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## The infinite summations of perturbation theory in atomic multiphoton ionization

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**Abstract.** The infinite summations over the complete set of unperturbed atomic states appearing in the  $N$ th-order time-dependent perturbation theory applied to atomic multiphoton ionization are performed using the Green's function formalism. In order to test the method extended calculations of the cross section for two- and three-photon ionization for atomic hydrogen are made and numerical comparison is shown with the values obtained by different methods. The resonant character of the process is made evident since the poles of the radial part of the Green's function represent the actual energy spectrum of the atom. The relevant transition matrix elements are written in closed form and then computed exactly without averaging over the intermediate states. The cross section values vanish for circularly polarized light for some incident photon energies between two successive intermediate resonances and close to them: this explains the deep valleys that are present in the ratio of the cross sections for circularly and linearly polarized light.

### 1. Introduction

Perturbation methods are currently employed in order to describe theoretically multiphoton absorption and to calculate the multiphoton ionization probability rate under the action of strong electromagnetic fields for incident photon fluxes when the theory is still valid. When  $N$ th-order time-dependent perturbation theory is applied, a major difficulty found in such calculations is the infinite summation over the complete set of unperturbed atomic states, discrete plus continuum, related to the transition matrix of perturbation theory (see equation (6)).

Different approaches were used in order to solve this problem. Bebb and Gold (1966) performed, in an approximate manner, the summation by introducing an average frequency  $\bar{\omega}$  related to the real energy spectrum of the atom. In this fashion the infinite summation is replaced by an average term so that the closure property of Hilbert vector space for the Schrödinger wavefunctions can be utilized to remove the intermediate-state transitions from the problem. Morton (1967) carried out similarly an averaging over the numerators replacing each set of intermediate levels by one effective level and using the classical oscillators strengths to estimate the matrix elements. Gontier and Trahin (1968) made exact calculations for atomic hydrogen relating the infinite summations to the numerical solutions of a set of first-order differential equations.

Recently the Green's function method was used in order to perform the summations (Zon *et al* 1972, Arnous *et al* 1973). This presents the advantage that for the particular case of a pure Coulomb potential, i.e., for hydrogenic atoms, the relevant transition matrix elements can be evaluated analytically in closed form since the radial Coulomb Green's function for angular momentum  $l$  is known explicitly, then the exact calculations are possible. In order to test this last method extended calculations are presented in this work for the multiphoton ionization cross sections in atomic hydrogen produced by the absorption of two and three photons. Comparison is made with exact computations published elsewhere using different methods.

## 2. Fundamental equations

We analyse the theory of multiphoton absorption by direct application of the  $N$ th-order time-dependent perturbation theory using the concept of the evolution operator. Since these theoretical tools are only occasionally used in atomic physics, we give a brief deduction of the cross section expression for multiphoton atomic ionization using the path-integral method, taking special care to discuss the meaning of the intermediate virtual states.

In the interaction representation the probability amplitude for the process in which the system, initially in the state represented by the free ket  $|g\rangle$  at time  $-\tau$ , should be in the  $|f\rangle$  state at time  $+\tau$  is given by:

$$\langle f|U_1(\tau, -\tau)|g\rangle$$

where  $U_1(\tau, -\tau)$  is the evolution operator which is formally defined by the integral equation

$$U_1(t, t_0) = 1 + i^{-1} \int_{t_0}^t H'_1(t') U_1(t', t_0) dt' \quad (1)$$

in atomic units.

$H'_1(t)$  is the interaction Hamiltonian between the electron and the field in the interaction representation,  $H_1$  being the interaction Hamiltonian in the Schrödinger one:

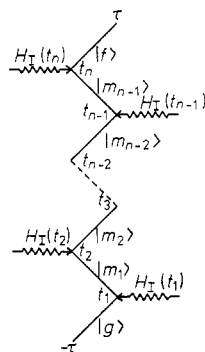
$$H'_1(t) = e^{iH_0 t} H_1 e^{-iH_0 t}$$

where  $H_0$  is the Hamiltonian of the free system.

When we make  $\tau \rightarrow \infty$  the evolution operator  $U_1$  becomes the  $S$  operator but it is necessary to make the interaction time  $\tau \rightarrow \infty$  only when all the mathematical calculations have been performed and the physical quantities obtained.

We obtain the following expression for the  $N$ th-order contribution to the probability amplitude for the transition from  $|g\rangle$  to  $|f\rangle$  by successive iteration of the integral equation (1):

$$\begin{aligned} \langle f|U_1^{(N)}(\tau, -\tau)|g\rangle &= i^{-N} \sum_{m_{N-1}} \sum_{m_{N-2}} \dots \sum_{m_k} \dots \sum_{m_2} \sum_{m_1} \int_{-\tau}^{\tau} dt_N \int_{-\tau}^{t_N} dt_{N-1} \dots \int_{-\tau}^{t_{N-1}} dt_k \dots \\ &\times \int_{-\tau}^{t_2} dt_1 \exp[i(E_f - E_{m_{N-1}})t_N] \exp[i(E_{m_{N-1}} - E_{m_{N-2}})t_{N-1}] \dots \\ &\times \exp[i(E_{m_k} - E_{m_{k-1}})t_k] \dots \exp[i(E_{m_1} - E_g)t_1] \langle f|H_1|m_{N-1}\rangle \\ &\times \langle m_{N-1}|H_1|m_{N-2}\rangle \dots \langle m_k|H_1|m_{k-1}\rangle \dots \langle m_1|H_1|g\rangle. \end{aligned}$$



**Figure 1.** Formal diagram of a multiphoton absorption process in  $N$ th-order time-dependent perturbation theory.

This expression may be written again in the following form

$$\begin{aligned}
 & \langle f | U^{(N)}(\tau, -\tau) | g \rangle \\
 &= i^{-N} \sum_{m_{N-1}} \dots \sum_{m_k} \dots \sum_{m_1} \langle f | H_1 | m_{N-1} \rangle \dots \langle m_k | H_1 | m_{k-1} \rangle \dots \\
 & \times \langle m_1 | H_1 | g \rangle \int_{-\tau}^{\tau} dt_N \int_{-\tau}^{t_N} dt_{N-1} \int_{-\tau}^{t_{N-1}} dt_{N-2} \dots \int_{-\tau}^{t_{k-1}} dt_k \dots \int_{-\tau}^{t_2} dt_1 \\
 & \times \exp [i(E_f - E_g)t_N] \exp [i(E_{m_{N-1}} - E_g)(t_{N-1} - t_N)] \\
 & \times \exp [i(E_{m_{N-2}} - E_g)(t_{N-2} - t_{N-1})] \dots \exp [i(E_{m_k} - E_g)(t_k - t_{k+1})] \dots \\
 & \times \exp [i(E_{m_1} - E_g)(t_1 - t_2)]. \quad (2)
 \end{aligned}$$

This last term is related to the formal diagram indicated on figure 1 which describes the system evolution from  $|g\rangle$  to  $|f\rangle$  via the intermediate states  $|m_1\rangle, |m_2\rangle, \dots, |m_{N-1}\rangle$  under the effect of  $N$  transitions at times  $t_1, \dots, t_N$ .

In order to obtain the  $N$ th-order contribution it is necessary to make all the paths of this kind interfere by integrating over  $t_N$  from  $-\tau$  to  $\tau$  and over  $(t_{N-1} - t_N), \dots, (t_1 - t_2)$  between  $-\tau$  and 0 and summing over the intermediate states  $|m_{N-1}\rangle, |m_{N-2}\rangle, \dots, |m_1\rangle$ .

The interference between the different paths are defined in the sense of the path-integral method where the phase factors in formula (2) play an essential role (Feynman 1948, Feynman and Hibbs 1965). Finally we introduce the limit  $\tau \rightarrow \infty$ , this operation yields the distribution.

It is important in the path-integral formalism to analyse the different cases that may occur when different possibilities are considered in relation to the phase factors. First of all let us fix the intermediate states  $|m_{N-1}\rangle, \dots, |m_1\rangle$  and their respective time durations  $(t_{N-1} - t_N), \dots, (t_1 - t_2)$ . The integration of  $\exp[i(E_f - E_g)t_N]$  in expression (1) makes the interference between the different paths destructive

if  $(E_f - E_g)\tau \gg 1$ . It is evident that the probability amplitude vanishes when the energy of the initial state is not equal to that of the final state since

$$i^{-1} \int_{-\tau}^{\tau} \exp [i(E_f - E_g)t_N] dt_N = -2\pi i \delta^{(\tau)}(E_f - E_g)$$

where

$$\delta^{(\tau)}(E_f - E_g) = \frac{1}{\pi} \frac{\sin(E_f - E_g)\tau}{(E_f - E_g)}. \quad (3)$$

This function has no limit when  $\tau \rightarrow \infty$  but in the distribution sense  $\delta^{(\tau)}(E_f - E_g)$  yields the Dirac distribution  $\delta(E_f - E_g)$ .

Now let us suppose that  $E_f = E_g$  and let us integrate over the intermediate transition time intervals  $(t_{N-1} - t_N), \dots, (t_1 - t_2)$ , after fixing the intermediate states  $|m_{N-1}\rangle, \dots, |m_1\rangle$ . Then two cases may occur.

(i) If we choose an energy value such that  $E_{m_k} = E_f = E_g$ , the phase factor in the relevant integral in equation (2) is the same for every value of the interval  $(t_k - t_{k+1})$ . Then all the paths interfere constructively and the intermediate transition time duration can give all the possible values. We then have a real intermediate state and the relevant transition represents a resonance.

(ii) If we take  $E_{m_k} \neq E_f, E_g$ , from one path to another the phase varies. There is a partially destructive interference and we have to calculate the integral

$$\lim_{\tau \rightarrow \infty} i^{-1} \int_{-2\tau}^0 \exp [-i(E_g - E_{m_k})u] du \quad (4)$$

where  $u = t_k - t_{k+1}$ .

This integral has no limit in the sense of a function but from the point of view of the distribution theory the limit of the integral (4) when  $\tau \rightarrow \infty$  is defined by

$$\lim_{\epsilon \rightarrow 0+} \frac{1}{E_g - E_{m_k} + i\epsilon}$$

where the convergence factor  $\epsilon$  introduced into the phase can be as small as is wanted. It is obvious that when  $E_g \neq E_{m_k}$  the result of (4) is equal to  $(E_g - E_{m_k})^{-1}$ . We are thus faced with a virtual transition and this may be the physical meaning of these transitions when the  $N$ th-order time dependent perturbation theory is applied to a multiphoton absorption process.

Following this formalism, taking into account equations (2), (3), (4), and using the non-relativistic dipole approximation, it is not difficult to obtain the differential cross section per atom for multiphoton ionization derived previously using somewhat different methods (Bebb and Gold 1966).

$$\frac{d\sigma_{f,g}^{(N)}(\theta_k, \phi_k)}{I^{N-1} d\Omega_k} = \frac{1}{(2\pi)^2} (2\pi\alpha)^N \omega |K_{f,g}^{(N)}|^2 k \quad (5)$$

where  $K_{f,g}^{(N)}$  is the matrix element for the transition from the initial atomic state  $g$  to the final one  $f$  of the ejected electron, after disentangling the radiation from the atomic states, and is given by:

$$K_{f,g}^{(N)} = \sum_{a_{N-1}} \sum_{a_{N-2}} \dots \sum_{a_2} \sum_{a_1} \frac{\langle f|R|a_{N-1}\rangle \langle a_{N-1}|R|a_{N-2}\rangle \dots \langle a_1|R|g\rangle}{\omega_{a_{N-1},g} - (N-1)\omega} \dots \frac{\langle a_1|R|g\rangle}{\omega_{a_1,g} - \omega}. \quad (6)$$

$R$  is the dipolar momentum operator and  $\omega_{a_i,g} = E_{a_i} - E_g$ ,  $\omega$  is the photon frequency,  $\alpha$  the electromagnetic interaction constant,  $I$  the intensity of incident radiation,  $k$  and  $\theta_k$ ,  $\phi_k$  are respectively the radial and angular parts of the ejected-electron wave-vector  $k$ .

The total cross section is obtained by integrating the angular part of  $k$ .

### 3. Green's function method

As we have shown, to the first non-vanishing order in the non-relativistic approximation, the cross section for the  $N$ -photon ionization is related to the term  $K_{f,g}^{(N)}$  which is the matrix element for the transition from the initial state  $g$  to the final one  $f$  of the ejected electron. The main difficulty that arises is the evaluation of  $K_{f,g}$  since this is expressed as an infinite summation through the complete set of real atomic states. We have calculated this by using the Green's function method. If the eigenfunction development of the Green's function is used  $K_{f,g}$  may be written as follows:

$$K_{f,g}^{(N)} = \langle f(r_1) | (r_1 \cdot \epsilon) G(E_g + (N-1)\omega; r_1, r_2) (r_2 \cdot \epsilon) G(E_g + (N-2)\omega; r_2, r_3) \dots \\ \times (r_{N-1} \cdot \epsilon) G(E_g + \omega; r_{N-1}, r_N) (r_N \cdot \epsilon) | g(r_N) \rangle \quad (7)$$

where  $\epsilon$  is the unit polarization vector,  $r$  the electron radius vector and  $G(E, r, r')$  the valence-electron Green's function for virtual or real electron states of energy  $E$ . After separating the angular variables, this last may be written as:

$$G(E; r, r') = \sum_{l,m} g_l(E; r, r') Y_l^m(\theta, \phi) Y_l^{m*}(\theta', \phi') \quad (8)$$

where  $g_l$  is the Green's function of the radial Schrödinger's equation for angular momentum  $l$ . In order to assess the method, this was applied to atomic hydrogen where exact calculations are possible, so avoiding any approximation. In this case  $g_l$  may be expressed for the case of electron bound states ( $E < 0$ ) as

$$g_l(E; r, r') = \frac{\Gamma(l+1-\nu)}{\Gamma(2l+2)} \frac{\nu}{rr'} W_{\nu, l+\frac{1}{2}}\left(\frac{2r_{>}}{\nu}\right) M_{\nu, l+\frac{1}{2}}\left(\frac{2r_{<}}{\nu}\right) \quad (9)$$

(Zon *et al* 1972),  $W$  and  $M$  being the Whittaker functions;  $r_{>}$  ( $r_{<}$ ) is the larger (smaller) of the variables  $r$  and  $r'$ , and the principal quantum number  $\nu$  (for real or virtual states) is given by  $\nu = (-2E)^{-1/2}$ .

The general expression of the Whittaker functions are (Bateman 1953).

$$M_{k,\mu}(x) = e^{-x/2} x^{c/2} \Phi(a, c, x) \quad (10)$$

$$W_{k,\mu}(x) = e^{-x/2} x^{c/2} \Psi(a, c, x) \quad (11)$$

with  $a = \frac{1}{2} - k + \mu$  and  $c = 2\mu + 1$ .

In this work several developments of the functions  $\Phi$  and  $\Psi$  were used according to the values presented by the argument, small or large ones.

Knowing that in our case  $c = 2\mu + 1 = 2l + 2$  is always an integer, we can use the logarithmic expansion for  $\Psi$ :

$$\begin{aligned} \Psi(a, n+1; x) = & \frac{(-1)^{n-1}}{n! \Gamma(a-n)} \left( \Phi(a, n+1; x) \log x + \sum_{r=0}^{\infty} \frac{(a)_r}{(n+1)_r} \right. \\ & \times [\psi(a+r) - \psi(1+r) - \psi(1+n+r)] \frac{x^r}{r!} \Big) \\ & + \frac{(n-1)!}{\Gamma(a)} \sum_{r=0}^{n-1} \frac{(a-n)_r}{(1-n)_r} \frac{x^{r-n}}{r!} \quad (n = 0, 1, 2, \dots). \end{aligned} \quad (12)$$

The last sum is to be omitted if  $n = 0$ .  $\psi(x)$  is the logarithmic derivative of  $\Gamma(x)$ .

Also we have used the asymptotic expansion given by

$$\Psi(a, c, x) = \sum_{n=0}^{N-1} (-1)^n \frac{(a)_n (a-c+1)_n}{n!} x^{-a-n} + O(|x|^{-a-N-1}) \quad (13)$$

where the  $N$ th term is the smallest in the expansion.

For  $\Phi$  we have used the expansion

$$\Phi(a, c, x) = \sum_{n=0}^{\infty} \frac{(a)_n (x)^n}{(c)_n n!} \quad (14)$$

and the asymptotic expansion

$$\begin{aligned} \Phi(a, c, x) = & \frac{\Gamma(c)}{\Gamma(c-a)} (e^{i\pi\epsilon}/x) \sum_{n=0}^{M-1} \frac{(a)_n (a-c+1)_n (-x)^{-n}}{n!} + O(|x|^{-a-M-1}) \\ & + \frac{\Gamma(c)}{\Gamma(a)} e^{x\chi^{a-c}} \sum_{n=0}^{N-1} \frac{(c-a)_n (1-a)_n x^{-n}}{n!} + O(|e^{x\chi^{a-c}} x^{-N-1}|). \end{aligned} \quad (15)$$

$\epsilon = 1$  if  $\text{Im } x > 0$ ,  $\epsilon = -1$  if  $\text{Im } x < 0$ , where the  $M$ th and  $N$ th terms are the smallest in the expansion.

The four expansions in power series given by (12) (13) (14) and (15) have in fact been used to calculate the Whittaker functions  $W$  and  $M$ . The expansions (12) and (14) are infinite and are used only for small values of the argument modulus, less than 10 au approximately. The expressions (13) and (15) are limited and are used for great values of the argument modulus, more than 10 au approximately. Extended numerical computations have been made showing that the junction between the non-asymptotic and the asymptotic expansions is made in a large range around 10 au. This fact permits us to use the asymptotic development for large values of the argument giving the same results as the non-asymptotic one, the great advantage being the reduction of the calculation time.

## 4. Two-photon ionization

### 4.1. Linearly polarized radiation

In the case of the photon-ionization of the hydrogen in the ground state we take as the initial 1S eigenfunction

$$|g\rangle = 2 e^{-r} Y_0^0(\hat{r})$$

written in atomic units, and as the final state a Coulomb wavefunction.

$$|f\rangle = \left(\frac{\pi}{2k}\right)^{1/2} \sum_l i^l (2l+1) e^{-i\eta_l} R_{k,l}(r) P_l(k, r) \quad (16)$$

with

$$P_l(k, r) = \frac{4\pi}{2l+1} \sum_m Y_l^{m*}(\hat{k}) Y_l^m(\hat{r})$$

and

$$\eta_l = \arg \Gamma(l+1-i/k)$$

and

$$R_{k,l}(r) = \frac{C_k}{(2l+1)!} \frac{i^{-(l+1)}}{2k^{3/2}r} M_{-i/k, l+\frac{1}{2}}(2ikr) \quad (17)$$

with

$$C_k = \left(\frac{2}{\pi}\right)^{1/2} k e^{\pi/2k} |\Gamma(l+1-i/k)|.$$

Now we have to evaluate

$$K_{f,g}^{(2)} = \langle f(r_1) | (r_1 \cdot \epsilon_L) G_{E_g+w}(r_1, r_2) (r_2 \cdot \epsilon_L) | g(r_2) \rangle. \quad (18)$$

In the case of the linearly polarized light we take the polar axis of the spherical coordinates along the direction of the photon unit polarization vector:

$$r \cdot \epsilon_L = \left(\frac{4\pi}{3}\right)^{1/2} r Y_1^0(\hat{r}) \quad (19)$$

thus we obtain for  $K_{f,g}^{(2)}$

$$\begin{aligned} K_{f,g}^{(2)} = & + \frac{16\pi^2}{3k} v e^{\pi/2k} \sum_{l_f, m_f} \sum_{l, m} Y_{l_f}^{m_f}(\hat{k}) \exp(i\eta_{l_f}) \frac{|\Gamma(l_f+1-i/k)|}{(2l_f+1)!} \\ & \times \frac{\Gamma(l+1-\nu)}{\Gamma(2l+2)} \int_0^\infty r dr M_{i/k, l_f+\frac{1}{2}}(-2ikr) \int_0^\infty r'^2 dr' e^{-r'} M_{\nu, l+\frac{1}{2}}\left(\frac{2r'}{v}\right) \\ & \times W_{\nu, l+\frac{1}{2}}\left(\frac{2r}{v}\right) \int d\Omega_1 Y_{l_f}^{m_f*} Y_1^0 Y_l^m \int d\Omega_2 Y_l^{m*} Y_1^0 Y_0^0. \end{aligned} \quad (20)$$

Integrating over the angular part and using the properties of the  $3J$ -Wigner symbols we can see that the only possible final angular momentum  $l$  are  $l_f = 0$  and  $l_f = 2$  (Edmonds 1960).

Thus we have two possible channels for  $l$

$$0 \rightarrow 1 \rightarrow 2 \quad \text{and} \quad 0 \rightarrow 1 \rightarrow 0.$$

The selection rules also impose  $\Delta m = 0$  during the transitions. Thus we obtain

$$\begin{aligned} K_{f,g}^{(2)} = & - \frac{2\pi i}{qk} v e^{\pi/2k} e^{i\eta_0} |\Gamma(1-i/k)| \Gamma(2-\nu) \mathcal{M}_{1,0} Y_0^0(\hat{k}) \\ & - \frac{i\pi}{2 \cdot 3^3 \cdot 5^{3/2} k} v e^{\pi/2k} e^{i\eta_2} |\Gamma(3-i/k)| \Gamma(2-\nu) \mathcal{M}_{1,2} Y_2^0(\hat{k}) \end{aligned} \quad (21)$$



where

$$\begin{aligned} \mathcal{M}_{l,l_f} = & \int_0^\infty r \, dr \, M_{i/k, l_f + \frac{1}{2}}(-2ikr) W_{v, l + \frac{1}{2}}(2r/v) \int_0^r r'^2 \, dr' \, M_{v, l + \frac{1}{2}}(2r'/v) e^{-r'} \\ & + \int_0^\infty r \, dr \, M_{i/k, l_f + \frac{1}{2}}(-2ikr) M_{v, l + \frac{1}{2}}(2r/v) \int_r^\infty r'^2 \, dr' e^{-r'} W_{v, l + \frac{1}{2}}(2r'/v). \end{aligned} \quad (22)$$

For the first integral in the expression for  $\mathcal{M}_{l,l_f}$ , the condition  $r' < r$  is always satisfied and it is then possible to make  $r_< \equiv r'$ . On the other hand, for the second integral, the condition  $r' > r$  is satisfied thus permitting us to make the identification  $r_> \equiv r'$ . Obviously, in both cases the logical definitions of  $r_>$  and  $r_<$  have been taken into account.

#### 4.2. Circularly polarized light

In this case we take the polar axis of the spherical coordinates along the wavevector of the incoming photons. So we have

$$r \cdot \epsilon_C = - \left( \frac{4\pi}{3} \right)^{1/2} r Y_1^1(\hat{r}) \quad (23)$$

and we obtain for  $K_{f,g}^{(2)}$

$$\begin{aligned} K_{f,g}^{(2)} = & \frac{16i\pi^2}{3k} v e^{\pi/2k} \sum_{l_f, m_f} \sum_{l, m} Y_{l_f}^{m_f}(\hat{k}) \exp(i\eta_{l_f}) |\Gamma(l_f + 1 - i/k)| \frac{\Gamma(l + 1 - v)}{\Gamma(2l + 2)} \mathcal{M}_{l, l_f} \\ & \times \int d\Omega_1 Y_{l_f}^{m_f*} Y_1^1 Y_l^m \int d\Omega_2 Y_l^{m*} Y_1^1 Y_0^0. \end{aligned} \quad (24)$$

In this case the selection rules are given again by the properties of the  $3J$ -Wigner symbols and we can see easily that the only possible final angular momentum is  $l_f = 2$ . Then we have only one possible channel for  $l$

$$0 \rightarrow 1 \rightarrow 2$$

and as the selection rules impose that  $\Delta m = 1$  during the transitions, that is to say  $m \rightarrow 0 \rightarrow 1 \rightarrow 2$ , finally we obtain for  $K_{f,g}^{(2)}$

$$K_{f,g}^{(2)} = \frac{\pi}{2^{3/2} \cdot 3^{5/2} \cdot 5^{3/2} k} v \Gamma(2 - v) e^{\pi/2k} |\Gamma(3 - i/k)| \mathcal{M}_{1,2} Y_2^2(\hat{k}). \quad (25)$$

### 5. Three-photon case

#### 5.1. Linearly polarized light

It is necessary to evaluate the following expression:

$$K_{f,g}^{(3)} = \langle f(\mathbf{r}_1) | (\mathbf{r}_1 \cdot \epsilon_L) G_{E_g + 2\omega}(\mathbf{r}_1, \mathbf{r}_2) (\mathbf{r}_2 \cdot \epsilon_L) G_{E_g + \omega}(\mathbf{r}_2, \mathbf{r}_3) (\mathbf{r}_3 \cdot \epsilon_L) | g(\mathbf{r}_3) \rangle. \quad (26)$$

Here we have two intermediate transitions via the states of principal quantum number  $v_1$  after the absorption of two photons and  $v_2$  after the absorption of one photon. We obtain for  $K_{f,g}^{(3)}$

$$K_{f,g}^{(3)} = \frac{(4\pi)^{5/2}}{3^{3/2}k} i v_1 v_2 \sum_{l_f, m_f} \sum_{l_1, m_1} \sum_{l_2, m_2} Y_{l_f}^{m_f}(\hat{k}) \exp(i\eta_{l_f}) \\ \times \frac{|\Gamma(l_f + 1 - i/k)|}{(2l_f + 1)!} \frac{\Gamma(l_1 + 1 - v_1)}{\Gamma(2l_1 + 2)} \frac{\Gamma(l_2 + 1 - v_2)}{\Gamma(2l_2 + 2)} \mathcal{P}_{l_2, l_1, l_f} \\ \times \int d\Omega_1 Y_{l_f}^{m_f*} Y_{l_1}^{m_1} Y_1^0 \int d\Omega_2 Y_{l_1}^{m_1*} Y_1^0 Y_{l_2}^{m_2} \int d\Omega_3 Y_{l_2}^{m_2*} Y_1^0 Y_0^0 \quad (27)$$

with

$$\mathcal{P}_{l_2, l_1, l_f} = \int_0^\infty \int_0^\infty \int_0^\infty r_1 dr_1 M_{i/k, l_f + \frac{1}{2}}(-2ikr_1) r_2 dr_2 W_{v_1, l_1 + \frac{1}{2}}\left(\frac{2r_>}{v_2}\right) \\ \times M_{v_1, l_1 + \frac{1}{2}}\left(\frac{2r_<}{v_1}\right) r_3^2 dr_3 W_{v_2, l_2 + \frac{1}{2}}\left(\frac{2r_>}{v_2}\right) M_{v_2, l_2 + \frac{1}{2}}\left(\frac{2r_<}{v_2}\right) e^{-r_3}. \quad (28)$$

According to the definitions of  $r_>$  and  $r_<$  for the case corresponding to  $v_1$ ,  $r_>(r_<)$  is the larger (smaller) of the variables  $r_1$  and  $r_2$ ; for the other case corresponding to  $v_2$ ,  $r_>(r_<)$  is the larger (smaller) of the variables  $r_2$  and  $r_3$ . Making the same reasoning as for the expression of  $\mathcal{M}_{l, l_f}$ , the integrals occurring in  $\mathcal{P}_{l_2, l_1, l_f}$  may be written as follows:

$$\mathcal{P}_{l_2, l_1, l_f} = \int_0^\infty r_1 dr_1 M_{i/k, l_f + \frac{1}{2}}(-2ikr_1) W_{v_1, l_1 + \frac{1}{2}}\left(\frac{2r_1}{v_1}\right) \int_0^{r_1} r_2 dr_2 M_{v_1, l_1 + \frac{1}{2}}\left(\frac{2r_2}{v_2}\right) \\ \times W_{v_2, l_2 + \frac{1}{2}}\left(\frac{2r_2}{v_2}\right) \int_0^{r_2} r_3^2 dr_3 e^{-r_3} M_{v_2, l_2 + \frac{1}{2}}\left(\frac{2r_2}{v_2}\right) \\ + \int_0^\infty r_1 dr_1 M_{i/k, l_f + \frac{1}{2}}(-2ikr_1) W_{v_1, l_1 + \frac{1}{2}}\left(\frac{2r_1}{v_1}\right) \\ \times \int_0^{r_1} r_2 dr_2 M_{v_1, l_1 + \frac{1}{2}}\left(\frac{2r_2}{v_1}\right) M_{v_2, l_2 + \frac{1}{2}}\left(\frac{2r_2}{v_2}\right) \int_{r_2}^\infty r_3^2 dr_3 e^{-r_3} \\ \times W_{v_2, l_2 + \frac{1}{2}}\left(\frac{2r_3}{v_2}\right) + \int_0^\infty r_1 dr_1 M_{i/k, l_f + \frac{1}{2}}(-2ikr_1) M_{v_1, l_1 + \frac{1}{2}}\left(\frac{2r_1}{v_1}\right) \\ \times \int_{r_1}^\infty r_2 dr_2 W_{v_1, l_1 + \frac{1}{2}}\left(\frac{2r_2}{v_1}\right) W_{v_2, l_2 + \frac{1}{2}}\left(\frac{2r_2}{v_2}\right) \\ \times \int_0^{r_2} r_3^2 dr_3 e^{-r_3} M_{v_2, l_2 + \frac{1}{2}}\left(\frac{2r_3}{v_2}\right) + \int_0^\infty r_1 dr_1 M_{i/k, l_f + \frac{1}{2}}(-2ikr_1) \\ \times M_{v_1, l_1 + \frac{1}{2}}\left(\frac{2r_1}{v_1}\right) \int_{r_1}^\infty r_2 dr_2 W_{v_1, l_1 + \frac{1}{2}}\left(\frac{2r_2}{v_1}\right) \\ \times M_{v_2, l_2 + \frac{1}{2}}\left(\frac{2r_2}{v_2}\right) \int_{r_2}^\infty r_3^2 dr_3 e^{-r_3} W_{v_2, l_2 + \frac{1}{2}}\left(\frac{2r_3}{v_2}\right). \quad (29)$$

Integrating over the angular part and using the properties of the 3J-Wigner symbols we can see that the only possible final angular momentum values are  $l_f = 1$  and  $l_f = 3$ . Then we have three possible channels for  $l$

$$0 \rightarrow 1 \rightarrow 0 \rightarrow 1$$

$$0 \rightarrow 1 \rightarrow 2 \rightarrow 1$$

$$0 \rightarrow 1 \rightarrow 2 \rightarrow 3.$$

The selection rules also impose  $\Delta m = 0$  during the transitions. Thus we obtain

$$\begin{aligned} K_{f,g}^{(3)} &= \frac{i\pi}{3^{7/2}k} \Gamma(2 - v_2) |\Gamma(2 - i/k)| e^{\pi/2k} v_1 v_2 e^{i\eta_1} Y_1^0(\hat{k}) \\ &\times \left( \Gamma(1 - v_1) \mathcal{P}_{1,0,1} + \frac{\Gamma(3 - v_1)}{2 \cdot 3 \cdot 5^2} \mathcal{P}_{1,2,1} \right) + \frac{i\pi}{2^5 \cdot 3^4 \cdot 5^3 \cdot 7^{3/2}k} \\ &\times \Gamma(2 - v_2) \Gamma(3 - v_1) |\Gamma(4 - i/k)| e^{\pi/2k} v_1 v_2 e^{i\eta_3} Y_3^0(\hat{k}) \mathcal{P}_{1,2,3}. \end{aligned} \quad (30)$$

### 5.2. Circularly polarized light

We obtain

$$\begin{aligned} K_{f,g}^{(3)} &= \frac{(4\pi)^{5/2}}{3^{3/2}k} v_1 v_2 e^{\pi/2k} \sum_{l_f, m_f} \sum_{l_1, m_1} \sum_{l_2, m_2} \exp(i\eta_{l_f}) \frac{\Gamma(l_1 + 1 - v_1)}{\Gamma(2l_1 + 2)} \\ &\times \frac{\Gamma(l_2 + 1 - v_2)}{\Gamma(2l_2 + 2)} \frac{\Gamma(l_f + 1 - i/k)}{(2l_f + 1)!} \mathcal{P}_{l_2, l_1, l_f} \int d\Omega_1 Y_{l_f}^{m_f*} Y_1^1 Y_{l_1}^{m_1} \\ &\times \int d\Omega_2 Y_{l_1}^{m_1*} Y_1^1 Y_{l_2}^{m_2} \int d\Omega_3 Y_{l_2}^{m_2*} Y_1^1 Y_0^0. \end{aligned} \quad (31)$$

In this case the properties of the 3J-Wigner symbols again mean that the only possible final angular momentum is  $l_f = 3$ . We have, therefore, only one channel for  $l$

$$0 \rightarrow 1 \rightarrow 2 \rightarrow 3$$

and for  $m$  the selection rules give  $\Delta m = 1$  during the transitions. We obtain

$$\begin{aligned} K_{f,g}^{(3)} &= \frac{\pi}{2^{11/2} \cdot 3^4 \cdot 5^{5/2} \cdot 7^{3/2}k} \Gamma(2 - v_1) \Gamma(3 - v_2) |\Gamma(4 - i/k)| \\ &\times v_1 v_2 e^{\pi/2k} e^{i\eta_3} Y_3^3(\hat{k}) \mathcal{P}_{1,2,3}. \end{aligned} \quad (32)$$

## 6. Numerical results

The Whittaker functions occurring in the expressions (22) and (29) of  $\mathcal{M}_{l,l_f}$  and  $\mathcal{P}_{l_2, l_1, l_f}$  respectively have been calculated by means of the expansions into convergent power series given by the expressions (12, 13, 14, 15). The low integration limit in (22) and (29) cannot be taken as zero because of the unphysical divergence of the  $W$  function at  $r = 0$ . We have taken as the lowest integration limit  $r = 1 \times 10^{-6} a_0$ ,

**Table 1.** Dispersion values of  $\sigma_L^{(2)}/I$  versus wavelength for two-photon ionization of H from ground state by linearly ( $\sigma_L^{(2)}$ ) and circularly ( $\sigma_C^{(2)}$ ) polarized incident radiation in  $\text{cm}^4 \text{W}^{-1}$ . The results ascribed to Bebb and Gold (1966) are estimated from dispersion curves.

$\lambda(\text{\AA})$	$\sigma_L^{(2)}/I$				$\sigma_C^{(2)}/I$	$\sigma_C^{(2)}/\sigma_L^{(2)}$
	Present work	Gontier and Trahin (1971)	Chan and Tang (1969)	Bebb and Gold (1966)	Present work	Present work
925	2.044(−34)				1.249(−35)	0.061
975	4.923(−33)		5.152(−33)		6.882(−33)	1.397
1020	7.080(−33)	5.522(−33)	6.752(−33)		7.235(−33)	1.021
1100	4.035(−34)	4.049(−33)	4.013(−34)	1.0(−33)	4.284(−34)	1.061
1200	6.417(−32)	5.803(−32)	6.303(−32)	6.6(−33)	7.725(−32)	1.203
1300	1.277(−32)	1.283(−32)	1.276(−32)	1.1(−32)	1.879(−32)	1.471
1400	8.470(−33)	8.453(−33)	8.450(−33)	7.0(−33)	1.270(−32)	1.499
1600	9.182(−33)	9.143(−33)	9.154(−33)	6.8(−33)	1.358(−32)	1.479
1700	1.028(−32)	1.023(−32)	1.025(−32)	8.4(−33)	1.498(−32)	1.457

$a_0$  being the Bohr radius. We have found that the numerical results are not sensitive with respect to the low integration limit provided that the  $r$  values are chosen sufficiently small. All the calculations have been made in double precision using an IBM/370 computer.

The numerical results computed in this work are reported in table 1 and 2 and they are compared with those published elsewhere and calculated using different methods (Bebb and Gold 1966, Chan and Tang 1969, Gontier and Trahin 1971, 1973).

The complexity of the calculations necessary to evaluate the integrals like (22), (29) and the specific numerical methods here involved imply that the final results are approximate and subject to computation errors. Thus it appears necessary to estimate the overall accuracy of our calculations. Errors may occur from the following sources:

**Table 2.** Dispersion values of  $\sigma_L^{(3)}/I^2$  versus wavelength for three-photon ionization of H from ground state by linearly ( $\sigma_L^{(3)}$ ) and circularly ( $\sigma_C^{(3)}$ ) polarized incident radiation in  $\text{cm}^6 \text{W}^{-1}$ . The results ascribed to Bebb and Gold (1966) and to Gontier and Trahin (1973) are estimated from dispersion curves.

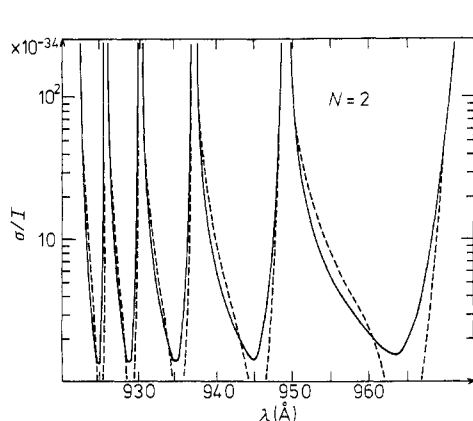
$\lambda(\text{\AA})$	$\sigma_L^{(3)}/I^2$				$\sigma_C^{(3)}/I^2$	$\sigma_C^{(3)}/\sigma_L^{(3)}$
	Present work	Gontier and Trahin (1973)	Bebb and Gold (1966)		Present work	Present work
1840	1.484(−48)				3.610(−48)	2.432
1860	3.604(−47)				6.857(−47)	1.902
1900	1.186(−46)		8.2(−47)		2.479(−46)	2.089
2000	5.581(−48)	5 (−48)	1.2(−47)		1.365(−47)	2.446
2100	2.542(−47)	2.5(−47)	2.2(−47)		5.771(−47)	2.269
2200	1.593(−47)	1.7(−47)	9.8(−48)		3.957(−47)	2.483
2300	2.650(−47)	2.5(−47)	1.3(−47)		3.853(−47)	1.453
2400	7.125(−46)	7 (−46)	4.4(−46)		3.935(−47)	0.055
2500	2.980(−46)	3 (−46)	3.2(−46)		3.998(−47)	0.134
2600	1.008(−46)	1 (−46)	3.6(−47)		3.947(−47)	0.391

(i) truncation of the series expansions used for the Whittaker functions; (ii) the numerical quadrature in calculating the integrals; (iii) the finite number of digits used in the calculation. We will analyse these three points beginning with the last one.

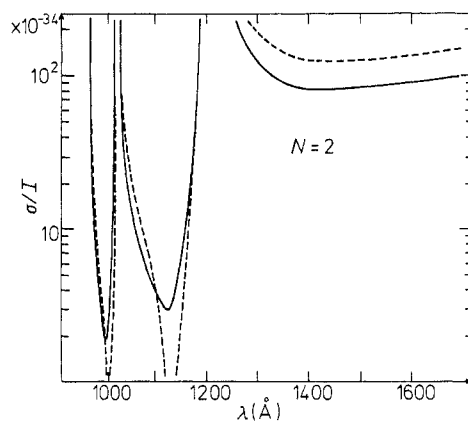
In the last case we have tested the numerical stability of final results by varying the number of digits with which the computation has been made: overall good stability was found. This is to be expected since IBM double precision was used and there is not a significant amount of cancellation in the calculation.

Concerning the truncation error of the series expansion (point (i)), all the series have been calculated using tests of convergence such that the accuracy of the final results is overall accurate to  $10^{-8}$  per cent i.e. the truncation of the series was taken in such form that the numerical stability was obtained on the 10th significant digit. We have also verified that the results are not perturbed when changing the order of operations.

The most important source of error was found to be the numerical quadrature (point (ii)). In fact when calculating an integral with an infinite superior limit, this must first be replaced by a finite one; second the integral is calculated through a finite series expansion which is more or less complicated according to the computing subroutines employed. In our case the calculated integrals are rather rapidly convergent so the error due to the substitution of the infinite limits can be neglected if the high integration limit is large enough. Finally, of the remainder, the use of the finite expansions is the essential cause of error. In order to calculate the integrals occurring in (22) and (29) the different kernels were tabulated and integration subroutines were used yielding the results as a vector (in the sense of numerical computation) of the integral values for a given equidistant  $r$  interval of the  $r$  function values for those integrals involving a variable limit  $r$ ; similar methods and subroutines were used to calculate the final integrals with fixed limits. The absolute error of the quadrature methods depends on the integration step  $h$ , including the truncation and the rounding ones. In fact the local absolute truncation error  $\epsilon$  for each step is proportional to the power of the step  $h^p$ ,  $p$  being an integer number. However, this last error may accumulate so it is necessary to take as the total truncation error the product  $N\epsilon$ ,  $N = L/h$ ,  $N$  and  $L$  being the number of steps and the whole integration interval, respectively. In our case the subroutine employed presents a local truncation error proportional to  $h^6$ . On the other hand the rounding error is given by  $cL/h$  where  $c$  is the rounding error for each step; so this last is proportional to  $1/h$ . Therefore there exists an optimum step value for which the total quadrature error is a minimum, i.e. it is not possible to choose a step value as small as wanted. It was observed that the numerical stability also depends on the wavelength  $\lambda$  of the incident photons via the high integration limit: for small values of the wavelength the limit must be chosen to be greater than for large values of  $\lambda$ , thus the whole integration interval depends on the wavelength. In fact we have taken as the high integration limit the values of  $r$  given by  $r = 160v_f/2$  atomic units where  $v_f$  is the principal quantum number of the virtual state before ionization. Finally the practical computation was performed in the following manner for sufficiently small ranges around the different wavelength values: some initial step value  $h_1$  was chosen, successive calculations were made with decreasing values of  $h$  until the best numerical stability was obtained for a step  $h_0$  which was considered the optimum; smaller values than  $h_0$  lead to broken stability. For instance, for the three-photon case in a range around 2600 Å the numerical result given in table 2 was calculated with a step of 0.3 au. If recalculated with step values of 0.15 and 0.5 au the differences



**Figure 2.** Dispersion rate  $\sigma/I$  in  $\text{cm}^4 \text{W}^{-1}$  for the two-photon ionization of H in the ground state. Full curves: linearly polarized light; broken curves: circularly polarized light.



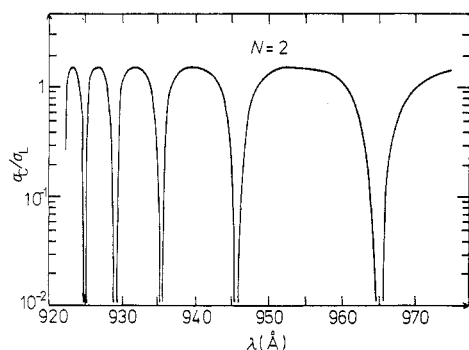
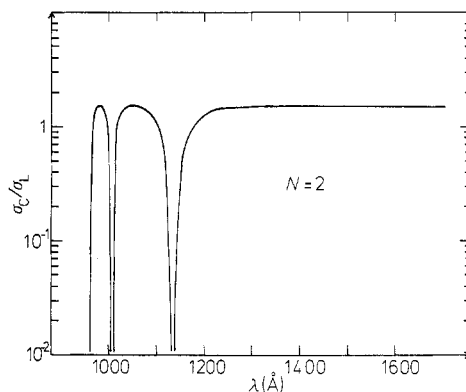
**Figure 3.** Dispersion rate  $\sigma/I$  in  $\text{cm}^4 \text{W}^{-1}$  for the two-photon ionization of H in the ground state. Full curves: linearly polarized light; broken curves: circularly polarized light.

with respect to the first result were of the order of 0.15 per cent and 1 per cent respectively. This kind of error is by far greater than the other errors previously discussed. This same calculation was repeated for every result indicated on tables 1 and 2: as a final conclusion we may say that the overall accuracy in final results is of 1 per cent in the wavelength intervals analysed and that the use of finite series expansions in order to perform the numerical quadratures is the essential source of error in this work.

We have calculated the cross sections for linearly and circularly polarized light and the ratio circular/linear for atomic hydrogen for the two- and three-photon cases in the ranges 920–1700 Å and 1835–2700 Å respectively.

In the first case some of the calculated values are shown in table 1 and compared, for linearly polarized light, with the results published by Bebb and Gold (1966), Chan and Tang (1969) and Gontier and Trahin (1971). The transition rates  $\sigma_L^{(2)}/I$  and  $\sigma_C^{(2)}/I$  are plotted against the wavelength in figures 2 and 3. The ratio  $\sigma_C^{(2)}/\sigma_L^{(2)}$  against wavelength is given in figures 4 and 5. As is shown in table 1 we can see that a good agreement is obtained with the results obtained using other methods of calculation, especially with those presented by Chan and Tang (1969) and Gontier and Trahin (1971, 1973). We point out that intermediate resonances through real atomic states are obtained as well and that the maximum allowed values of the ratio  $\sigma_C^{(2)}/\sigma_L^{(2)}$  predicted by perturbation theory equal to 3/2 (Lambropoulos 1972, Klarsfeld and Maquet 1972, Arnous *et al* 1973) is also obtained in this work as may be seen in table 1. On the other hand we can see that there are values of  $\lambda$  where the cross section  $\sigma_C^{(2)}/\sigma_L^{(2)}$  in circularly polarized light collapses. This is due to the fact that for the linearly polarized radiation there are two possible channels for  $l$ , i.e. there are two matrix elements in the probability amplitude, but in the case of the circularly polarized radiation there is only one possible channel, i.e. one matrix element. This matrix element collapses between two successive intermediate resonances, although in the linear case they do not collapse at the same wavelength.

In the three-photon case some of the calculated values are shown in table 2 and are compared with those estimated from the dispersion curves given by Bebb and Gold (1966) and by Gontier and Trahin (1973). The dispersion curves  $\sigma_L^{(3)}/I^2$  and

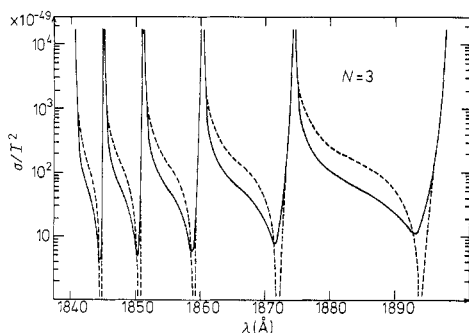
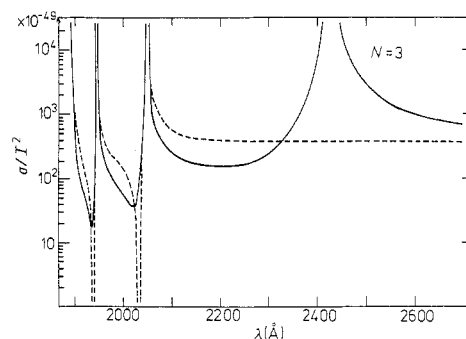
Figure 4. Ratio  $\sigma_c/\sigma_L$  for the two-photon case.Figure 5. Ratio  $\sigma_c/\sigma_L$  for the two-photon case.

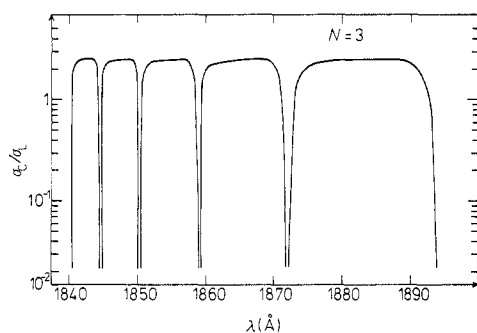
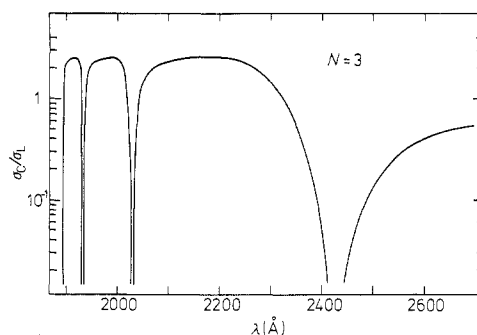
$\sigma_c^{(3)}/I^2$  are plotted against the wavelength in figures 6 and 7 and the ratio  $\sigma_c^{(3)}/\sigma_L^{(3)}$  is plotted in the figures 8 and 9. As we can see a good agreement is obtained, in particular, with the results computed by Gontier and Trahin using another theoretical method. We point out that the intermediate resonances are obtained as well and that the maximum allowed value of the ratio  $\sigma_c^{(3)}/\sigma_L^{(3)}$  predicted by perturbation theory equal to  $5/2$  is also obtained (Klarsfeld and Maquet 1972). The same observation as in the two-photon case is made for the circularly polarized light: there are wavelength values where the transition rate  $\sigma_c^{(3)}/I^2$  collapses.

Finally we observe that in figure 7 for  $\lambda = 2430.045 \text{ \AA}$  a resonance is obtained with linearly polarized light but not with circularly polarized radiation. This is a resonance due to an intermediate  $2S$  state produced by absorption of two photons: this is possible with linearly polarized light but not with circularly polarized light since the atomic  $2D$  state does not exist.

## 7. Conclusion

The infinite summations over the complete set of the unperturbed atomic eigenfunctions appearing in perturbation theory have been performed in exact fashion employing the

Figure 6. Dispersion rate  $\sigma/I^2$  in  $\text{cm}^6 \text{ W}^{-2}$  for the three-photon ionization of H in the ground state. Full curves: linearly polarized light, broken curves: circularly polarized light.Figure 7. Dispersion rate  $\sigma/I^2$  in  $\text{cm}^6 \text{ W}^{-2}$  for the three-photon ionization of H in the ground state. Full curves: linearly polarized light, broken curves: circularly polarized light.

Figure 8. Ratio  $\sigma_C/\sigma_L$  for the three-photon case.Figure 9. Ratio  $\sigma_C/\sigma_L$  for the three-photon case.

Green's function method; no approximations in the sense of averaging over the atomic states were made at all. For the particular case of atomic hydrogen the relevant transition matrix elements to  $N$ th order were calculated exactly since the radial Coulomb Green's function is known explicitly as a combination of Whittaker functions: this makes it possible to write the matrix elements in closed form. The method was applied to atomic hydrogen and extended calculations of the multiphoton ionization cross section for two and three photons were made: overall good numerical stability was found and the final results are in reasonable agreement with others computed with different methods. This approach makes it possible to sum the infinite series of perturbation theory, including the continuous spectrum. Since the poles of the radial Green's function represent the actual energy spectrum of the atom, the resonant character of the multiphoton process is made evident: for every photon energy such that the ionization takes place through an intermediate real atomic state an enhancement of the cross section is obtained (figures 2, 3, 6 and 7). On the other hand for circularly polarized incident radiation the cross section vanishes for some photon energies that lie between two successive resonances but close to them: this explains the deep valleys shown on the curves of the ratio  $\sigma_C/\sigma_L$  (figures 4, 5, 8 and 9).

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