

## Two-Photon Processes in Real Atoms

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We present a general method for calculating two-photon processes in real atoms by a variant of the usual multichannel quantum-defect theory (MQDT). Most notably, this method enables us to describe processes in which a single photon has enough energy to ionize the atom (above-threshold processes). All effects of intermediate Rydberg series, continua, or autoionizing series are treated on an equal footing and with the same ease; the final state is also treated properly by standard MQDT. This method should also work for many three- or four-photon processes.

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The development of high-intensity lasers has enabled the experimental exploration of nonlinear interactions of atoms with electromagnetic fields. The current state of theory cannot describe the full atom-laser field interaction; in this paper we emphasize the atomic dynamics while treating the electron-laser interaction at the level of perturbation theory. In perturbation theory, these nonlinear (multiphoton) processes are described by amplitudes which contain summations over all possible intermediate states. These summations are difficult enough without adding to it the internal dynamics of the atom (e.g., electron correlations), especially when one of the intermediate photons is above threshold. There have been very few attempts at realistic calculations for complicated atoms with intermediate energy near or above threshold [1-5]. Fink and Zoller [6] have proposed a parametrization of two-photon processes utilizing the ideas of multichannel quantum-defect theory (MQDT). However, the calculation of those parameters has not been pursued. Consequently, the lion's share of the theoretical work in this field simplifies the atomic physics by using model atoms or atomic hydrogen. In contrast, theory for one-photon processes has matured to the point where calculation of accurate cross sections is nearly routine.

In this paper, we describe how to weld techniques and ideas developed for the description of one-photon processes to multiphoton processes. We show that the  $R$ -matrix technique, now highly developed for one-photon processes, combined with the ideas in Ref. [6] describe two-photon processes with the accuracy previously achieved in one-photon calculations. The  $R$ -matrix procedure takes advantage of the finite range of both the complicated electron-electron interactions and the electron-laser interaction. The parametrization of the multiphoton matrix elements by MQDT allows the compact description of these processes over *large* frequency ranges. The method we use is only restricted by the requirement that  $2\omega$  should be less than the energy needed for double ionization. This is the same restriction presently limiting the theory of one-photon processes. In particular, we can study the effect of intermediate-state Rydberg series, autoionizing resonances, and continua.

We will sketch the theory for two-photon processes; its application to higher-order processes can be treated by iterative techniques. Also, we stress that the techniques developed here are applicable to the description of other physical processes involving perturbative calculations. This paper deals with Al as the target atom only because one of us has some familiarity with this element through previous study. In future publications we will spell out our method in more detail; we also plan to initiate a study of multiphoton processes akin to the fuller study of single-photon processes already carried out [7] (e.g., our first step will be to examine these processes in the alkaline earths, Be, Mg, Ca, for the similarities and differences among these elements).

The two-photon amplitude for going from state  $i$  to state  $f$  has the structure

$$T_{f \leftarrow i}^{(2)} = \sum \int d\varepsilon \langle f | D | \varepsilon \rangle (\varepsilon_i + \omega - \varepsilon + i\eta)^{-1} \langle \varepsilon | D | i \rangle, \quad (1)$$

$$\eta \rightarrow 0^+,$$

where  $D$  is the dipole operator (we will always use the length gauge) and  $\omega$  is the light frequency. Energy conservation requires  $\varepsilon_i + 2\omega = \varepsilon_f$  for two-photon absorption. The Raman effect consists of absorbing a photon of frequency  $\omega$  and emitting a photon of frequency  $\Omega$ , with  $\varepsilon_i + \omega = \varepsilon_f + \Omega$ . Dynamic polarizability consists of absorbing and reemitting (or emitting and reabsorbing) a photon of frequency  $\omega$  with  $|f\rangle = |i\rangle$  in this case. We will only consider the cases where  $|i\rangle$  is a localized bound state.

We solve Eq. (1) by the procedure of Dalgarno and Lewis [8], setting  $T_{f \leftarrow i}^{(2)} = \langle f | D | \Lambda \rangle$  with  $|\Lambda\rangle$  a solution of the inhomogeneous equation

$$(\varepsilon_i + \omega - H) |\Lambda\rangle = D | i \rangle, \quad (2)$$

where the limit  $\eta \rightarrow 0^+$  in Eq. (1) translates into imposing outgoing wave boundary conditions on  $|\Lambda\rangle$  in the open channels. We solve for  $|\Lambda\rangle$  by noting that  $|\Lambda\rangle = |\Lambda_0\rangle + \sum_i |\psi_i\rangle A_i$ , where  $|\Lambda_0\rangle$  is any solution of Eq. (2) and the  $|\psi_i\rangle$  are solutions of the homogeneous equation

$$(\varepsilon_i + \omega - H) |\psi_i\rangle = 0. \quad (3)$$

MQDT [9] now comes into play by judiciously choosing the  $A_i$  to give the correct boundary conditions for  $|\Lambda\rangle$  as  $r \rightarrow \infty$ . MQDT takes advantage of the fact that once an electron leaves the core region it only feels an average potential due to the core electrons, thus simplifying its dynamics. The wave function of the electron in this average potential can be solved analytically. We can now simply impose the physical boundary conditions on  $|\Lambda\rangle$  because the asymptotic form of  $|\Lambda_0\rangle$  and  $|\psi_i\rangle$  are known analytically once their logarithmic derivatives are specified at a finite radius, typically 15–20 a.u. The boundary conditions at  $r \rightarrow \infty$  are completely ignored when calculating  $|\Lambda_0\rangle$  and  $|\psi_i\rangle$ , thus making these functions insensitive to the energy. The form of these functions outside of the core region is given by

$$\psi_i = \sum_{i'} \phi_{i'} [f_{i'}(r) \delta_{i'i} - g_{i'}(r) K_{i'i}] \quad (4)$$

and

$$\Lambda_0 = \sum_{i'} \phi_{i'} [f_{i'}(r) \lambda_{i'}^{(f)} - g_{i'}(r) \lambda_{i'}^{(g)}], \quad (5)$$

where  $\phi_{i'}$  is the  $i'$  channel function and  $f(g)$  is the solution of the Schrödinger equation for the long-range field [9] which the outgoing electron feels. For neutral atoms,  $f(g)$  is a Coulomb function. The coefficients  $A_i$  are determined by enforcing the boundary conditions at large distances (i.e.,  $|\Lambda\rangle$  must converge to zero in the closed channels and must have only outgoing waves in the open channels). This procedure is similar to the treatment in Sec. 8.4 of Ref. [9]. The coefficients  $A_i$  are thus very sensitive to the energy. However, the  $A_i$  depend on the inverse of a small matrix times a vector, and so we can afford to calculate it much more often. Specifically,

$$\mathbf{A} = -(\mathbf{K} + \mathbf{B})^{-1}(\boldsymbol{\lambda}^{(g)} + \mathbf{B}\boldsymbol{\lambda}^{(f)}), \quad (6)$$

where  $\mathbf{B}$  is a diagonal matrix with components  $\tan \pi \nu_j$  if the  $j$  channel is closed and  $i = \sqrt{-1}$  if the  $j$  channel is open and  $\mathbf{K}$  and  $\boldsymbol{\lambda}$  are from Eqs. (4) and (5).

In all that follows, the method of solving Eqs. (2) and (3) is largely a matter of taste. We use the eigenchannel  $R$ -matrix method in its streamlined formulation [10] to solve Eq. (3). The  $R$ -matrix procedure is a variational principle for determining the logarithmic derivatives of the wave function on a boundary. In practice, the wave function is expanded in a superposition of basis functions; thus the variational principle reduces to a generalized eigenvalue problem where the eigenvectors are coefficients of the basis expansion and the eigenvalues are the logarithmic derivatives. A variant of this method also works for Eq. (2).  $\Lambda_0$  is constructed by a superposition of basis functions inside an  $R$ -matrix box. The coefficients of the superposition are determined by

$$(\Gamma - b_\lambda \sigma) \mathbf{C}_\lambda = 2\mathbf{Z}, \quad (7)$$

with  $Z_j = \langle y_j | D | i \rangle$ ;  $\Gamma$  is proportional to the energy minus the Hamiltonian plus Bloch operator [Eq. (2a) of Ref.

[10]],  $\sigma$  is the surface operator [Eq. (2b) of Ref. [10]], and  $b_\lambda$  is minus the logarithmic derivative of  $\Lambda_0$  at the surface of the  $R$ -matrix box.  $b_\lambda$  can be chosen to be any value which leaves  $\mathbf{C}_\lambda$  finite. Equation (7) can be “streamlined.” This has the advantage that the logarithmic derivative of  $|\Lambda_0\rangle$  is (in some sense) found variationally and also that computer programs that were developed for one-photon processes can be easily converted to calculate two-photon processes.

We chose Al to be the atomic target to test this procedure. It is, for our purposes, a three-electron atom having the ground-state symmetry  $3s^2 3p^2 P^o$  outside of a Ne-like core. The energy needed to ionize Al leaving behind two electrons in the states  $3s^2$ ,  $3s 3p^3 P$ , and  $3s 3p^1 P$  is 0.22, 0.39, and 0.49 a.u., respectively. Upon absorbing a photon, the atom has either  $^2S^e$ ,  $^2P^e$ , or  $^2D^e$  symmetry. The five channels used for the  $^2D^e$  symmetry are  $3s^2 + d$ -wave electron,  $3s 3p^3 P + p$ -wave or  $f$ -wave electron, and  $3s 3p^1 P + p$ -wave or  $f$ -wave electron. After absorbing two photons the atom can have either  $^2S^o$ ,  $^2P^o$ ,  $^2D^o$ , or  $^2F^o$  symmetry.

We have calculated the frequency-dependent polarizability,  $\chi^{(1)}(\omega)$ , of Al which provides a sensitive test for the inhomogeneous solution because  $\sigma_T \propto \omega \text{Im}(\chi^{(1)})$ . The total photoabsorption cross section  $\sigma_T$  can be easily calculated using completely different techniques. We calculated the  $\sigma_T$  in the length gauge for the  $^2D^e$  final-state symmetry over the energy range between the  $3s^2$  and  $3s 3p^1 P$  thresholds using the eigenchannel  $R$ -matrix approach, obtaining good agreement with previous work [7]. Using the same basis functions we then calculated the dynamic polarizability using the solution to Eq. (2) with outgoing wave boundary conditions. The difference in  $\sigma_T$  was less than one part in a billion. This agreement reflects the stability of this method of calculating  $|\Lambda\rangle$  and shows that it is as accurate as the homogeneous solution in this energy range.

In Fig. 1, we graph the real and imaginary parts of

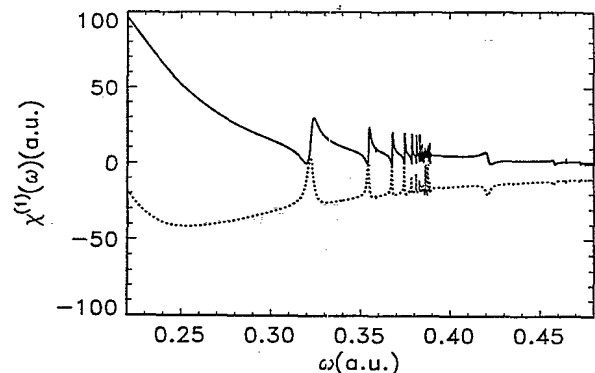


FIG. 1. The real (dotted line) and imaginary (solid line) parts of the dynamic polarizability for the  $^2D^e$  intermediate-state symmetry. The imaginary part is positive for all frequencies.

$\chi^{(1)}(\omega)$  which arise from the two sequences  $3s^2 3p^2 P^o \pm \hbar\omega \rightarrow {}^2D^e \rightarrow 3s^2 3p^2 P^o \pm \hbar\omega$ . We plot  $\chi^{(1)}$  only for this pathway for reasons of clarity. The lowest threshold ( $3s^2$ ) of Al lies at  $\omega \sim 0.22$  a.u.; the second threshold ( $3s 3p^3 P$ ) is at  $\omega \sim 0.39$  a.u. Not surprisingly, every structure in the real part of  $\chi^{(1)}$  corresponds to a structure in the imaginary part. On the whole the real part is negative above the lowest ( $3s^2$ ) threshold. For frequencies less than  $\sim 0.22$  a.u.,  $\chi^{(1)}$  is purely real with a Rydberg series of divergences proportional to  $(\epsilon_i + \omega - \epsilon_n)^{-1}$ . The total  $\chi^{(1)}(0)$  summed over all intermediate-state symmetries ( ${}^2S^e, {}^2P^e, {}^2D^e$ ) is equal to 57.6 a.u., which compares favorably with the value 56.3 a.u. obtained by Reinsch and Meyer [11]. Note that the real part changes sign between  $\omega=0$  and 0.22 a.u. This is probably due to the very broad  $3s 3p^2 {}^2D^e$  perturber centered threshold. Another striking feature of Fig. 1 is that the autoionizing series,  $3s 3p({}^3P)np^2 D^e$ , converging to the threshold at  $\omega \sim 0.39$  a.u., produces nearly Lorentzian peaks in the real part, while the autoionizing series,  $3s 3p({}^1P)np^2 D^e$ , converging to the threshold at  $\omega \sim 0.49$  a.u. produces dips. This is correlated with the Fano  $q$  parameter characterizing the imaginary part.  $q_R$ , the  $q$  value of  $\text{Re}(\chi^{(1)})$ , appears related to  $q_I$ , the  $q$  value of  $\text{Im}(\chi^{(1)})$ , roughly by  $q_R \sim (1+q_I)/(1-q_I)$ . Another notable feature of Fig. 1 is the difference in magnitude of the two curves. We will need to gain experience with  $\chi^{(1)}$  by calculating it for several elements in different columns of the periodic table before knowing how ubiquitous is this feature.

Figure 2 shows the two-photon absorption cross section through the path  $3s^2 3p^2 P^o + 2\hbar\omega \rightarrow {}^2D^e + \hbar\omega \rightarrow {}^2F^o$ . This pathway is relevant to absorption of circularly polarized photons by optically pumped atoms, though we did not choose this process because of its physical relevance but because it facilitates disentangling the effects of intermediate- and final-state resonances. The small peak at  $\sim 0.165$  ( $3s 3p^3 P 3d^2 F^o$ ) is the lowest member of the final-state Rydberg series with threshold at  $2\omega \sim 0.39$  a.u. The large resonance in the two-photon cross section at  $\sim 0.15$  a.u. stems from the lowest  ${}^2D^e$  intermediate state; the large resonance at  $\sim 0.175$  a.u. is the next state of this symmetry (i.e.,  $3s^2 3d$  and  $4d$ , respectively). These are the first two resonances of the intermediate Rydberg series approaching 0.22 a.u. The cross section for higher energies pertains to above-threshold ionization (ATI). ATI is greatly enhanced near the frequencies 0.231 ( $3s 3p^1 P 4d^2 F^o$ ) and 0.237 a.u. ( $3s 3p^1 P 5d^2 F^o$ ) which are autoionizing resonances in the final state. ATI should also be enhanced near autoionizing resonances of the intermediate state; probably the largest enhancement of ATI will be near autoionizing resonances in both the intermediate and final states.

We can take advantage of the generalization of MQDT [12] to extend the range of applicability of this procedure. For example, we should be able to calculate multiphoton amplitudes of negative ions by utilizing the ana-

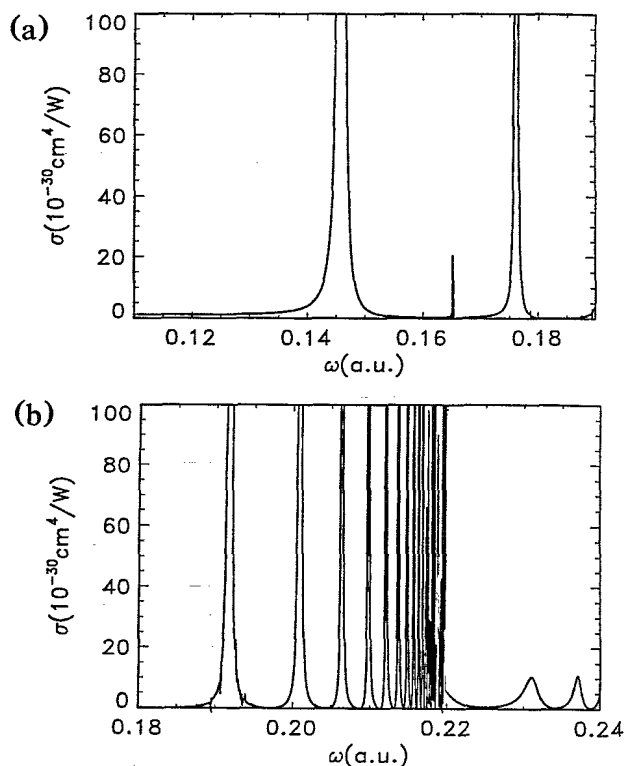


FIG. 2. The two-photon ionization cross section only for the  ${}^2F^o$  final-state symmetry. (a)  $0.11 \text{ a.u.} < \hbar\omega < 0.19 \text{ a.u.}$  (b)  $0.18 \text{ a.u.} < \hbar\omega < 0.24 \text{ a.u.}$

lytic solution of Schrödinger's equation for a polarization potential. Another interesting possibility would be to study second-harmonic generation by neutral atoms in a constant electric field. It should be interesting to follow the evolution of this process from perturbative in the electric field at low photon energies to highly nonperturbative in the electric field as twice the photon energy approaches threshold. This process near doubly excited states should also display interesting effects which may well have qualitatively different behavior depending on whether or not the doubly excited state can decay to the ground state. These seem to be the two most interesting situations to be explored, but any of the generalizations of QDT explored by previous workers for one-photon processes should also be incorporated in the present method of calculating multiphoton processes.

The procedure we have described can be easily applied to any two-photon processes (Raman scattering, two-photon absorption, and dynamic polarizability). Particularly, this method is not restricted to the cases where the inhomogeneous function,  $|\Lambda\rangle$ , is described by an  $L^2$  basis. The variant of MQDT for  $|\Lambda\rangle$  applied here requires the same computational effort far below the threshold as near the thresholds. This feature allows for a more unified and automated treatment of two-photon processes in multielectron atoms whose atomic physics is fully developed.

Higher-photon processes should be equally amenable to this formulation after overcoming the single difficulty that arises when the inhomogeneous term in Eq. (2) extends outside of the  $R$ -matrix box. In this situation, the inhomogeneous solution outside of the box is not simply Coulomb functions. We will try to adapt the techniques of Ref. [13] to resolve this difficulty. This method eventually runs out of steam for high-order processes due to the propagation of the errors in the inhomogeneous equation. We are confident that this method is sufficiently accurate up to four-photon processes.

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