Multiphoton Processes in a Hydrogen Atom

Y. Gontier and M. Trahin

Service de Physique Atomique Centre d'Etudes Nucléaires de Saclay, Gif-sur-Yvette, France

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Within the framework of time-dependent perturbation theory, general expressions are derived for the cross section of multiphoton processes induced by radiation acting on a hydrogen atom. Bound-bound transitions involving emission of a single quantum and bound-free transitions are calculated for a wide range of photon energies. In the case of resonance, the transition probability is also discussed. The procedure used to evaluate the sums over intermediate states is described. The numerical computation allows one to compare the results obtained for various competing processes.

I. INTRODUCTION

The interaction of radiation with atomic systems has been the subject of a considerable amount of recent theoretical work.¹⁻¹⁷ Most of this concerns two-photon processes. In this paper, we shall present calculations for the treatment of many-photon problems. First, we shall discuss any process involving absorption of several photons and emission of a single quantum sufficient to conserve energy in a transition of a bound hydrogenic electron. This study will enable us to compute numerical cross sections for processes involving a quantum emission in the region of low photon energies as well as in the vacuum ultraviolet range of the spectrum. Next, the transition probability for the absorption of N photons will be derived. Finally, we shall investigate the multiphoton ionization of atomic hydrogen in the ground state and in the metastable 2s state.

Section II contains explicit formulas for multiphoton transition and multiphoton ionization. The case of resonance is discussed using a procedure developed by Low¹⁸ to take radiation corrections into account.

The evaluation of the Nth-order matrix element is performed in Sec. III. The sums over intermediate states, discrete plus continuum, are carried out through the Schwartz and Tieman method.¹⁹ However, the generalization of this technique described in a previous paper,¹² is rewritten in a form involving the momentum operator.

In Sec. IV, the numerical procedure is described and the precision of the solution obtained from our computer program is discussed. This latter investigation has led to the verification of an interesting theorem due to Cohan and Hameka, ⁵ which concerns the role played by the quadratic A^2 term arising from the interaction Hamiltonian. Some of our numerical results are reported in Sec. V.

II. MULTIPHOTON CROSS SECTIONS

The differential cross section for absorption of

(N-1) photons and emission of a single quantum may be derived by direct application of time-dependent perturbation theory.

The nonrelativistic interaction Hamiltonian between the radiation field and an atomic electron is

$$H_{I} = -(e/m)\vec{\mathbf{p}}\cdot\vec{\mathbf{A}} + (e^{2}/2m)\vec{\mathbf{A}}^{2} .$$
 (1)

But the problem is greatly simplified by using an interesting proposition due to Cohan and Hameka.⁵ It may be shown that for any multiphoton process involving more than two photons, the quadratic \vec{A}^2 term does not contribute to the transition probability. In such a statement the vector potential \vec{A} is assumed to be constant throughout the atomic volume.

Therefore, considering only the linear $(\vec{p} \cdot \vec{A})$ term in the dipole approximation, we have, for transitions between two hydrogenic bound states,

$$\frac{d\sigma_{(E)}}{d\Omega} = r_0^2 \left(\frac{I}{I_0}\right)^{N-2} E_p E_s \left|\frac{1}{E_p^{N-1}} \mathfrak{M}^{(N)}(E_p, E_s)\right|^2 .$$
(2)

 $d\sigma_{(E)}/d\Omega$ is the differential cross section per atom, in cm²/sr, for an electron described by quantum numbers (n, l, m). r_0 is the classical electron radius, I is the incident intensity in W/cm², and I_0 is 14.038×10¹⁶ W/cm². The incoming photon energy E_{p} , the outgoing photon energy E_{s} , and the remaining quantities are expressed in atomic units.

The Nth-order matrix element may be set up in the form

$$\mathfrak{M}^{(N)}(E_{p},E_{s})=\sum_{\nu=1}^{N}M_{\nu}.$$
(3)

Using the notations

$$d_{k,\nu} = (\vec{\epsilon} \cdot \vec{p}) + \delta_{\nu,k} [(\vec{\epsilon}' \cdot \vec{p}) - (\vec{\epsilon} \cdot \vec{p})], \qquad (4)$$

$$\Omega_{k,\nu} = \Omega_{(k-1),\nu} + E_{p} - \delta_{k,\nu} (E_{p} + E_{s}) , \quad \Omega_{0,\nu} = 0$$
 (5)

we have M.=

$$M_{\nu} = \langle f | d_{N,\nu} \left(\sum_{i_{N-1}} \frac{|i_{N-1}\rangle \langle i_{N-1} | d_{N-1,\nu}}{E_{\varepsilon} - E_{N-1} + \Omega_{N-1,\nu}} \right) \cdots$$

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$$\times \left(\sum_{i_{k}} \frac{|i_{k}\rangle \langle i_{k}|d_{k,\nu}}{E_{g} - E_{k} + \Omega_{k,\nu}} \right) \cdots \left(\sum_{i_{1}} \frac{|i_{1}\rangle \langle i_{1}|d_{1,\nu}}{E_{g} - E_{1} + \Omega_{1,\nu}} \right) |g\rangle.$$
(6)

In Eq. (6), E_{ξ} and E_k denote the energies of the initial state $|g\rangle$ and intermediate state $|i_k\rangle$, respectively. $|f\rangle$ is the final state function and $\vec{p} = -i \vec{\nabla}$ is the momentum operator. $\vec{\epsilon}$ is the unit vector in the direction of polarization of the incident radiation. $\vec{\epsilon}'$ is the final unit polarization vector of the emitted radiation.

For the value N = 2, it can be seen that Eq. (2) gives the Raman scattering dispersion formula.

When the energy E_s goes to zero, Eq. (2) is no longer valid. However, within the framework of time-dependent perturbation theory, the differential cross section for absorption of N photons may be directly derived. We get the result

$$\sigma_{(A)} = (2\pi)^2 r_0 c \left(\frac{I}{I_0}\right)^{N-1} \frac{1}{E_p} \left| \frac{1}{E_p^{N-1}} \mathfrak{M}^{(N)} (E_p, 0) \right|^2 g (NE_p) .$$
(7)

The Nth-order matrix element $\mathfrak{M}^{(\nu)}(E_{p},0)$ is obtained from Eq. (6), for the particular value $\nu = 0$,

$$\mathfrak{M}^{(N)}(E_p, \mathbf{0}) = M_0$$
 (8)

 $g(NE_p)$ is the atomic line-shape function in sec.

The special case of $E_s = E_p$ and N = 2 corresponds to the coherent scattering from a bound electron. This interaction is clearly described by the wellknown Kramers-Heisenberg dispersion formula

$$\frac{d\sigma_{(C)}}{d\Omega} = r_0^2 \left| \left(\vec{\epsilon} \cdot \vec{\epsilon}' \right) + \mathfrak{M}^{(2)} \left(E_{p,} E_{p} \right) \right|^2 . \tag{9}$$

Equation (9) has been treated in some detail by several authors.^{1,10,11} The method discussed in Sec. III will allow us to check some available results.

The last process we wish to investigate is the multiphoton ionization. The expression of the differential cross section, derived elsewhere, ^{6,12} can be rewritten in the form

$$\frac{d\sigma_{(I)}}{d\Omega} = \frac{r_0^2}{2\pi\alpha^3} \left(\frac{I}{I_0}\right)^{N-1} \frac{k}{E_p} \left| \frac{1}{E_p^{N-1}} \operatorname{\mathfrak{M}}^{(N)}(E_p, 0) \right|^2,$$
(10)

where k is the wave number of the ejected electron and α is the fine-structure constant. Since the atom is left ionized, the final state function must belong to the continuum. In contrast with the calculations reported in a previous paper, ¹² the evaluation of the matrix element M_0 will be performed by using the momentum operator instead of the position operator. Obviously, it must be expected that the previous way of operating will also lead to the same final result.

In spherical polar coordinates, the hydrogenic wave functions are expressed as a product of two functions, $\Psi_{nlm} = R(n, l \mid r) Y_{lm}(\theta, \phi)$. Therefore, the calculation of a given matrix element may be carried out in evaluating separately the contributions arising from angular and radial parts, respectively. We must rewrite Eq. (3) in a more convenient form for numerical computation. Each state is denoted by its index $|k\rangle \equiv |i_k\rangle$, $|0\rangle \equiv |g\rangle$, and $|N\rangle \equiv |f\rangle$. By defining the quantities

$$\langle i | \mathbf{\tilde{p}} | j \rangle = \mathbf{\tilde{p}}_{ij}, \quad \langle i | \mathbf{\tilde{\epsilon}} \cdot \mathbf{\tilde{p}} | j \rangle = p'_{ij}, \quad E_i - E_j = E_{i,j},$$

we have

$$\mathfrak{M}^{(N)}(E_{p},E_{s}) = \frac{\vec{\epsilon}\cdot\vec{\epsilon}'}{3} \left(\sum_{i_{1}\cdots i_{k}\cdots i_{(N-1)}} \frac{(\vec{p}_{01}\cdot\vec{p}_{12})p'_{23}\cdots p'_{(N-2)-(N-1)}p'_{(N-1)N}}{(E_{\varepsilon,1}+\Omega_{1,1})(E_{\varepsilon,2}+\Omega_{2,1})\cdots(E_{\varepsilon,(N-1)}+\Omega_{(N-1),1})} \right) \\ + \sum_{i_{1}\cdots i_{k}\cdots i_{(N-1)}} \frac{p'_{01}(\vec{p}_{12}\cdot\vec{p}_{23})p'_{34}\cdots p'_{(N-2)(N-1)}p'_{(N-1)N}}{(E_{\varepsilon,1}+\Omega_{1,2})(E_{\varepsilon,2}+\Omega_{2,2})\cdots(E_{\varepsilon,(N-1)}+\Omega_{(N-1),2})} + \cdots \\ + \sum_{i_{1}\cdots i_{k}\cdots i_{(N-1)}} \frac{p'_{01}p'_{12}p'_{23}\cdots p'_{(N-3)(N-2)}(\vec{p}_{(N-2)(N-1)}\cdot\vec{p}_{(N-1)N})}{(E_{\varepsilon,1}+\Omega_{1,(N-1)})(E_{\varepsilon,2}+\lambda_{2,(N-1)})\cdots(E_{\varepsilon,(N-1)}+\Omega_{(N-1),(N-1)})} \\ + \sum_{i_{1}\cdots i_{k}\cdots i_{(N-1)}} \frac{p'_{01}p'_{12}p'_{23}\cdots p'_{(N-3)(N-2)}(\vec{p}_{(N-2)(N-1)}\cdot\vec{p}_{(N-1)}N)}{(E_{\varepsilon,1}+\Omega_{1,(N-1)})(E_{\varepsilon,2}+\lambda_{2,(N-1)})\cdots(E_{\varepsilon,(N-1)}+\Omega_{(N-1),(N-1)})} \right)$$
(11b)

(11a)

To compute the matrix components of the interaction Hamiltonian, we use the following notations for the well-known relations between spherical harmonics²⁰:

$$\nabla_{z} [R(n, l | r) Y_{Im}] = [A(l, m) Y_{(l+1)m} q^{+} + B(l, m) Y_{(l-1)m} q^{-}]R(n, l | r),$$

$$(\nabla_{x} + i \nabla_{y}) [R(n, l | r) Y_{Im}] = [C(l, m) Y_{(l+1)(m+1)} q^{+} + D(l, m) Y_{(l-1)(m+1)} q^{-}]R(n, l | r),$$

$$(\nabla_{x} - i\nabla_{y})[R(n, l, |r)Y_{lm}] = [E(l, m)Y_{(l+1)(m-1)}q^{*}]$$
(12)

+
$$F(l, m) Y_{(l-1)(m-1)} q^{-1} R(n, l|r)$$
,

where the q^{\pm} operators are given by

$$q^{*}(l,r) = \left(\frac{d}{dr} - \frac{l}{r}\right), \quad q^{-}(l,r) = \left(\frac{d}{dr} + \frac{l+1}{r}\right). \quad (13)$$

In order to have formulas in as simple a form as possible, we shall next define the quantities

$$Q_{0}(l_{j+1}, l_{j}) = [A(l_{j}, m_{j}) \delta(l_{j+1}, l_{j} + 1) \\ + B(l_{j}, m_{j}) \delta(l_{j+1}, l_{j} - 1)],$$

$$Q_{*}(l_{j+1}, l_{j}) = [C(l_{j}, m_{j}) \delta(l_{j+1}, l_{j} + 1) \\ + D(l_{j}, m_{j}) \delta(l_{j+1}, l_{j} - 1)],$$

$$Q_{-}(l_{j+1}, l_{j}) = [E(l_{j}, m_{j}) \delta(l_{j+1}, l_{j} + 1)$$

$$Q_{-}(l_{j+1}, l_{j}) = [E(l_{j}, m_{j}) \delta(l_{j+1}, l_{j} + 1)]$$

$$+F(l_{j}, m_{j})\delta(l_{j+1}, l_{j}-1)]$$

and

$$q(l_{j},r) = \left(\frac{l_{j+1} - l_{j} + 1}{2} q^{*}(l_{j},r) + \frac{l_{j} - l_{j+1} + 1}{2} q^{-}(l_{j},r)\right),$$
(15)

where $\delta(i, j)$ is used for the Kronecker symbol δ_{ij} . From Eqs. (12), (14), and (15), we can write

$$\langle \psi_{j+1} | \nabla_{\mathbf{z}} | \psi_j \rangle = Q_0(l_{j+1}, l_j) \langle R_{j+1} | q | R_j \rangle ,$$

$$\langle \psi_{j+1} | (\nabla_{\mathbf{x}} + i \nabla_{\mathbf{y}}) | \psi_j \rangle = Q_+(l_{j+1}, l_j) \langle R_{j+1} | q | R_j \rangle ,$$

$$\langle \psi_{j+1} | (\nabla_{\mathbf{x}} - i \nabla_{\mathbf{y}}) | \psi_j \rangle = Q_-(l_{j+1}, l_j) \langle R_{j+1} | q | R_j \rangle ,$$

$$(16)$$

 R_i being an abbreviation for the radial wave function $R(n_i, l_i | r_i)$.

In combining expressions such as Eq. (16), the

Nth-order matrix element for transitions from the initial state characterized by the three quantum numbers (n, l, m) to the final state described by (n', L, M), may be transformed in a more convenient form for the numerical calculations. All the transitions allowed by the selection rules are determined in computing the angular contributions to $\mathfrak{M}^{(N)}(E_p, E_s)$. By assuming that the unit polarization vector is along the z axis, we have

$$G_{\nu}(l_{1}, m_{1}; \dots; l_{k}, m_{k}; \dots; L, M)$$

$$= Q_{0}(L, l_{N-1}) Q_{0}(l_{N-1}, l_{N-2})$$

$$\times Q_{0}(l_{N-2}, l_{N-3}) \cdots Q_{0}(l_{k+2}, l_{k+1})$$

$$\times \{ Q_{0}(l_{k+1}, l_{k}) Q_{0}(l_{k}, l_{k-1}) + \frac{1}{2} [1 - \delta(\nu, 0)]$$

$$\times [Q_{+}(l_{k+1}, l_{k}) Q_{-}(l_{k}, l_{k-1}) + Q_{-}(l_{k+1}, l_{k}) Q_{+}(l_{k}, l_{k-1})] \}$$

$$\times Q_{0}(l_{k-1}, l_{k-2}) \cdots Q_{0}(l_{1}, l) . \quad (17)$$

In connection with the evaluation of each factor $G_{\nu}(l_1, m_1; \ldots; l_k, m_k; \ldots; L, M)$, the calculation of the corresponding radial contribution must be performed. This quantity may be written in the form

$$P_{\nu}(l_{1},\ldots,l_{k},\ldots,L|E_{p},E_{s})$$

$$=\sum_{n(N-1)\cdots n_{k}\cdots n_{1}}\frac{\langle R_{f}|q|R_{N-1}\rangle}{\langle E_{\varepsilon},(N-1)+\Omega_{(N-1),\nu}\rangle}\cdots$$

$$\times\frac{\langle R_{k+1}|q|R_{k}\rangle\langle R_{k}|q|R_{k-1}\rangle}{\langle E_{\varepsilon,k}+\gamma_{k,\nu}\rangle}\cdots\frac{\langle R_{1}|q|R_{\varepsilon}\rangle}{\langle E_{\varepsilon,1}+\beta_{1}+\beta_{1,\nu}\rangle}.$$
 (18)

The total cross section $\sigma_{(n, l,m)}$ is obtained by squaring $\mathfrak{M}^{(N)}(E_p, E_s)$, then summing over the final states of polarization when the emission of photons occurs, and finally integrating over the solid angle Ω . Finally we have

$$\mathfrak{M}^{(N)}(E_{p}, E_{s})|^{2} = K \left| \sum_{\nu=1}^{N} \sum_{i_{1}\cdots i_{k}\cdots i_{(N-1)}} G_{\nu}(l_{1}m_{1}; \ldots; l_{k}m_{k}; \ldots; LM) \right| \times P_{\nu}(l_{1}, \ldots, L|E_{p}, E_{s})|^{2}.$$
(19)

When $E_s = 0$, then Eq. (19) reduces to

$$|\mathfrak{M}^{(N)}(E_{p}, \mathbf{0})|^{2} = K | \sum_{i_{1}\cdots i_{k}\cdots i(N-1)} \\ \times G_{\mathbf{0}}(l_{1}m_{1}; \ldots; l_{k}m_{k}; \ldots; LM) \\ \times P_{\mathbf{0}}(l_{1}, \ldots, l_{k}, \ldots, L | E_{p}, E_{s})|^{2}.$$
(20)

The coefficient K arising from the previous man-

ipulations takes the values $8\pi/27$, 1, $8\pi/27$, and $8\pi^3/k$ for the processes described by Eqs. (2), (7), (9), and (10), respectively.

The dispersion formulas Eqs. (2), (7), (9), and (10), are not valid in the case of resonances, i.e., if $E_g - E_k + \Omega_{k,\nu} = 0$. Then, the expression of M_{ν} may be rederived by using the procedure developed by Low¹⁸ for the resonance scattering. As a principal consequence of this treatment, every energy term appearing in the denominator of Eq. (6) is modified by the introduction of a complex damping term $(\frac{1}{2}i\gamma)$. Then, we can expect that the inclusion of the natural linewidth must lead to finite results.

The probability of a spontaneous transition²⁰ of an atom from a state $|n\rangle$ to a state $|n'\rangle$ may be written

$$(W_{(S)})_{n,n'} = \frac{4}{3} \alpha^3 \frac{\alpha^3 c}{\gamma_0} E_s |\langle n'|\vec{\epsilon}', \vec{p}|n\rangle|^2, \qquad (21)$$

and the natural linewidth as

$$\gamma_n = \sum_{n' \le n} (W_{(S)})_{n,n'} .$$
 (22)

For a transition from an initial state $|g\rangle$ to a final state $|f\rangle$ via a resonant state $|R\rangle$, the multiphoton process may be described in terms of transition probability per unit time W_{ef} . By combining Eq. (2) or (10) with Eq. (7), (9), or (21), we easily find

$$(W_{(E,I)}^{(N)})_{ef} = \frac{(W_{(A)}^{(K)})_{eR}(W_{(E,I)}^{(N-K)})_{Rf}}{(\frac{1}{2}\gamma_R)^2} \frac{K_1}{2\pi} \frac{1}{g(KE_p)} \quad .$$
(23)

In Eq. (23), the transition probabilities W_{ij} and γ_R are expressed in sec⁻¹ and the incident photon energy is taken in atomic units. $K_1 = 1$ unless W_{Rf} is identical with $(W_{(C)})_{Rf}$ or $(W_{(S)})_{Rf}$; in these cases we have $K_1 = (1/9)$.

III. METHOD OF EVALUATING RADIAL MATRIX ELEMENTS

The chief difficulty in calculating the $P_{\nu}(l_1, \ldots, l_k, \ldots, L | E_p, E_s)$ function stands in the correct evaluation of the (N-1) summations over the n_i , which are extended over the complete set of all possible intermediate states of the unperturbed Hamiltonian, discrete plus continuum. In a previous paper¹² it has been shown how a particular technique, introduced by Dalgarno and Lewis²¹ and reformulated by Schwartz and Tieman¹⁹ could be generalized to calculate the sums contained in transition matrix elements built up from the matrix components of the position operator. We present here the method of operating with Nthorder matrix elements $|\mathfrak{M}^{(N)}(E_p, E_s)|$ expressed as functions of the momentum operator.

Let us write the radial contribution in the form

$$P_{\nu}(l_{1}, \ldots, l_{j}, \ldots, L \mid E_{p}, E_{s}) = \int_{0}^{\infty} dr \, r^{2} R(n, l \mid r)$$

$$\times [q(l_1, r) V_{\nu}(l_1, \ldots, l_j, \ldots, L | r, E_p, E_s)] \quad .$$
 (24)

From Eqs. (6), (18), and (24), we find

$$V_{\nu}(l_{1},\ldots,l_{j},\ldots,L|r,E_{p},E_{s}) = \sum_{n_{1},\ldots,n_{j},\ldots,n_{(N-1)}} R(n_{1}l_{1}|r) \frac{\langle R_{1}|q|R_{2}\rangle}{(E_{\varepsilon,1}+\Omega_{1,\nu})} \cdots \frac{\langle R_{N-1}|q|R_{f}\rangle}{(E_{\varepsilon,(N-1)}+\Omega_{(N-1),\nu})}$$
(25)

This function is a special case of a more general function defined by

$$V_{\nu}(l_{j}, l_{j+1}, \dots, L \mid r, E_{p}, E_{s}) = \sum_{n_{j}} R(n_{j}l_{j} \mid r) \int_{0}^{\infty} dr_{j} r_{j}^{2} R(n_{j}, l_{j} \mid r_{j}) \frac{1}{(E_{\varepsilon, j} + \Omega_{j, \nu})} q(l_{j+1}, r_{j}) V_{\nu}(l_{j+1}, l_{j+2}, \dots, L \mid r, E_{p}, E_{s}),$$
(26)

$$V(L | r, E_{p}, E_{s}) = R(n', L | r) .$$
(27)

To perform the *j*th sum over n_j , we must consider the Schrödinger equation

$$D_{j}(r) R(n_{j}l_{j}|r) = \left(\frac{1}{2} \frac{d^{2}}{dr^{2}} + \frac{1}{r} \frac{d}{dr} + \frac{1}{r} - \frac{l_{j}(l_{j}+1)}{2r^{2}}\right) R(n_{j}l_{j}|r)$$
$$= -E_{j} R(n_{j}, l_{j}|r) .$$
(28)

Equation (28) can be transformed in order to involve the $V_{\nu}(l_j, l_{j+1}, \ldots, L \mid r, E_p, E_s)$ functions. It may be checked that we have

$$(E_{\boldsymbol{g}} + \Omega_{j,\boldsymbol{\nu}} + D_j) V_{\boldsymbol{\nu}}(l_j, l_{j+1}, \ldots, L \mid \boldsymbol{r}, E_{\boldsymbol{p}}, E_{\boldsymbol{s}})$$

. .

$$= \int_{0}^{\infty} dr_{j} (r_{j} / r) \sum_{n_{j}} rR(n_{j}, l_{j} | r)$$

$$\times r_{j}R(n_{j}, l_{j} | r_{j})[q(l_{j+1}, r_{j})$$

$$\times V_{\nu}(l_{j+1}, l_{j+2}, \dots, L | r_{j}, E_{\phi}, E_{\phi})]. \quad (29)$$

By means of the closure condition, Eq. (29) becomes

$$(E_{g} + \Omega_{j,\nu} + D_{j}) V_{\nu}(l_{j}, l_{j+1}, \dots, L \mid r, E_{p}, E_{s})$$

= $q(l_{j+1}, r) V_{\nu}(l_{j+1}, l_{j+2}, \dots, L \mid r, E_{p}, E_{s})$. (30)

Finally, we have shown how the (N-1) sums included in Eq. (25) can be evaluated by solving (N-1) equations analogous to Eq. (30).

To go further into the computation, a more explicit expression for the radial contribution must be obtained. The bound-state wave function is used in the form

$$R(n, l | r) = \beta(n, l) \sum_{s=0}^{n-l-1} (-1)^{s} \alpha(n, l, s) r^{l+s} \exp(-r/n) ,$$
(31)

where

$$\beta(n, l) = \frac{1}{2} \left(\frac{2}{n}\right)^{l+2} \left(\frac{(n+l)!}{(n-l-1)!}\right)^{1/2} , \qquad (32)$$

$$\alpha(n, l, s) = \frac{(n-l-1)! (2/n)^s}{(n-l-1-s)! (2l+1+s)! s!} \quad . \tag{33}$$

The exponential included in R(n, l|r) allows us to express the quantity $P_{\nu}(l_1, \ldots, l_j, \ldots, L | E_p, E_s)$ as

a finite sum of derivatives of the Laplace transform of $V_{\nu}(l_1, \ldots, l_j, \ldots, L \mid r, E_p, E_s)$ computed at the point p = 1/n. Let us define

$$S_{\nu}(l_{j}, l_{j+1}, \ldots, L \mid p)$$

= $\int_{0}^{\infty} dr \, V_{\nu}(l_{j}, l_{j+1}, \ldots, L \mid r, E_{p}, E_{s}) \, e^{-pr} \,, \quad (34)$

and

$$y_{\nu}(l_{j}, l_{j+1}, \dots, L \mid p) = \left(\frac{d}{dp}\right)^{l_{j}+1} S_{\nu}(l_{j}, l_{j+1}, \dots, L \mid p) .$$
(35)

As a consequence of definitions in Eqs. (34) and (35), it will be noted that $S_{\nu}(l_j, l_{j+1}, \ldots, L | p)$ and all its derivatives are finite for all p such that $\operatorname{Re}(p) > 0$. After some algebra, Eq. (24) becomes

$$P_{\nu}(l_{1},\ldots,l_{j},\ldots,L|E_{p},E_{s}) = \beta(n,l) \left\{ \sum_{s=0}^{n-l-1} (-1)^{l} \alpha(n,l,s) \left[\delta(l,l_{1}+1) \left((2l+s+1) \left(\frac{d}{dp} \right)^{s+1} + p \left(\frac{d}{dp} \right)^{s+2} \right) + \delta(l,l_{1}-1) \right\} \times \left(s \left(\frac{d}{dp} \right)^{s-1} + p \left(\frac{d}{dp} \right)^{s} \right) \left[y_{\nu}(l_{1},\ldots,l_{j},\ldots,L|p) \right]_{p=1/n} \right\}$$
(36)

Thus, we have expressed the radial contribution to $|\mathfrak{M}^{(N)}(E_p, E_s)|$ as a function of $y_{\nu}(l_1, \ldots, l_j, \ldots, L | p)$. But the function $y_{\nu}(l_j, l_{j+1}, \ldots, L | p)$ is the analytic solution of the first-order differential equation derived by taking the Laplace transform of Eq. (30) and by differentiating the result l_j times with respect to p. Then, in defining $\alpha_{j,\nu}^2 = -2(E_{\xi} + \Omega_{j,\nu})$, we have

$$\begin{pmatrix} (p^2 - \alpha_{j,\nu}^2) \frac{d}{dp} + 2[(l_j + 1)p - 1] \end{pmatrix} y_{\nu}(l_j, l_{j+1}, \dots, L | p) \\ = \begin{cases} \delta(l_{j+1}, l_j - 1) \left[2p \left(\frac{d}{dp} \right)^2 + (4l_j + 2) \frac{d}{dp} \right] \\ + \delta(l_{j+1}, l_j + 1) (2p) \end{cases} y_{\nu}(l_{j+1}, l_{j+2}, \dots, L | p) .$$
(37)

From Eq. (37), a hierarchy of inhomogeneous differential equations may be set up. The solution to the first is used to construct the right-hand side of the second, and so on. In this way, the first equation is

$$\left(\left(p^{2} - \alpha_{(N-1),\nu}^{2} \right) \frac{d}{dp} + \left[\left(l_{N-1} + 1 \right) p - 1 \right] \right) y_{\nu} \left(l_{N-1}, L \mid p \right)$$

$$= \left\{ \delta(L, l_{N-1} - 1) \left[2p \left(\frac{d}{dp} \right)^{2} + \left(4l_{N-1} + 2 \right) \frac{d}{dp} \right] + \delta(L, l_{N-1} + 1) \left(2p \right) \right\} y_{\nu} \left(L \mid p \right), \quad (38)$$

and it depends on the y(L|p) function which must be specified. From Eqs. (27), (34), and (35), we get

$$y(L|p) = \left(\frac{d}{dp}\right)^{L+1} \int_0^\infty dr R(n', L|r) e^{-pr} .$$
 (39)

Equation (39) leads to the following results. (i) For a bound radial function,

$$y^{b}(L \mid p) = (-1)^{L+1} \beta(n', L)(p - 1/n')^{n'-L-1} \times (p + 1/n')^{-n'-L-1}.$$
 (40)

(ii) For a continuum radial function,¹

$$y^{F}(L \mid p) = \left(\frac{-2}{p^{2} + k^{2}}\right)^{L+1} \prod_{j=1}^{L} (1 + j^{2}k^{2})^{1/2} \\ \times \frac{\exp[-2k^{-1} \operatorname{arc} \cot(p/k)]}{[1 - \exp(-2\pi/k)]^{1/2}} \quad .$$
(41)

The other equations are defined without difficulties. To solve Eq. (37), we need to know an initial value of $y_{\nu}(l_j, \ldots, L | p)$. This one will be simply determined at the positive value $p = \alpha_{j,\nu}$. $[(E_{\varepsilon} + \Omega_{j,\nu}) < 0]$ for which the coefficient of the derivative vanishes. The unique solution of the set of Eq. (37) is the desired $y_{\nu}(l_1, \ldots, l_j, \ldots, L | p)$ function, which has been defined by Eqs. (34) and (35) as an analytic function.

IV. NUMERICAL COMPUTATION

The two-photon ionization cross sections have

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been calculated in using different computational procedures. For the second-order matrix element, Klarsfeld¹⁵ derives an exact analytic formula in terms of hypergeometric functions of Appell's type, which may be computed at any degree of accuracy. To eliminate the sums over the intermediate states, Gold and Bebb⁶ replace the atomic energies appearing in Eq. (6) by an average energy independent of the state. Chan and Tang¹⁴ evaluate the ionization rate by utilizing the fact that Eq. (38) may be reduced to quadrature by the use of an integration factor. To solve Eq. (38), Zernik and Klopfenstein¹ have developed a method based on Taylor-series expansions. From the initial value $y_{\nu}(l_{(N-1)}, L \mid \alpha_{(N-1),\nu})$, a Taylor series is formed about the point $p_0 = \alpha_{(N-1),\nu}$. The function $y_{\nu}(l_{(N-1)}, L \mid p)$ is evaluated at the point p_1 in the re-

gion of convergence. Then, a new Taylor series is formed about the point $p = p_1$ and the process is continued until the solution can be computed at the desired value p = 1/n.

This method was employed to calculate the multiphoton ionization cross sections presented in a previous paper. For the two-photon ionization of the 2s metastable state, our results were in excellent agreement with those obtained by Zernik; but later, the comparison with new available values related to the ionization of the ground state^{1,14,15} exhibited some discrepancies. This disagreement gave rise to a delicate question, since any error in the second-order calculation may tend to grow and accumulate until the accuracy of the solution for the higher-order processes is eventually impaired. To remove any kind of doubt, our previous results have been improved in performing new calculations with a more powerful computer. For this purpose a numerical program has been written for the CDC 6600. With this computer it is possible to store informations related to 300 Taylor series containing 50 terms each. Because of the big size of the 300×50 array, the value of each p may be chosen in such a way that the convergence of each Taylor expansion is quickly obtained. Thus, a

diminution of the truncation error is to be expected. Another source of uncertainty arises from the necessity of rounding off each entry. This error may be simply minimized by performing the computation in double precision. For CDC 6600, this technique procures about 30 significant figures which must give a sufficient precision. In fact, truncation errors and round-off errors must necessarily coexist and interact in any numerical computation. Their presence cannot be avoided and the best we can do is to estimate an upper bound $\epsilon_B^{(N)}$ on the relative error in the matrix element $|\mathfrak{M}^{(N)}(E_{b}, E_{s})/$ E_{b}^{N-1} . The derivation of this bound can be obtained at the expense of additional calculations which may take a long machine time and be costly for higherorder processes. The analysis of errors and the evaluation of upper bounds are given in the Appendix.

Some typical results for the two-photon ionization of hydrogen in the ground state are summarized in Table I. It may be seen that our new data agree quite well with those obtained by Klarsfeld.¹⁵ Except for some wavelengths around 1100 Å, the agreement is good also with the values given by Chan and Tang.¹⁴ With the possibility of storing more information for each equation, the discrepancy resulting from the comparison between our present and former results has been simply resolved by using a larger number of Taylor expansions.

In Table II, we present some results concerning the anti-Stokes Raman scattering and the coherent scattering from the metastable 2s state. For these second-order processes, our data are in good accordance with those obtained by Zernik.¹ The disagreement around the Balmer- α resonance seems to be due to the factor relating energy and wavelength. The calculation performed in keeping a maximum number of significant digits in each arithmetic operation leads to precise values and small bounds ($\epsilon_B^{(2)} \leq 10^{-20}$) on the total error. For the processes higher than second order, we have carried out an additional verification of our data. Starting from the conclusions of Cohan and Hameka⁵

TABLE I. Values of the two-photon ionization rate σ/I (cm⁴/W) for atomic hydrogen in the ground state. The numbers in the parentheses indicate powers of 10. The results ascribed to Bebb and Gold are estimated from the dispersion curves of Ref. 6. The first column of values headed Gontier-Trahin has former values given in Ref. 12 and the second is present data calculated with an upper bound $\epsilon_{\mu}^{(2)} < 10^{-20}$.

λ(Å)	Bebb-Gold (Ref. 6)	Gontier-Trahin (Ref. 12)	Chan-Tang (Ref. 19)	Klarsfeld (Ref. 15)	Gontier-Trahin (present work)
1020		1.887 (-32)	6.752 (-33)	5,521 (-33)	5,522(-33)
1100	1.0 (-33)	2.103 (-33)	4.013(-34)	4,049 (-34)	4.049(-34)
1200	6.6 (-32)	8.938 (-32)	6.303 (-32)	5,803(-32)	5,803(-32)
1300	1.1 (-32)	4.953 (-33)	1.276 (-32)	1,283 (-32)	1,283(-32)
1400	7.0 (-33)	3.251 (-33)	8.450 (-33)	8,453 (-33)	8,453 (-33)
1600	6.8 (-33)	5.528 (-33)	9.154 (-33)	9.143 (-33)	9.143(-33)
1700	8.4 (-33)	8.054 (-33)	1.025 (-32)	1.024 (-32)	1.023 (- 32)

TABLE II. Values of the cross section σ (cm²) for the (2s-1s) anti-Stokes Raman scattering and the coherent scattering from the metastable 2s state. The numbers in the parentheses indicate powers of 10. In both cases, the upper bound is $\epsilon \frac{(2)}{B} < 10^{-20}$.

	$\sigma_r(2s-1s) \ (\mathrm{cm}^2)$		$\sigma_c(2s-2s) \ (\mathrm{cm}^2)$		
λ(Å)	Zernik (Ref. 1)	Gontier-Trahin (present work)	Zernik (Ref. 1)	Gontier-Trahin (present work)	
5 000 5 300 6 000 6 550 6 570 6 934 8 000	2.171 (-23) 7.166 (-24) 8.069 (-20) 1.285 (-19) 1.263 (-22) 2.361 (-23) 	2.208 (- 23) 1.908 (- 24) 7.077 (- 24) 6.022 (- 20) 1.971 (- 19) 1.273 (- 22) 2.364 (- 23)	$\begin{array}{c} 7.779 \ (-25) \\ \dots \\ 3.495 \ (-24) \\ 1.102 \ (-20) \\ 1.70 \ (-20) \\ 1.025 \ (-23) \\ 7.02 \ (-24) \\ 0.200 \ (-25) \end{array}$	$\begin{array}{c} 8.044 (-25) \\ 1.264 (-25) \\ 3.473 (-24) \\ 8.246 (-21) \\ 2.616 (-20) \\ 1.036 (-23) \\ 7.042 (-24) \\ \end{array}$	
9 000 10 000 10 600	1.298 (-23) 1.298 (-23)	1.209 (- 23) 1.299 (- 23) 1.219 (- 23)	2.322 (- 25) 1.083 (- 26)	$\begin{array}{c} 2.327 (-25) \\ 1.086 (-26) \\ 7.487 (-26) \end{array}$	

reported in Sec. II, we have numerically checked that the sum of matrix elements containing one quadratic term (matrix elements constructed from one double-photon jump and a certain number of one-photon jumps) does not give any contribution to the multiphoton transition probability. The proof seems to be significant since the calculation has been performed in adding up the N(N-1) independent solutions obtained in solving N(N-1) sets of differential equations. In such a computation,



FIG. 1. Dispersion rate σ_E/l^2 for four-photon transition of a hydrogenic electron in the ground state. The solid line corresponds to a $1_S \rightarrow 1_S$ transition. The dashed line gives the results for a $1_S \rightarrow 2_S$ transition; at 3647 Å, the $\lambda_A^{(3)}(1_S \rightarrow 2_p)$ threshold is $\sigma_A/g(3E_p)l^2 = 8.9 \times 10^{-31}$. The "dot-dashed" line represents a $1_S \rightarrow 3d$ transition; at 3077 Å, the $\lambda_A^{(3)}(1_S \rightarrow 3_p)$ threshold is $\sigma_A/g(3E_p)l^2 = 2.9 \times 10^{-32}$. The upper bound is $\epsilon_B^{(4)} < 10^{-11}$.



FIG. 2. Dispersion rate σ_E/I^4 for six-photon transition from the ground state. The solid line corresponds to a $1_S \rightarrow 1_S$ transition. The dashed line represents a $1_S \rightarrow 2_S$ transition; at 6078 Å, the $\lambda_A^{(5)}(1_S \rightarrow 2_p)$ threshold is $\sigma_A/g(5E_p)I^4 = 9.6 \times 10^{-61}$; at 4863 Å, the $\lambda_A^{(4)}(1_S \rightarrow 2_S)$ threshold is $\sigma_A/g(4E_p)I^3 = 1.8 \times 10^{-46}$. The "dot-dashed" line gives the results for a $1_S \rightarrow 3_S$ transition; at 5129 Å, the $\lambda_A^{(5)}(1_S \rightarrow 3_p)$ threshold is $\sigma_A/g(5E_p)I^4 = 2 \times 10^{-59}$. The upper bound is $\epsilon \frac{g}{6} < 10^{-5}$.

an accumulation of errors should necessarily appear; we have observed nothing but the usual roundoff error.

V. NUMERICAL RESULTS

The total cross section σ has been computed for the competing processes which may be produced by the interaction of radiation with atomic hydrogen. When necessary, these quantities have been evaluated by summing over the final quantum numbers (L, M). The calculation of Raman-like processes from hydrogen in the ground state has been carried out for a range of wavelengths from 1000 up to 7200 Å. The agreement is good with the values obtained by Saslow and Mills¹⁶ for a 1s - 2stwo-photon transition. But our results will be presented only for radiations which are accessible experimentally by the light from ruby or neodymium-glass lasers.

In Figs. 1-3, the rate σ/I^{N-2} is given as a function of wavelength, for transitions from the ground state to states with n=1, n=2, and n=3, and perturbation orders 4, 6, and 7. The dispersion curves are plotted for wavelengths between the (N-1)-photon ionization threshold $\lambda_I^{(N-1)}$ and the (N-1)-photon absorption threshold $\lambda_A^{(N-1)}$. Within these limits, the scattered photon energy E_s varies



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FIG. 3. Dispersion rate σ_{E}/I^{5} for seven-photon transition from the ground state. The solid line corresponds to a $1s \rightarrow 2p$ transition; at 7294 Å, the $\lambda_A^{(6)}(1s \rightarrow 2s)$ threshold is $\sigma_A/g(6E_p)I^5 = 4.9 \times 10^{-75}$. The dashed line represents a $1s \rightarrow 3p$ transition; at 6154 Å, the $\lambda_A^{(6)}(1s \rightarrow 3s)$ threshold is $\sigma_A/g(6E_p)I^5 = 2.2 \times 10^{-73}$ and the $\lambda_A^{(6)}(1s \rightarrow 3d)$ threshold is $\sigma_A/g(6E_p)I^5 = 2 \times 10^{-72}$. The upper bound is $\epsilon_B^{(7)} < 10^{-2}$.

from the final state energy $|E_f|$ to zero energy (Fig. 4). With the particular values $E_s = E_b$ and $E_s = (|E_f| - E_p)$, the wavelength reaches the (N-2)- photon absorption threshold $\lambda_A^{(N-2)}$ and the (N)-photon ionization threshold $\lambda_I^{(N)}$ successively (Fig. 4). Since the damping corrections to the perturbation theory results have been neglected, Figs. 1-3 and Figs. 5-7 exhibit the expected peaks arising from the resonant structure of M_{ν} . The transition rate goes to zero below the $\lambda_A^{(N-1)}$ threshold and between two consecutive resonances. At the wavelength $\lambda_A^{(N)}$, one can note that the absorption cross section defined by Eq. (7) is very useful to compute the resonant process determined from Eq. (23), which is, indeed, the dominant one. Out of resonances, the most intense processes seem to be those which involve emission of ultraviolet photons. In particular, the Nth-order 1s - 1s transitions have an appreciable cross section.

In Fig. 5, we present plots of σ/I for some thirdorder processes which can occur from the metastable 2s state. For a range of wavelengths from 8000 to 11000 Å, this graph exhibits the general feature of the transition rate for the generation of excited states. Within the preceding frequency limits, the three-photon ionization rate of the metastable 2s state is given in Fig. 6. In each case, the computed upper bound $\epsilon_B^{(N)}$ is indicated in the relevant figure caption.

In Figs. 7(a) and 7(b), we present the dispersion curves obtained from our new computer program for six-photon and eight-photon ionization of H in the ground state, respectively. In general, the dispersion curves show an increase in cross sections with respect to our former results. For N = 6, our data deviate from those computed by Bebb and



FIG. 4. Resonant energies and relevant thresholds in a portion of the hydrogen spectrum between the excited final state (E.F.S.) and the continuum. The dashed lines correspond to the virtual intermediate states. The photon energy decreases from the left- to the right-hand side of the graph.



FIG. 5. Dispersion rate σ_E/I for three-photon transition from the metastable 2s state. The solid line corresponds to a $2s \rightarrow 2p$ transition. The dashed line represents a $2s \rightarrow 3p$ transition. The "dot-dashed" line gives the results for a $2s \rightarrow 4p$ transition; at 9725.5 Å, the $\lambda_A^{(2)}$ $(2s \rightarrow 4s)$ threshold is $\sigma_A/g(2E_p)I = 3 \times 10^{-18}$. The upper bound is $\epsilon_B^{(3)} < 10^{-15}$.

Gold; on the other hand, they come nearer for N=8. In this last case, the upper-bound calculation is impractical because of the great number of allowed transitions to free final states (the selection rules give 70 contributions to the total cross section). However, in varying the parameter $(p_{i+1}-p_i)$, we have observed a great stability in our results.

VI. CONCLUSION

In performing the calculations described in the previous sections, our purpose was to collect more quantitative information about transitions induced by incoming photons. The detection of stimulated radiation in rubidium vapor by Korolev et al., 22 and the experimental observations of the multiphoton ionization effect in alkali vapors and noble gases by Bystrova et al.²³ and by Agostini et al.²⁴ are sufficient to motivate the present computations. The recent observation of singly stimulated twophoton emission and anti-Stokes Raman scattering from metastable deuterium atoms by Braünlich and Lambropoulos²⁵ shows that it is useful to determine the relative importance of the transition probabilities from various processes. The generation of excited states should be of considerable importance for a better understanding of the mechanism producing the ionization of atoms. The analysis of the results shows that the transition rate depends



FIG. 6. Dispersion rate σ_I/I^2 for three-photon ionization of H in the 2s state versus the wavelength λ_p of the incident light. The upper bound is $\epsilon_B^{(3)} < 10^{-15}$

strongly on the radiation wavelength. However, in comparing a bound-free transition with a bound-bound transition, we can define an I_s threshold as the particular photon intensity for which the ioniza-



FIG. 7. (a) Dispersion rate σ_I/I^5 for six-photon ionization of H in the ground state. The upper bound is $\epsilon_B^{(6)}$ <10⁻⁵. (b) Dispersion rate σ_I/I^7 for eight-photon ionization of H in the ground state. Presently calculated, solid lines; results obtained from a former computation (Ref. 12), dashed lines; data calculated by Bebb and Gold (Ref. 6), "dot-dashed" lines.

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tion cross section Eq. (10) is equal to the Ramanlike transition cross section Eq. (2) $[\sigma_{(I)}(I_s)/\sigma_{(E)}(I_s)]$ = 1]. Then, we observe that the direct multiphoton ionization process is the dominant one when the intensity I is greater than I_s . From the values taken by the two cross sections $\sigma_{(I)}$ and $\sigma_{(E)}$ in some particular cases, we have deduced interesting results for the I_s threshold. At 6943 Å, we have obtained $I_s = 10^9 \text{ W/cm}^2$ for a 1s - 2p transition [Figs. 3 and 7(b)]. At 5300 Å, the threshold is $I_s = 5 \times 10^6$ W/cm^2 for a 1s - 1s transition [Figs. 2 and 7(a)]. At 3471.5 Å, we find the intensities $I_s = 10^8 \text{ W/cm}^2$ for a 1s - 1s transition, and $I_s = 2 \times 10^5 \text{ W/cm}^2$ for a 1s - 2s transition (Fig. 1 and Fig. 3 of Ref. 12). From these results, we shall conclude that each case requires a detailed analysis of multiphoton processes.

We can go further in our investigations by considering the case of resonance. At 5128.65 Å, the five-photon energy coincides with the energy of the Lyman-(1s - 3p) line. The sixth-order (1s - 3p - c) ionization rate of hydrogen in the ground state and the sixth-order (1s - 3p - 2s)transition rate both are resonant process [Figs. 2 and 7(a)]. The related probabilities per unit time can be evaluated by means of Eq. (23). To do that, we need to know the probabilities $W_s^{(1)}(3p-2s)$, $W_I^{(1)}(3p - c) \simeq 20I, \gamma_{3p}$ which have been discussed in literature, ²⁰ and the fifth-order (1s - 3p) absorption probability which is $W_A^{(5)}(1s - 3p) = 4.8 \times 10^{-41} I^5 g(5E_p)$. The computed values of each rate are $W_I^{(6)}(1s - 3p - c) = 2 \times 10^{-56} I^6$ and $W_E^{(6)}(1s - 3p - 2s)$ = 2. $4 \times 10^{-51} I^5$. In order to determine the role played by resonances in multiphoton processes, these probabilities have to be compared with the corresponding data in a different situation. Out of resonance, at 5100 Å, one finds $W_I^{(6)}(1s - c) = 2 \times 10^{-68} I^6$ and $W_E^{(6)}(1s \to 2s) = 8 \times 10^{-63} I^5$. If the intensity is increased by a factor of 100 for incoming photons at 5100 Å, we can note that the corresponding probabilities may reach the values obtained in the case of resonance.

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APPENDIX

To discuss the accuracy of numerical results, it is necessary to determine the sources of uncertainty and to calculate upper bounds. It seems to be impractical to try to correct errors after each step in the computation; but it is possible to improve a prior routine in order to derive smaller upper bounds. The estimation of these bounds is simultaneous with the evaluation of the numerical solution.

As a consequence of definition [Eqs. (34) and (35)], the solution of Eq. (37) is an analytic function $y_{\nu}(l_{j+1}, l_{j+2}, \ldots, L | p)$. It may be expanded in a Taylor series

$$y^{j}(p_{i+1}) = \sum_{m=0}^{\max} a_{m}^{j}(i) (p_{i+1} - p_{i})^{m}, \qquad (A1)$$

about some point $p_i > 0$. But it is more convenient to use the following form:

$$y^{j}(p_{i+1}) = \sum_{m=0}^{\max} A^{j}_{m}(p_{i}) .$$
 (A2)

The computational procedure which has been described by Zernik, ¹ leads to recursion relations between the $A_m^j(p_i)$'s. For j=N, the (L+1)th derivative of the Laplace transform of the final state function may be determined by formulas in the form

$$A_{m}^{N}(p_{i}) = \beta_{m-2}(i)A_{m-2}^{N}(p_{i}) + \gamma_{m-1}(i)A_{m-1}^{N}(p_{i}).$$
 (A3)

 $\beta_{m-2}(i)$ and $\gamma_{m-1}(i)$ are coefficients depending on L, m, and p_i , which exist only when $m \ge 0$. The absolute error in $A_m^N(p_i)$ is denoted by $\epsilon_m^N(i)$. The error due to the necessity of rounding off each result is ϵ_R , and the relevant error affecting $A_m^N(p_i)$ is $|\epsilon_R A_m^N(p_i)|$. The absolute error $\epsilon_0^N(i)$ in the function $y^N(p_i)$ may be easily computed from analytic expressions such as Eqs. (40) and (41). It propagates through Eq. (A3) into all following terms of the Taylor series. The error resulting from this process is

$$\lambda_m^N(i) = \left| \beta_{m-2}(i) \epsilon_{m-2}^N(i) \right| + \left| \gamma_{m-1}(i) \epsilon_{m-1}^N(i) \right| .$$
 (A4)

We define $\theta_{m-2}(i)$ and $\theta'_{m-1}(i)$ as the errors committed in the computation of $\beta_{m-2}(i)$ and $\gamma_{m-1}(i)$, respectively. They combine to give the term

$$\mu_{m}^{N}(i) = \left| A_{m-2}^{N}(p_{i}) \theta_{m-2}(i) \right| + \left| A_{m-1}^{N}(p_{i}) \theta_{m-1}'(i) \right| .$$
(A5)

Neglecting the contributions to $\epsilon_m^N(i)$ that involve products of errors, the uncertainty in $A_m^N(p_i)$ is

$$\epsilon_m^N(i) = \left| \epsilon_R A_m^N(p_i) \right| + \lambda_m^N(i) + \mu_m^N(i) .$$
 (A6)

In order to follow the accumulation of errors, we must examine how $\epsilon_m^N(i)$ propagates into the next equation with j = N - 1, and then into the following ones. The coefficients of the Taylor series formed about the initial point $p_i = \alpha_j$ verify recursion relations in the form

$$A_{m}^{j}(\alpha_{j}) = \eta_{m+2}(i)A_{m+2}^{j+1}(\alpha_{j}) + \chi_{m+1}(i)A_{m+1}^{j+1}(\alpha_{j}) + \beta_{m-1}(i)A_{m-1}^{j}(\alpha_{j}) .$$
(A7)

Proceeding as before, we can obtain

$$\lambda_{m}^{j}(i) = \left| \eta_{m+2}(i) \epsilon_{m+2}^{j+1}(i) \right| + \left| \chi_{m+1}(i) \epsilon_{m+1}^{j+1}(i) \right|$$

(10)

$$\mu_{m}^{j}(i) = \left| A_{m+2}^{j+1}(\alpha_{j}) \phi_{m+2}(i) \right| + \left| A_{m+1}^{j+1}(\alpha_{j}) \phi_{m+1}'(i) \right|$$

$$+ \left| A_{m-1}^{j}(\alpha_{j}) \theta_{m-1}(i) \right| , \quad (A9)$$

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where $\phi_{m+2}(i)$ and $\phi'_{m+1}(i)$ represent the errors in $\eta_{m+2}(i)$ and $\chi_{m+1}(i)$, respectively. Finally, we obtain

$$\epsilon_m^j(i) = \left| \epsilon_R A_m^j(\alpha_j) \right| + \lambda_m^j(i) + \mu_m^j(i) .$$
 (A10)

Starting from the solution at the point p_i , we must solve the equation at the point p_{i+1} . We have

$$y^{j}(p_{i+1}) = \sum_{m=0}^{\max} A^{j}_{m}(p_{i}) = A^{j}_{0}(p_{i+1}) .$$
 (A11)

The total error in $A_0^j(p_{i+1})$ is

$$\epsilon_{0}^{j}(i+1) = \sum_{m=0}^{\max} \epsilon_{m}^{j}(i) + \epsilon_{T}^{j}(i) + \left| \epsilon_{R} A_{0}^{j}(p_{i+1}) \right| , \quad (A12)$$

where $\epsilon_T^j(i)$ denotes the truncation error committed by summing only a finite number of terms in Eq. (A11). The error $\epsilon_m^j(i+1)$ in $A_m^j(p_{i+1})$ and all other successive errors can be computed as $\epsilon_m^j(i)$.

Since the Taylor series considered in Eq. (A1) depends on the difference $(p_{i+1} - p_i)$, it can be made as quickly convergent as desired. In addition, it

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may be noted that two successive a_i^j coefficients have opposite signs. In most cases, $(p_{i+1} - p_i)$ is positive and Eq. (A2) represents an alternating convergent series that is terminated after calculating about 50 terms. In doing this, we introduce a truncation error which is no greater than the first term neglected. In Raman scattering calculations it happens that $(p_{i+1} - p_i) < 0$; then the truncation error is estimated to be less than the last term retained. But in all cases, experience has shown that the errors caused by truncating the infinite series are usually small for the $(p_{i+1} - p_i)$ values employed in the computation. Thus, it appears that the errors affecting the precision of the solution are mainly due to the use of numbers that are subjected to round-off. From the $\epsilon_m^j(i)$'s, we can derive an upper bound ϵ_B^j on the relative error committed in the numerical evaluation of $|\mathfrak{M}^{(N)}(E_p, E_s)/E_p^{N-1}|$. This bound is generally smaller than the error introduced by the physical constants such as r_0 and I_0 . Although ϵ_B^j probably does not represent the smallest upper bound, it has the advantage of being easily evaluated without a prohibitive expense of machine time. When the parameter $(p_{i+1} - p_i)$ is varied, the values taken by the upper bound present minima; in contrast, the first significant figures of the numerical solution remain unchanged so that the final result seems to possess a good stability and a sufficient precision.

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