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# Microwave Ionization and Excitation of Rydberg Atoms

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A classical theory gives excellent agreement with the Bayfield-Koch experiment on microwave ionization of Rydberg hydrogen atoms. The time dependence of excitation and ionization is presented, and classical trajectories are divided into four significant categories. The results suggest that nonresonant laser ionization of atoms in states of low quantum number can also take place as a result of extremely high-order processes with large numbers of intermediate states of excitation.

In the recent experiments of Bayfield and Koch[1] and of Bayfield, Gardner, and Koch[2] beams of highly excited hydrogen atoms were passed through a microwave cavity. The probability of ionization was measured[1] and excitation to states higher than the initial states detected.[2] The experiments were suggested by them to be a useful scaled model of laser ionization of atoms in low states.

Their experimental results can be summarized as follows: (EX1) For given field frequency (i.e., microwave) the ionization probability rises from zero to unity with increasing field strength. Considerable ionization is observed even when the peak electric field strength is small by comparison with the static electric field strength needed to ionize the atom. (EX2) The ionization probability depends on the field frequency $\omega_F$. (EX3) Multiphoton excitations take place.

It is clear that very large numbers of quantum states are involved. The usual theories of laser ionization[3] have not been applied. The Keldysh dynamic barrier-penetration theory[4,5] is clearly inadequate because barrier penetration decreases approximately as $\exp(-n)$ and is utterly negligible for $n \approx 66$. However the parameter $\gamma$ introduced by Keldysh has a classical interpretation which is important in this Letter.

In our theory both atom and microwave field are treated classically and the magnetic effects of the field neglected. While the atom is in the interior of the microwave cavity its electron moves in a classical orbit satisfying Hamilton's equations with the Hamiltonian function

$$H(\vec{r}, \vec{p}) = \tfrac{1}{2}p^2 - r^{-1} + zF_{\max}\cos\omega t, \quad (1)$$

where $\vec{r}$ is the position and $\vec{p}$ the momentum of the electron and units have been chosen for which the charge and mass of the electron are unity. Entry to and exit from the cavity are represented by adiabatic increase and decrease of the envelope of the oscillating field.

The initial conditions are chosen by a Monte Carlo method from a classical microcanonical distribution corresponding to equal population of the degenerate $(l, m)$ states of a given $n$. The equations of motion are solved by stepwise numerical integration. Details of the method and checking procedures are given by Leopold and Percival.[6] The theory and method were both adapted from well-tried procedures for collision processes.[7]

The method was subject to the following errors: (E1) The precise conditions of the laboratory experiment, such as the initial distribution over $(l, m)$ states produced by charge transfer, and the form of the rise and fall of the microwave field, were not known. (E2) The quantized atom and field are represented by a classical model. (E3) There are errors in computation, mainly inadequate statistics.

Experimental results without errors E1 were unavoidable to us, the errors E3 are probably slightly smaller, and the errors E2 are certainly completely negligible by comparison. Thus the theoretical model adequately represents the experiments[1,2] and this is confirmed for the experiment of Ref. 1.

The classical dynamics of excitation and ionization processes depends only on the dimensionless ratios

$$\omega_F/\omega_{at} \tag{2}$$

and

$$F_{max}/F_{at}, \tag{3}$$

where $\omega_{at}$ is the angular frequency of the electron in its orbit,

$$\omega_{at} = (1\text{ hartree})/n^3\hbar, \tag{4}$$

and for unperturbed circular orbits $F_{at}$ is the force exerted on the electron by the proton.

The quantity $\gamma$ is given by

$$\gamma = \frac{\omega_F/\omega_{at}}{F_{max}/F_{at}} = \frac{P_{at}}{F_{max}/\omega_F}, \tag{5}$$

where $\omega_F$ and $F_{max}$ are the frequency and the peak amplitude of the applied field, respectively. In our units $P_{at}$ is the momentum of the electron in a classical orbit corresponding to the quantum state characterized by the quantum number $n$. The ratio $F_{max}/\omega_F$ is the maximum momentum induced by the field in the absence of the proton.

Because only the dimensionless ratios (2) and (3) are important, the same calculation can be used for any value of $n$, provided these ratios remain constant and classical mechanics is valid.

Calculations were performed for atoms with $n = 66$ and a field of 9.9 GHz, giving $\omega/\omega_{at} = 0.43$.

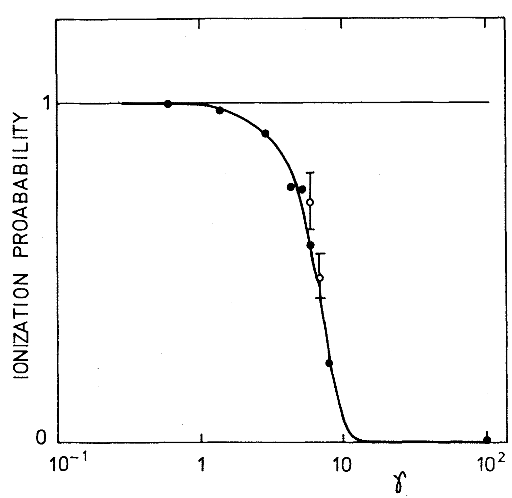


FIG. 1. Ionization probability vs $\gamma$ for 9.9-GHz microwave field. (Full circles are Bayfield-Koch experimental results, open circles correspond to our calculations.)

The field amplitudes were $F_{max}/F_{at} = 0.061$ and 0.072 which corresponds to $\gamma = 7$ and 6, respectively. We chose these field amplitudes since they are lower than any classical adiabatic threshold field calculated by us.[8] Thus, during the adiabatic rise of the envelope of the field to its peak value almost none of the trajectories ionized. The times of integration corresponded to 10-keV atoms passing through cavities of lengths ranging from 3 mm to 3 cm. The results are compared with the Bayfield-Koch experiment[1] in Fig. 1. The ionization probabilities calculated by us are close to the experimental result for the two values of $\gamma$ for which calculations were performed. For $\gamma = 7$ and 6 Bayfield and Koch observed an ionization probability of 50% and 62%, respectively. Our calculations give (40–50)% and (62–80)% for the same respective values of $\gamma$. Considering the differences between the laboratory experiment and the computer simulation the agreement is excellent. The most important differences are in the initial distribution of $(l, m)$ states. In the laboratory experiment this distribution is broad but unknown while in our case it is classical microcanonical. There is also a

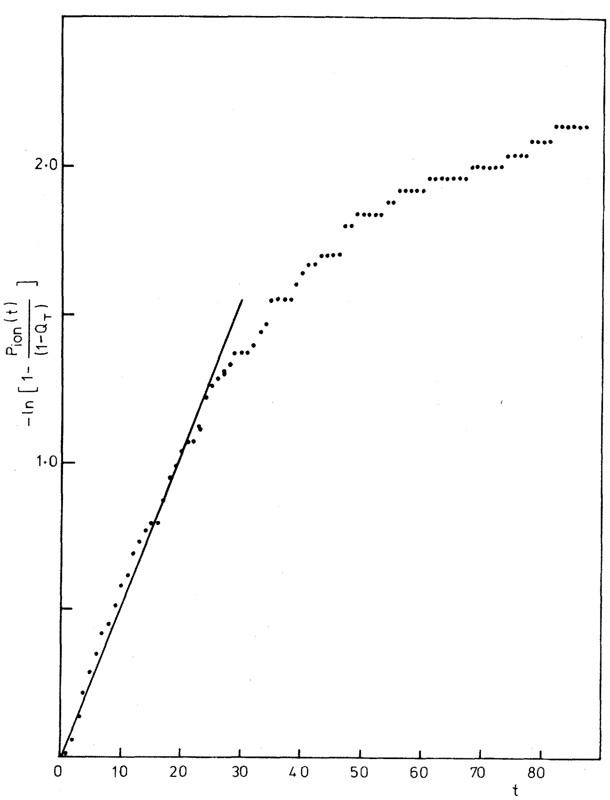


FIG. 2. Ionization probability plot.

laboratory distribution of $n$ (63–69) which corresponds to a range of $\gamma$'s (or for fixed $\gamma$ and $\omega/\omega_{at}$ to a range of $F/F_{at}$). We chose $n=66$, fixed $\gamma$, $\omega/\omega_{at}$, and $F/F_{at}$.

In addition to the above comparison we have been able to investigate the time dependence of the atomic processes both for the whole sample and for individual trajectories.

The probability of ionization $P_{\rm ion}(t)$ obeys the law

$$P_{\rm ion}(t) \simeq (1-Q_T)\{1-\exp[-\beta(t)t]\}. \qquad (6)$$

The constant $Q_T$ is the estimated probability that the trajectories lie in invariant tori in phase space.[9] Such trajectories never ionize. In Fig. 2 we can see that until about 90% of the ionization is completed $\beta(t)$ is nearly independent of time.

We find that the individual trajectories can be classified into four distinct categories, illustrated by example in Fig. 3: (C1) trajectories in invariant tori, (C2) rapid-ionization trajectories, (C3) trajectories with excitation to extremely highly excited (EHE) states, with subsequent ionization, (C4) trajectories with excitation to EHE states without subsequent ionization.

All categories are important. Most of the C2 trajectories ionize in the linear part of Fig. 2

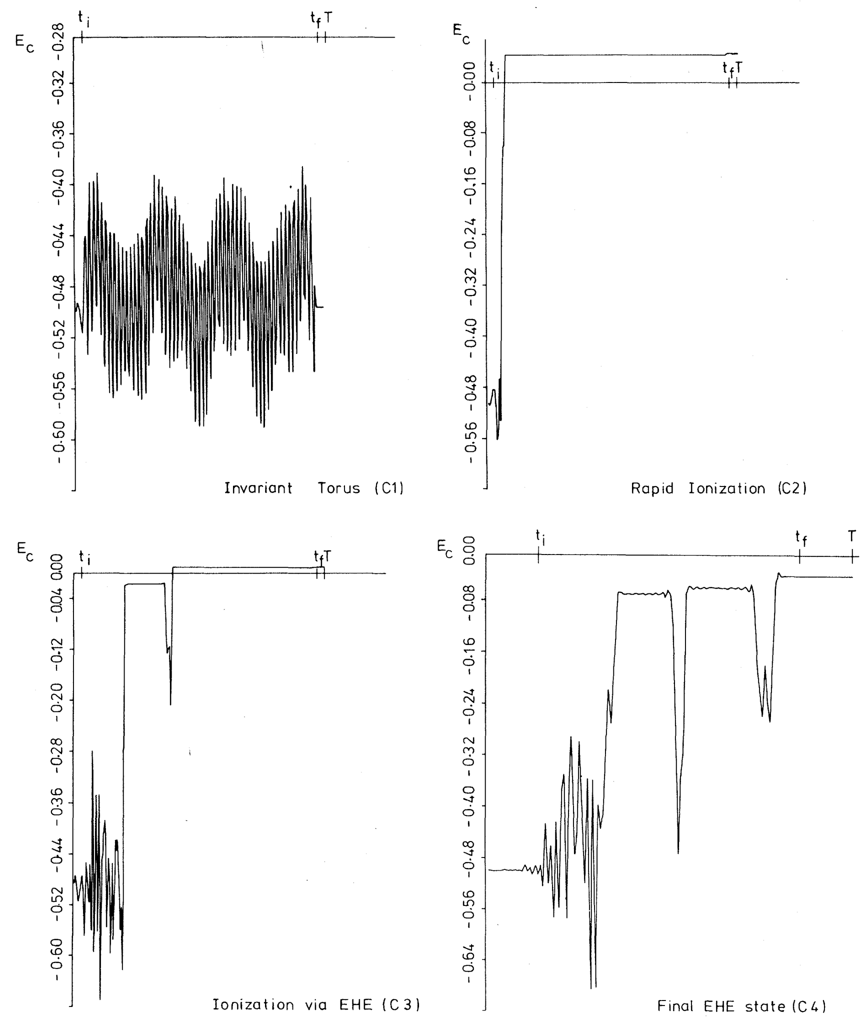


FIG. 3. Examples of the four types of trajectories. The compensated energy is plotted against time or equivalently cavity length. The field is gradually turned on to its peak amplitude from zero time to $t_i$. It is gradually turned off between $t_f$ and $T$. The effective cavity is between $t_i$ and $t_f$. (For the samples here it was 1 cm for trajectories C1, C2, and C3 and 3 mm for the trajectory of type C4.) $E_c$ is in scaled atomic units, for which the energy of the initial state is always $-\frac{1}{2}$.

while the remaining EHE orbits are longer lived and ionize with a lower $\beta(t)$.

The energy $E_c$ plotted in Fig. 3 is the "compensated energy"

$$E_c = -r^{-1} + \tfrac{1}{2}\{p_x^2 + p_y^2 + [p_z - (F_{\max}/\omega)\sin\omega t]^2\}, \quad (7)$$

which is constant in the presence of the microwave field along. $E_c$ is much more stable than the actual energy. When it is greater than zero, it is a good indication that ionization has taken place, as shown by the removal of the electron from the proton; this is not so for the actual energy. In the more interesting categories C3 and C4 the electron gains energy early as in C2, but not enough to ionize. It moves away from the proton into an elliptical orbit upon which is superimposed the sinusoidal oscillations of the field, with many oscillations around the ellipse. The orbit is often highly eccentric. The compensated energy $E_c$ is very stable in the outer parts of the orbits. The sudden changes in $E_c$ take place when the electron is near perihelion. Notice that the *weaker* the binding the *more stable* the atom is in the presence of the oscillating field. These orbits correspond to the EHE states. Although they are remarkably stable in the microwave field, they would be very sensitive to collisions or to stray static or adiabatic fields, which would affect the comparison between theory and experiment. For $\gamma = 6$ and a 3-mm effective cavity, 17% EHE states with ionization energies more than 50 times lower than the initial energy are observed. Bayfield, Gardner, and Koch[2] have observed higher excitations with $\Delta n = 1, 2$ from initial $48 \leq n \leq 57$ but their experimental setup did not allow for observing EHE states.

Because of the dependence on the dimensionless ratios (1) and (2), the classical calculation can be used for states of low quantum number and laser frequencies. It then becomes a classical model of laser ionization, with the disadvantage that it neglects all quantal effects. The classical approximation may be considered as the zeroth term in an asymptotic expansion in powers of $1/\hbar$, but both the correspondence identities[10] and comparison of classical collision-ionization calculations with experiment[11] show that in practice the agreement between them, even for ground-state ionization, is very much better than asymptotic theory would suggest. A satisfactory general explanation for this agreement is not yet available.

The classical calculation has the advantage that it is independent of any form of perturbation theory. The action of the radiation field on the atom is included to all orders. The results suggest that significant ionization results from extremely high-order processes, with large numbers of intermediate states of excitation. Our conclusions are very similar to those of Walker and Preston[12] who treated an anharmonic oscillator in a driving field classically as was suggested to them by W. E. Lamb.

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