Field-Ionization Processes in Excited Atoms

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We identify two different processes by which free atoms are ionized in a static electric field. The first process is by tunneling and is described accurately by theory developed for hydrogen. The second process, important for all atoms except hydrogen, is similar to autoionization and arises from the effect of level mixing. Data are presented on field ionization in lithium which display behavior due to each of these ionization mechanisms.

The problem of how an atom is ionized in an applied electric field has attracted wide theoretical and experimental interest. Considering the level of activity, it is remarkable that there is such poor agreement between rigorous theories, developed for hydrogen, and experimental observations on highly excited atoms in hydrogenic states. It is also remarkable that a simple "back-of-the-envelope" theory successfully predicts the field values at which ionization becomes significant. Our aims are to reconcile the conflicting theoretical pictures of field ionization, and to provide a useful insight into the underlying processes.

To put the problem into perspective, let us contrast two views of field ionization. In the first view, ionization occurs by tunneling of the electron through the potential barrier along the axis
of the applied field. The potential is taken to be (in atomic units)

\[ V(r) = -r^{-1} - Fz. \]  

(1)

The field \( F \) defines the \( z \) axis. Tunneling rates have been calculated to high precision by a variety of methods. Among the most useful results are those of Bailey, Hiskes, and Riviere. In Fig. 1(b), ionization rates are shown for levels with principal quantum numbers \( n = 18-20 \), and azimuthal quantum number \( |m| = 1 \). The field values at which the ionization rates equal the radiative decay rates are indicated by tick marks. Beyond these points the ionization rates increase so rapidly that the levels broaden into the continuum.

Experimental studies of field ionization on hydrogen have been carried out using collisionally excited fast beams, and in one case the tunneling rate for a laser-selected hydrogenic state has been measured precisely. The observations agree with the theory developed for hydrogen, and the process seems to be well understood.

The second view of the ionization process is entirely classical and is based on simple energy arguments. The potential of Eq. (1) has a saddle point on the \( z \) axis where it has the value \( V_{sp} = -2\sqrt{F} \). According to this model, which we shall call the "saddle-point" model, an atomic state is stable or ionized according to whether its energy \( W \) is lower or higher than \( V_{sp} \), respectively. Thus, bound states are allowed only for levels which satisfy

\[ W < -2\sqrt{F}. \]  

(2)

If one ignores the Stark effect and substitutes the value \( W = 1/2n^2 \), where \( n^* \) is the effective quantum number, then Eq. (2) predicts that states will ionize at the threshold field value \( F_{th} = 1/16n^4 \).

This behavior has been noted by numerous observers. Recently, Cooke and Gallagher have pointed out that the analysis requires modification for states with nonzero angular momentum. For the case \( |m| \ll n \), the saddle point of the effective potential is \( V_{sp} \approx -2\sqrt{F} + |m| F^{3/4} + (3/16)n^2 F \), and the region of stability is

\[ W < -2\sqrt{F} + |m| F^{3/4} + \frac{3}{16} n^2 F. \]  

(3)

The dotted lines in Fig. 1 mark this boundary for \( |m| = 1 \).

Generally there are natural connections between quantum mechanical and classical descriptions of systems, and it is tempting to regard the saddle-point model as a limiting case of the tunneling model. There are, however, fundamental conflicts between these two descriptions. In fact, as Fig. 1(b) illustrates, they do not even agree qualitatively. Consider, for instance, the order in which the sublevels of a given term ionize with increasing field. According to the tunneling picture, as the field increases the levels of a given term begin to decay by ionization in order of increasing energy. According to the saddle-point model, however, levels ionize in order of decreasing energy. The two pictures predict that a given state ionizes at fields which can differ by a factor greater than 2. It is apparent that the tunneling and classical descriptions are in serious conflicts notwithstanding that there is experimental evidence to support each view.

We believe that both tunneling and classical saddle-point phenomena play important roles in field ionization, but that the underlying quantum mechanical processes are fundamentally different and need to be distinguished clearly. We shall illustrate this point with data on field ionization in lithium, obtained by experimental techniques similar to those used in earlier studies of sodium.

A thermal atomic beam of lithium is excited to a Rydberg state by tunable pulsed lasers (5-ns pulse length) in a three-step process: 2s - 2p (671 nm), 2p - 3s (813 nm), and 3s - Rydberg state (-626 nm, \( n = 19 \)). The Rydberg state is characterized by \( |m| = 0 \) or 1 according to whether the light exciting the final step is polarized parallel to or perpendicular to the electric field, respectively. Excitation takes place between parallel plates which are used for applying a dc electric field and a pulsed field, as needed. To detect levels which do not ionize rapidly, a 10-kV/cm pulsed electric field, large enough to ionize all Rydberg atoms present, is applied 3 \( \mu \)s after laser excitation. (The 3-\( \mu \)s delay time was chosen to be somewhat shorter than the transit time of the atoms across the detector, ~10 \( \mu \)s.) The ions are collected in a gated time window which begins with the applied field pulse, so that the only states observed are those which spontaneously ionize at a rate less than (3 \( \mu \)s)\(^{-1} = 3 \times 10^5 \text{ s}^{-1} \). This collection method serves to detect only those excited atoms which are essentially stable in the static applied field. Spontaneous radiation is not important since the radiation rates for the levels studied are ~10\(^5 \text{ s}^{-1} \) or less.

Data for the states of lithium in the vicinity of \( n = 19 \) are shown in Fig. 1(a). The energies are in agreement with calculation for hydrogen, Fig. 1(b). The most interesting feature of the data is
FIG. 1. Tunneling and saddle-point ionization in lithium. (a) Experimental map of the energy levels of lithium, $|m|=1$, in a static electric field. The horizontal peaks arise from ions collected after laser excitation. Energy is measured relative to the one-electron ionization limit. Disappearance of a level with increasing field indicates that the ionization rates exceed $3 \times 10^5 \text{ s}^{-1}$, as explained in the text. The dotted line is the prediction of saddle-point theory, Eq. (3). One state has been emphasized by shading. (b) Energy levels for hydrogen ($n=18-20$, $|m|=1$) according to fourth-order perturbation theory. Levels from nearby terms are omitted for clarity. Symbols used to denote the ionization rate are defined in the legend. The tick mark indicates the field where the ionization rate equals the spontaneous radiative rate. (c) Experimental map as in (a) except that the collection method is sensitive only to states whose ionization rate exceeds $3 \times 10^5 \text{ s}^{-1}$. At high fields, the levels broaden into the continuum in agreement with tunneling theory for hydrogen.
the abrupt disappearance of the states at intermediate fields, indicating that the spontaneous ionization rate exceeds $3 \times 10^5$ s$^{-1}$. The onset of ionization is in striking agreement with the predictions of the saddle-point theory. The observed threshold does not change appreciably as the delay time is decreased by a factor as great as 5, which suggests that the ionization rates increase rapidly at the saddle-point threshold.

Equally striking is the behavior of the Stark levels in fields above the saddle-point ionization limit. To investigate this region we took data as before except that the timing window, 3 $\mu$s long, was started immediately after laser excitation, and the pulsed field was omitted. Now only states which spontaneously ionize at a rate greater than $3 \times 10^5$ s$^{-1}$ are observed. The results are shown in Fig. 1(c). The levels are conspicuously sharp and well defined at fields far above the saddle-point limit. By “sharp” we mean that the level width is small compared with the laser linewidth, 0.25 cm$^{-1}$, which requires an ionization rate of less than $5 \times 10^{10}$ s$^{-1}$. The relative stability of the states, shown in Fig. 1(c), is fundamentally inconsistent with tunneling behavior. According to tunneling theory, if the field is increased beyond the point where a state starts to ionize appreciably, the level rapidly broadens into the continuum. Such tunneling behavior is, in fact, evident in Fig. 1(c) though not at the saddle-point limit. For instance, the shaded $n=19$ sublevel in Fig. 1(c) starts to broaden at a field of about 6.2 kV/cm, and effectively merges with the continuum by 6.6 kV/cm. The observed broadening of this level, and all other levels in the $n=19$ manifold, is in good agreement with the behavior calculated for hydrogen. It is apparent that the Stark states eventually ionize according to hydrogenic tunneling theory, but that they are also capable of ionizing, although at relatively low rates, as soon as they reach the saddle-point limit.

At this point it is helpful to recognize a peculiarity of simple tunneling theory, namely that most pure hydrogenic states are stable even if their total energies lie above a local potential maximum. These states correspond to electron orbits that simply miss the saddle point. It is also helpful to realize that there is a paradox inherent in the saddle-point approach: As explained below, if the central potential is strictly Coulombic, the saddle-point theory does not apply.

Non-Coulombic effects on field ionization are perhaps best understood in the context of a hydrogen model. In the nonrelativistic theory of hydrogen, states from different terms have different symmetry and can cross. As a consequence, stable levels can exist degenerately with rapidly ionizing states from higher terms. Any perturbation of the Coulomb field breaks the symmetry and leads to level mixing. The effects can be dramatic. For example, the perturbation of a spherically symmetric core of inner-shell electrons leads to avoided crossings between stable states with the same value of $m$. In the case of a crossing between a stable state and an ionizing state with the same value of $m$, the perturbation leads to level mixing which quenches the stable state. In the absence of such level mixing (e.g., in hydrogen) the saddle-point model fails. Note that the perturbation due to the core also influences the zero-field energy-level structure and thus information concerning the quantum defects may be used to estimate the amount of level mixing in the applied field. If the quantum defects (modulo 1) of any the levels of a given $m$ are large, then we may expect extensive mixing, and likewise if they are all small, then we may expect negligible mixing. In our example of lithium ($|m|=1$) level mixing is neither extensive nor negligible. Here the largest of the quantum defects, that of the $p$ state, is only 0.05.

There is a close analogy between saddle-point ionization and autoionization. In first approximation a localized electron state is embedded in a continuum with which it cannot interact. Under the influence of a perturbation, the bound level is coupled to the continuum and the level ionizes. In the case of autoionization the perturbation is due to configuration interaction. In the case of saddle-point ionization the perturbation is due to the core.

In a previous study we have shown how coupling between a stable and an ionizing level at a localized level crossing can be analyzed by projecting the excited-state wave functions onto a basis set of hydrogen wave functions. Unfortunately the generalization of this procedure is unwieldy. A quantitative understanding of field ionization of atoms other than hydrogen is needed, nonetheless, and further work towards this end is in progress.

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1 Cf. T. Yamabe, A. Tachibana, and H. J. Silverstone,


\textsuperscript{6}W. Cooke and T. Gallagher, Phys. Rev. A \textbf{17}, 1226 (1978). Equation (3) of this work is derived following considerations of their comment.
