properties of the Padé approximants.[19]

I acknowledge important conversations with
R. Damburg, G. Hatton, H. Silverstone, and Yale
University colleagues. R. Damburg, G. Hatton,
H. Silverstone, J. Leopold, D. Bailey, and
J. Hiskes kindly performed some calculations.
E. Rock and H. Venkataramania assisted in the
early stages of the experiment. This research
was supported in part by National Science Founda-
tion Contract No. PHY 76-84469 and by Yale Uni-
versity.

[1]H. A. Bethe and E. E. Salpeter, *Quantum Mechanics
of One- and Two-Electron Atoms* (Academic, New York,
1955); E. U. Condon and G. H. Shortley, *The Theory of
Atomic Spectra* (Cambridge Univ. Press, Cambridge,
1963), Chap. 17.

[2]E. C. Titchmarsh, *Eigenfunction Expansions As-
sociated with Second-Order Differential Equations
Part II* (Oxford Univ. Press, Oxford, 1958).

[3]J. Killingbeck, Rep. Prog. Phys. **40**, 963 (1977).

[4]B. H. Bransden, *Atomic Collision Theory* (Benjamin,
New York, 1970), p. 166.

[5]F. J. Dyson, Phys. Rev. **85**, 631 (1952).

[6]H. J. Silverstone, Phys. Rev. A (to be published),
and private communication.

[7]D. S. Bailey, J. R. Hiskes, and A. C. Riviere, Nucl.
Fus. **5**, 41 (1965). See also the following: Quantal:
R. J. Damburg and V. V. Kolosov, J. Phys. B **9**, 3149
(1976); G. J. Hatton, Phys. Rev. A **16**, 1347 (1977).
Classical: D. Banks and J. G. Leopold, J. Phys. B **11**,
L5, 37 (1978), and to be published, and private com-
munication.

[8]Damburg and Kalosov, Ref. 7; Hatton, Ref. 7; Banks
and Leopold, Ref. 7.

[9]M. Hehenberger, H. V. McIntosh, and E. Brandas,
Phys. Rev. A **10**, 1494 (1974); C. Cerjan, W. P. Rein-
hardt, and J. E. Avron, J. Phys. B **11**, L201 (1978),
and references therein.

[10]D. F. Blossey, Phys. Rev. B **2**, 3976 (1970).

[11]P. M. Koch, L. D. Gardner, and J. E. Bayfield, in
Beam-Foil Spectroscopy, edited by D. J. Pegg and
I. A. Sellin (Plenum, New York, 1976), Vol. 2.

[12]J. E. Bayfield, Rev. Sci. Instrum. **47**, 1450 (1976).

[13]P. M. Koch, Opt. Commun. **20**, 115 (1977).

[14]J. E. Bayfield, L. D. Gardner, and P. M. Koch,
Phys. Rev. Lett. **39**, 76 (1977).

[15]P. M. Koch, Bull. Am. Phys. Soc. **22**, 1318, 1319
(1977), and **23**, 563 (1978).

[16]T. Y. Chang. Opt. Commun. **2**, 77 (1970).

[17]H. W. Mocker, Appl. Phys. Lett. **12**, 20 (1968).

[18]J. E. Bayfield and P. M. Koch, Phys. Rev. Lett. **33**,
258 (1974).

[19]P. M. Koch, to be published.

[20]G. A. Baker, Jr., *Essentials of Padé Approximants*
(Academic, New York, 1975).

Field-Ionization Processes in Excited Atoms

Michael G. Littman, Michael M. Kash, and Daniel Kleppner
*Research Laboratory of Electronics and Department of Physics, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139*
(Received 10 April 1978)

We identify two different processes by which free atoms are ionized in a static elec-
tric field. The first process is by tunneling and is described accurately by theory de-
veloped 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 pre-
sented 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 theoreti-
cal[1,2] and experimental[3] interest. Considering
the level of activity, it is remarkable that there
is such poor agreement between rigorous theo-
ries, developed for hydrogen, and experimental
observations on highly excited atoms in hydro-
genic states. It is also remarkable that a simple
"back-of-the-envelope" theory successfully pre-
dicts the field values at which ionization becomes
significant. Our aims are to reconcile the con-
flicting theoretical pictures of field ionization,
and to provide a useful insight into the underlying
processes.

To put the problem into perspective, let us con-
trast two views of field ionization. In the first
view, ionization occurs by tunneling of the elec-
tron through the potential barrier along the axis

of the applied field. The potential is taken to be (in atomic units)

$$V(r) = -r^{-1} - Fz. \tag{1}$$

The field F defines the z axis. Tunneling rates have been calculated to high precision by a variety of methods.[1] Among the most useful results are those of Bailey, Hiskes, and Riviere.[2] 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,[4] and in one case the tunneling rate for a laser-selected hydrogenic state has been measured precisely.[5] 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

$$W \leq -2\sqrt{F}. \tag{2}$$

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 $F_c = 1/16n^{*4}$. This behavior has been noted by numerous observers.[3] Recently, Cooke and Gallagher[6] 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 $V_{sp} \cong -2\sqrt{F} + |m| F^{3/4} + (3/16)m^2 F$, and the region of stability is

$$W \leq -2\sqrt{F} + |m| F^{3/4} + \tfrac{3}{16} m^2 F. \tag{3}$$

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.[7] 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: $2s \to 2p$ (671 nm), $2p \to 3s$ (813 nm), and $3s \to$ Rydberg state ($\sim$626 nm, $n \sim 19$). 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 μs after laser excitation. (The 3-μs delay time was chosen to be somewhat shorter than the transit time of the atoms across the detector, $\sim$10 μs.) 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 $(3 \ \mu s)^{-1} = 3 \times 10^5 \ s^{-1}$. 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 $10^5 \ s^{-1}$ 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
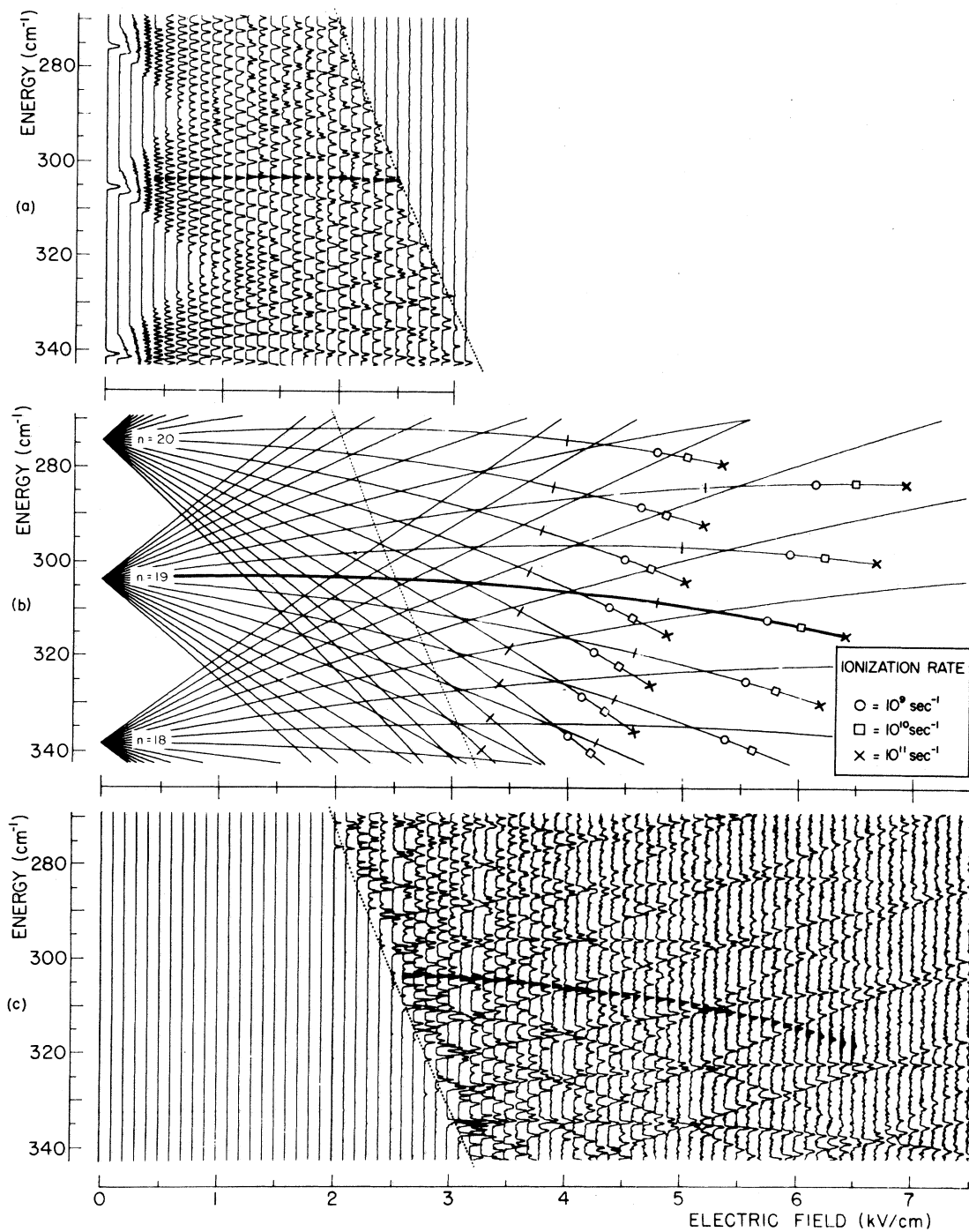
FIG. 1. Tunneling and saddle-point ionization in lithium. (a) Experimental map of the energy levels of lithium, $|m| = 1$, in a static electric field. The horizontal peaks arise from ions collected after laser excitation. Energy is measured relative to the one-electron ionization limit. Disappearance of a level with increasing field indicates that the ionization rates exceed 3×10^5 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 3×10^5 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 inter-
mediate fields, indicating that the spontaneous
ionization rate exceeds 3×10^5 s^{-1}. The onset of
ionization is in striking agreement with the pre-
dictions of the saddle-point theory. The observed
threshold does not change appreciably as the de-
lay 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 lev-
els in fields above the saddle-point ionization lim-
it. To investigate this region we took data as be-
fore except that the timing window, 3 μs long,
was started immediately after laser excitation,
and the pulsed field was omitted. Now only states
which spontaneously ionize at a rate *greater* than
3×10^5 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 5×10^{10} s^{-1}. The relative stability of the
states, shown in Fig. 1(c), is fundamentally in-
consistent with tunneling behavior. According to
tunneling theory, if the field is increased beyond
the point where a state starts to ionize appreci-
ably, the level rapidly broadens into the continu-
um. 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 lev-
el, 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 tunnel-
ing theory, but that they are also capable of ion-
izing, although at relatively low rates, as soon
as they reach the saddle-point limit.

At this point it is helpful to recognize a peculi-
arity 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 in-
herent in the saddle-point approach: As explained
below, if the central potential is strictly Coulomb-
ic, the saddle-point theory does not apply.

Non-Coulombic effects on field ionization are
perhaps best understood in the context of a hydro-
gen model. In the nonrelativistic theory of hydro-

gen, states from different terms have different
symmetry[8] and can cross. As a consequence, sta-
ble levels can exist degenerately with rapidly ion-
izing states from higher terms. Any perturbation
of the Coulomb field breaks the symmetry and
leads to level mixing. The effects can be dramat-
ic. For example, the perturbation of a spherical-
ly 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 hydro-
gen) the saddle-point model fails. Note that the
perturbation due to the core also influences the
zero-field energy-level structure and thus infor-
mation 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 mix-
ing. In our example of lithium ($|m| = 1$) level mix-
ing 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 approxima-
tion 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 local-
ized level crossing can be analyzed by projecting
the excited-state wave functions onto a basis set
of hydrogen wave functions.[5] 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.

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

Phys. Rev. A 16, 877 (1977), and references therein;
B. M. Smirnov and M. I. Chibisov, Zh. Eksp. Teor.
Fiz. 49, 841 (1965) [Sov. Phys. JETP 22, 585 (1966)];
D. Banks and J. G. Leopold, J. Phys. B 11, L5 (1978).

[2]D. S. Bailey, J. R. Hiskes, and A. C. Riviere, Nucl.
Fusion 5, 41 (1965).

[3]Cf. R. F. Stebbings, C. J. Lattimer, W. P. West,
F. B. Dunning, and T. B. Cooke, Phys. Rev. A 12,
1453 (1975); T. W. Ducas, M. G. Littman, R. R. Free-
man, and D. Kleppner, Phys. Rev. Lett. 35, 366 (1975);
T. F. Gallagher, L. M. Humphrey, W. E. Cooke, R. M.
Hill, and S. A. Edelstein, Phys. Rev. A 16, 1098 (1977).

[4]P. N. Il'in, in Atomic Physics 3, edited by S. J.
Smith and G. K. Walters (Plenum, New York, 1973),
p. 309.

[5]M. G. Littman, M. L. Zimmerman, and D. Kleppner,
Phys. Rev. Lett. 37, 486 (1976).

[6]W. Cooke and T. Gallagher, Phys. Rev. A 17, 1226
(1978). Equation (3) of this work is derived following
considerations of their comment.

[7]M. G. Littman, M. L. Zimmerman, T. W. Ducas,
R. R. Freeman, and D. Kleppner, Phys. Rev. Lett. 36,
788 (1976).

[8]K. Helfrich, Theor. Chim. Acta 24, 271 (1972).

Measurement of Dielectronic Recombination Rates for the Iron Ions Fe IX–XI

R. L. Brooks, R. U. Datla, and Hans R. Griem
Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742
(Received 11 April 1978)

Iron is injected into a well-diagnosed θ-pinch plasma. The intensities of lines from
various ionization stages are measured as functions of time and interpreted by means of
a time-dependent corona ionization-recombination model. Effective coefficients for di-
electronic recombination at electron densities $N_e \approx 3 \times 10^{16}$ cm^{-3} are equal to or smaller
than presently accepted theoretical values for low-density plasmas. Rate coefficients
for ionization tend to be smaller than theoretical values.

The distribution of (heavy) atomic ions over
ionization stages remains an important quantity
in astrophysics and solar physics, and has now
also become very important in controlled fusion
research. To calculate this distribution, one
needs ionization and recombination rate coeffi-
cients for the dominant processes—usually elec-
tron-impact ionization for increases in the ionic
charge and, more often than not, for decreases
in the charge, "dielectronic" recombination.[1]
The latter process involves radiationless capture
of a plasma electron, accompanied by excitation
of a bound electron, into doubly excited (autoion-
izing) states. These captures are followed by
stabilizing radiative transitions which give rise
to satellites of the resonance lines of the recom-
bining ions. Finally, the captured electron cas-
cades radiatively or by collisions from its nor-
mally rather highly excited state. Calculations
of such complex processes are necessarily very
uncertain and depend on many approximate cross
sections and spontaneous transition rates that
have not been tested experimentally.

To provide an experimental test of the overall
dielectronic recombination process, two methods
come to mind. One approach would be based on

an absolute measurement of all important satel-
lite lines in a plasma with known concentration
of recombining ions and electrons. The sum of
all corresponding photon emission rates could
then yield the desired recombination rate. This
approach has may difficulties and has not yet
been successful. Our approach is a generaliza-
tion of a method[2,3] for the determination of effec-
tive ionization-rate coefficients from a compari-
son of measured and calculated line emission
from impurity ions in a transient plasma whose
electron temperature and density have been meas-
ured independently.

We assume that practically all ions are in their
respective ground states and consider the coupled
rate equations for the corresponding densities,
N_z, in a plasma of electron density N_e:

$$dN_z/dt = N_e[S_{z-1}N_{z-1} + \alpha_{z+1}N_{z+1} - (S_z + \alpha_z)N_z].$$

The ionization and recombination coefficients,
S_z and α_z, are functions of electron temperature,
T. The shape of these functions is assumed to
be known,[1,2] as is the shape of the excitation rate
coefficients [$\sim \exp(-E/kT)/E$] which relate N_z to
the observed line intensities. (Here E is the ex-
citation energy.) By introducing temperature-