Time-Dependent Calculation of Photoelectron Spectra in Mg Involving Multiple Continua

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We report the first successful attempt at the time-dependent nonperturbative calculation of multiphoton ionization and above threshold ionization in the presence of several open channels leaving the ion in excited states. After an outline of the theoretical approach based on a discretized basis constructed in terms of B-splines, we also present illustrative results on atomic magnesium. [S0031-9007(96)01144-1]

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The photoelectron energy spectrum of an atom under a strong laser pulse, especially in connection with above threshold ionization (ATI) [1,2], contains the imprint of nonperturbative behavior expected above certain intensities. Although much has been learned about this behavior in the single active electron (SAE) approximation, where all but one of the electrons are assumed frozen and unaffected by the field, very little is known theoretically about the expected behavior beyond that approximation. Yet, it has been known for quite some time that, in the alkaline earths, under the appropriate combination of intensity and frequency, significant double electron excitation takes place, leaving the ion not only in the ground but also in excited states [3–5]. Even in perturbation theory in single-photon processes this is a difficult problem as it involves several open channels (continua) [6–9].

In previous preparatory work, we have developed the essentials of the approach and have studied the ATI spectrum of He, where, however, the ionized electron is hardly affected by the other electron which is left in the ionic ground state. This was not totally unexpected since, in He, correlation is not very strong, being most important in the ground state. Thus the energy gap between the two thresholds is relatively large, as a consequence of which, for optical or even UV photons, most of the observable ATI peaks are produced between the two thresholds, with negligible influence of correlation. In Mg and the other alkaline earth atoms, on the other hand, the situation is quite different. Continua associated with more than one ionization threshold lie much closer to the lowest one (see Fig. 1) which makes them much more accessible at intensities, frequencies, and pulse durations currently available. That is why excited ionic states have been observed in such atoms. An important question therefore is: How does one calculate branching ratios in photoelectron spectra corresponding to different ionization channels under strong-field multiphoton excitation, and how do they depend on laser intensity? In other words, what is the nonperturbative behavior of processes with several open channels? It is the purpose of this paper to present the first time-dependent nonperturbative treatment of this problem, including specific results on Mg.

Discrete atomic bases obtained inside a finite space have been used to carry out nonperturbative time-dependent calculations in He [10,11]. The main difference between the two atoms is the inner-shell electrons, Mg having 10 of them. These core electrons are relatively inactive in the laser intensity range we are considering, so we treat them as frozen in their Hartree-Fock orbitals. The outer two valence electrons are treated in the same way as the two electrons in He [12]. The boundary condition we use at the outer boundary of the box is $\psi(r = R_{\max}) = 0$. This condition selects continuum orbitals, resulting in the discretization, and modifies slightly the bound orbitals [13]. With unit normalization, the discretization is equivalent to

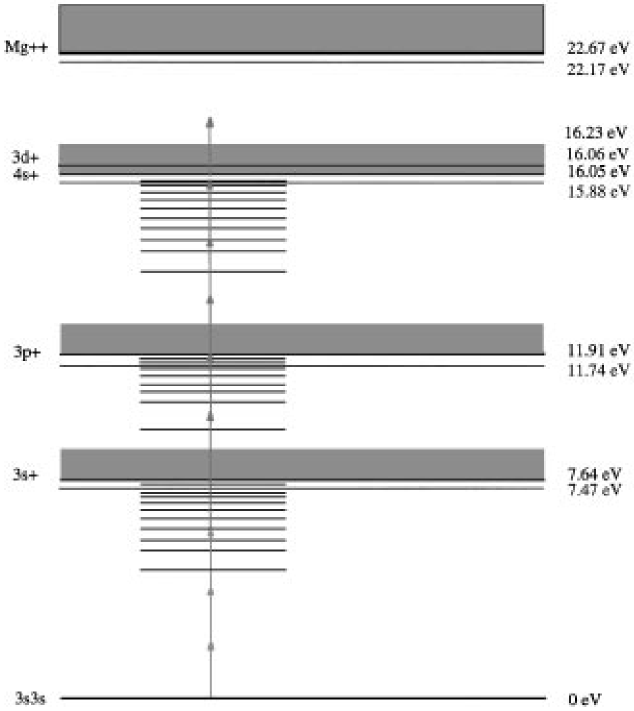

FIG. 1. Mg energy level diagram, solid numbers are experimental values and dotted numbers are calculated values.

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a numerical quadrature for a single continuum [14]. The criterion for the "box" size is that it be large enough for all physics of interest to be confined within the box, during the interaction time. For Mg, $R_{\max} = 800$ a.u. is necessary, and we obtain 700 one-electron radial orbitals for each angular momentum component of the ionic state by diagonalizing the single electron Hamiltonian on a set of 702 B-splines defined in $R = [0, R_{\max}]$. By contrast, a larger box would be required if higher ATI contributions are significant, as, for example, in He at higher intensity.

Two-electron states are antisymmetrized products of one-electron orbitals obtained in the box, and we select the configuration space to be $3snl + 3pnl + 4snl + 3dnl$. Higher ionization thresholds are left out. As long as we focus on the study of branching ratios below and including the $3d$ threshold, this basis is sufficient. Including more and more high lying thresholds is important if we are to study the double electron ejection. This extension presents a major challenge to any method, both mathematically and computationally. We limit ourselves to the study of single electron ionization in this paper. The resulting two-electron eigenstates can be denoted as $\psi_{nL}(\vec{r}_1, \vec{r}_2, (M = 0))$. We use only the $M = 0$ states, because we are interested in linearly polarized laser fields. A chosen set of $[nL]$ defines a basis. The time-dependent Schrödinger equation can then be solved on this basis set, as described in [10,11,15], providing the time-dependent "exact" (within the finite space) wave function $\Psi(t)$.

The extraction of the photoelectron energy spectrum from $\Psi(t)$ in the region of the multiple continua is neither evident nor straightforward. The reason is that now we need to find the partial photoelectron spectra associated with different ionization thresholds, but each discrete two-electron state at a particular energy is a box-dependent superposition of physical states. In other words, we want to expand the time-dependent wave function in the proper basis,

$$\Psi(t) = \sum_{n,L} C_{nL}(t)\psi_{E_{nL}} + \sum_i \int C_E^i(t)\psi_E^{i-}\,dE\,, \tag{1}$$

where i indicates the ionization channel associated with the ith threshold, Φ_i represents the corresponding ionic state and the angular momentum factor. Asymptotically,

$$\psi_E^{i-} \xrightarrow{r\to\infty} \frac{1}{r}\sqrt{\frac{2}{\pi k_i}}\,\frac{1}{2i}\left(\Phi_i e^{i\theta_{k_i}} - \sum_j S_{ij}\Phi_j e^{-i\theta_{k_j}}\right), \tag{2}$$

where

$$\theta_{k_i} = k_i r - \frac{1}{2} l_i \pi - \frac{1}{k_i}\ \ln(2k_i r) + \arg\left[\Gamma\left(l_i + 1 - i\,\frac{1}{k_i}\right)\right] \tag{3}$$

is the Coulomb phase shift in the nuclear field of charge 1, and S_{ij} are matrix elements of the S matrix that determine the interaction between the channels i and j. The photoelectron energy spectrum is then given by $|C_E^i(t \to \infty)|^2$, corresponding to leaving the ion in state i with $k_i^2/2 = E - E_{th}^i$.

Before we discuss the relation between the discrete basis functions and the correct wave functions satisfying Eq. (2), we first look at the relation between the eigenchannels used in the multichannel quantum defect (MQDT) theory [16,17] and the desired wave functions with an outgoing spherical wave in one channel and an incoming spherical wave in all channels. The MQDT eigenchannel wave functions can be written as

$$\psi_\beta \xrightarrow{r\to\infty} \sum_i U_{\beta i}\Phi_i'\ \sin(\theta_i + \delta_\beta)\,. \tag{4}$$

They relate to the channel wave functions, each corresponding to an outgoing spherical wave in one channel and an incoming wave in all channels, through a linear transformation

$$\psi^{i-} = \sum_\beta (U_{i\beta}e^{-i\delta_\beta})\pi_\beta\,, \tag{5}$$

$$\xrightarrow{r\to\infty} \frac{1}{2i}\left(\Phi_i' e^{i\theta_i} - \sum_j S_{ij}\Phi_j' e^{-i\nabla_j}\right). \tag{6}$$

The physical nature of the N-fold continua determines that there should be N linearly independent solutions at each energy. Therefore, in principle, any linear transformation of the eigenchannel solutions leads to an alternative set of solutions. Consider now an arbitrary "rotation" of the eigenchannels,

$$\chi^\alpha = \sum_\beta A_\beta^\alpha \psi_\beta\,, \tag{7}$$

$$\xrightarrow{r\to\infty} \sum_i B_i^\alpha \Phi_i' \sin(\theta_i + \delta_i^\alpha)\,. \tag{8}$$

These solutions differ from the eigenchannel solutions in that there is no characteristic phase shift associated with each channel. Any one of these solutions (for a certain α) can be understood as having behavior similar to one discrete state in the basis. If one can find N linearly independent basis functions at each energy, they can be transformed to the desired final wave functions exactly. Consequently, the time-dependent coefficients can be found as

$$C_E^i(t) = \sum_\alpha \langle\psi^{i-} \mid \chi_E^\alpha\rangle C_E^\alpha(t) = \sum_\alpha \langle\psi^{i-}|\psi_i^\alpha\rangle C_E^\alpha(t) B_i^\alpha\,. \tag{9}$$

Unfortunately, the discrete basis with a fixed boundary condition does not possess the N-fold degeneracy, simply because the energies of two discretized states of different channels in the continuum would coincide only accidentally. In fact, it is safe to say that practically there is no degeneracy at all. This can be seen clearly even in the structure of uncoupled channels. Since each single electron continuum is discretized approximately quadratically, continua associated with different thresholds have different discretization at a given two-electron energy. [Neglecting the complicated behavior of the wave function near the nucleus, we have $k_n R_{\max} \approx \pi n$, so that

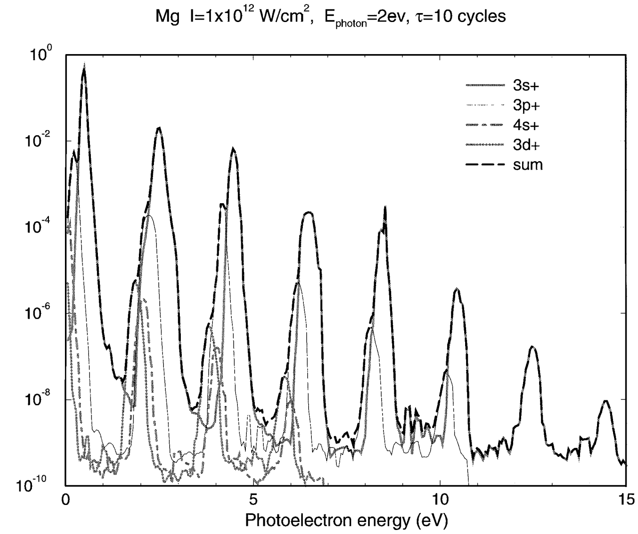

FIG. 2. Photoelectron energy spectra at $\hbar\omega = 2$ eV, $I_0 = 10^{12}$ W/cm^2. The vertical axis is population per energy in (1/a.u.).

$E_n = k_n^2/2 = \pi^2 n^2/(2R_{\text{max}}^2)$, proportional to n^2.] Note that we do not know the projection coefficient $\langle \psi^{i-} \mid \psi_i^{\alpha} \rangle$ within our discretized basis, since we do not know ψ^{i-}. Even if we know it, we still cannot regenerate the lost degeneracy.

To circumvent that difficulty, instead of the transformation in Eq. (9), we replace the summation over α by a summation weighted by a window function over neighboring states

$$|C_E^i(t)|^2 = \sum_j W(E_j - E)\,|C_{E_j}(t) B_i(E_j)|^2. \tag{10}$$

This approximation implies an interpolation between discretized states, which can be understood as recovering the degeneracy within a small energy interval. As long as the window width is comparable to the energy spacing, the resulting spectra are not very sensitive to the width, as we have verified numerically. The window function we use here is a Lorentzian type of function normalized to unity [18].

Using this method, we have studied photoelectron energy spectra in Mg. The time-dependent calculation is performed as described in Ref. [11]. We show only the interaction Hamiltonian here,

$$V(t) = -\frac{e}{m_e}\,\hat{\epsilon} \cdot (\vec{p}_1 + \vec{p}_2) A(t)\,, \tag{11}$$

where the $A(t)^2$ term has been transformed away, $\hat{\epsilon}$ is the polarization vector of the electric field and the vector potential $A(t) = A_0 \exp[-\frac{1}{2}(t/\tau)^2]\cos(\omega t)$, where τ is approximately the HWHM for the electric field. We integrate the time-dependent differential equations from -3τ to $+3\tau$.

In Fig. 2, we show the total and partial photoelectron energy spectra at the end of a Gaussian pulse of $\tau = 10$ optical cycles at photon energy =2eV. The peak intensity of the laser pulse is 10^{12} W/cm^2. In this case, the spectrum associated with the $3p$ threshold is almost completely hidden under the dominant contribution related to the $3s$ threshold. This overlap can be attributed to the fact that the $3s$ and $3p$ thresholds are about 4.27 eV apart, so the first photoelectron peak above the $3p$ threshold has only 0.27 eV energy less than the first peak above the $3s$ threshold.

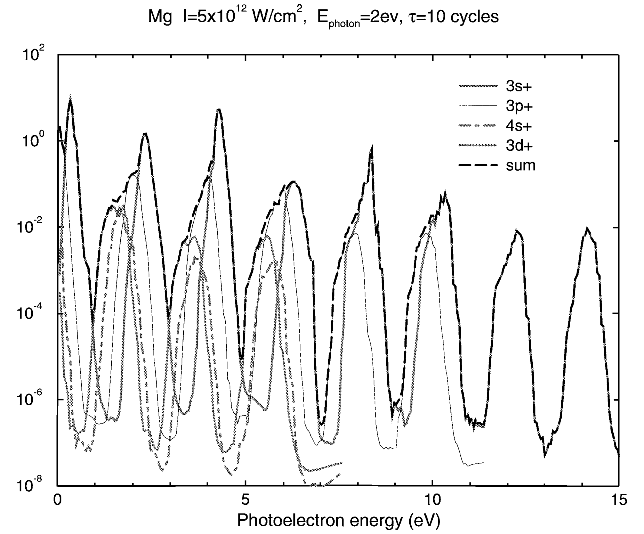

FIG. 3. Photoelectron energy spectra at $\hbar\omega = 2$ eV, $I_0 = 5 \times 10^{12}$ W/cm^2.

The spectra under the same conditions as Fig. 2 but with higher peak intensity 5×10^{12} W/cm^2 are shown in Fig. 3. It can be seen that different branches of the spectra shift relative to each other compared to the lower intensity case. And the branching ratios are also changed; contributions from higher thresholds become more significant. Recall that, in perturbation theory, branching ratios are independent of intensity.

At different photon energies, spectra associated with different thresholds may be well separated in energy.

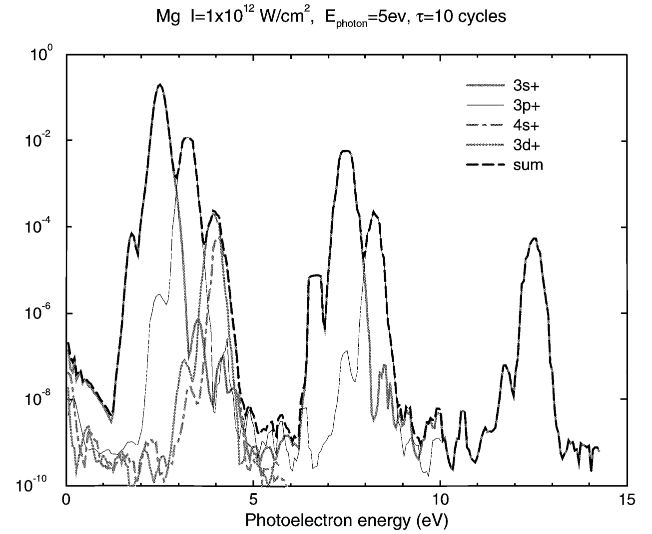

FIG. 4. Photoelectron energy spectra at $\hbar\omega = 5$ eV, $I_0 = 10^{12}$ W/cm^2.

An example is shown in Fig. 4, calculated for photon energy 5 eV. The last example we show in Fig. 5, for yet another photon energy, has more interesting features. (For viewing purposes, we show only the two most important partial spectra.) Namely, not only are the two spectra related to the $3s$ and $3p$ thresholds well separated in energy, but, also, each of them shows a splitting. The origin of this splitting is the near resonant two-photon coupling of the ground state to the $(3s5s)^1S$ state. In fact, at this photon frequency, there is also a three-photon resonance between the ground state and the $(3p4s)^1P$ autoionizing state, but this process is completely masked by the two-photon resonance transition.

To the best of our knowledge, this is the first successful attempt at one of the long standing problems in strong field interactions. The advantage of our approach is that it is relatively straightforward to build the basis, since all states with a given angular momentum L are obtained in one diagonalization. A minor disadvantage is the limited resolution, constrained by the energy spacing, but it is still superior to the typical experimental resolution. A more serious related shortcoming is that the photoelectron angular distribution cannot be calculated, since the phase information cannot be extracted from the averaging. Also, obtaining a sufficiently high density of states becomes cumbersome owing to the quadratic discretization.

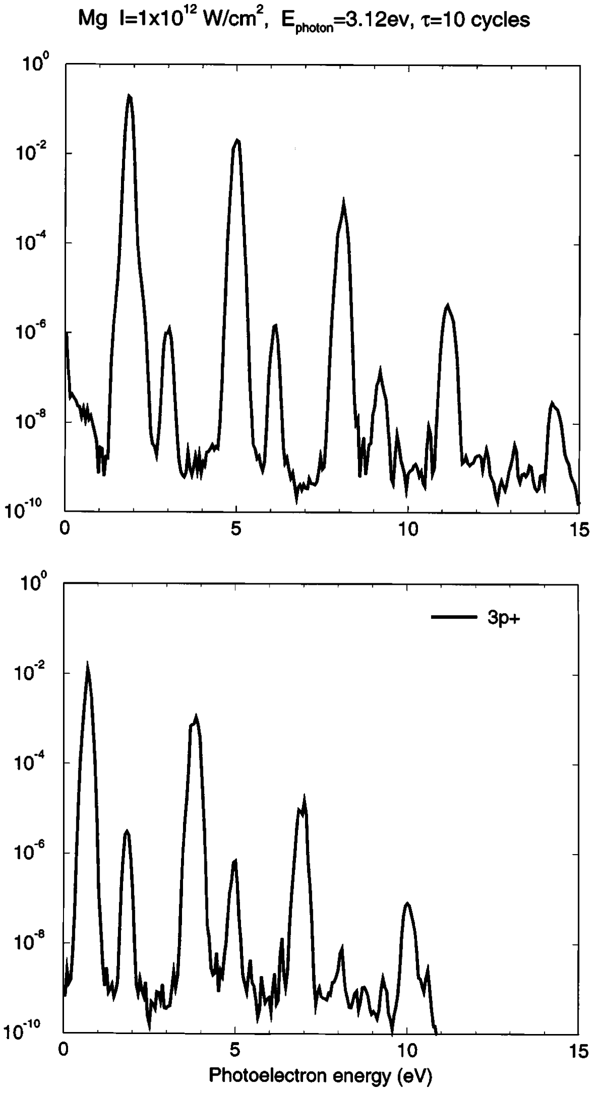

FIG. 5. Photoelectron energy spectra at $\hbar\omega = 3.12$ eV, $I_0 = 10^{12}$ W/cm^2.

The above difficulty can, however, be overcome by restructuring the construction of the discrete basis. We have been able to show that, by choosing different boundary conditions, the continuum can be discretized uniformly which restores the necessary degeneracy. This involves a number of technical details that will be presented elsewhere. For the moment, it should suffice to say that we have developed a method in two stages: a more straightforward one providing everything except photoelectron angular distributions and a more demanding but tested stage that provides angular distributions and a somewhat more refined ATI spectra. This has also allowed us to verify in yet another way the reliability of the results reported here.

The intensities and photon energies employed in all of our examples are readily available. It should not be too surprising that nonperturbative effects in Mg set in at intensities as low as 5×10^{12} W/cm^2, as it is a rather soft atom compared to He.

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