-1)^n/\sqrt{4\pi}(na)^{3/2}\Gamma(n+1)]\,(2r/na)^{n-1} \times e^{-r/na}\, {}_2F_0(1-n,-n;-na/2r)\,. \tag{2}$$

We note that when extended to nonintegral n this expression provides a solution

$$\psi_{n^*} = [C(n^*)/\sqrt{4\pi}\,]\,(2r/n^*a)^{n^*-1} \times e^{-r/n^*a}\,{}_2F_0(1-n^*, -n^*; -n^*a/2r) \qquad (3)$$

to the Schrödinger equation which is regular at infinity and irregular at the origin. The formal hypergeometric series for ${}_2F_0$ has zero radius of convergence but provides an asymptotic series for $r \gg n^*a/2$. Replacement of n by nonintegral n^* in Eq. (1) would yield an unnormalizable wave function which is irregular at infinity. In spite of the irregular behavior at the origin, the wave function in Eq. (3) is normalizable. The normalization constant $C(n^*)$ is determined by the condition that

$$4\pi \int_0^\infty dr\, r^2 |\psi_{n^*}|^2 = 1\,, \qquad (4)$$

and is found to be given by

$$|C(n^*)| = [2/(n^*a)^{3/2}]\,[1/\Gamma(n^*+1)]\,|S(n^*)|\,, \qquad (5)$$

with

$$|S(n^*)| = [\pi/|\sin(n^*\pi)|\,] \times \left(\tfrac{1}{2}\sum_{m=0}^{\infty} 1/(n^*-m-1)^2(n^*-m)^2\right)^{-1/2}. \qquad (6)$$

The derivation of $C(n^*)$ is sketched in the Appendix. $|S(n^*)|$ is found to be exactly equal to one for positive integer n^* and very close to one for all nonintegral $n^* > \frac{1}{2}$, which is the range of n^* in which we are interested.

In principle, the true wave function could be determined by matching its asymptotic form ψ_{n^*} with a wave function that is regular at the origin and determined by the effective potential at short distances. However, it is the asymptotic part of the wave function that is sampled in the process of field ionization and the primary effect of short-distance deviation from Coulombic behavior is to make n^* nonintegral and change the normalization. Because the radial integration in the wave function normalization integral has an r^2 weight, the true normalization constant is not very sensitive to the wave function at small distances. Thus one is justified in using $C(n^*)$ given by Eq. (5) as the normalization constant. The small-distance effects of non-Coulombic potentials essentially appear in our final-rate expression purely through n^*.

We choose to work in parabolic coordinates, $\eta = r - z$ and $\xi = r + z$, which are the natural coordinates to use for a superposition of a Coulomb and a homogeneous electric field in the $+z$ direction. Following Landau and Lifshitz,[9] we note the existence of a potential barrier in the η coordinate associated with the removal of an electron from the atom in the direction $z \to -\infty$ corresponding to tunneling through a region of large η and small ξ.

From Eq. (3), we find that the asymptotic form of the wave function for arbitrary principal quantum number n^* and angular-momentum quantum number $L = 0$ in the absence of an electric field, is given by

$$\psi_{n^*} = \left(\frac{C(n^*)}{\sqrt{4\pi}}\right) e^{-\xi/2n^*a} e^{-\eta/2n^*a} \left(\frac{\eta}{2n^*a}\right)^{n^*-1} \times \left(1 - \frac{n^{*2}(n^*-1)a}{\eta} + \cdots\right), \qquad (7)$$

$$\eta \gg n^{*2}|n^*-1|a\,. \qquad (8)$$

The Schrödinger equation for an electron in an attractive Coulomb field along with a homogeneous electric field F is given by

$$\frac{4}{(\xi+\eta)}\left[\partial_\xi(\xi\partial_\xi\psi_{n^*}) + \partial_\eta(\eta\partial_\eta\psi_{n^*})\right] + \frac{2m}{\hbar^2}\left(-B + \frac{2e^2}{4\pi\epsilon(\xi+\eta)} - \frac{eF(\xi-\eta)}{2}\right)\psi_{n^*} = 0\,, \qquad (9)$$

where B, the binding energy is given by

$$B = \left(\frac{e^2}{4\pi\epsilon a}\right)\frac{1}{2n^{*2}}\,. \qquad (10)$$

Writing

$$\psi_{n^*} = \frac{X_1(\xi)}{\sqrt{\xi}}\,\frac{X_2(\eta)}{\sqrt{\eta}}\,, \qquad (11)$$

this equation can be separated in ξ and η coordinates as

$$\frac{d^2X_1}{d\xi^2} + \left[\frac{1}{4\xi^2} - \left(\frac{eFm}{4\hbar^2}\right)\xi - \frac{mB}{2\hbar^2} + \frac{\beta_1}{\xi}\right]X_1 = 0\,, \qquad (12a)$$

$$\frac{d^2X_2}{d\eta^2} + \left[\frac{1}{4\eta^2} + \left(\frac{eFm}{4\hbar^2}\right)\eta - \frac{mB}{2\hbar^2} + \frac{\beta_2}{\eta}\right]X_2 = 0\,, \qquad (12b)$$

where β_1 and β_2 are separation constants which satisfy

$$\beta_1 + \beta_2 = 1/a\,. \qquad (13)$$

It is important to note that the exact wave function for nonintegral n^* does not separate in parabolic coordinates. However, separation can be accomplished for the asymptotic form of the wave function. The basic philosophy is that we choose a value of η within the barrier (η_0) such that the wave function at this point is the asymptotic wave function in the absence of the external field. This is valid for weak fields such that terms linear in F in Eqs. (12a) and (12b) can be neglected at this point within the barrier. Substituting the asymptotic form (7) into Eqs. (12a) and (12b) we find that

$$\beta_1 = \frac{1}{2n^*a} \qquad (14a)$$

and

$$\beta_2 = \frac{(2n^* - 1)}{2n^* a} \tag{14b}$$

which are consistent with Eq. (13).

In the presence of an applied electric field F, the dependence of ψ_{n*} on ξ may be considered to be the same as in Eq. (7). This is due to the fact that ξ is small in the range which contributes most to the tunneling current. The η dependent equation can be written as

$$\frac{d^2X_2}{d\eta^2} + p^2(\eta)X_2 = 0\,, \tag{15}$$

where

$$p(\eta) = \left(-\frac{mB}{2\hbar^2} + \frac{Fem}{4\hbar^2}\,\eta + \frac{\beta_2}{\eta} + \frac{1}{4\eta^2}\right)^{1/2}. \tag{16}$$

To obtain the tunneling rate, we apply the WKB approximation to the η barrier in which $p(\eta)$ is imaginary. We remind the reader that η_0 is some value of η within the barrier such that,

$$n^{*2}|n^* - 1|a \ll \eta_0 \ll \eta_1\,, \tag{17}$$

where η_1 is the outermost classical turning point. Following Ref. 9, we use the asymptotic form of the wave function given by Eq. (7) at $\eta = \eta_0$. Outside the barrier, the exponent in the WKB wave function contributes a pure phase factor and the amplitude decreases as $1/\sqrt{p}$ with increasing η and we have for $\eta > \eta_1$:

$$|X|^2 = \left(\frac{n^* a|\,C(n^*)|^2}{2\pi}\right) e^{-(\xi + \eta_0)/n^* a} \left(\frac{|p_0|}{p}\right) \times \left(\frac{\eta_0}{2n^* a}\right)^{2n^* - 1} \exp\left(-2\int_{\eta_0}^{\eta_1} |p|\,d\eta\right), \tag{18}$$

where

$$\psi_{n*} = X/\sqrt{\eta} = X_1 X_2/\sqrt{\xi\eta}\,, \tag{19}$$

$|p|$ is the effective wave vector in the barrier and $|p_0|$ is the value of $|p|$ at $\eta = \eta_0$. After performing the integral in Eq. (18), we find that the asymptotic η_0 dependence disappears from Eq. (18). Assuming the validity of the inequality (17) the ionization rate R is found by integrating the probability current $|\psi_{n*}|^2 v_z$ over a plane perpendicular to the z axis. We find

$$R(F) = \omega(\alpha/F)^{2n^* - 1} \exp(-\alpha/F)\,, \tag{20}$$

where

$$\alpha = 2\hbar^2/3me(n^* a)^3\,, \tag{21}$$

$$\omega = [me^4/\hbar^3(4\pi\epsilon)^2](\tfrac{1}{4})6^{2n^* - 1} n^* a^3 |C(n^*)|^2\,. \tag{22}$$

We believe that this result can provide a reasonably good estimate of field ionization from atomic levels which are well described in the asymptotic region by quantum-defect hydrogenic wave functions. In the limit $n^* \to 1$, Eq. (20) reduces to the standard-rate formula[3,9] for the ground state of hydrogen. Direct comparisons with purely Coulombic results (no quantum defect) for integer $n > 1$ are not possible because we treat field ionization of nondegenerate $L = 0$ states. Quantum defects are associated with the lifting of the degeneracy of states with various L values.

In addition to the $n^* \to 1$ limit we are able to examine another limit and compare it with published results. This is the limit[10] in which the binding energy is held fixed while $n^* \to 0$. From Eq. (10) we see that in this limit the charge e, and hence the Coulombic part of the potential, must vanish with the binding energy maintained at a fixed value by the short-range potential which is responsible for the quantum defect. We see that in this limit our rate formula reduces exactly to the "δ-function" rate formula of Demkov and Drukarev.[11] This relies essentially on our normalization factor $|S(n^*)|$ which is one for integer $n^* \geq 1$ and $\sqrt{2}$ for $n^* = 0$. To determine the explicit condition of validity of the WKB approximation, we solve the equation $|p(\eta)| = 0$ to obtain

$$\eta_1 = 2B/eF - 2\hbar^2\beta_2/Bm \tag{23}$$

for small F, i.e., with the requirement that

$$eF|n^* - \tfrac{1}{2}| \ll 2B(2mB)^{1/2}/\hbar\,. \tag{24a}$$

Inequality (17) therefore yields the constraints on F and n^* for the rate formula (20) to be valid as

$$eF[n^*|n^* - 1| + 2(2n^* - 1)] \ll 2B(2mB)^{1/2}/\hbar\,. \tag{24b}$$

This inequality becomes trivial for values of n^* for which the quantity $[n^*|n^* - 1| + 2(2n^* - 1)]$ is small. In that case the inequality (24a) gives stronger restriction of F. Defining the classical critical field[1] as $F_c = B/8\,ean^{*2}$ inequalities (24) can be rewritten as

$$|1 - 2/n^*| \ll 16F_c/F \tag{25a}$$

and

$$|n^* - 1| + 4 - 2/n^* \ll 16F_c/F\,. \tag{25b}$$

The WKB approach is therefore valid at fields sufficiently below the classical critical field, so that electrons must tunnel through an appreciable barrier width. The largest n^* for which the approximation is valid for a given field F can be determined by the stronger of the conditions obtained from (25) as

$$n^{*3}|n^* - \tfrac{1}{2}| \ll [m^2e^5/\hbar^4(4\pi\epsilon)^3]/F \tag{26a}$$

and

$$n^{*4}|n^*-1|+2n^{*3}(2n^*-1)\ll[m^2e^5/\hbar^4(4\pi\epsilon)^3]/F. \tag{26b}$$

A quick comparison of ionization rates for different values of m, n^*, and the dielectric constant K, may be obtained by noting that the ionization rate is a rapidly varying function of (D/F), where $D=m^2/K^3n^{*3}$. A given rate which occurs at a field F_0 in a system with m_0, n_0^*, K_0, will occur at a field value approximately given by

$$F\simeq F_0(m/m_0)^2(K_0/K)^3(n_0^*/n^*)^3, \tag{27}$$

in a system with m, K, and n^*. This provides a convenient comparison between field ionization of isolated atoms and field ionization of shallow impurity levels in semiconductors using the Kohn-Luttinger approach[12] in which the solid is characterized by the dielectric constant and the charge carriers by an effective mass m^*. The Kohn-Luttinger approach involves approximations of varying reliability depending on the nature of the impurity[5] and the degree of intervalley mixing.[13,14]

Our treatment above does not incorporate effects of unequal longitudinal and transverse effective masses. When this anisotropy is important, it is simplest to make the further approximation of using a single effective mass as introduced by Kohn and Luttinger[12] in their studies of approximate hydrogenic wave functions. Precise measurements of field-ionization rates may reveal the need for improving this method of handling the effects of anisotropy.

The results derived here have already been applied to studies of the dynamics of field ionization from localized impurity levels in a semiconductor at low temperatures in an externally applied electric field.[15] Results of these theoretical studies have been found to be in agreement with experiments using silicon-pin diodes.[6] More precise measurements are currently underway. Studies[16] have also been made of quantum-mechanical limitations on the charge release time associated with field ionization of localized ground-state impurity levels in semiconductors. That work was motivated by possible applications to charge-storage devices and memory elements.

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APPENDIX

In this appendix, we present a sketch of our derivation of the normalization constant $C(n^*)$ of the wave function

$$\psi_{n^*}=[C(n^*)/\sqrt{4\pi}\,](2r/n^*a)^{n^*-1}\times e^{-r/n^*a}\,{}_2F_0(1-n^*,-n^*;-n^*a/2r). \tag{A1}$$

We first write $C(n^*)$ as

$$C(n^*)=[2/(n^*a)^{3/2}\Gamma(n^*+1)]\,S(n^*) \tag{A2}$$

such that the quantity in brackets is the normalization constant of the radial part of the wave function for integer n^*. The normalization condition is given by

$$I=4\pi\int_0^\infty r^2dr\,|\psi_{n^*}|^2=1. \tag{A3}$$

Substituting (A1) into (A3) gives

$$\begin{aligned}I&=\int_0^\infty r^2dr\,|C(n^*)|^2\left(\frac{2r}{n^*a}\right)^{2n^*-2}e^{-2r/n^*a}\,|{}_2F_0(1-n^*,-n^*,-n^*a/2r)|^2\\&=|C(n^*)|^2(n^*a/2)^3\int_0^\infty dx\,e^{-x}x^{2n^*}|{}_2F_0(1-n^*,-n^*,-1/x)|^2\\&=|S(n^*)|^2\frac{1}{2\Gamma^2(n^*+1)}\int_0^\infty dx\,e^{-x}x^{2n^*}|{}_2F_0(1-n^*,-n^*;-1/x)|^2\end{aligned} \tag{A4}$$

The hypergeometric function ${}_2F_0$ may be written in terms of the integral representation[8]

$${}_2F_0(p,q;-1/x)=\frac{x^q}{\Gamma(q)}\int_0^\infty e^{-xt}t^{q-1}(1+t)^{-p}dt,\quad \mathrm{Re}(q)>0. \tag{A5}$$

Substituting (A5) into (A4) gives

$$I=|S(n^*)|^2\frac{1}{2\Gamma^2(n^*+1)\Gamma^2(-n^*)}\int_0^\infty dx\,e^{-x}\int_0^\infty ds\int_0^\infty dt\,e^{-x(s+t)}(st)^{-n^*-1}(1+t)^{n^*-1}(1+s)^{n^*-1}. \tag{A6}$$

This equation is valid for negative n^* only. We shall continue to work with $n^*<0$ and subsequently obtain the desired result for $S(n^*)$ by analytically continuing the function defined by the integrals in Eq. (A6) back to $n^*>0$. By making the substitutions, $u=1+1/s$ and $v=1+1/t$, integral I reduces

to

$$I=|S(n^*)|^2\frac{2\sin^2(\pi n^*)}{\pi^2}\times\int_1^\infty du\int_1^\infty dv(uv)^{n^*-2}(u-1)(v-1)/(1-1/uv).$$

Now expanding $(1-1/uv)^{-1}$ in a power series in $1/uv$, the integral reduces to a sum of integrals. Carrying out these integrals yields

$$I=|S(n^*)|^2\frac{2\sin^2(\pi n^*)}{\pi^2}\left(\sum_{m=0}^{\infty}\frac{1}{(n^*-m-1)^2(n^*-m)^2}\right).$$

Note that the function defined by the sum can now be analytically continued to $n^*>0$. From the normalization condition $I=1$ we obtain

$$|S(n^*)|=\frac{\pi}{|\sin(n^*\pi)|}\left(\tfrac{1}{2}\sum_{m=0}^{\infty}\frac{1}{(n^*-m-1)^2(n^*-m)^2}\right)^{-1/2}.$$

The quantity $|S(n^*)|$ is easily seen to be exactly equal to one for positive integer n^* by examining the poles of $1/\sin(n^*\pi)$ and the double poles appearing in the sum. Since $|S(n^*)|$ is obviously unbounded at negative integral n^*, it is clear that $|S(n^*)|$ cannot be identically equal to one. Numerical evaluation of $|S(n^*)|$ shows that it is very close to one even for nonintegral $n^*>\frac{1}{2}$.

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