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Space localization and bound-state population in short-pulse resonant multiphoton ionization

P. Agostini

Service de Recherches sur les Surfaces et l'Irradiation de la Matière, Centre d'Etudes Nucleáires de Saclay, 91191 Gif Sur Yvette, France

L. F. DiMauro

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973

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A numerical analysis using the resolvent-operator method shows that the space and time localization of ionization is in fact the key needed to understand the residual population that is left in the excited state in Stark-induced resonant multiphoton ionization. The two viewpoints recently opposed in the literature [G. N. Gibson, R. R. Freeman, and T. J. McIllrath, Optics and Photonics News **3**, 22 (1992)] are therefore compatible. However, the excited-state population can easily be destroyed if the resonance intensity or the pulse duration is increased.

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Picosecond and subpicosecond pulses have revealed [1] the resonant nature of multiphoton ionization (MPI). In short, the optical field required to observe MPI is usually strong enough to induce Stark resonances, which temporarily increases the ionization rate and dominates, in general, the nonresonant process. Due to averaging over the pulse space-time intensity distribution, the resonances are normally unobservable in the total ionization yield, but easily appear as sharp structures (typically 30 to 50 meV wide) in the photoelectron energy spectrum produced by short pulses. Due to a ponderomotive shift of the ionization limit, the energy at which the structure appears is uniquely determined by the corresponding state's binding energy and the photon energy [1]. From the uncertainty principle, it may be argued that the sharp structures indicate that the atomic state remains in resonance for a time comparable to the inverse of its width (100 fs). It was therefore asserted [2] that the resonant structures originate only from the region of the interaction volume where the intensity (I_r) needed to bring the state into resonance is reached at the *top* of the pulse's temporal envelop where the shift rate is close to zero. This scenario results in a long-enough time scale for adiabatic passage to occur from the ground state to the excited state, which is then immediately ionized at a constant intensity, namely I_r. This model, which is based on a generalized Landau-Zener (LZ) level-crossing theory, led to the "shell" model of ionization, owing to the spatial shape of such a region in a Gaussian pulse. While the model was consistent with the photoelectron results, de Boer and Muller made the most interesting discovery that a population may survive in the Stark-shifted excited state after the end of the strong pulse [3]. From this observation, it was alternatively proposed that the excited state may indeed be populated when the resonance occurs during the rise of the pulse and subsequently ionized at various intensities during the rest of the pulse. The resulting photoelectron energy remains unchanged *provided* that the state has the *same* rate of shift as the ionization limit, i.e., the ponderomotive shift. An obvious characteristic of this scenario is that it contradicts the shell model, since now the resonance intensity may be reached at any time during the pulse and therefore *anywhere* in the interaction volume. However, a recent experiment provided reconfirmation of the "shell" model by observing ionization through a state that has a shift rate *different* from the ponderomotive shifted threshold. The resulting photoelectron spectrum showed a sharp resonance [4], which apparently refutes the de Boer and Muller scenario and raises questions about the origin of the observed excited-state population [5].

The key result to be asserted in this Rapid Communication is that the shell model is perfectly compatible with a residual excited-state population. This assertion results from a calculation using realistic atomic parameters to describe the physics of the aforementioned experiments. To make the demonstration, it is sufficient to consider a model that uses an isolated resonance. To compute the residual population on the excited state, as well as the ionization probability or the electron-energy spectra, it is convenient to use the well-known resolvent-operator technique. When applied to a two-level atom, it has proved extremely successful in accounting for all the low-intensity resonant MPI experiments [6]. While it cannot compete with a Floquet calculation in dealing with a large basis [7], it does provide some advantages in the present discussion, since it is completely analytical and therefore is not computer intensive. A general objection would be that it is basically a time-independent model and therefore inadequate to describe the situation at hand. However, this limitation is the same for the Floquet theory, which has nevertheless proven effective in treating the case of even very short pulses [8]. The single excited state involved in this calculation should be adequate to describe the situation in which the resonant state is sufficiently isolated from adjacent states. The specific case studied here is the (7+1)-photon ionization of H atoms having a seven-photon dynamical resonance

with the $4f$ state. The photon energy used is 0.0738 a.u. (618 nm), and is chosen to closely match the experiment [3].

In our two-state model, the ground state at zero energy has a Stark coefficient α_g and the resonant state has energy E_r and Stark coefficient α_r. The relevant parameters of the problem in atomic units are the static detuning from the resonance $\Delta_0 = m\omega_p - E_r$ (where ω_p is the photon energy and m the number of photons coupling the two states); the resonance intensity $I_r = \Delta_0/(\alpha_r + \alpha_g)$; the generalized Rabi frequency $R_{\rm gr} I^{m/2}$; and the ionization width of the excited state $\gamma_r I$, where I is the laser intensity and a one-photon coupling γ_r of the excited state to the continuum is assumed. The probabilities that the system is ionized (P_i) or left in the excited state (P_r) at time t, are given by (for a complete derivation see, for example [6])

$$P_i(I,t) = 1 - \frac{1}{|\, Z^+ - Z^- \,|^2} \times [\, |\, Z_r^+ e^{-iZ^+t} - Z_r^- e^{-iZ^-t} \,|^2 + R_{\rm gr}^2 I^m |\, e^{-iZ^+t} - e^{-iZ^-t} \,|^2 \,], \tag{1}$$

$$P_r(I,t) = \frac{R_{\rm gr}^2 I^m}{|\, Z^+ - Z^- \,|^2} [\, |\, e^{-iZ^+t} - e^{-iZ^-t} \,|^2 \,]. \tag{2}$$

Here Z^+ and Z^- denote the two poles of the resolvent operator:

$$Z^\pm = \frac{1}{2}\{\tilde{E}_r + \tilde{E}_g - i\gamma_r I \pm \sqrt{[\Delta_0 - (\alpha_r + \alpha_g)I + i\gamma_r I]^2 + 4R_{\rm gr}^2 I^m}\} \tag{3}$$

and

$$Z_r^\pm = Z^\pm - \tilde{E}_r + i\gamma_r I, \tag{4}$$

with $\tilde{E}_{r,g} = E_{r,g} + \alpha_{r,g} I$. The direct coupling of the ground state to the continuum can normally be neglected and, in the present case, $\alpha_g \ll \alpha_r$. The values of the atomic parameters are [9]: $R_{\rm gr} = 0.65 \times 10^9$, $\gamma = 1.1$, $\alpha_r = 184.421, \alpha_g = 4.625\,52$, $E_r = 0.468\,75$ a.u., and the intensity unit is 1.4038×10^{17} W cm^{-2}.

Figure 1(a) shows the real part of the poles as a function of intensity in the region of the level crossing (actually a small avoided crossing) at this photon energy. All of the physics of the resonance is contained in this crossing diagram and in the pulse duration. Figure 1(b) displays P_i and P_r in the same intensity range for a time $t \simeq 2500$ a.u., which is long enough for the resonance to build up (see below). Note that the ionization and residual bound-state population are localized at the resonant intensity defined by the crossing point.

Figure 2 shows the probabilities for the system to end up in the continuun, excited state, and ground state after a square pulse of intensity I_r. It is clear that, if the pulse is not too long, some population may subsist in the excited state (up to 17.5% for a 120-fs pulse). However,

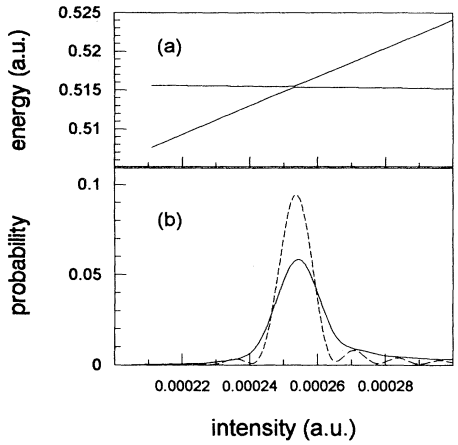

FIG. 1. (a) Real parts of Z^+ and Z^- and (b) P_i (solid line) and P_r (dashed line) as a function of intensity (1 a.u. $\equiv 1.4038 \times 10^{17}$ W cm^{-2}).

the amount that is left strongly depends on the static detuning (through the resonance intensity), the ionization rate ($\gamma_r I$) of the excited state, and the pulse duration (τ). The space localization of the probabilities (basis of the shell model) has obviously its origin in their sharp dependences on intensity, shown above. For a Gaussian beam, the intensity is given by

$$I(r,z,t) = \frac{\exp\left(-\frac{r^2}{1+z^2}\right)}{1+z^2} \exp\left(-\frac{(t-z/c)^2}{\tau^2}\right). \tag{5}$$

As $I(r,z,t)$ evolves in time along the pulse, the resonance intensity is reached in different regions of the beam. However, the effective time $\tau_{\rm eff}$ it remains on resonance also varies along the pulse. It will stay on resonance longer, if $\dot{I}_r$ is reached at the top rather than during the rise or fall of the pulse. One can easily evaluate $\tau_{\rm eff}$ from the width of the curves in Fig. 1(b) and the profile of the Gaussian pulse $e^{-(t/\tau)^2}$. It can be shown that $\tau_{\rm eff}$ is divided by 6 from the top of the pulse to $\tau/2$. Con-

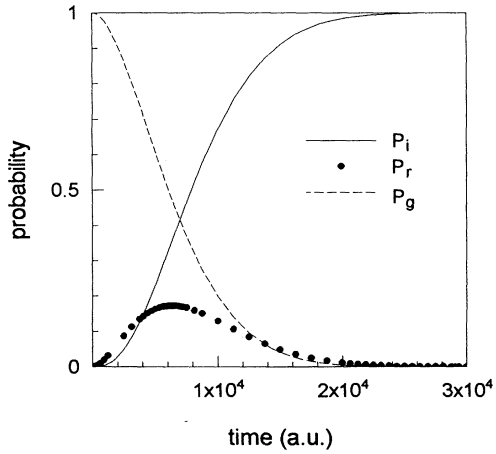

FIG. 2. Time dependence of the ground state (dashed line), excited-state (solid circles), and ion (solid line) populations for a square pulse of intensity I_r.

tour plots of $P_\tau(I(r,z,t),\tau_{\rm eff})$ (where r and z are the space coordinates) for a pulse with a peak intensity $2I_r$ illustrate this point in Fig. 3. They provide snapshots of the populations as the pulse evolves in time. In the rising edge of the pulse, some of the population is nonresonantly driven at the center of the beam, but at a virtually undetectable level. When the pulse reaches its maximum at $t = 0$, most of the population transfer occurs in the spatial regions of the beam where the intensity is I_r, in full agreement with the LZ analysis [4]. Note that we observe identical localization and time dependence of the ionization probability P_i. The significant addition of this calculation is that it allows evaluation of the residual excited-state population, which is observed to be *appreciable and localized* after the pulse. The basic reason for this occurrence is that, even at the top of the pulse, $\tau_{\rm eff}$ may be too short to saturate the transition, since $\tau_{\rm eff} < \tau$. However, an increase of the resonance intensity results in both an increase of the peak population and a rapid decrease of its lifetime. For instance, a 2% increase

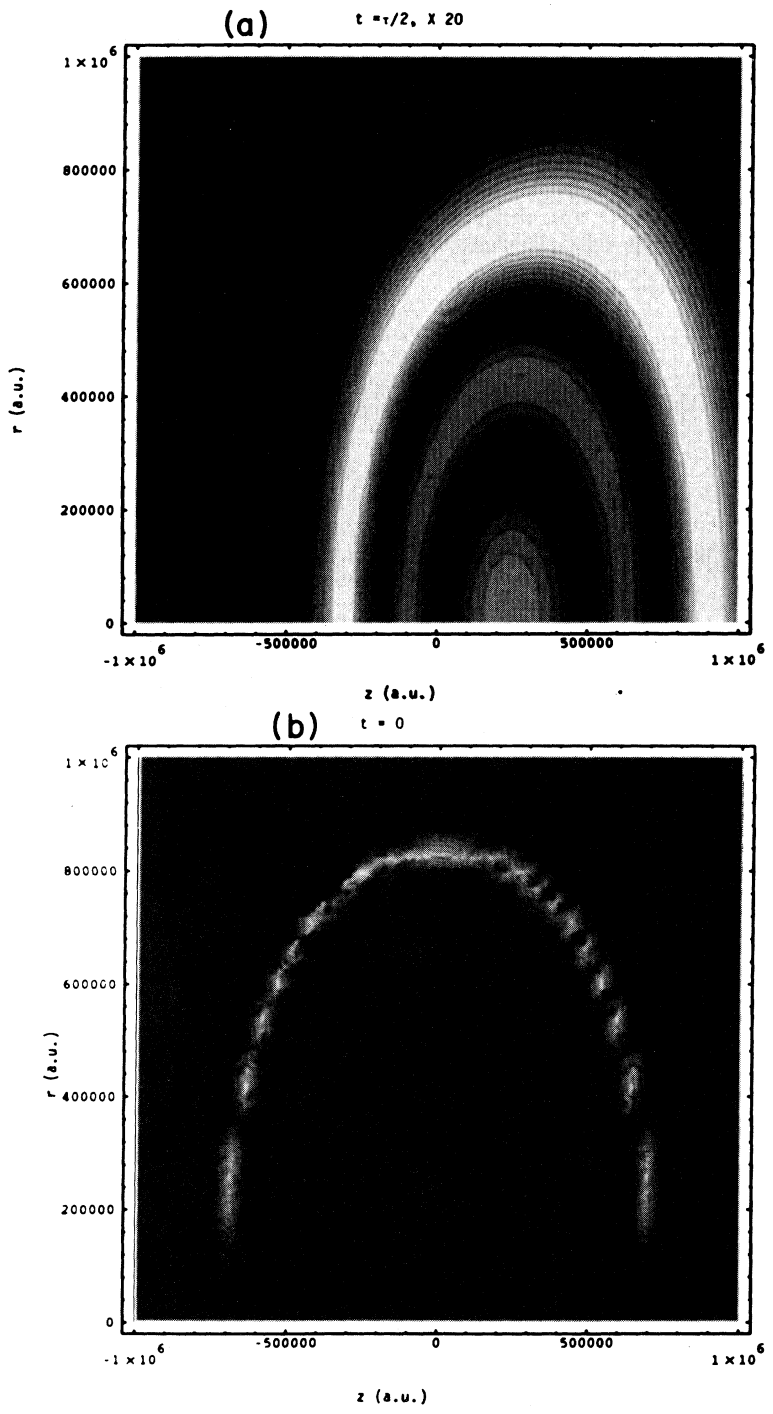

FIG. 3. Contour plots of the excited-state population as a function of r and z, the coordinates in the Gaussian beam at (a) $t = \tau/2$ ($\tau_{\rm eff}$ = 456 a.u.) and (b) t=0 ($\tau_{\rm eff}$ = 2680 a.u.). The peak intensity is twice I_τ and τ = 10000 a.u. The excited-state population in the highlighted shell in (b) is $\sim$ 9% and (a) is magnified by a factor of 20.

in the photon energy results in a maximum excited-state population of 30% (to be compared to the 17.5% in Fig. 2), but it is reduced to zero after a time of only 10^4 a.u. For a 5% photon-energy increase, this time is reduced to 5000 a.u. If approximately 10% of the total population is left in the $4f$ state at 618 nm, the model predicts that this value would be reduced to zero for 590 nm photons, in agreement with the experiment [10].

Finally, we have examined the photoelectron spectrum that arises when a resonant state has a shift different from the continuum limit. First, it must be realized that ionization always occurs over some intensity range, albeit small. Therefore, the question of the structure broadening is always present, but our analysis demonstrates that the energy shift is not expected to play a major role. This is confirmed in Fig. 4, where the electron-energy spectra (the ionization probability as a function of the energy mapping of the intensity) are simulated for three values (1.5, 1, 0.5) of the ratio α_p/α_r (α_p ponderomotive shift coefficient) by linearly mapping the energy K to intensity as $K = 8\omega_p - E_I - \alpha_p I$, where E_I is the ionization potential. In spite of an obvious broadening and a trivial shift, the structures remain narrow. At the same time, the amount of population left in the excited state remains constant and spatially localized.

In conclusion, both the LZ and the present calculation predict a sharp dependence of the ionization probability around the resonance intensity. Both time and space localizations of ionization follow. However, the LZ level crossing theory implies that all the ground-state population is transferred to the excited state (most efficiently in the regions of the interaction volume where the resonance intensity is reached at the top of the pulse) and that any residual excited population will be returned to the ground state during the fall of the pulse. This may be a very good approximation for high Rydberg states with very low ionizing rates, but it does not seem to be adequate for realistic couplings in the case of the $4f$ state. The dynamics of the system is more accurately described by the present calculation in which the amount of population left in the excited-state clearly *depends on the excited-state ionization rate and the effective interaction time.* Furthermore, this localization produces sharp photoelectron energy structures, even in the case of a state that shifts very differently from the continuum limit (ponderomotive). However, the above calculation clearly shows that the de Boer and Muller result is rather atypical and fragile, since a small increase in I_r or in the pulse duration will in general be sufficient to remove all of the excited-state population. Finally, it should be stressed that the present calculation is only a first approximation to describe situations where such large shifts are observed. In particular, all the couplings are described to lowest order. The agreement between the experiment and the present prediction must be ascribed to the fact that the $4f$ state is very weakly coupled to other states. More complete treatments using a larger basis or time-dependent solution of the Schrödinger equation are required to make accurate predictions in the general case.

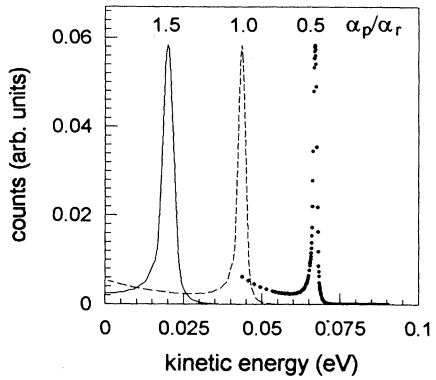

FIG. 4. Simulated electron kinetic-energy spectra for three different value of the Stark coefficient relative to the ponderomotive coefficient. (See text.)

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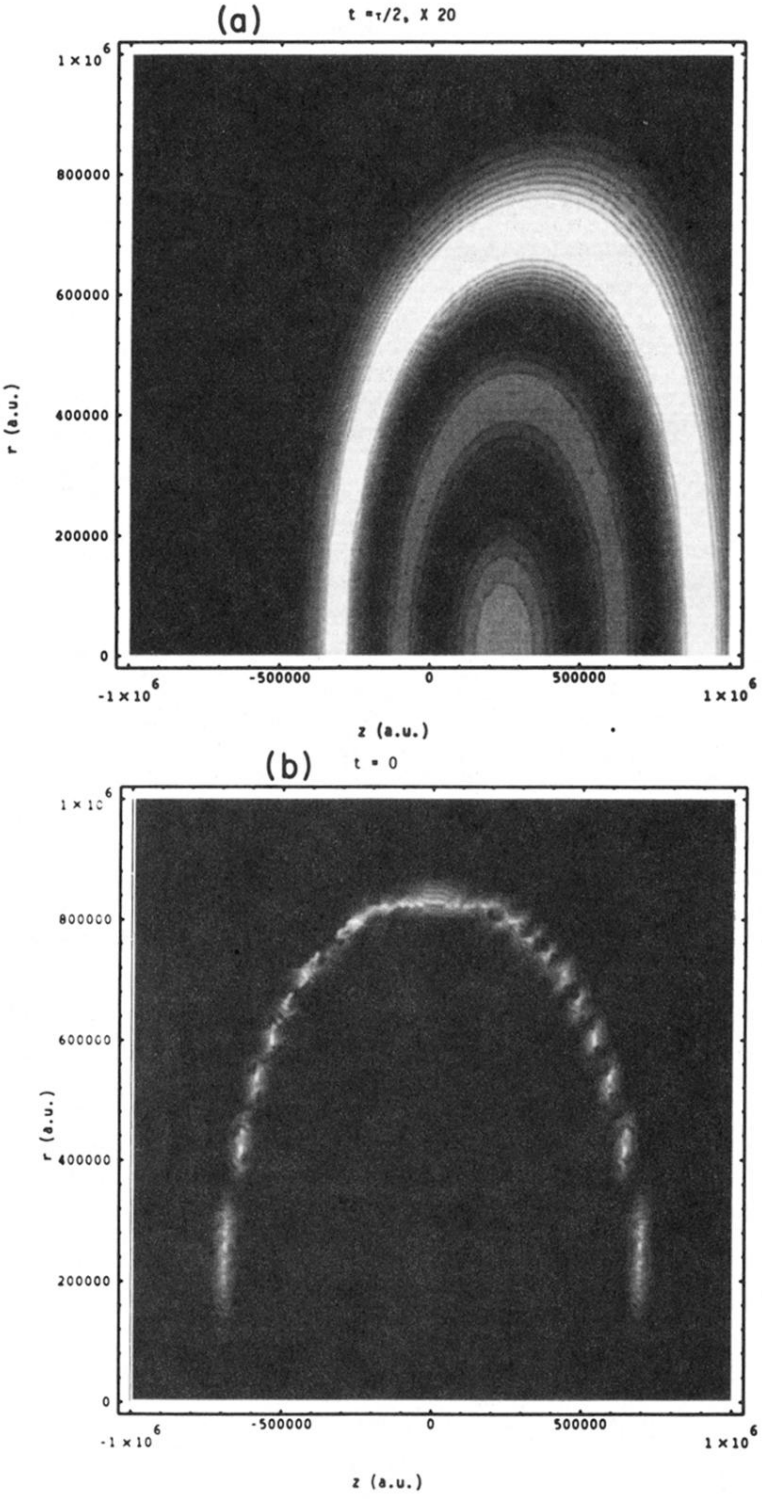

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