New Photoelectric Ionization Peak in the Hydrogen Atom

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We present here analytical and numerical evidence which establishes that, for highly excited hydrogen atoms irradiated by microwaves, a large ionization peak occurs at frequencies much below those required for the conventional one-photon photoelectric effect. Indeed, we find that this ionization peak can, for suitable parameters values, be much higher than that of the usual photoelectric effect, a theoretical prediction which is currently being tested in the laboratory. A striking property of this ionization peak is that its frequency width is jointly determined by two independent effects: the classical chaotic threshold and the quantum delocalization border.

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The cross section for one-photon ionization in the hydrogen atom can be calculated by use of elementary quantum mechanics and, consequently, its properties are now quite well understood. For frequencies below the one-photon ionization threshold, two or more photons are required to cause ionization and, for sufficiently small fields, the probability of such processes is much less than that for the standard one-photon ionization.

On the other hand, for large fields, several investigators[1–10] have shown that strong excitation and ionization can take place even for frequencies well below the one-photon ionization threshold. Indeed, many authors[2–9] have noted that this ionization of the quantum hydrogen atom occurs concurrent with the appearance of chaotic motion in the corresponding classical atom. This connection is quite reasonable since classical chaos is known to yield ionization via a diffusion process of the Fokker-Planck type; the correspondence principle then permits (but does not require) us to anticipate similar behavior in the quantum motion.

While rough agreement has been found between experimental results and the predictions of classical dynamics,[5] the validity of using classical dynamics to predict quantum results is a theoretical problem in itself. Indeed, it is known that the quantum dynamics for classically chaotic systems may predict behavior which differs from the classical even in the semiclassical region. In particular, previous numerical simulations[3,4] of a quantum model for the hydrogen atom in a microwave field have exposed a parameter range in which no diffusive-type excitation takes place even though the corresponding classical case does exhibit diffusion.

For some time now, we have been conducting a fully quantal computer investigation of ionization mechanisms in hydrogen using a model which includes continuum effects. Indeed, we have previously established conditions under which classical chaos is relevant to quantum dynamics.[4] In the present paper, we announce a particularly striking result of our recent studies. A detailed report will appear elsewhere.[8] Specifically, we find that the hydrogen atom can exhibit a large ionization peak at frequencies much below that of the conventional photoelectric effect. As incident microwave frequency increases away from zero, appreciable ionization first occurs at the threshold for classical chaos ω_c as expected, following which the ionization probability increases extremely rapidly to its large maximum value. As frequency continues to rise, the ionization probability remains high until a strictly quantal effect—the so-called quantum delocalization border[4]—is encountered at frequency ω_d above which the hydrogenic electron can no longer mimic classical diffusion. Above ω_d, the hydrogenic wave function becomes localized precluding ionization. In short, a frequency window of large-amplitude ionization can occur in hydrogen at frequencies much below that of the conventional photoelectric effect. No empirical test of these predictions has yet been completed, but such investigations are currently in progress.

Turning now to specifics, let us consider ionization mechanisms for the hydrogen atom when a linearly polarized monochromatic electric field induces transitions from initial states having principal quantum number $n_0 \gg 1$. For simplicity, we restrict ourselves

to the study of very elongated quantum states having parabolic quantum numbers $n_1 = n_0 - 1$, $n_2 = 0$, and magnetic quantum number $m = 0$. Since to a good approximation these wave functions have nonzero values only along the direction of the applied field, we are at liberty here to treat the hydrogen atom as it if were one dimensional, having the Hamiltonian

$$H = p^2/2 - 1/x + \epsilon x \cos(\omega t), \quad x > 0, \tag{1}$$

where ϵ and ω are the microwave electric field strength and frequency, respectively, in atomic units. The validity of this one-dimensional approximation is due to the small value of matrix elements for transitions having $\Delta n_2 \neq 0$. As a consequence, the atom remains one dimensional during the relevant interaction times.[3,4] This important fact has also been verified in laboratory experiments which produce such states and excite them by microwave fields.[11]

Classical analysis[2,9] reveals that for microwave field strengths $\epsilon_0 = \epsilon n_0^4$ larger than the critical value

$$\epsilon_c \approx 1/50\omega_0^{1/3}, \tag{2}$$

a chaotic excitation of the hydrogenic electron occurs which obeys a diffusion law, where n_0 denotes the classical action of the initially excited state and where $\omega_0 = \omega n_0^3$ is required to be greater than unity. The diffusion rate is given[2] by

$$D = (\Delta n)^2/\tau \approx 2\epsilon_0^2 n^3/(\omega_0^{7/3} n_0) = 2\epsilon^2 n^3/\omega^{7/3}, \tag{3}$$

where $\tau = \omega t/2\pi$ is the time measured as number of microwave periods and where Δn is the spread in the classical action n at time τ. Since the diffusion coefficient given by Eq. (3) increases rapidly like n^3, the dispersion Δn becomes infinite in a finite time.[2,8] In short, the classical electron ionizes in a finite time τ_D. A rough estimate for τ_D has been obtained[2,8] under the assumption that τ_D is not appreciably different from the time at which Δn becomes on the order of n_0. The validity of this assumption clearly improves with increasing n_0. With this assumption in Eq. (3) and with the approximation of n by n_0, it has been found that

$$\tau_D \sim \omega_0^{7/3}/\epsilon_0^2. \tag{4}$$

In closing this paragraph, let us discuss the reason why we have required $\omega_0 > 1$ in the preceding Eqs. (2)–(4). First, note that Eqs. (2)–(4) were calculated under the assumption of a classical chaos arising from the overlap of first-order resonances specified by the equations $\omega - s\Omega = 0$,[2,9] where ω is the frequency of the monochromatic microwave field and Ω is the classical frequency of the electron. But if there is to be full diffusion due to the overlap of all resonances down to the lowest ($s = 1$), clearly the microwave frequency ω must be on the order of the electron's fundamental (or lowest) frequency Ω, i.e., $\omega \approx \Omega$. Indeed, if we neglect higher-order resonances as well as the width of this lowest first-order resonance, then there can be no resonance overlap and hence no chaos when $\omega < \Omega$. But from the unperturbed action-angle Hamiltonian for the hydrogen atom, we have $\Omega = 1/n_0^3$. Hence under the above assumptions, $\omega \approx n_0^{-3}$ provides the lowest critical value ω_{cr} ($\approx n_0^{-3}$) of the microwave frequency at which chaos can occur. In terms of ω_0, we have

$$\omega_0 > \omega_c \sim 1, \tag{5}$$

where $\omega_c = \omega_{cr} n_0^3$ is a normalized critical frequency, approximately equal to unity, which we call the *chaotic threshold* in frequency on the understanding that ϵ_0 must be greater than the critical value given[12] by Eq. (2).

A recent analysis[4] of the quantum behavior of the microwave-driven hydrogen atom has revealed the existence of a critical field value ϵ_q, called the *quantum delocalization border,* below which quantum effects suppress diffusive excitation. However, for field values ϵ_0 above this border, the quantum excitation proceeds in much the same way as the classical. The critical field value has been shown to be given[4] by

$$\epsilon_q \approx \omega_0^{7/6}/(6n_0)^{1/2} \quad (\omega_0 \gtrsim 1). \tag{6}$$

Notice here that for states having $n_0 \leq 400\omega_c$, as frequently occurs in laboratory experiments, diffusive excitation will occur only for microwave field strengths above the quantum delocalization border given by $\epsilon_q > \epsilon_c$.

It is interesting to compare quantal diffusive ionization with the conventional one-photon process. According to Goreslavsky, Delone, and Krainov,[13] the ionization rate for the one-photon process is

$$\tau_\Phi^{-1} \approx 1.7\epsilon_0^2 n_0^2/\omega_0^{13/3}. \tag{7}$$

This rate achieves its maximum value γ_Φ, given by $\gamma_\Phi \approx 34\epsilon_0^2/n_0^{7/3}$, at the frequency threshold value $\omega_0 = \omega_\Phi \approx n_0/2$. On the other hand, the diffusive ionization rate τ_D^{-1} reaches its maximum [see Eq. (4)] $\gamma_D \sim \epsilon_0^2$ at $\omega_0 \approx \omega_c \ll \omega_\Phi$. The truly striking result here is not merely that the quantum diffusive ionization occurs at frequencies low compared to the one-photon threshold but that its rate is much higher, namely

$$\gamma_D/\gamma_\Phi \sim n_0^{7/3}/34. \tag{8}$$

It is important to recall that the classical expression for γ_D used in Eq. (8) is also the quantal expression (since here the field intensity is above the delocalization border) and that the rates given in Eq. (8) refer to time measured in periods of the microwave field. In terms of physical time $t = (2\pi/\omega)\tau$, this ratio becomes

$$\Gamma_D/\Gamma_\Phi \sim n_0^{4/3}/17. \tag{9}$$

At first glance, the dimensionless ratios of Eqs. (8) and (9) might be expected to be equal until one notices that both rates until one notices that both rates in Eq. (8) are specified after the same fixed number of periods but at two distinct frequencies, whereas the rates in Eq. (9) are specified at a fixed time. From these estimates, we see that, for highly excited initial states, the diffusive ionization process gives larger ionization probability than does the one-photon process.

We have checked the above predictions against numerical solutions of Schrödinger's equation for the model discussed in Ref. 1. In these computations, we used a Sturm basis in order to account explicitly for the continuous part of the spectrum. A detailed description of our numerical technique will be given elsewhere.[8] We now turn to a graphical presentation of results with accompanying discussion.

In accordance with common usage in laboratory experiments, we say that the hydrogenic atom has ionized when it reaches a state having some large preassigned value of the principal quantum number $n = \bar{n}$. We let the symbol W_I denote the ionization probability. In Fig. 1, we present our main results on the comparison between the diffusive and one-photon ionization mechanisms at fixed field intensity ϵ_0, initial state n_0, and physical time t. In this figure, the solid curve was obtained from the quantum calculations, while the dotted curve provides the classical predictions. The much higher ionization probability for the quantum diffusive ionization process *vis-à-vis* the one-phonon process is striking. Moreover, the frequency of onset for the quantum diffusive ionization peak is almost 2 orders of magnitude below that of the one-photon process. We perhaps should note that the classical results were obtained by numerical integration of Newton's equations of motion for 250 trajectories with the same initial action n_0 as for the quantum case but with the phases chosen to be homogeneously distributed over the interval $[0, 2\pi]$. In this way, the classical calculation is made to correspond with the quantum computation. The frequency of onset for the new photoelectric ionization peak is, as mentioned earlier, given by the classical chaotic border. The fact that the numerically computed ω_c in Fig. 1 lies below unity merely means that the effect of higher-order resonances and the width of the lowest resonance is not entirely negligible here.[12]

In Fig. 1, for the range $\omega_c \leq \omega_0 \leq \omega_d \approx (6n_0\epsilon_0^2)^{3/7}$ [from Eq. (6)], the curves of ionization probability computed for the classical and quantum hydrogen atom are seen to be quite close thus verifying our ear-

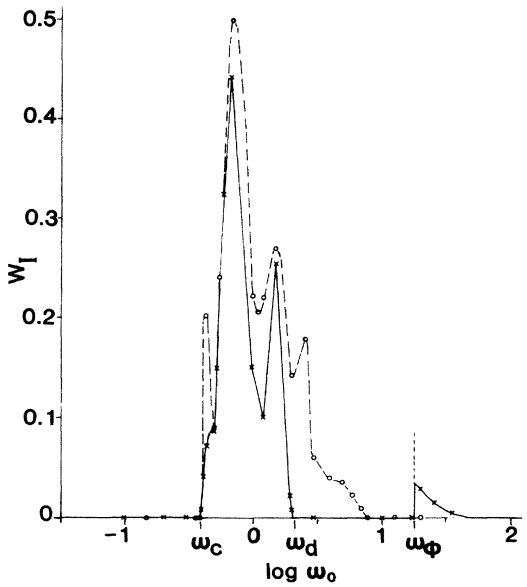

FIG. 1. Ionization probability $W_I = \sum_{n>\bar{n}} |c_n|^2$ vs field frequency ω_0 after a time $\tau = 40\omega_0$ which corresponds to the same real physical time t for all frequencies. We have set $n_0 = 66$, $\epsilon_0 = 0.05$, $\bar{n} = 99$. Crosses, quantum theory; circles, classical theory. Notice that ω_Φ is here somewhat less than $n_0/2$ because, in our definition of the ionization probability, the contribution of states with $n > \bar{n}$ is also included.

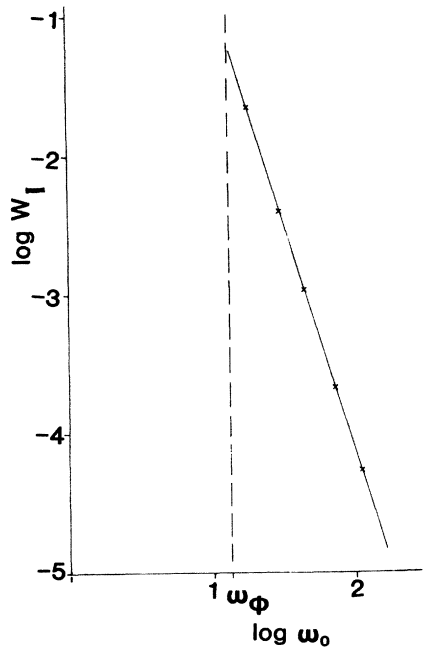

FIG. 2. Ionization probability for frequencies above the one-photon threshold ω_Φ for parameter values similar to those of Fig. 1. The crosses are the results of our numerical quantum calculations. The straight line is not a least-squares fit to the crosses but is rather the line given by the theoretical quantum mechanical expression. The excellent agreement with theory shown in Fig. 2 even at very large frequencies validates our entire numerical procedure and shows that the Sturm base takes into account the continuous spectrum quite effectively.

lier assertion regarding the effect of quantum delocalization. For $\omega_0 > \omega_d$, however, quantum localization occurs[4] and the ionization probability drops sharply below the classical prediction. Finally for the one-photon region $\omega_0 > \omega_\Phi$, our numerical results are in excellent agreement with theory as is seen in Fig. 2. Indeed, this agreement provides a very good check on our whole numerical procedure; specifically, it verifies that the Sturm basis quite effectively incorporates the effects of the continuous spectrum. Numerous results similar to those shown in Figs. 1 and 2 have been obtained for various parameter values, and they will be reported elsewhere.

In this Letter, we have provided numerical and theoretical evidence for the existence of a frequency window inside which a strong excitation and ionization of hydrogen atoms can occur. The present high level of experimental technique[5,11,14,15] encourages the hope that this phenomenon can be observed in the laboratory.

This article is but one product of a long-standing international collaboration linking far-flung outposts in Atlanta, Milano, and Novosibirsk. On this particular paper, however, only Milano and Novosibirsk explicitly appear on the by-line; nonetheless, knowledgeable readers will likely appreciate Atlanta's contribution to the final draft as much as the authors do themselves. The authors also delight in taking this opportunity publicly to thank R. Bonifacio, G. Mantica, L. Perotti, and F. M. Izraelev for stimulating discussions, and to express their warmest gratitude to G. Bellini and A. Pullia for much kind assistance and generosity in providing computer time, without which this paper most certainly could not have been written. This work was supported by the Consiglio Nazionale delle Ricerche, Italy.

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[12]The case $\omega_0 < 1$ has been considered in Refs. 2 and 9. However, since discussion of this point is not crucial for this paper, we delay further elaboration until a future date (Ref. 8). Nonetheless, we must emphasize that, because of the presence of higher-order resonances, ω_c may be less than unity and that Eq. (2) as well as other estimates given in this paper yield approximate values. More accurate results are provided by numerical experiments.

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