

Multiphoton ionization of magnesium with configuration-interaction calculations

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(Received 22 February 1990)

A simple configuration-interaction calculational procedure with a finite- L^2 -basis set constructed from B splines is presented and applied to a multiphoton ionization process. An initial application of this theoretical procedure to the four-photon nonresonant ionization of Mg at 532 nm has led to excellent agreement with the experimental photoelectron angular distribution measurement. The atomic structure effects due to the multielectron interactions are also examined in detail.

The reliable and accurate calculation of multiphoton transitions in multielectron atoms even within perturbation theory remains a difficult problem. The major obstacle stems from the fact that the multiple summations over virtual intermediate states should involve complete sets of multiconfigurational wave functions, even if the final state results in excitation or ionization of only one electron. Certain aspects of multiphoton transitions, e.g., photoelectron angular distributions, are quite sensitive to the multielectron character of the virtual intermediate states. This sensitivity is more pronounced when a real (resonant) intermediate state is involved or when transitions are affected by the presence of doubly excited states.

Within the framework of perturbation theory, three methods are available for multiple summations over intermediate states. The truncated summation method has the advantage of total flexibility as to the type of wave functions that can be employed while availing itself to the inclusion of configuration interaction in all states (initial, intermediate, and final) involved. Its disadvantage stems from the truncation which often limits the sum to the discrete spectrum.¹ Procedures of the Dalgarno-Lewis type² or Green's-function³ techniques allow for the complete sum but do not lend themselves to a convenient way for the inclusion of configuration interaction in the intermediate states. Finally, variational methods^{4,5} may include multielectron effects but cannot be extended easily to more than third-order processes. A further drawback, common to the last two methods, is that they tend to be rather time consuming.

In this paper, we introduce a simple configuration-interaction (CI) approach employing an L^2 -basis set in a calculation of multiphoton transitions for a divalent atom such as magnesium. We have chosen Mg as our first application due to the availability of angularly resolved nonresonant multiphoton experiment presented in detail recently.⁶ This experiment is sufficiently refined to provide a stringent test of the calculation. The spectra of alkaline-earth atoms are also quite complicated with a rich structure of autoionizing states above the first ionization threshold. As a result, the energies and the oscillator strengths below the threshold are often affected by configuration mixing with doubly excited states,⁷ thus

providing an ideal atomic system for the systematic study of electron correlation effects in multiphoton processes.

The use of L^2 -basis methods has a long tradition in physics and chemistry. Extensive applications by using the Sturmian basis to multiphoton processes have been carried out for the higher-order transitions in hydrogen.^{8,9} However, besides hydrogen, its applicability is limited. For multielectron atoms, Moccia and Spizzo^{10,11} have employed a self-consistent-field-type L^2 basis in the calculation of two-photon ionization cross sections for Be and Mg. Work similar in spirit for two- and four-photon processes including autoionizing states has been performed by Bachau and Lambropoulos¹² using a Slater-type L^2 basis. In this paper we implement an L^2 -basis technique involving finite basis sets constructed from B splines.¹³ The effectiveness of such basis sets has been demonstrated in recent relativistic many-body perturbation calculations¹⁴ as well as in nonrelativistic CI calculations.¹⁵ The generalization of this method to multiphoton processes, presented in this paper, appears to be equally promising.

The simple CI procedure with finite basis constructed from B splines has been presented in detail previously.¹⁵ Similar to some of its recent applications,^{15,16} the radial part χ_{vl} of the one-particle orbital wave function corresponding to an orbital energy eigenvalue ε_{vl} satisfies the eigenequation

$$h_l^{\text{HF}} \chi_{vl} = \varepsilon_{vl} \chi_{vl}. \quad (1)$$

The one-particle frozen-core Hartree-Fock (FCHF) Hamiltonian h_l^{HF} is given explicitly by Eq. (7) in Ref. 17. The eigenfunction χ is constructed¹⁵ from a set of B splines of order k and total number n defined between two end points $r_{\min} = 0$ and $r_{\max} = R$. The value of R is chosen to cover the estimated interaction region of the Green's function for the N -photon process at energy $E_g + (N-1)\omega$, where E_g is the energy of the initial state and ω is the photon energy. For example, in our calculation of four-photon ionization from the ground state of Mg at 532 nm, the values of R are varied from $200a_0$ to $250a_0$ to ensure numerical convergence. The numerical procedure for the solution χ of Eq. (1) is discussed in Ref. 15. In practice, the finite L^2 -basis set consists of a number of two-

electron configuration series nll' . Each configuration series consists of a series of configuration wave functions corresponding to one electron in a fixed one-electron orbital nl and the other electron in orbitals with fixed orbital angular momentum l' but variable energy eigenvalues ϵ_{vl} , both negative and positive, over an entire set of χ_{vl} from Eq. (1). As a result, the continuum contribution, represented by the positive energy orbitals, is effectively included in our CI calculation.

In lowest-order perturbation theory, the N -photon generalized ionization cross section σ_N in $\text{cm}^{2N} \text{sec}^{N-1}$ is given by the expression

$$\sigma_N = 2\pi \frac{ac}{\alpha_0} \left[\frac{\omega}{F_0} \right]^N \sum_{J_f} |D^{(N)}|^2 \quad (2)$$

similar to Eq. (29) of Ref. 1. The summation in Eq. (2) includes contribution from all final states with allowed total angular momentum J_f . The N -photon transition amplitude $D^{(N)}$ from an initial state g to a final state f is given by

$$D^{(N)} = \sum_{v,\mu,\dots,\lambda} \frac{F_{fv}F_{v\mu} \cdots F_{\lambda g}}{[E_v - E_g - (N-1)\omega] \cdots (E_\lambda - E_g - \omega)} \quad (3)$$

The transition amplitude $F_{ji} = \langle j | \hat{\epsilon} \cdot \mathbf{D} | i \rangle$ for a polarized

radiation field of polarization vector $\hat{\epsilon}$ is defined by

$$F_{ji} = \sum_{n_j, l_j, n_j, l_j, n_i, l_i, n_i, l_i} C^{S_j L_j J_j} (n_j l_j n_j l_j) C^{S_i L_i J_i} (n_i l_i n_i l_i) D_{ji}, \quad (4)$$

where $C^{S_j L_j J_j}$ and $C^{S_i L_i J_i}$ are the expansion coefficients which form the eigenvectors for the eigenstates j and i . The dipole operator \mathbf{D} represents \mathbf{r} and $\omega \mathbf{V}$ in the length and velocity approximation, respectively. The dipole transition matrix D_{ji} between configurations $(n_j l_j n_j l_j)$ and $(n_i l_i n_i l_i)$ is given by

$$D_{ji} = [d(j' j, i' i; \Lambda_j \Lambda_i) + d(jj', ii'; \Lambda_j \Lambda_i)] + (-1)^{S_i} [d(j' j, ii'; \Lambda_j \Lambda_i) + d(jj', i' i; \Lambda_j \Lambda_i)], \quad (5)$$

where $\Lambda_\mu \equiv (S_\mu L_\mu J_\mu M_{J_\mu})$ represents the quantum numbers S, L, J , and M_J associated with the eigenstate μ . For configurations with two equivalent electrons, a factor of $\sqrt{2}$ should be included in D_{ji} . The matrix element d is the product of the angular factor ρ and the one-particle radial integrals, i.e.,

$$d(j' j, i' i; \Lambda_j \Lambda_i) = \rho(l_j l_j l_i l_i; \Lambda_j \Lambda_i) \langle \chi_{n_j l_j} | \chi_{n_i l_i} \langle \chi_{n_j j'} | t | \chi_{n_i i'} \rangle, \quad (6)$$

where t in radial integral $\langle \chi_{n_j j'} | t | \chi_{n_i i'} \rangle$ represents the radial part of \mathbf{r} and $\omega \mathbf{V}$ in the length and velocity approximation, respectively. In the FCHF approximation, $\langle \chi_{n_j l_j} | \chi_{n_i l_i} \rangle = \delta_{n_j n_i} \delta_{l_j l_i}$. The angular factor ρ is given by

$$\rho(l_1 l_2 l_3 l_4; \Lambda' \Lambda) = (-1)^{J'+J+L'+L+S+l_2-M_J} \delta_{SS'} \delta_{l_2 l_4} [(2J'+1)(2J+1)(2L'+1)(2L+1)(2l_1+1)(2l_3+1)]^{1/2} \times \begin{pmatrix} l_1 & 1 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ -M_{J'} & q & M_J \end{pmatrix} \begin{Bmatrix} L' & J' & S \\ J & L & 1 \end{Bmatrix} \begin{Bmatrix} l_1 & L' & l_2 \\ L & l_3 & 1 \end{Bmatrix}, \quad (7)$$

where $q=0$ for linearly polarized light and $q=\pm 1$ for circularly polarized light.

To calculate the angular distribution for a photoelectron leaving an ion characterized by l_c, m_c , and m_s , the final state is expanded (with the incoming-wave normalization¹) in terms of a sum over all J_f and its associated partial waves, represented by l, m , and m_s , for the outgoing photoelectron, i.e.,

$$|f_{l_c m_c j_c}(k)\rangle = \sum_{J_f, l, m, m_s} i^l e^{-i\delta_l} Y_{lm}^*(\hat{\mathbf{k}}) (SLJ_f M_{J_f} | SM_S L M_L) (ss SM_S | sm_s c m_s) (l_c l M_L | l_c m_c l m) |SLJ_f M_{J_f}\rangle, \quad (8)$$

where δ_l is the sum of the Coulomb and short-range phase shift, \mathbf{k} is the momentum of the photoelectron, and $\hat{\mathbf{k}} = (\theta, \varphi)$ defines the direction of \mathbf{k} with respect to the polarization axis or the propagation axis for linearly or circularly polarized light, respectively. At 532 nm, the photoelectron energy in the four-photon ionization from Mg ground state is far from any autoionization structure dominated by doubly excited states. For simplicity, a single-channel one-particle radial function χ_{kl} , subject to a screening Hartree-Fock potential^{17,18} given by Eq. (11) in Ref. 17, is used to represent the outgoing photoelectron as $r \rightarrow \infty$ with asymptotic form

$$\chi_{kl} \rightarrow \left[\frac{2}{\pi k} \right]^{1/2} \sin \left[kr + \frac{1}{k} \ln(2kr) - \frac{l\pi}{2} + \delta_l \right]. \quad (9)$$

Finally, the differential cross section for the N -photon ionization is given by

$$\frac{d\sigma_N(l_c; \hat{\mathbf{k}})}{d\Omega} = 2\pi \left[\frac{ac}{\alpha_0} \right] \left[\frac{\omega}{F_0} \right]^N \sum_{m_c, m_s} |M^{(N)}(l_c, m_c, m_s; \hat{\mathbf{k}})|^2, \quad (10)$$

where the N -photon ionization partial amplitude is given by

$$M^{(N)}(l_c, m_c, m_s; \hat{\mathbf{k}}) = \sum_{J_f, l, m, m_s} i^l e^{i\delta_l} (-1)^{L-S+l-l_c-M_{J_f}-M_S-M_L} Y_{lm}(\hat{\mathbf{k}}) [(2J_f+1)(2L+1)(2S+1)]^{1/2} D^{(N)} \times \begin{pmatrix} S & L & J_f \\ M_S & M_L & -M_{J_f} \end{pmatrix} \begin{pmatrix} s & s & S \\ m_s & m_s & -M_S \end{pmatrix} \begin{pmatrix} l_c & l & L \\ m_c & m & -M_L \end{pmatrix}. \quad (11)$$

The usefulness of L^2 -basis constructed from B splines as a substitution for a complete intermediate basis set in the perturbation calculation has been demonstrated in a recent relativistic many-body calculation.¹⁴ In the present study, we first examine the N -photon ionization for hydrogen by using the nonrelativistic single-particle basis constructed from B splines in a pure nuclear Coulomb potential as the intermediate states. The accuracy of our numerical calculation has been tested by varying the values of R and n for each intermediate basis corresponding to different orbital angular momentum l . For N up to six, we have varied R from $150a_0$ to $200a_0$ and n from 40 to 60. Our calculation has shown that σ_N converges rapidly to four or more digits with nearly identical length and velocity results. In Table I, we list the values of σ_N for hydrogen in a linearly polarized light at selected wavelengths. The results of our finite basis calculation are in excellent agreement with that from the well established Green's-function technique.³ By selecting $R=200a_0$ and $n=60$, which are sufficiently large to cover the interaction region for N up to 6, the frequency independent finite basis generated in our calculation can be used repeatedly for ionization at other photon frequency of interest.

The ability of the simple CI procedure incorporating B splines L^2 basis to generate reliable one-photon transition probability for light alkaline-earth atoms has been demonstrated in recent applications.^{15,16} For Be and Mg, the length and velocity results for one-photon oscillator strengths agree to about 1%-2%, except for a few weak transitions where the difference could be as large as 5%-6%. When the number of configuration series (i.e., the size of the basis set) is reduced substantially from the usual number of about 16 to a minimum of three or four strongly mixed series, the calculated one-photon oscillator strengths change only slightly with a modest increase in the difference between the length and velocity results. To examine quantitatively the agreement between the length and velocity results for the N -photon bound-bound transitions from the Mg ground state in a scaled-down CI calculation, the size of the basis set is reduced by including only the dominant $3s^l$ configuration series and a few other strongly mixed $3pl'$ series with a maximum number of configurations ranging from 150 to 250 instead of the usual 600 to 700 in a one-photon calculation. In Table II, we list the N -photon transition amplitude $D^{(N)}$ in a.u. for some of the allowed two- and three-photon bound-bound transitions. The agreement between length and velocity results remains satisfactory despite the use of a smaller number of configuration series. By including only the

TABLE II. The length and velocity N -photon bound-bound transition amplitudes $D^{(N)}$ in a.u. from the $3s^2 1S$ ground state of Mg.

N	Final state	Length	Velocity
2	$3s 3d^1 D$	56.8	49.4
2	$3s 4s^1 S$	75.5	73.6
2	$3s 4d^1 D$	-36.5	-36.0
2	$3s 5s^1 S$	-28.9	-28.7
3	$3s 3p^1 P$	1.42×10^3	1.15×10^3
3	$3s 4p^1 P$	6.25×10^3	5.68×10^3
3	$3s 4f^1 F$	2.90×10^3	2.48×10^3

strongly mixed configuration series, we are able to reduce substantially the rapidly growing numerical calculation required for $D^{(N)}$. We also note that when we vary the values of R and n , the velocity result converges somewhat faster than the length result. This is consistent with the need for larger R as N increases, so as to account for the increasingly greater contribution from the larger r interaction region to $D^{(N)}$ in the length calculation.

To compare the theoretical results with the experimental data, we have carried out a nonresonant four-photon ionization calculation at 532 nm from Mg ground state. In particular, we compare in Fig. 1 the theoretical and experimental results for the photoelectron angular distribution. The experimental data represented by the solid dots agree very well with the theoretical velocity results shown by the solid curve. Qualitatively, the length result, which is approximately 30% smaller than the velocity result, is also in close agreement with the experimental data. To illustrate the effect due to the atomic structure, we have evaluated the four-photon ionization cross section by excluding the multielectron interactions in a CI calculation, including only the singly excited $3s^l$ configuration series both for the ground and the intermediate excited states. The calculated angular distribution in this single-configuration series CI calculation, represented by the dashed curve, is significantly different from the angularly resolved

TABLE I. Values of σ_N in $\text{cm}^{2N} \text{sec}^{N-1}$ for hydrogen atom from finite-basis (L^2) and Green's-function calculations as functions of photon energy $h\nu$.

N	$h\nu$ (cm^{-1})	L^2	Green's function
2	57 868.66	1.216×10^{-50}	1.216×10^{-50}
3	38 579.12	6.171×10^{-83}	6.171×10^{-83}
4	28 934.33	1.138×10^{-115}	1.138×10^{-115}
5	23 147.47	3.855×10^{-148}	3.855×10^{-148}
6	19 289.56	2.12×10^{-179}	2.12×10^{-179}

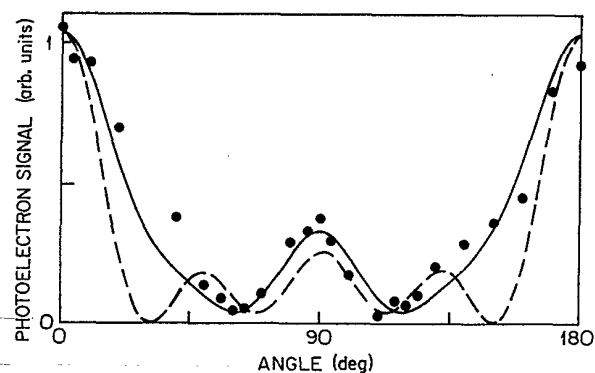


FIG. 1. Photoelectron angular distribution for four-photon ionization at 532 nm from the ground state of Mg. The experimental data, the multiconfiguration CI results, and the single-configuration series CI results are represented by the solid dots, solid curve, and dashed curve, respectively.

experiment result shown in Fig. 1. We have also evaluated the angular distribution for the four-photon ionization in a *single-channel* quantum defect calculation.³ This result is again substantially different from the experiment but in reasonable agreement with the result from the single-configuration series CI calculation.

At 532 nm, our calculated four-photon ionization cross section σ_4 in the velocity approximation converges rapidly to a value of $2.41 \times 10^{-113} \text{ cm}^8 \text{ sec}^3$, as we increase the values of R from $200a_0$ to $250a_0$ and n from 45 to 60. The value of σ_4 in the length approximation is $1.66 \times 10^{-113} \text{ cm}^8 \text{ sec}^3$, which does not converge as fast and is about 30% smaller. In the single-configuration series CI calculation, the σ_4 from velocity approximation, at $1.30 \times 10^{-113} \text{ cm}^8 \text{ sec}^3$, is about a factor of 2 smaller, again, indicating a significant atomic structure effect due to the multielectron interactions. The large difference between σ_4 from the single- and multiconfiguration series CI calculations, which measures the atomic structure effects, re-

sults from the combined contribution from differences in the transition amplitude F_{ji} as well as the energy denominators in Eq. (3). We are unable to measure the absolute (angle integrated) σ_4 , but given the good agreement in photoelectron angular distribution, which represents a much more stringent test, the total cross section should also be reliable quantitatively. Having so far tested the method for up to six-photon processes, we are fairly optimistic about its usefulness and versatility in the study of multiphoton processes including intense field effects.

This work is supported by NSF under Grants No. PHY89-13521, No. PHY89-03384, and No. PHY88-96134, and by Department of Energy (DOE) under Grant No. DE-FG03-87ER60504. The research was carried out at Brookhaven National Laboratory under DOE Contract No. DE-AC02-76CH00016 and supported in part by its Division of Chemical Sciences, Office of Basic Energy Sciences.

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