

## Two-photon ionization of alkali-metal atoms in the framework of infinite summations and spin-orbit coupling

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A theoretical method previously developed for the two-photon ionization of alkali-metal atoms is extended to the spin-orbit coupling scheme. We have obtained the Green's function of this problem in the framework of quantum-defect theory and so we have been able to perform the infinite summations related to perturbation theory. The generalized transition probability rates are calculated in the off-resonant and resonant regions, respectively, for polarized incident radiation. Destructive interference effects between the unperturbed atomic states in the infinite summations producing a finite deep minimum in the off-resonant region, are predicted by our theory, both for linearly and circularly polarized incident radiation. A detailed calculation of electron-spin polarization is given. Comparisons of values predicted by the present work with experiment and other theoretical calculations are made for the case of atomic cesium initially in the ground  $6S$  state.

### I. INTRODUCTION

In the last few years, considerable interest has been shown in the study of experimental and theoretical multiphoton processes due to the interaction of intense laser fields with atomic systems. Since in most of the experiments the external laser field strength is small compared to the internal atomic field strength, the theoretical analysis may be based on the time-dependent perturbation theory developed to the lowest nonvanishing order. In the last few years, experimental work has been carried out to determine probability rates for the two-photon ionization of the cesium atom,<sup>1,2</sup> where it is possible to use laser intensities which are not too strong. This permits the application of perturbation theory, which leads to predicted values that may be compared to the measured ones, provided an acceptable atomic model is adopted.

The spin-orbit coupling in unpolarized atoms causes the existence of an important property of the ejected electron beam, the electron-spin polarization, that was theoretically predicted by Fano<sup>3</sup> in the single-photon ionization by circularly polarized light. Although differences exist between the single and multiphoton cases, the physical basis is the same: The spin-orbit interaction in bound states and in the continuum produces the spin orientation of the photoelectrons, the projection axis being the direction of the wave vector  $\mathbf{k}$  of the incident circular light. While in Fano's analysis the electron polarization is only due to the spin-orbit coupling in the  $\epsilon p$  continuum states because the initial state is chosen as the  $6S$  discrete ground state of Cs, in multiphoton processes the spin-orbit coupling in bound states plays an important role when the ionization takes place through a real state, i.e., when an intermediate

resonance is present. On the other hand, in the off-resonance region, when the multiphoton process is performed through virtual states, the influence of the spin-orbit coupling is indirect in the sense that it introduces a greater number of channels than those that exist in its absence, so that it adds more contributions to the total transition amplitude for the same photon energy. This fact may significantly change the behavior of total cross sections as a function of the incident photon energy as will be shown in this paper, for instance, in the Cooper minimum region. This prediction has been recently confirmed by experimental work performed at Saclay.<sup>4</sup>

Measurements have been reported on the photoelectron spin polarization in the two-photon ionization of cesium via the  $7^2P_{1/2, 3/2}$  intermediate states.<sup>5</sup> Theoretical work has been developed in order to obtain characteristic features for the same system.<sup>6,7</sup> In both papers, perturbation theory to the lowest nonvanishing order was employed and the relevant matrix elements were calculated semiempirically using models for the atomic structure such as quantum-defect theory and model potentials as well as experimental oscillator strengths. Truncated summations over a finite number of states served as substitutes for the infinite summations over the unperturbed atomic states appearing in the  $N$ th-order perturbation theory. Recently the same problem has been analyzed in detailed theoretical form when the two-photon ionization takes place via a resonant intermediate state using a density matrix formulation.<sup>8</sup>

In the last years we have developed a theoretical analysis for multiphoton processes in alkali atoms based on the Green's-function formalism,<sup>9-11</sup> a method that allows us to perform in close form the infinite summations over the unperturbed atomic

states appearing when perturbation theory is applied to orders higher than the first and thus suppressing the ambiguities related to the truncated summation methods. In the present paper the spin-orbit coupling has been added, thus extending this theory. Since the Green's function represents the partial-wave projection of the valence-electron propagator, that formalism combined with the quantum-defect theory yields information not only around the poles of the Green's function, i.e., for real intermediate resonant transitions, but also for virtual transitions, thus allowing closed calculations in the off-resonant region. The layout of the paper is as follows. Section II summarizes the

fundamental features of the theory here employed emphasizing the Green's-function method and its consequences; in Sec. III we introduce the spin-orbit coupling, discussing the physical conditions by which we may find the correct Green's function on the basis of the quantum-defect theory. Section IV shows the theoretical calculations derived from the theory and is followed in Sec. V by the numerical results making a detailed comparison with measured values and results of other theoretical calculations of the transition probability per unit of time, ion asymmetry, and electron-spin polarization.

## II. FUNDAMENTAL THEORY

Time-dependent perturbation theory developed to the first nonvanishing order in the nonrelativistic approximation gives the transition probability rate per atom (atomic units are used) for the absorption of  $N$  photons from the initial atomic state  $|i\rangle$  to the final one  $|f\rangle$  as<sup>12</sup>

$$W^{(N)} = \frac{1}{(2\pi)^2} (2\pi\alpha F\omega)^N \int |K_{fi}^{(N)}|^2 d\hat{k} \quad (2.1)$$

for an ejected electron of wave vector  $\vec{k}$ , where  $\omega$  is the angular photon frequency,  $F$  the photon flux, and  $\alpha$  the fine-structure constant.  $\hat{k} \equiv (\theta_k, \phi_k)$  represents the angular part of the ejected electron wave vector  $\vec{k}$  and the total probability rate is obtained by integrating over  $\vec{k}$ . The matrix element  $K_{fi}^{(N)}$  for the transition between the unperturbed atomic states in the  $N$ th-order approximation includes infinite summations over the complete set of unperturbed atomic states  $|a_j\rangle$ , discrete plus continuum, and it may be written as<sup>10</sup>

$$K_{fi}^{(N)} = \sum_{a_{N-1}} \sum_{a_{N-2}} \cdots \sum_{a_2} \sum_{a_1} \langle f | \hat{V} | a_{N-1} \rangle \frac{\langle a_{N-1} | \hat{V} | a_{N-2} \rangle}{E_{a_{N-1}} - E_{a_i} - (N-1)\omega} \frac{\langle a_{N-2} | \hat{V} | a_{N-3} \rangle}{E_{a_{N-2}} - E_{a_i} - (N-2)\omega} \\ \times \cdots \times \frac{\langle a_2 | \hat{V} | a_1 \rangle}{E_{a_2} - E_{a_i} - 2\omega} \frac{\langle a_1 | \hat{V} | a_i \rangle}{E_{a_1} - E_{a_i} - \omega}, \quad (2.2)$$

where  $E_{a_j}$  are the atom eigenvalues in a.u.  $\hat{V}(\vec{\epsilon}, \vec{r})$  is the interaction operator between the radiation (unit polarization vector  $\vec{\epsilon}$ ) and the valence electron (radius vector  $\vec{r}$ ). That operator is reduced to a simple expression in the electric dipole approximation which we use in this work:

$$\hat{V}(\vec{\epsilon}, \vec{r}) = \hat{V}^D E = \vec{\epsilon} \cdot \vec{r}, \quad (2.3)$$

the electric field of the incident radiation being taken at the nucleus position ( $\vec{r}=0$ ).

One of the main difficulties experienced when calculating probability rate (2.1) is related to the infinite summations appearing in expression (2.2). As is known, infinite summations appear in perturbation theory as a theoretical condition due to the use of the closure properties of the Hilbert space spanned by the atomic unperturbed eigenfunctions. Here, we performed these infinite summations with the help of the Green's-function method now described. If the expansion in eigenfunctions is used, the Green's function related to the problem for an arbitrary energy  $E$  may be written in the following form in the coordinate representation:

$$G(E; \vec{r}, \vec{r}') = \sum_j \frac{\langle \vec{r} | a_j \rangle \langle a_j | \vec{r}' \rangle}{E_j - E} + \int_{E', > 0} \frac{\langle \vec{r} | E' \rangle \langle E' | \vec{r}' \rangle}{E' - E} dE', \quad (2.4)$$

where the unperturbed kets belonging to the discrete and continuum one-electron spectra are introduced with the corresponding eigenvalues  $E_j$  and  $E'$ . Thus, from (2.2) and (2.4) we see that the transition matrix element is

$$K_{fi}^{(N)} = \langle f(\vec{r}_N) | \hat{V}(\vec{\epsilon}_N, \vec{r}_N) G(E_i + (N-1)\omega; \vec{r}_N, \vec{r}_{N-1}) \hat{V}(\vec{\epsilon}_{N-1}, \vec{r}_{N-1}) G(E_i + (N-2)\omega; \vec{r}_{N-1}, \vec{r}_{N-2}) \\ \times \cdots \times \hat{V}(\vec{\epsilon}_2, \vec{r}_2) G(E_i + \omega; \vec{r}_2, \vec{r}_1) \hat{V}(\vec{\epsilon}_1, \vec{r}_1) | i(\vec{r}_1) \rangle. \quad (2.5)$$

One recognizes that the Green's function is no more than the partial-wave projection of the one-electron propagator in the atom. Thus, the relevant transition matrix elements can be evaluated analytically in closed form if an approximate theoretical atomic model is adopted. In this sense, as we are dealing with single valence-electron atoms, we may reasonably assume that if the atomic core and the single outer electron interact according to a central potential, the Green's function may be factorized as follows:

$$G(E; \vec{r}, \vec{r}') = \sum_{l, m_l} g_l(E; r, r') Y_l^{m_l}(\hat{r}) Y_l^{m_l*}(\hat{r}'), \quad (2.6)$$

where the radial part  $g_l(E; r, r')$  is the solution of a Green's differential equation associated to the Schrödinger equation of the single valence electron whose angular momentum is  $l$ . The symbol  $\hat{r}$  ( $\hat{r}'$ ) in the spherical harmonics  $Y_l^{m_l}$  means the angular part of the electron radius vector  $\vec{r}$  ( $\vec{r}'$ ).

The method of the Green's function applied here is limited to the cases where the requisite solution of the Green's differential equation can be determined. Since precise solutions are available for systems whose coordinates are separable, the required solution is useful only for these cases. However, in our problem the factorized Green's function given by expression (2.6) provides that condition. Now, it is essential to fix the form of the central potential through which the single outer electron interacts with the atomic core in order to attempt to find a precise solution. In this sense the assumption is made that the single valence electron interacts with the atomic core of radius  $r_c$  according to an attractive Coulomb potential with net charge  $z$  (for neutral atoms  $z = 1$ ) in the range  $r > r_c$ . Thus this makes it possible to apply the quantum-defect method (QDM) that yields the possibility of calculating the Green's function, which introduces single-electron wave functions.<sup>13-15</sup> We point out that the one-channel theory is applicable to this case since we are dealing with alkali atoms which may be described as an electron added to an atomic core which has a large first excitation potential.<sup>16,17</sup> With these assumptions, we can determinate the Green's and wave functions for alkali-metal atoms.

In that framework, and an expansion based on relation (2.6), the Green's differential equation associated with the radial Schrödinger equation may be written as

$$\left[ \frac{1}{2} \left( \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) - \frac{1}{r} - E \right] g_l(E; r, r') = \frac{\delta(r-r')}{rr'}. \quad (2.7)$$

The solution of this equation, the Coulomb Green's function, was fully analyzed in previously published works.<sup>18,19</sup> In the case of alkali metal atoms and the Coulomb potential being limited to  $r > r_c$ , we must add a non-Coulomb term to the pure Coulomb Green's function and consider for  $r > r_c$  (Ref. 20)

$$g_l(E; r, r') = \frac{\nu}{rr'} \frac{\Gamma(l+1-\nu)}{\Gamma(2l+2)} M_{\nu, l+1/2} \left( \frac{2r_{<}}{\nu} \right) W_{\nu, l+1/2} \left( \frac{2r_{>}}{\nu} \right) + A \frac{\nu}{rr'} W_{\nu, l+1/2} \left( \frac{2r}{\nu} \right) W_{\nu, l+1/2} \left( \frac{2r'}{\nu} \right), \quad (2.8)$$

where  $r_{<}$  ( $r_{>}$ ) is the smaller (larger) of the two quantities  $r$  and  $r'$ ,  $M$  and  $W$  are the Whittaker functions,<sup>21</sup>  $\nu$  is the effective quantum number defined by  $E = -(2\nu^2)^{-1}$  for  $E < 0$ , and  $A$  is a coefficient that takes into account the non-Coulomb feature of the potential through which the outer electron of an alkali-metal atom interacts with the atomic core. To evaluate this coefficient we consider the QDM which connects the non-Coulomb phase  $\delta_l$  to the quantum defect  $\mu_l(E)$  extrapolated to  $E > 0$  from its values  $\mu_{n_l}$  at the eigenvalues  $E_{n_l} < 0$ . The energy is defined by  $E_{n_l} = -(2\nu_{n_l}^2)^{-1}$  with  $\mu_{n_l} = n - \nu_{n_l}$ ,  $n$  being the principal quantum number and  $\nu_{n_l}$  the effective quantum number. Indeed from a result of the study of Ham<sup>13</sup> about the quantum-defect theory, we have

$$\cot \delta_l = (1 - e^{-2\pi/k}) \left( \cot \pi \mu_l(E) + \frac{i}{1 - e^{2\pi/k}} \right) \quad (2.9)$$

for  $2E = k^2 > 0$ . From the asymptotic behavior of the radial part of the Green's function at  $E > 0$  and using (2.9), we have from an analytic continuation at  $E < 0$  (Ref. 22)

$$A = \frac{\Gamma(l+1-\nu)}{\Gamma(l+1+\nu)} \frac{\sin[\pi \mu_l(E) + l]}{\sin[\pi \mu_l(E) + \nu]}. \quad (2.10)$$

Now, we can obtain the radial part of the eigen-solutions  $R_{n_l}(E)$  at  $E < 0$  from the residues  $R_{\epsilon_l}(E_{n_l})$  of  $g_l(E; r, r')$  at the poles  $E = E_{n_l}$ . From the general definition (2.4) and the fact that we can separate coordinates, we obtain from (2.6)

$$g_l(E; r, r') = \sum_{n, E_{n_l} < 0} \frac{R_{n_l}(r) R_{n_l}^*(r')}{E_{n_l} - E} + \int_{E', > 0} \frac{R_{\epsilon_l}(r) R_{\epsilon_l}^*(r')}{E' - E} dE', \quad (2.11)$$

where the functions  $R_{\epsilon_l}$  are normalized on the energy scale from the definition of the Green's function. With the definition of the residue  $R_{\epsilon_l}$  and Eq. (2.11), we have

$$R_{\epsilon_l}(E_{n_l}) = \lim_{E \rightarrow E_{n_l}} [(E - E_{n_l}) g_l(E; r, r')] = R_{n_l}(r) R_{n_l}^*(r'). \quad (2.12)$$

Calculating the value of this residue with relations (2.8) and (2.10) for  $E < 0$ , it results that

$$R_{E_1}(E_{n_1}) = -\frac{1}{r r'} \frac{1}{\nu_{n_1}^2} \times \frac{W_{\nu_{n_1}, l+1/2}(2r/\nu_{n_1}) W_{\nu_{n_1}, l+1/2}(2r'/\nu_{n_1})}{\Gamma(l+1+\nu_{n_1}) \Gamma(\nu_{n_1}-l)} \times \frac{1}{1 + [\partial \mu_l(E)/\partial \nu]_{\nu=\nu_{n_1}}}. \quad (2.13)$$

So, considering that

$$\left( \frac{\partial \mu_l(E)}{\partial \nu} \right)_{\nu=\nu_{n_1}} = \frac{1}{\nu_{n_1}^2} \left( \frac{\partial \mu_l(E)}{\partial E} \right)_{E=E_{n_1}} \ll 1,$$

we have

$$R_{n_1}(r) = \frac{1}{r} [\nu_{n_1}^2 \Gamma(l+1+\nu_{n_1}) \Gamma(\nu_{n_1}-l)]^{-1/2} W_{\nu_{n_1}, l+1/2} \left( \frac{2r}{\nu_{n_1}} \right). \quad (2.14)$$

The assumption  $[\partial \mu_l(E)/\partial E]_{E=E_{n_1}} \ll 1$  corresponds to the condition of applicability of QDM and is very well satisfied through the full length of the alkali-metal atom spectrum.

Likewise, we note that the Green's function defined by (2.11) has a pole for any positive eigenenergy. Moreover, this Green's function is also defined for  $E > 0$  by (2.8) with (2.10), where  $\nu = i/k$ , which has an asymptotic behavior corresponding to an outgoing wave. So, following the collision theory,<sup>23</sup> this Green's function may be looked on as the matrix element of the operator

$$G^* = \lim_{\epsilon \rightarrow 0^+} \frac{1}{H_0 - (E + i\epsilon)}.$$

Therefore, we are led to consider in the expression (2.11)  $1/(E' - E)$  as a distribution; then we write

$$\frac{1}{E - E'} = \lim_{\epsilon \rightarrow 0^+} \frac{1}{E' - (E + i\epsilon)} = P \left( \frac{1}{E' - E} \right) + i\pi \delta(E' - E), \quad (2.15)$$

where  $\delta$  is the Dirac distribution and  $P[1/(E' - E)]$  is the principal value of  $1/(E' - E)$  in the Cauchy's sense. Note that in expression (2.11) we have

$$\sum_{n, E_{n_1} < 0} \lim_{\epsilon \rightarrow 0^+} \frac{R_{n_1}(r) R_{n_1}^*(r')}{E_{n_1} - (E + i\epsilon)} = \sum_{n, E_{n_1} < 0} \frac{R_{n_1}(r) R_{n_1}^*(r')}{E_{n_1} - E}$$

because  $E$  is positive; thus in that case this term has no poles for  $E_{n_1} < 0 \forall n$ . Thus we have for  $E > 0$

$$g_l(E; r, r') = \sum_{n, E_{n_1} < 0} \frac{R_{n_1}(r) R_{n_1}^*(r')}{E_{n_1} - E} + P \int_0^{\infty} \frac{R_{E_1}(r) R_{E_1}^*(r')}{E' - E} dE' + i\pi R_{E_1}(r) R_{E_1}^*(r'). \quad (2.16)$$

Moreover, we can write the expression (2.8) using the non-Coulomb term like (2.10), but valid for  $E > 0$  in the form<sup>24</sup>

$$g_l(E; r, r') = \frac{i}{k r r'} e^{-\tau/k} \left( \frac{e^{i\sigma_l} e^{i\delta_l}}{(i)^{l+1}} W_{i/k, l+1/2}(-2ikr) \right) \times 2 \operatorname{Re} \left( \frac{e^{i\sigma_l} e^{i\delta_l}}{(i)^{l+1}} W_{i/k, l+1/2}(-2ikr') \right), \quad (2.17)$$

where  $k = (2E)^{1/2}$ ,  $\operatorname{Re}$  means real part, and  $\sigma_l$  is the Coulomb phase shift defined by  $\sigma_l = \arg[\Gamma(l+1 - i/k)]$ . If we assume  $R_{E_1}$  to be real in the general definition (2.16) of  $g_l(E; r, r')$ , we have

$$\operatorname{Im}[g_l(E; r, r')] = \pi R_{E_1}(r) R_{E_1}(r'), \quad (2.18)$$

where  $\operatorname{Im}$  means that the imaginary part of  $g_l$  has to be taken. By putting (2.17) into (2.18) we have

$$\operatorname{Im}[g_l(E; r, r')] = \frac{2}{k r r'} e^{-\tau/k} \times \operatorname{Re} \left( \frac{e^{i\sigma_l} e^{i\delta_l}}{(i)^{l+1}} W_{i/k, l+1/2}(-2ikr) \right) \times \operatorname{Re} \left( \frac{e^{i\sigma_l} e^{i\delta_l}}{(i)^{l+1}} W_{i/k, l+1/2}(-2ikr') \right), \quad (2.19)$$

which is the product of a function of  $r$  by the same function of  $r'$  as in (2.18) with  $R_{E_1}$  real. Thus, this last assumption is valid, and the solution  $R_{E_1}(r)$  of our problem is real and equal to

$$R_{E_1}(r) = \frac{1}{r} \left( \frac{2}{\pi k} \right)^{1/2} e^{-\tau/2k} \times \operatorname{Re} \left( \frac{e^{i\sigma_l} e^{i\delta_l}}{(i)^{l+1}} W_{i/k, l+1/2}(-2ikr) \right). \quad (2.20)$$

Therefore, we have determined the radial parts of the Green's function with (2.8) and (2.10), and of the eigenfunctions for  $E_{n_1} < 0$  with (2.14) and  $E > 0$  with (2.20). In the study of multiphoton ionization of alkali-metal atoms, we consider the initial state  $|a_i\rangle$  of expression (2.2) as the fundamental  $S$  state. So, we write the radial part of this state as follows:

$$R_{n_1 0}(r) = \frac{1}{r} [\nu_{n_1 0}^2 \Gamma(\nu_{n_1 0} + 1) \Gamma(\nu_{n_1 0})]^{-1/2} W_{\nu_{n_1 0}, 1/2} \left( \frac{2r}{\nu_{n_1 0}} \right) \quad (2.21)$$

with  $\nu_{n_1 0} = -(2E_{n_1 0})^{-1/2}$  and  $E_{n_1 0}$  is equal to the ionization energy of the studied atom. This function diverges near the origin, but due to the fact that the expression (2.8) is valid only for  $r > r_c$ , we can perform the integration over  $r$  occurring in (2.2) from  $r_c$  to infinity, in order to calculate the radial matrix elements. Moreover,  $\nu_{n_1 0}$  is always finite and the argument is limited by  $2r_c/\nu_{n_1 0}$ . Finally,

in the neighborhood of zero, the Whittaker's function  $W_{\nu, n_0, 1/2}(2r/\nu_{n_0})$  behaves such that expression (2.21) diverges less quickly than  $1/r$  for small values of  $r$ .<sup>21</sup>

Consequently, this divergence does not affect the calculations for the values of the argument which are interesting for us ( $r > r_c$ ). Then we shall retain expression (2.21) for the radial part of the initial wave function. In this way, the complete initial wave function appearing in (2.5) will be taken as

$$i(\vec{r}_1) = R_{n_1 0}(r_1) Y_0^0(\hat{r}_1). \quad (2.22)$$

Finally, in the expression (2.1), the matrix element  $K_{fi}^{(N)}$  involves a final state of the electron whose wave vector is  $\vec{k}$ . So we must consider the final wave function in (2.5) as  $f_{\vec{k}}(\vec{r}_N)$ , which describes a stationary state of collision which can be expanded on the basis of partial waves [ $R_{E1}(r_N) Y_l^{m_l}(\hat{r}_N)$ ],  $R_{E1}(r_N)$  being defined by (2.20). Following the method proposed by Messiah<sup>23</sup> to treat the scattering by a Coulomb potential plus a short-range interaction, the requisite decomposition is given by

$$f_{\vec{k}}(r_N) = 4\pi \left(\frac{\pi}{2k}\right)^{1/2} \sum_{l=0}^{\infty} \sum_{m_l=-l}^l (i)^l e^{-i(\sigma_l + \delta_l)} Y_l^{m_l}(\hat{k}) \times R_{E1}(r_N) Y_l^{m_l}(\hat{r}_N). \quad (2.23)$$

These wave functions are normalized so that

$$\rho(\vec{k}) \int f_{\vec{k}}^*(\vec{r}) f_{\vec{k}}(\vec{r}) d\vec{r} = \delta(\vec{k} - \vec{k}') \quad (2.24)$$

with

$$\rho(\vec{k}) = (2\pi)^{-3}, \quad (2.25)$$

which is taken into account in the expression (2.1) where we have introduced the density of states<sup>12</sup>  $\rho(E) = k/(2\pi)^3$ . But, in the same way as above, we note that in the expression (2.23) the function  $R_{E1}$  defined by (2.20) depends on a quantity which diverges for small values of the argument. In our problem, we can reach such small positive values of energy so that  $|2ikr|$  lies into the region of divergence of  $W_{l/h, l+1/2}(-2ikr)$  even with  $r > r_c$ . Indeed, if we consider that for these small values  $E > 0$  this divergence takes place for  $r < r_1$ ,  $r_1$  corresponding to the first inflexion point of the Whittaker's function and being equal to  $l(l+1)/2$  for  $l \neq 0$  (this is obtained from the radial Schrödinger equation with  $E \simeq 0$  and  $d^2W/dr^2 = 0$ ), then we can have  $r_c < r_1$  so that the function  $W$  diverges in the interval of variation  $r_c \leq r \leq r_1$ . In order to reduce this divergence, we are led to introduce a cutoff factor  $B_l$  so that for small values of  $r$  we have  $R_{E1}(r) \propto r^l$  as is required by the general theory of

central fields, and  $B_l = 1$  for  $r > r_1$ . In this way, we finally obtain

$$R_{E1}(r) = \frac{1}{\pi} \left(\frac{2}{\pi k}\right)^{1/2} e^{-\tau/2k} \times \text{Re} \left( \frac{e^{i\sigma_l}}{(i)^{l+1}} W_{l/h, l+1/2}(-2ikr) \times (\cos \delta_l + i B_l \sin \delta_l) \right) \quad (2.26)$$

with

$$B_l = (1 - e^{-\tau/r})^{2l+1} \quad (2.27)$$

and  $\tau_l r_l = 5 \forall l$ , as previously used.<sup>15</sup> Therefore we consider the final wave function defined by the relations (2.23) and (2.26)–(2.28).

Finally, we must evaluate the core radius  $r_c$  according to the QDM from which we have obtained the above-mentioned expressions. In order to do this, we use the Slater's orbital method and we take  $r_c$  as the radius of the outer complete electronic shell of the residual ion (i.e.,  $r_c$  is of the order of 1 a.u. for alkali-metal atoms). In this way we have all the elements to calculate the probability rate (2.1). In the coming sections, we will treat the same problem but will introduce spin-orbit coupling.

### III. TWO-PHOTON ABSORPTION WITH SPIN-ORBIT COUPLING

We now consider the coupling between the angular momentum vector  $\vec{L}$  and the spin vector  $\vec{S}$  of the outer electron. From Dirac's relativistic equation we obtain the following Schrödinger equation for the outer electron in the core field  $V(r)$  which is assumed to be central:

$$\left[ -\frac{1}{2} \left( \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\vec{L}^2}{r^2} \right) + V(r) + \frac{1}{2c^2 r} \frac{dV}{dr} \vec{L} \cdot \vec{S} \right] \Psi(\vec{r}) = E \Psi(\vec{r}), \quad (3.1)$$

where  $c$  is the velocity of light in a.u. In order to solve this equation we introduce the total angular momentum  $\vec{J} = \vec{L} + \vec{S}$  and we can write as usual  $\vec{L} \cdot \vec{S} = \frac{1}{2} (\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$  where the operators  $\vec{L}$  and  $\vec{S}$  commute. So it follows that

$$\left[ -\frac{1}{2} \left( \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\vec{L}^2}{r^2} \right) + V(r) + \frac{1}{4c^2 r} \frac{dV}{dr} (\vec{J}^2 - \vec{L}^2 - \vec{S}^2) \right] \Psi(\vec{r}) = E \Psi(\vec{r}).$$

In this way, we are led to consider the spin spherical harmonics  $Y_{j l m_j}(\theta, \phi)$  defined by<sup>25</sup>

$$Y_{jlm_j}(\theta, \phi) = \sum_{m_1=-l}^l \sum_{m_s=-s}^s Y_{l m_1}^{m_l}(\theta, \phi) \chi_{m_s} \times \langle l, s, m_1, m_s | l, s, j, m_j \rangle, \quad (3.2)$$

where  $m_s$  takes the two possible values  $\pm \frac{1}{2}$  of the electron-spin projection upon some  $z$  axis,  $\chi_{m_s}$  are the eigenspin vectors of the spin operators  $S^2$  and  $S_z$ ,  $\langle l, s, m_1, m_s | l, s, j, m_j \rangle$  is the Clebsch-Gordan coefficient, which is real, relative to an angular momentum  $l$  and a total angular momentum  $j$ ,  $m_j$  being the eigenvalue of the  $J$  projection on the  $z$  axis of the problem. This  $z$  axis will be subsequently defined from the incident light polarization, a fact that will make it possible to particularize the spin projection direction on that  $z$  axis. The spin spherical harmonics defined by (3.2) are eigenfunctions of  $J^2$  and  $J_z$  and we write

$$\Psi(\vec{r}) = R(r) Y_{jlm_j}(\hat{r}).$$

So the radial Schrödinger equation (3.1) is reduced to

$$\left[ -\frac{1}{2} \left( \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) + V_{l s j}(r) \right] R(r) = ER(r) \quad (3.3a)$$

with

$$V_{l s j}(r) = V(r) + \frac{j(j+1) - l(l+1) - \frac{3}{4}}{4c^2 r} \frac{dV}{dr}, \quad (3.3b)$$

which is the same equation as in the case of a particle without spin in a central field. But, now, the "effective radial field" varies from one doublet ( $lj$ ) to another. On the other hand, considering the model potential used in QDM, we can note from (3.3b) that for  $r > r_c$  where  $V(r) = -1/r$ , the corrective radial term due to the spin-orbit coupling is negligible compared to the potential  $V(r)$  itself with the ratio of these two terms being of the order of  $10^{-4}$ – $10^{-5}$  for  $r > r_c$ . In other words, we may write in a more precise form that the spin-orbit potential departs from the attractive Coulomb potential by amounts that converge to zero faster than  $1/r$ . This fact leads to the possibility of introducing phase shifts into the radial part of the outer electron wave function in order to take into account the departures from the Coulomb potential, a method widely used in relation to the formulation of atomic-structure problems and the quantum-defect treatments.<sup>26,27</sup> So, we can write, as a good approximation to the problem, the following differential equation valid for  $r > r_c$ :

$$\left[ -\frac{1}{2} \left( \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) - \frac{1}{r} \right] R(r) = ER(r), \quad (3.4a)$$

considering that the effects of spin-orbit coupling

on the radial parts are only important into the core region. Then we use an "effective central field" such that for  $r > r_c$ ,  $V_{l s j}(r) = -1/r$ ; for  $r < r_c$ ,  $V_{l s j}(r)$  is defined by (3.3b) where  $V(r)$  is the atomic-core part of the field approximated by the non-Coulomb part of the QDM potential. We note that if  $V(r)$  is assumed to have the mathematical properties required by the one-channel QDM for  $r < r_c$ ,<sup>13</sup> the "effective central field"  $V_{l s j}(r)$  will fulfil the same properties as well. In this way, we can apply the QDM to the  $V_{l s j}$  potential in which the non-Coulomb features explicitly depend on the values of  $j$  and  $l$ . Consequently, from the results of QDM in this configuration, we are led to make explicit the ( $lj$ ) dependence of the radial solutions throughout the quantum defect  $\mu_{j l}(E)$  obtained from a ( $lj$ ) series based on the values  $\mu_{j l}(E_{n j l})$  at the measured eigenvalues of energy  $E_{n j l}$  and defined as

$$E_{n j l} = -(2\nu_{n j l}^2)^{-1}, \quad \nu_{n j l} = n - \mu_{j l}(E_{n j l}). \quad (3.4b)$$

Based on these considerations, the solution of the differential Green's equation associated with the Schrödinger equation with spin-orbit coupling (3.1) can be factorized just like the earlier Green's function, but now in the new form

$$G(E; \vec{r}, \vec{r}') = \sum_{j l m_j} g_{j l}(E; r, r') Y_{j l m_j}(\hat{r}) Y_{j l m_j}(\hat{r}') \quad (3.5a)$$

with the radial part  $g_{j l}(E; r, r')$  a solution of the following equation, valid for  $r > r_c$ :

$$\left[ -\frac{1}{2} \left( \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) - \frac{1}{r} - E \right] g_{j l}(E; r, r') = \frac{\delta(r - r')}{r r'}. \quad (3.5b)$$

The ( $lj$ ) dependence of this function is due to the "effective potential". Equation (3.5b) leads us to the same analytic form of  $g_{j l}(E; r, r')$  as shown previously [relation (2.8)], but now, in order to take into account the ( $lj$ ) dependence of the considered "effective potential" accordingly to the QDM, we must choose the quantum defect  $\mu_{j l}(E)$  defined by (3.4b) and we write for  $r > r_c$

$$\begin{aligned} g_{j l}(E; r, r') &= \frac{\nu}{r r'} \frac{\Gamma(l+1-\nu)}{\Gamma(2l+2)} \\ &\times M_{\nu, l+1/2} \left( \frac{2r'}{\nu} \right) W_{\nu, l+1/2} \left( \frac{2r}{\nu} \right) \\ &+ \frac{\nu}{r r'} \frac{\Gamma(l+1-\nu)}{\Gamma(2l+2)} \frac{\sin \pi [\mu_{j l}(E) + l]}{\sin \pi [\mu_{j l}(E) + \nu]} \\ &\times W_{\nu, l+1/2} \left( \frac{2r}{\nu} \right) W_{\nu, l+1/2} \left( \frac{2r'}{\nu} \right). \quad (3.6a) \end{aligned}$$

This introduces an analogous term like  $A$  in Eqs. (2.8) and (2.10) that represents the non-Coulomb contributions to the QDM potential, including the central spin-orbit coupling. Here the energy  $E$  must be regarded as a given value into the  $(lj)$  series associated with the "effective potential"  $V_{lsj}$  corresponding to the radial part (3.6a). Consequently, the energy  $E$  and the effective quantum number  $\nu$  are implicit functions of  $j$  and  $l$  by the following definition:

$$E(jl) = -[2\nu^2(jl)]^{-1}. \quad (3.6b)$$

To simplify the notation, we omit this implicit  $(lj)$  subscript dependence of  $E$  and  $\nu$ , this dependence being explicit as in (3.4b) on the eigenvalues. As done previously, we can obtain the radial part of the initial wave function from (3.6a), since the method here proposed uses some general properties of the Green's function deduced from the "central field"  $V_{lsj}(r)$ . Consequently we have for  $r > r_c$

$$R_{n_i, 1/2, 0}(r) = \frac{1}{r} \left\{ \psi_{n_i, 1/2, 0}^2 \Gamma(\nu_{n_i, 1/2, 0} + 1) \Gamma(\nu_{n_i, 1/2, 0}) \times \left[ 1 + \left( \frac{\partial \mu_{1/2, 0}(E)}{\partial \nu} \right)_{\nu = \nu_{n_i, 1/2, 0}} \right] \right\}^{-1/2} \times W_{\nu_{n_i, 1/2, 0}, 1/2} \left( \frac{2r}{\nu_{n_i, 1/2, 0}} \right), \quad (3.7)$$

which specifies only one value  $j = \frac{1}{2}$  since the initial state is an  $S$  state described by  $l = 0$  and  $j = \frac{1}{2}$ . We must now take into consideration the fact that we have incomplete information about the real initial state which is degenerate with respect to  $m_j$ . So, in order to calculate the transition probability rate  $W^{(2)}$  we shall compute the following.

(i) The transition probability rate  $W_+^{(2)}$  relative to the value  $m_j = +j = +\frac{1}{2}$ , the total initial wave function being

$$f_{\mathbf{k}, m_s}(\vec{\mathbf{r}}_2) = 4\pi \left( \frac{\pi}{2k} \right)^{1/2} \sum_{l=0}^{\infty} \sum_{j=l-1/2}^{l+1/2} \sum_{m_j=-j}^j \sum_{m_s=-l}^l (i)^l e^{-i(\sigma_l + \sigma_j)l} Y_l^{m_j}(\hat{\mathbf{k}}) \langle l, \frac{1}{2}, j, m_j | l, \frac{1}{2}, m_l, m_s \rangle R_{Ej1}(r_2) Y_{jl m_j}(\hat{\mathbf{r}}_2). \quad (3.11)$$

These wave functions are normalized so that

$$\rho(\vec{\mathbf{k}}, m_s) \int f_{\vec{\mathbf{k}}, m_s}^* f_{\vec{\mathbf{k}}', m_s'}(\vec{\mathbf{r}}) d\vec{\mathbf{r}} = \delta(\vec{\mathbf{k}} - \vec{\mathbf{k}}') \delta_{m_s m_s'} \quad (3.12)$$

with

$$\rho(\vec{\mathbf{k}}, m_s) = (2\pi)^{-3}. \quad (3.13)$$

The density of these states on the energy scale is  $\rho(E, m_s) = k/(2\pi)^3$  and the transition probability rate  $W_+^{(2)}$  relative to a given initial state  $|i\rangle = |j_i, l_i; m_{j_i}\rangle$

$$i(\vec{\mathbf{r}}_1) = R_{n_i, 1/2, 0}(r_1) Y_{1/2, 0, 1/2}(\hat{\mathbf{r}}_1). \quad (3.8a)$$

(ii) The transition probability rate  $W_-^{(2)}$  relative to the value  $m_j = -j = -\frac{1}{2}$ , the total initial wave function being

$$i(\vec{\mathbf{r}}_1) = R_{n_i, 1/2, 0}(r_1) Y_{1/2, 0, -1/2}(\hat{\mathbf{r}}_1), \quad (3.8b)$$

and weighting them by the degree of degeneracy of these states which is equal to  $(2j+1) = 2$  and considering that

$$W^{(2)} = \frac{1}{2} W_+^{(2)} + \frac{1}{2} W_-^{(2)}. \quad (3.9)$$

In the same manner we can obtain the radial part of the eignesolutions for positive energy so that

$$R_{Ej1} = \frac{1}{r} \left( \frac{2}{\pi k} \right)^{1/2} e^{-\tau/2k} \operatorname{Re} \left( \frac{e^{i\sigma_l}}{(i)^{l+1}} W_{i/k, l+1/2}(-2ikr) \times (\cos \delta_{jl} + iB_l \sin \delta_{jl}) \right) \quad (3.10)$$

with  $\delta_{jl} = \pi \mu_{jl}$ , where  $\mu_{jl}$  is extrapolated to the positive energies as explained before. The cutoff factor  $B_l$  is defined by (2.27) and (2.28) and is reasonably assumed to be independent of  $j$  since the term due to the spin-orbit coupling which appears in the radial Schrödinger equation does not significantly affect the values of  $r$  corresponding to the divergence of the solution. Finally, we must expand the final wave function as in Eq. (2.23) on the coupled partial waves  $R_{Ej1}(r) Y_{jl m_j}(\hat{\mathbf{r}})$ . We now apply the previously described method in Sec. II but in the  $\vec{\mathbf{L}} \cdot \vec{\mathbf{S}}$  coupling scheme. We are led to consider some final states described by wave functions presenting an asymptotic behavior and characterized by a given wave vector  $\vec{\mathbf{k}}$  and a well defined spin number projection  $m_s$ . Consequently we note the final wave function with  $f_{\vec{\mathbf{k}}, m_s}(\vec{\mathbf{r}})$  and in this way the requisite decomposition is given by

with  $m_{j_i} = \pm \frac{1}{2}$  as it is defined in (3.8a) is given by

$$W_{\pm}^{(2)} = \sum_{m_s=-1/2}^{+1/2} m_s W_{\pm}^{(2)} = {}_+W_{\pm}^{(2)} + {}_-W_{\pm}^{(2)}. \quad (3.14)$$

The left indices  $+$  and  $-$  correspond, respectively, to  $m_s = +\frac{1}{2}$  and  $m_s = -\frac{1}{2}$ , that is,  ${}_+W_{\pm}^{(2)}$  are defined by the corresponding final wave function given by (3.11).

In this way, the transition probability rate  $W^{(2)}$  defined by (3.9) may be written as

$$W^{(2)} = \frac{1}{2}({}_+W_+^{(2)} + {}_-W_+^{(2)}) + \frac{1}{2}({}_+W_-^{(2)} + {}_-W_-^{(2)}) \quad (3.15)$$

or

$$W^{(2)} = {}_+W^{(2)} + {}_-W^{(2)} \quad (3.16)$$

with

$$\begin{aligned} {}_+W^{(2)} &= \frac{1}{2}({}_+W_+^{(2)} + {}_-W_+^{(2)}), \\ {}_-W^{(2)} &= \frac{1}{2}({}_+W_-^{(2)} + {}_-W_-^{(2)}). \end{aligned} \quad (3.17)$$

So, from the previous considerations involving the initial states and from the definition of  ${}_+W_+^{(2)}$ , the two quantities  ${}_+W^{(2)}$  and  ${}__-W^{(2)}$  defined by (3.17) are exactly the probability rates relative to some final states which are described by wave functions having an asymptotic behavior corresponding to

pure spin states. In this sense, we can define a spin polarization  $P^{(2)}$  similar to that introduced by Fano<sup>3</sup> for the one-photon ionization and for the multiphoton case by Lambropoulos<sup>28,6</sup> as

$$P^{(2)} = \frac{{}_+W^{(2)} - {}_-W^{(2)}}{{}_+W^{(2)} + {}_-W^{(2)}} = \frac{{}_+W^{(2)} - {}_-W^{(2)}}{W^{(2)}}. \quad (3.18)$$

This gives the relative excess of spins up compared to spins down along the  $z$  axis of the problem at large distance from the nucleus after a two-photon ionization. The upper asymptotic conditions apply, so that  ${}_+W^{(2)}$  and  ${}__-W^{(2)}$  can be regarded respectively as the two-photon transition probability rates relative to a "well defined final spin state."

#### IV. CALCULATIONS IN THE ELECTRIC DIPOLE APPROXIMATION

The matrix element  $K_{fi}^{(2)}$  is developed in the case of the electric dipole approximation for a given polarization of the incident light. For linearly polarized light we take the polar axis of the spherical coordinates along the direction of the photon polarization unit vector, and then the interaction operator defined by (2.3) has the form

$$\hat{V}(\vec{\epsilon}, \mathbf{r}) = \vec{\mathbf{r}} \cdot \vec{\epsilon}_L = \left(\frac{4\pi}{3}\right)^{1/2} r Y_1^0(\hat{\mathbf{r}}). \quad (4.1)$$

For circularly polarized light, we use as polar axis the wave-vector direction of the incoming photons and we have:

$$\hat{V}(\vec{\epsilon}, \vec{\mathbf{r}}) = \vec{\mathbf{r}} \cdot \vec{\epsilon}_C = -\left(\frac{4\pi}{3}\right)^{1/2} r Y_1^{\pm 1}(\hat{\mathbf{r}}), \quad (4.2)$$

where  $Y_1^1(\hat{\mathbf{r}})$  and  $Y_1^{-1}(\hat{\mathbf{r}})$  correspond, respectively, to right and left circularly polarized light.

In this way, the matrix elements for the two-photon absorption have the following form:

$$\begin{aligned} K_{m_s \pm}^{(2)} &= 4\pi \left(\frac{\pi}{2k}\right)^{1/2} \left(\frac{4\pi}{3}\right) \\ &\times \sum_{l_f=0}^{\infty} \sum_{j_f=|l_f-1/2|}^{l_f+1/2} \sum_{m_{j_f}=-j_f}^{j_f} \sum_{m_{l_f}=-l_f}^{l_f} (-i)^{l_f} e^{i(\sigma_{l_f} + 6j_f l_f)} \langle l_f, \frac{1}{2}, j_f, m_{j_f} | l_f, \frac{1}{2}, m_{l_f}, m_s \rangle Y_{l_f}^{m_{l_f}}(\hat{\mathbf{k}}) \\ &\times \sum_{l'=0}^{\infty} \sum_{j'=|l'-1/2|}^{l'+1/2} \sum_{m_{j'}=-j'}^{j'} \langle R_{E, j_f l_f}(\mathbf{r}_2) | r_2 g_{j' l'}(E_{n_i, 0, 1/2} + w; \mathbf{r}_1, \mathbf{r}_2) r_1 | R_{n_i, 0, 1/2}(\mathbf{r}_1) \rangle \\ &\times \int Y_{j_f l_f m_{j_f}}^*(\hat{\mathbf{r}}_2) Y_1^m(\hat{\mathbf{r}}_2) Y_{j' l' m_{j'}}(\hat{\mathbf{r}}_2) d\hat{\mathbf{r}}_2 \int Y_{j' l' m_{j'}}^*(\hat{\mathbf{r}}_1) Y_1^m(\hat{\mathbf{r}}_1) Y_{1/2, 0, 1/2}(\hat{\mathbf{r}}_1) d\hat{\mathbf{r}}_1, \end{aligned} \quad (4.3)$$

where the index "f" is relative to the final states, the symbol ' occurs for the intermediate states,  $m=0, \pm 1$  according to the light polarization used and the index + (-) corresponds to an initial state such as  $m_{j_i} = +\frac{1}{2}$  ( $m_{j_i} = -\frac{1}{2}$ ), the index  $m_s$  being the value of the spin number associated with the particular final wave function as previously explained. So, the transition probability rate  ${}_+W_+^{(2)}$  relative to a given initial state  $|i\rangle \equiv |n_i, \frac{1}{2}, 0, \pm \frac{1}{2}\rangle$  and a fixed value of  $m_s = \pm \frac{1}{2}$  is given by

$${}_+W_+^{(2)} = (\alpha F \omega)^2 k \int |K_{\pm\pm}^{(2)}|^2 d\hat{\mathbf{k}}, \quad (4.4)$$

where  $K_{\pm\pm}^{(2)}$  is given by (4.3). However, to work out

the angular integrals in (4.3) we must return to the noncoupled basis with the help of the development (3.2) of the spin spherical harmonics  $Y_{j l m_j}(\Omega)$ . In this manner, we have to calculate



integrals of the type

$$I = \int Y_{l_2}^{m_2*}(\Omega) Y_1^m(\Omega) Y_{l_1}^{m_1}(\Omega) d\Omega, \quad (4.5)$$

which can be easily evaluated. The orthogonality of the eigenspin vectors  $\chi_{m_s}$  and the nonvanishing conditions of the Clebsch-Gordan coefficients give us the following selection rules in the  $LS$  coupling scheme.

For linearly polarized light:

$$\Delta l = \pm 1, \quad \Delta j = 0, \pm 1, \quad \Delta m_j = 0. \quad (4.6)$$

For right circularly polarized light:

$$\Delta l = \pm 1, \quad \Delta j = 0, \pm 1, \quad \Delta m_j = +1.$$

The case  $\Delta j(0 \neq 0)$  is excluded since the initial state is labeled by the quantum number  $j = \frac{1}{2}$ . All these calculations are introduced into a numerical program using the Racah formula.<sup>29</sup> Now, if we note

$$A_{j_f l_f m_{j_f}}^{\pm} = \sum_{l_f'=0}^{\infty} \sum_{j_f'=|l_f'-1/2|}^{l_f'+1/2} \sum_{m_{j_f}'=-j_f'}^{j_f'} \langle R_{E_{j_f l_f}}(r_2) | r_2 g_{j_f l_f}(E_{n_i, 0, 1/2} + w; r_2, r_1) r_1 | R_{n_i, 0, 1/2}(r_1) \rangle \\ \times \int Y_{j_f l_f m_{j_f}}^*(\hat{r}_2) Y_1^m(\hat{r}_2) Y_{j_f l_f m_{j_f}}(\hat{r}_2) d\hat{r}_2 \int Y_{j_f l_f m_{j_f}}^*(\hat{r}_1) Y_1^m(\hat{r}_1) Y_{1/2, 0, 1/2}(\hat{r}_1) d\hat{r}_1, \quad (4.7)$$

the quantity  $A_{j_f l_f m_{j_f}}^{\pm}$  ( $A_{j_f l_f m_{j_f}}^{\pm}$ ) corresponds to an initial state such that  $m_{j_i} = +\frac{1}{2}$  ( $m_{j_i} = -\frac{1}{2}$ ) and we obtain

$$|K_{\pm\pm}^{(2)}|^2 = (4\pi)^2 \left(\frac{\pi}{2k}\right) \left(\frac{4\pi}{3}\right)^3 \sum_{l_f'=0}^{\infty} \sum_{j_f'=|l_f'-1/2|}^{l_f'+1/2} \sum_{m_{j_f}'=-j_f'}^{j_f'} \sum_{l_f''=0}^{\infty} \sum_{j_f''=|l_f''-1/2|}^{l_f''+1/2} \sum_{m_{j_f}''=-j_f''}^{j_f''} \sum_{l_f'''=0}^{\infty} \sum_{j_f'''=|l_f'''-1/2|}^{l_f'''+1/2} \sum_{m_{j_f}'''=-j_f'''}^{j_f'''} (-i)^{l_f-l_f''} \\ \times e^{i(\sigma_{l_f} - \sigma_{l_f'})} e^{i(\sigma_{l_f} - \sigma_{l_f'})} \langle l_f, \frac{1}{2}, j_f, m_{j_f} | l_f, \frac{1}{2}, m_{l_f}, \pm \frac{1}{2} \rangle \langle l_f', \frac{1}{2}, j_f', m_{j_f}' | l_f', \frac{1}{2}, m_{l_f}', \pm \frac{1}{2} \rangle \\ \times Y_{l_f l_f m_{j_f}}^*(\hat{k}) Y_{l_f l_f m_{j_f}}(\hat{k}) A_{j_f l_f m_{j_f}}^{\pm} A_{j_f l_f m_{j_f}}^{\pm}, \quad (4.8)$$

this because  $A_{j_f l_f m_{j_f}}^{\pm}$  is real. The radial matrix calculations involved in  $A_{j_f l_f m_{j_f}}^{\pm}$  related to the separation of the variables  $r_2$  and  $r_1$  are performed in the same manner as indicated in a previously published paper.<sup>10</sup> With the relation (4.4) and the condition of orthonormality of the functions  $Y_{l_f}^{m_{l_f}}(\Omega)$  we have

$$W_{\pm}^{(2)} = (\alpha F \omega)^2 \left(\frac{128\pi^5}{9}\right) \sum_{l_f'=0}^{\infty} \sum_{m_{l_f}'=-l_f'}^{l_f'} \left| \sum_{j_f'=|l_f'-1/2|}^{l_f'+1/2} \sum_{m_{j_f}'=-j_f'}^{j_f'} e^{i\sigma_{j_f l_f}} \langle l_f, \frac{1}{2}, j_f, m_{j_f} | l_f, \frac{1}{2}, m_{l_f}, \pm \frac{1}{2} \rangle A_{j_f l_f m_{j_f}}^{\pm} \right|^2. \quad (4.9)$$

Finally, from the selection rules (4.6) we can note that for a given value of  $m_{j_i}$ , we have only one possible value of the quantum number  $m_{j_f}$  (as for  $m_j$ ). So, in the electric-dipole approximation, with the obvious condition  $m_{j_f} = m_{l_f} + m_s$ , we obtain

$$W_{\pm}^{(2)} = (\alpha F \omega)^2 \left(\frac{128\pi^5}{9}\right) \sum_{l_f'=0}^{\infty} \left| \sum_{j_f'=|l_f'-1/2|}^{l_f'+1/2} e^{-i\sigma_{j_f l_f}} \langle l_f, \frac{1}{2}, j_f, m_{j_f} | l_f, \frac{1}{2}, [m_{j_f} - (\pm \frac{1}{2})], \pm \frac{1}{2} \rangle A_{j_f l_f m_{j_f}}^{\pm} \right|^2. \quad (4.10)$$

With this we are able to calculate  $W_L^{(2)}$  and  $W_C^{(2)}$  with relation (3.15) if we note  $W_L^{(2)}$  the total two-photon transition probability rate for a linearly polarized incident light and if  $W_C^{(2)}$  corresponds to the same concept in the right circularly case. After, from equation (3.18) we can also obtain  $P^{(2)}$ . We also study the ratio

$$\rho^{(2)} = \frac{W_C^{(2)}}{W_L^{(2)}}. \quad (4.11)$$

## V. NUMERICAL RESULTS

We have calculated the expressions  $W_C^{(2)}/F^2$ ,  $W_L^{(2)}/F^2$  (in  $\text{cm}^4 \text{s photon}^{-2}$ ),  $\rho^{(2)}$  and  $P^{(2)}$  for the wave numbers  $\omega$  (in  $\text{cm}^{-1}$ ) or wavelengths (in  $\text{\AA}$ ) corresponding either to the experimental values given by Morellec *et al.*<sup>4</sup> (Fig. 2) or to those obtained by Granneman *et al.*<sup>5</sup> (Fig. 5). We also compare our results with previous theoretical calculations<sup>6,7,9</sup> (Tables I and II). The differences

TABLE I. Generalized transition probability values per second  $W^{(2)}/F^2$  for the two-photon ionization of atomic cesium from the 6S ground state for circularly and linearly polarized radiation versus the incident photon energy. Comparison between different theoretical calculations and measured values for nine frequencies of the argon-ion laser. Theor. 1: Ref. 9. Green's-function formalism, QDM, and electric dipole plus quadrupole approximations. Theor. 2: Ref. 6. Truncated summations, QDM, and electric dipole approximation, and spin-orbit coupling. Theor. 3: Ref. 7. Truncated summations, model potential (Ref. 37), electric dipole approximation, and spin-orbit coupling. Present work: Green's-function formalism, QDM, electric dipole approximation, and spin-orbit coupling. Expt.: Refs. 1 and 2.

$\lambda$ (Å) $\omega$ (cm <sup>-1</sup> )	$\frac{W_C^{(2)}}{F^2}$ (cm <sup>4</sup> sphoton <sup>-2</sup> )		Present work (Theor.)		$\frac{W_L^{(2)}}{F^2}$ (cm <sup>4</sup> sphoton <sup>-2</sup> )		Present work (Theor.)
	Theor. 1	Theor. 2	Theor. 1	Theor. 3	Expt.		
5 145 19 436	4.20(-50)	4.58(-50)	4.26(-50)	3.05(-50)	7.90(-50)	2.6 ± 0.6 (-48)	3.03(-50)
5 017 19 932	1.44(-50)	1.66(-50)	1.18(-50)	9.83(-50)	4.62(-50)	9.4 ± 2.8 (-48)	7.91(-51)
4 965 20 140	5.85(-51)	7.57(-51)	3.95(-51)	3.90(-51)	3.39(-50)	1.3 ± 0.4 (-47)	2.77(-51)
4 880 20 491	1.52(-52)	2.35(-54)	1.40(-51)	1.54(-51)	1.54(-50)	1.3 ± 0.5 (-47)	3.99(-51)
4 765 20 986	5.08(-50)	4.07(-50)	6.01(-50)	5.06(-50)	3.81(-52)	1.6 ± 0.5 (-47)	5.92(-50)
4 727 21 155	1.32(-49)	1.05(-49)	1.38(-49)	1.24(-49)	7.34(-51)	1.8 ± 0.6 (-47)	1.29(-49)
4 658 21 468	9.96(-49)	6.75(-49)	7.59(-49)	8.86(-49)	1.41(-49)	1.8 ± 0.8 (-47)	6.72(-49)
4 579 21 839	3.89(-43)	1.53(-47)	1.58(-47)	3.36(-43)	4.14(-48)	5.6 ± 1.6 (-47)	1.07(-47)
4 545 22 002	5.28(-47)	4.44(-47)	4.57(-47)	4.91(-47)	1.81(-47)	2.8 ± 0.9 (-46)	3.76(-47)

TABLE II. Ratio between the generalized transition probabilities per second for circularly and linearly polarized incident radiation and spin-electron polarization values. Theoretical calculations: the same as in the caption of Table I. Experimental results: Ref. 2.

$\lambda$ (Å) $\omega$ (cm <sup>-1</sup> )	$\rho^{(2)} = \frac{W_C^{(2)}}{W_L^{(2)}}$				Present work (Theor.)	Theor. 2	$P_C^{(2)}$ Theor. 3	Present work (Theor.)
	Theor. 1	Theor. 2	Theor. 3	Expt.				
5 145 19 436	1.38	1.38	1.19	0.89 ±0.02	1.41	-0.0003	-0.06	-0.09
5 017 19 932	1.46	1.45	1.18	0.84 ±0.03	1.49	-0.03	-0.10	-0.22
4 965 20 140	1.50	1.49	1.18	0.92 ±0.02	1.42	-0.04	-0.13	-0.39
4 880 20 491	0.10	0.003	1.19	0.79 ±0.02	0.41	-0.08	-0.23	0.72
4 765 20 986	1.00	1.06	1.39	0.96 ±0.03	1.02	-0.08	0.82	0.05
4 727 21 155	1.07	1.12	1.15	0.86 ±0.02	1.07	-0.12	0.34	-0.02
4 658 21 468	1.12	1.18	1.15	0.94 ±0.03	1.13	-0.27	-0.11	-0.21
4 579 21 839	1.16	1.49	1.47	1.36 ±0.02	1.48	0.65	0.74	0.68
4 545 22 002	1.17	1.25	1.19	1.16 ±0.01	1.21	0.64	0.66	0.65

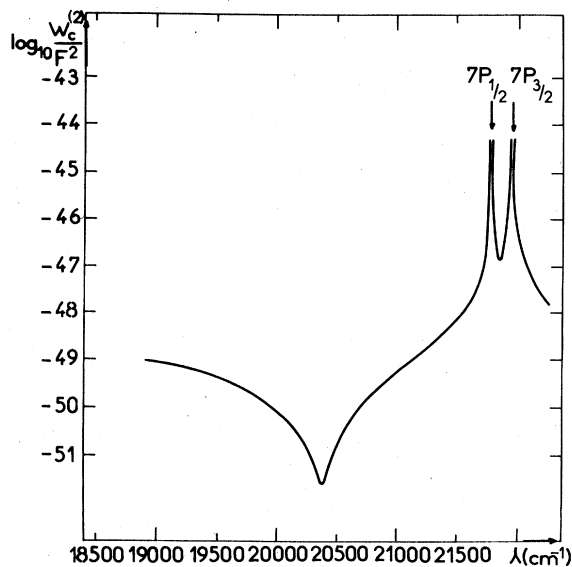


FIG. 1. Generalized transition probability rate in  $\text{cm}^4 \text{s photon}^{-2}$  for the two-photon ionization of atomic cesium from the 6S ground state for circularly polarized radiation versus the incident photon energy in  $\text{cm}^{-1}$ .

between the theoretical methods and the results of the comparison will be discussed in the last section of this paper. The curves on the Figs. 1-4 have been constructed from a series of calculated values lying in the wave-number range from 18 500 to 22 500  $\text{cm}^{-1}$ . Firstly we see in Fig. 2, where we have reported the experimental values of Ref. 4,

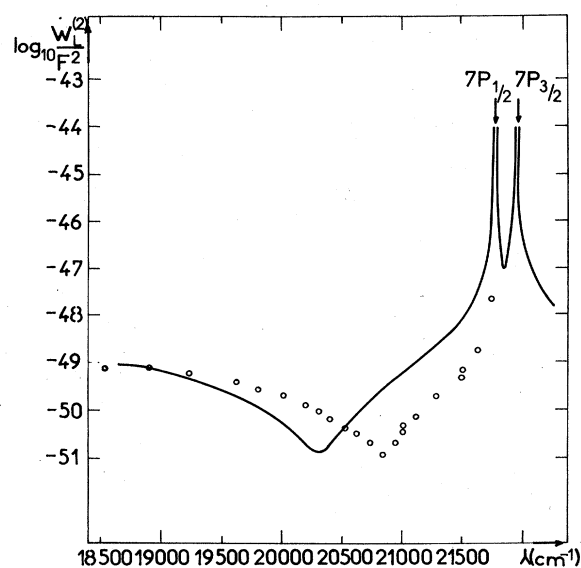


FIG. 2. Generalized transition probability rate in  $\text{cm}^4 \text{s photon}^{-2}$  for the two-photon ionization of atomic cesium from the 6S ground state for linearly polarized radiation versus the incident photon energy in  $\text{cm}^{-1}$ . Circles: experimental values (Ref. 4).

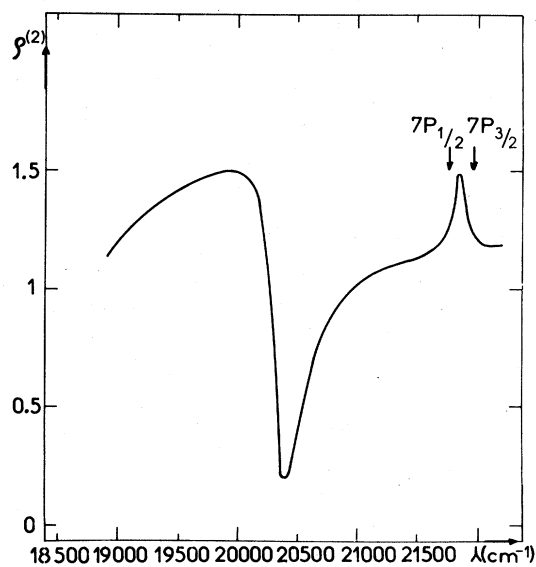


FIG. 3. Ratio of the generalized transition probability rates (circular over linear) for the two-photon ionization of atomic cesium from the 6S ground state. The values indicated by arrows have been extrapolated from calculations close to the intermediate  $7P$  states.

that we obtain a qualitative agreement with experiment, the main point being now that the experimental deep minimum actually exists. This invalidates the Granneman *et al.*<sup>1,2</sup> results since it has been shown<sup>4</sup> that in those works an important

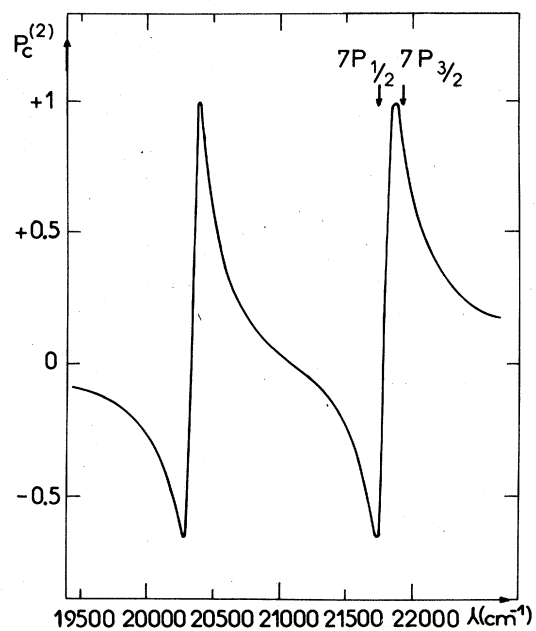


FIG. 4. Electron-spin polarization for the two-photon ionization of atomic cesium from the 6S ground state for incident circularly polarized radiation. The arrows indicate extrapolated values from calculations made close to the  $7P$  states.

molecular contribution was actually detected in the off-resonant region and not only the atomic signal as was claimed by the authors. We wish to point out that a finite deep minimum is now predicted for both polarizations, but with a higher value than that given in our earlier work.<sup>9</sup> In fact, taking the LS coupling into account we have a larger number of possible channels, so that the annulment due to the dipole-dipole contribution for circularly polarized light is suppressed, since radial matrix elements relative to the different allowed channels are not zero at the same photon frequency. The same characteristic is observed in the electric dipole plus quadrupole approximations,<sup>11</sup> but the present work shows that the spin-orbit coupling introduces a more important contribution in the off-resonant region when compared to the quadrupole effects. Now, before making comments on the curves of Figs. 3 and 4, we state precisely the different opened channels in both light polarizations and then detail the expressions of  $P^{(2)}$  and  $\rho^{(2)}$ . We must say that in this case, the comparison will be made with the experimental results of Ref. 5. This is not inconsistent with the previous remarks since the range of wavelengths studied for those quantities is limited around the atomic resonances  $7P_{1/2}$ ,  $7P_{3/2}$ , a region where the molecular contribution is weaker than the atomic one, the molecular absorption being at different wavelengths.<sup>4</sup>

#### A. Linearly polarized light case

Taking into account the selection rules given by (4.6) we have in this case the following possible transitions.

(i) For  $m_{j_i} = +\frac{1}{2}$

Initial states	Intermediate states	Final states	Spin number
$(j_i, l_i, m_{j_i})$	$(j', l', m_{j'})$	$(j_f, l_f, m_{j_f})$	$(m_s)$
$(1/2, 0, 1/2)$	$(1/2, 1, 1/2)$	$(1/2, 0, 1/2)$	$(+1/2)$
	$(3/2, 1, 1/2)$	$(3/2, 2, 1/2)$	$(+1/2, -1/2)$
		$(5/2, 2, 1/2)$	$(+1/2, -1/2)$

(5.1)

We have indicated the possible values of  $m_s$  so that the Clebsch-Gordan (CG) coefficient in (4.9) is non-zero for some given values of  $(j_f, l_f, m_{j_f})$ .

(ii) for  $m_{j_i} = -\frac{1}{2}$

Initial state	Intermediate states	Final states	Spin number
$(j_i, l_i, m_{j_i})$	$(j', l', m_{j'})$	$(j_f, l_f, m_{j_f})$	$(m_s)$
$(1/2, 0, -1/2)$	$(1/2, 1, -1/2)$	$(1/2, 0, -1/2)$	$(-1/2)$
	$(3/2, 1, -1/2)$	$(3/2, 2, -1/2)$	$(+1/2, -1/2)$
		$(5/2, 2, -1/2)$	$(+1/2, -1/2)$

(5.2)

On the other hand, the property of symmetry of CG coefficients

$$\langle l, 1/2, j, m_j | l, m_f, 1/2, m_s \rangle = (-1)^{l+1/2-j} \langle l, \frac{1}{2}, j, -m_j | l, -m_f, \frac{1}{2}, -m_s \rangle \quad (5.3)$$

implies

$$\int Y_{j_1 l_1 m_{j_1}}^*(\Omega) Y_{l_1}^0(\Omega) Y_{j_2 l_2 m_{j_2}}(\Omega) d\Omega = (-1)^{j_1+j_2} \int Y_{j_1 l_1 -m_{j_1}}^*(\Omega) Y_{l_1}^0(\Omega) Y_{j_2 l_2 -m_{j_2}}(\Omega) d\Omega. \quad (5.4)$$

With this and from schemes (5.1) and (5.2) and noting that the radial matrix elements are independent of the projection numbers  $m_j$ , we can conclude that the elements  $A_{j_f l_f m_{j_f}}^{\pm}$  defined by (4.7) verify the condition:

$$A_{j_f l_f m_{j_f}}^+ = (-1)^{j_f+3/2} A_{j_f l_f -m_{j_f}}^- \quad (5.5)$$

with  $m_{j_f} = \frac{1}{2}$  when  $j_i = \frac{1}{2}$  and if  $2J'$  is odd. At last, the property (5.3) also implies, after lengthy calculations,

$$\begin{aligned} \langle l_f, \frac{1}{2}, j_f, m_{j_f} | l_f, \frac{1}{2}, (m_{j_f} - \frac{1}{2}), \frac{1}{2} \rangle A_{j_f l_f m_{j_f}}^+ \\ = \langle l_f, \frac{1}{2}, j_f, -m_{j_f} | l_f, \frac{1}{2}, (\frac{1}{2} - m_{j_f}), -\frac{1}{2} \rangle A_{j_f l_f -m_{j_f}}^-, \end{aligned} \quad (5.6)$$

$$\begin{aligned} \langle l_f, \frac{1}{2}, j_f, m_{j_f} | l_f, \frac{1}{2}, (m_{j_f} + \frac{1}{2}), -\frac{1}{2} \rangle A_{j_f l_f m_{j_f}}^+ \\ = \langle l_f, \frac{1}{2}, j_f, -m_{j_f} | l_f, \frac{1}{2}, -(\frac{1}{2} + m_{j_f}), \frac{1}{2} \rangle A_{j_f l_f -m_{j_f}}^-, \end{aligned}$$

this when  $l_f$  is even and  $2j_f$  odd. From this and from the definition (4.9) of  $W_{\pm}^{(2)}$  we conclude that

$$\left. \begin{aligned} +W_{+}^{(2)} = -W_{-}^{(2)} \\ +W_{-}^{(2)} = -W_{+}^{(2)} \end{aligned} \right\} \Rightarrow W_L^{(2)} = +W_{+}^{(2)} + -W_{+}^{(2)}, \quad (5.7a)$$

and then with relations (3.17) and (3.18) we have

$$P_L^{(2)} = 0 \quad \forall \omega. \quad (5.7b)$$

Therefore with a linearly polarized light we cannot obtain polarized ejected electrons when starting from an S state. We define now some quantities which will be useful further to study the spin-electron polarization  $P^{(2)}$  and the ratio  $\rho^{(2)}$ .

The numerical program yields the result of the product of angular integrals occurring in (4.7) by the value of CG coefficient appearing in (4.10). The values of this product relative to the channel labeled (i) in relation (5.1) for a fixed quantum number  $m_s$  are ( $L$  is for linear)

Channel number	$m_s$	"Angular part"
(1)	$\frac{1}{2}$	$A_L = (12\pi)^{-1}$
(2)	$\frac{1}{2}$	$2A_L$
(3)	$\begin{cases} \frac{1}{2} \\ -\frac{1}{2} \end{cases}$	$\begin{cases} (2/\sqrt{5})A_L \\ -\sqrt{6/5}A_L \end{cases}$
(4)	$\begin{cases} \frac{1}{2} \\ -\frac{1}{2} \end{cases}$	$\begin{cases} (2/5\sqrt{5})A_L \\ -\frac{1}{5}\sqrt{6/5}A_L \end{cases}$
(5)	$\begin{cases} \frac{1}{2} \\ -\frac{1}{2} \end{cases}$	$\begin{cases} (18/5\sqrt{5})A_L \\ \frac{6}{5}\sqrt{6/5}A_L \end{cases}$

The corresponding radial matrix elements are noted as follows:

$$\begin{aligned}
 P_1 &= \langle R_{E(1/2)0}(r_2) | r_2 g_{(1/2)1}(E_{n,p(1/2)} + \omega; r_2, r_1) \\
 &\quad \times r_1 | R_{n,p(1/2)}(r_1) \rangle, \\
 P_2 &= \langle R_{E(1/2)0}(r_2) | r_2 g_{(3/2)1}(E_{n,p(1/2)} + \omega; r_2, r_1) \\
 &\quad \times r_1 | R_{n,p(1/2)}(r_1) \rangle, \\
 P_3 &= \langle R_{E(3/2)2}(r_2) | r_2 g_{(1/2)1}(E_{n,p(1/2)} + \omega; r_2, r_1) \\
 &\quad \times r_1 | R_{n,p(1/2)}(r_1) \rangle, \\
 P_4 &= \langle R_{E(3/2)2}(r_2) | r_2 g_{(3/2)1}(E_{n,p(1/2)} + \omega; r_2, r_1) \\
 &\quad \times r_1 | R_{n,p(1/2)}(r_1) \rangle, \\
 P_5 &= \langle R_{E(5/2)2}(r_2) | r_2 g_{(3/2)1}(E_{n,p(1/2)} + \omega; r_2, r_1) \\
 &\quad \times r_1 | R_{n,p(1/2)}(r_1) \rangle,
 \end{aligned} \quad (5.8)$$

With these relations, from the definition (4.9) of  $W_+^{(2)}$  and  $W_-^{(2)}$  and from schemes (5.1) and (5.2), we obtain:

$$\begin{aligned}
 \frac{W_+^{(2)}}{A_L^2} &\propto P_1^2 + 4P_2^2 + 4P_1P_2 + \frac{324}{125}P_5^2 + \frac{4}{5}P_3^2 \\
 &\quad + \frac{4}{125}P_4^2 + \frac{72}{25}P_3P_5 + \frac{72}{125}P_4P_5 + \frac{8}{25}P_3P_4 \quad (5.9)
 \end{aligned}$$

and

$$\begin{aligned}
 \frac{W_-^{(2)}}{A_L^2} &\propto \frac{216}{125}P_5^2 + \frac{6}{125}P_4^2 + \frac{6}{5}P_3^2 + \frac{12}{25}P_3P_4 \\
 &\quad - \frac{72}{25}P_3P_5 - \frac{72}{125}P_4P_5. \quad (5.10)
 \end{aligned}$$

So from Eq. (5.7a) we have

$$\frac{W_L^{(2)}}{A_L^2} \propto P_1^2 + 4P_2^2 + 2P_3^2 + \frac{2}{25}P_4^2 + \frac{108}{25}P_5^2 + 4P_1P_2 + \frac{4}{5}P_3P_4, \quad (5.11)$$

and the coefficient of proportionality is given by (4.10) and is equal to

$$\left(\frac{128}{5}\pi^5\right)(\alpha F\omega)^2.$$

### B. Circularly polarized light case

From identical considerations like the above-mentioned ones, we obtain the following opened channels, the notations being the same as previously. (i) For  $m_{j_i} = +\frac{1}{2}$

Initial state	Intermediate state	Final state	Spin number
$(j_i, l_i, m_{j_i})$	$(j', l', m_{j'})$	$(j_f, l_f, m_{j_f})$	$(m_s)$
$(1/2, 0, 1/2) \rightarrow (3/2, 1, 3/2) \xrightarrow{(6)} (5/2, 2, 5/2)$			$(+1/2)$

$$(5.12)$$

(ii) for  $m_{j_i} = -\frac{1}{2}$

Initial state	Intermediate state	Final state	Spin number
$(j_i, l_i, m_{j_i})$	$(j', l', m_{j'})$	$(j_f, l_f, m_{j_f})$	$(m_s)$
$(1/2, 0, -1/2) \rightarrow (1/2, 1, 1/2) \xrightarrow{(7)} (3/2, 2, 3/2) \xrightarrow{(8)} (5/2, 2, 3/2) \xrightarrow{(9)} (5/2, 2, 3/2)$			$(+1/2, -1/2)$

$$(5.13)$$

In the same way, the values of the "angular product" defined before are, considering the schemes (5.12) and (5.13).

Channel number	$m_s$	"Angular product"
(6)	$\frac{1}{2}$	$A_C = (1/4\pi)\sqrt{6/5}$
(7)	$\begin{cases} \frac{1}{2} \\ -\frac{1}{2} \end{cases}$	$\begin{cases} -A_C/3 \\ 2A_C/3 \end{cases}$
(8)	$\begin{cases} \frac{1}{2} \\ -\frac{1}{2} \end{cases}$	$\begin{cases} -A_C/15 \\ 2A_C/15 \end{cases}$
(9)	$\begin{cases} \frac{1}{2} \\ -\frac{1}{2} \end{cases}$	$\begin{cases} 2A_C/5 \\ A_C/5 \end{cases}$

The index C reminds us that the incident light is circularly polarized. We can also note that the radial parts involved in this case are the same as in the preceding one since the radial matrix elements (5.8) do not depend on the quantum number  $m_j$ . Now, considering the definition of  $W^{(2)}$  given by relation (4.10) we obtain in a similar fashion

$$\begin{aligned}
 \frac{W_+^{(2)}}{A_C^2} &\propto P_5^2, \quad \frac{W_-^{(2)}}{A_C^2} \propto 0, \\
 \frac{W_L^{(2)}}{A_C^2} &\propto \frac{4}{25}P_5^2 + \frac{1}{225}P_4^2 + \frac{1}{9}P_3^2 - \frac{4}{15}P_5P_3 - \frac{4}{75}P_5P_4 \\
 &\quad + \frac{2}{45}P_3P_4, \\
 \frac{W_-^{(2)}}{A_C^2} &\propto \frac{1}{25}P_5^2 + \frac{4}{225}P_4^2 + \frac{4}{9}P_3^2 + \frac{4}{15}P_5P_3 + \frac{4}{75}P_5P_4 \\
 &\quad + \frac{8}{45}P_3P_4,
 \end{aligned} \quad (5.14)$$

the coefficient of proportionality being also equal to  $(\frac{128}{5}\pi^5)(\alpha F\omega)^2$ . From Eqs. (3.15) and (3.14) we have

$$\frac{2W_C^{(2)}}{A_C^2} \propto \frac{5}{9}P_3^2 + \frac{1}{45}P_4^2 + \frac{6}{5}P_5^2 + \frac{2}{9}P_3P_4. \quad (5.15)$$

Therefore, in this case, we see from relations (5.14) and (3.18) that we can define an electron-spin polarization which is generally different from zero and equal to

$$\rho^{(2)} = 3 \left( \frac{54P_5^2 + P_4^2 + 25P_3^2 + 10P_3P_4}{108P_5^2 + 2P_4^2 + 50P_3^2 + 20P_3P_4 + 25P_1^2 + 100P_2^2 + 100P_1P_2} \right). \quad (5.17)$$

Finally, in order to make a rapid qualitative study of these two quantities considered as functions of the frequency  $\omega$ , we note from Eqs. (5.8) that the two radial matrix elements  $P_4$  and  $P_5$  differ only by the value of the quantum number  $j$  in their  $R_{Ej}(\nu)$  functions.

So, from relation (3.10) we can deduce from QDM results that this dependence is relatively weak, since the phase shift is sensibly constant for positive energies, and then we take  $P_4 \sim P_5$  in expressions (5.16) and (5.17), which we are now discussing.

### C. Study of $P_C^{(2)}$

Based on what we wrote before, we have

$$P_C^{(2)} \simeq \frac{9P_4^2 - 3P_3^2 - 6P_3P_4}{11P_4^2 + 5P_3^2 + 2P_3P_4}. \quad (5.18)$$

With respect to the photon frequency  $\omega$ , this expression is an extremum for

$$P_4 = -2P_3 \quad \text{and} \quad P_4 = P_3/7.$$

These values correspond, respectively, to

$$P_C^{(2)}(\max) = +1 \quad \text{and} \quad P_C^{(2)}(\min) = -\frac{2}{3}. \quad (5.19)$$

This has been previously theoretically obtained.<sup>6,2,8</sup> Therefore we can conclude that the minimum of  $P_C^{(2)}$ , which corresponds to  $P_4 = P_3/7$  (i.e.,  $P_3 > P_4$  with the same sign), lies before the  $7P_{1/2}$  resonance. In fact, close to the resonances the radial matrix elements  $P_3$  and  $P_4$  defined by (5.8) are theoretically proportional to  $(E_{n_i,0,1/2} + \omega - E_{n',1,1/2})^{-1}$  and  $(E_{n_i,0,1/2} + \omega - E_{n',1,3/2})^{-1}$ , respectively. Consequently, while  $P_3$  and  $P_4$  have the same sign,  $P_C^{(2)}(\min)$  is outside the interval  $(\omega_{P_{1/2}}, \omega_{P_{3/2}})$ , where  $\omega_{P_{1/2}} = (E_{n',1,1/2} - E_{n_i,0,1/2})$  and  $\omega_{P_{3/2}} = (E_{n',1,3/2} - E_{n_i,0,1/2})$ . Moreover, since in this case  $P_3 > P_4$ ,  $P_C^{(2)}(\min)$  is nearer to the  $7P_{1/2}$  resonance than to the  $7P_{3/2}$  one. At last, as  $\omega_{P_{3/2}} > \omega_{P_{1/2}}$ ,  $P_C^{(2)}(\min)$  lies before the  $7P_{1/2}$  resonance. From the same considerations, we can conclude that  $P_C^{(2)}(\max)$  lies in the interval  $(\omega_{P_{1/2}}, \omega_{P_{3/2}})$  and is nearer to the  $7P_{3/2}$  resonance than to the  $7P_{1/2}$  one. Finally, we can determine

$$P_C^{(2)} = \frac{3}{5} \left( \frac{84P_5^2 - P_4^2 - 25P_3^2 - 40P_3P_5 - 8P_4P_5 - 10P_3P_4}{54P_5^2 + P_4^2 + 25P_3^2 + 10P_3P_4} \right). \quad (5.16)$$

In the same way, we obtain the ratio of the transition probability rates:

the values of  $P_C^{(2)}$  close to the resonances. Close to the  $7P_{1/2}$  resonance we have  $P_3 \gg P_4$  and from equation (5.18) it is

$$P_C^{(2)}(7P_{1/2}) = -0.6. \quad (5.20)$$

However, close to the  $7P_{3/2}$  resonance, we have the opposite condition  $P_4 \gg P_3$ , and it follows that

$$P_C^{(2)}(7P_{3/2}) = +0.82. \quad (5.21)$$

We can remark that these two values are exactly those obtained in our calculations as can be verified from Fig. 4. We see also on the same figure that  $P_C^{(2)}$  has a similar behavior close to the deep valley (see Figs. 1 and 4). But in this region, it is the annulment of  $P_3$  and  $P_4$ , not their relative values that explains the behavior for  $P_C^{(2)}$ . A more detailed comparison of our theoretical values of  $P_C^{(2)}$  with the measured ones (Ref. 5, Fig. 2) corresponding to the resonant  $7P_{3/2}$ ,  $7P_{1/2}$  region has been made, which is shown on Fig. 5. We can note

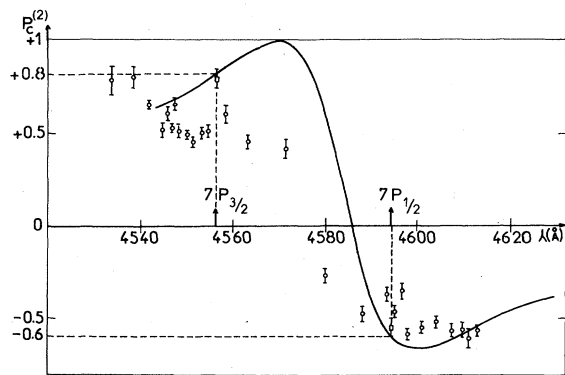


FIG. 5. Electron-spin polarization for the two-photon ionization of atomic cesium from the 6S ground state for circularly polarized radiation versus the incident photon wavelength in angstroms in the region of the  $7P_{3/2}$  and  $7P_{1/2}$  resonances. Circles: measured points (Ref. 5). Squares: measured points on resonances in the conditions indicated in the experimental work avoiding saturation. Solid line: present theoretical calculations. The arrows indicate the extrapolated values from calculations made close to the  $7P_{3/2}$  and  $7P_{1/2}$  intermediate states with wave numbers taken from Moore tables (Ref. 30).

that our theoretical values (5.20) and (5.21) (extrapolated from the calculated ones close to the resonances) approximately recover those obtained in the experiment, but between the two resonances the theoretical values are higher than the experimental ones. This last may be partly explained by considering that the light used in the experiment is not 100% right-hand circularly polarized a fact that tends to reduce the degree of spin polarization of the ejected electrons. Besides, we point out that the bandwidth of the laser used in the experiment is 12 Å (FWHM), this being comparable with the wavelength interval between resonances of the order of 40 Å, a fact that tends to mix the electron-spin polarization. This causes a tendency to reduce the values between resonances. The theoretical analysis here shown assumes fully polarized and monochromatic light without introducing level broadening or saturation effects due to the incident radiation. According to the authors of Ref. 5, the effect of the incomplete right-hand polarization may be partially compensated under experimental conditions related to the saturation of the intermediate resonant transitions. Thus they have measured

$$P_C^{(2)}(7P_{1/2}) = -0.55 \pm 0.05,$$

$$P_C^{(2)}(7P_{3/2}) = +0.80 \pm 0.05,$$

which may be considered in good agreement with our calculations. We have used for the  $7P$  resonances the transition wavelengths indicated on the Moore tables<sup>30</sup> which are 21 946.66 cm<sup>-1</sup> (4556.5 Å) and 21 765.65 cm<sup>-1</sup> (4594.4 Å) for the  $7P_{3/2}$  and  $7P_{1/2}$  states, respectively.

#### D. Study of the ratio $\rho^{(2)}$

With the previous conditions  $P_4 \sim P_5$ , Eq. (5.17) becomes

$$\rho^{(2)} = \frac{3}{2} \left( \frac{11P_4^2 + 5P_3^2 + 2P_3P_4}{11P_4^2 + 5P_3^2 + 2P_3P_4 + \frac{5}{2}(P_1 + 2P_2)^2} \right). \quad (5.22)$$

This ratio is maximum for  $P_1 = -2P_2$  and its corresponding value is

$$\rho_{\max}^{(2)} = \frac{3}{2}. \quad (5.23)$$

This result has been predicted in earlier published works.<sup>31</sup> With the same arguments as previously, we conclude that the maximum value of  $\rho^{(2)}$  lies in the interval  $(\omega_{P_{1/2}}, \omega_{P_{3/2}})$ , close to the  $7P_{1/2}$  resonance because  $P_1 > P_2$ . We note that the behavior of  $\rho^{(2)}$  in this region is different of our previous calculations<sup>9</sup> where the resonant enhancement of  $\rho^{(2)}$  was not found. Thus the present predicted values in the resonant region become comparable with the experimental results (Ref. 2, Fig. 3). This is a consequence of the introduction of the spin-orbit coupling in multiphoton ionization. For the other wavelengths in the off-resonance region, especially in the region of the deep minimum we could make the same observations as we reported in one of our previous works.<sup>11</sup> We do not present more precise values of  $\rho^{(2)}$  because we do not know the behavior of  $P_1$  and  $P_3$  very close to the  $7P_{1/2}$  resonance and the relative values of  $P_2$  and  $P_5$  close to the  $7P_{3/2}$  one. However, we can point out the behavior of  $\rho^{(2)}$  near the deep minimum which is explained by the rapid variations of the radial matrix elements in this region. In fact, there exist a greater number of possible channels for linearly polarized than for circularly polarized light. As a consequence, if one of the  $P_i$  matrix element is null, it would be possible to obtain  $W_L^{(2)} > W_C^{(2)}$  (i.e.,  $\rho^{(2)} < 1$ ) and thus  $\rho^{(2)}$  can be a minimum. Also the great variations of the radial matrix elements for frequencies lying close to that region are such that they make possible the existence of a wave number  $\omega$  corresponding to  $P_1 = -2P_2$ . Thus  $\rho^{(2)}$  can possess a maximum in that region as was previously pointed out and that is plotted in Fig. 3. We can also compare our theoretical values of  $\rho^{(2)}$  for those resonances (extrapolated from the calculated values close to the resonant wave numbers) with the experimental ones<sup>5</sup> and the theoretical values obtained with different methods<sup>6,7</sup> (finite summations, QDM, oscillator strengths and model potential) (see Table III). The discrepancy between the experimental and our own theoretical values for the  $7P_{1/2}$  resonance may be explained in two ways. First, according to the experimental information indicated in the preceding section, the laser light is not 100% right-hand cir-

TABLE III. Ratio between the generalized transition probabilities per second on the two intermediate resonances  $7P_{3/2}$  and  $7P_{1/2}$  for circularly and linearly polarized radiation. In the present work, the predicted values are calculated close to the resonances  $E(7P_{3/2}) - E(6S_{1/2}) = 21\,946.66$  cm<sup>-1</sup> or 4556.5 Å and  $E(7P_{1/2}) - E(6S_{1/2}) = 21\,765.65$  cm<sup>-1</sup> or 4594.4 Å.

$\rho^{(2)} = \frac{W_C^{(2)}}{W_L^{(2)}}$	Expt. Reference 4	Theor. Reference 5	Theor. Reference 6	Present work (Theor.)
$\rho^{(2)}(7P_{3/2})$	1.22 ± 0.01	1.28	1.23–1.28	1.23–1.24
$\rho^{(2)}(7P_{1/2})$	1.13 ± 0.01	1.36	1.33–1.36	1.32–1.39

cularly polarized, causing a weak contribution of photons with left-hand polarized light, a fact that makes possible transitions with the selection rule  $\Delta m_j = -1$ . This fact results in a weakening of the circular light contribution in the ratio  $\rho^{(2)} = W_C^{(2)}/W_L^{(2)}$  which tends to diminish its values. Second, the examination of the schemes (5.12) and (5.13) for circularly polarized light shows that there are more possibilities for the two-photon ionization via the  $7P_{3/2}$  intermediate state than there are for the  $7P_{1/2}$  one. This fact masks the influence of left-hand polarized photons for transitions through the  $7P_{3/2}$  state making those matrix elements in expression (4.7), where the  $7P_{1/2}$  intermediate state enters, more sensitive to the mixture of polarizations.

## VI. SUMMARY AND CONCLUSIONS

In this paper we have developed a theoretical analysis of the two-photon ionization of alkali-metal based on the Green's-function formalism using the quantum-defect theory extended to the spin-orbit coupling, which has not been done before. The essential points of the method may be summarized as follows. In the "effective central potential"  $V_{lsj}(r)$  formula (3.3b), the spin-orbit term converges to zero faster than  $1/r$ , thus in the framework of QDM approximations, the Green's function given by (3.6) may be considered as an exact solution of the corresponding differential equation for  $r > r_c$ . This yields correct information about real bound and about virtual states, and also for the continuum by extrapolation, where the departures of the Coulomb potential are considered by introducing the non-Coulomb phase shifts  $\delta_{jl}$ , when the quantum defects  $\mu$  are obtained from the study of measured energy states related to series of quantum numbers ( $jl$ ). In that sense, the matrix elements entering in the Green's function may be accepted as reliable as are the numerical results here presented.

In the resonant region, reasonable agreement is obtained between the predicted values obtained here and the measured ones as is shown in Secs. VC and VD. In the present analysis, neither a finite laser beam bandwidth nor saturation effects and mixing of polarizations were introduced, facts that may explain the discrepancies for the electron-spin polarization values between the two resonances (Fig. 5). On the other hand, in the off-resonant region, several observations can be made. As is shown in Fig. 1, annulment in the generalized cross section for the circularly polarized radiation in the range from 20 250 to 20 500  $\text{cm}^{-1}$  is suppressed, similarly the zero of the ratio circular to linear  $\rho^{(2)}$  (Fig. 3), since the matrix

elements of the different allowed channels are not zero at the same photon energy. Thus the influence of the spin-orbit coupling is relatively important there. The electron-spin polarization  $P_C^{(2)}$  shows very rapid variations (Figs. 4 and 1) in the region about the cross-section deep minimum, presenting both the minimum ( $-\frac{2}{3}$ ) and the maximum (+1) values in a short wave-number interval, behavior that is similar to that observed on the resonances, but the physical explanation is quite different. While in this last region these values are due to the dominance of the  $7P_{1/2}$  and  $7P_{3/2}$  states, respectively, on the deep valley characterized by virtual transitions, all the intermediate  $P$  states in the infinite summations contribute in such form that the interferences are destructive. However, the behavior of the transition rates related to a well defined final spin state, given by  ${}_+W^{(2)}$  and  ${}_-W^{(2)}$  [see Eq. (3.17)], is not exactly the same.<sup>32</sup> Indeed, the minima of  ${}_+W^{(2)}$  and  ${}_-W^{(2)}$  do not occur for the same wave number, since  ${}_+W^{(2)}$  reaches its minimum nonzero value before that of  ${}_-W^{(2)}$ , which is actually equal to zero. This fact explains in one hand that  $P_C^{(2)}(\text{min}) \neq -1$ , but on the other hand that  $P_C^{(2)}(\text{max}) = +1$ .

The comparison of very recent experimental work<sup>4</sup> to our theoretical predicted values of  $W^{(2)}/F^2$  for linearly polarized light has been made on Fig. 2 in the off-resonant region. We also report on Table I the comparison between previous experimental results<sup>1</sup> and other theoretical values. The new experiment of Saclay group shows that the deep minimum actually exists as is predicted in this paper. This result may lead to the conclusion that the Granneman et al.<sup>1</sup> experiment in the off-resonant region should be considered as being superceded. The reason for such a mistake can be found in the following remark: Close to the wavelength corresponding to the minimum, there exists a one-step ionization process of the molecule  $\text{Cs}_2$  which masks the two-photon atomic transition<sup>4</sup>-at the laser light intensities used in the experiments of Ref. 1. The similar behavior of the deep minimum is also obtained in another theoretical analysis<sup>33</sup> where a model potential and the Green's-function formalism on the basis of the Sturmian expansion was used. Similarly, the work of Rachman *et al.*,<sup>11</sup> where comparison between measured and predicted values is made for different cases of two- and three-photon ionization of alkali-metal atoms including the electric quadrupole contribution, shows the minimum. In order to attempt to explain the strong discrepancy between the second-order perturbation theory and the previous experimental results,<sup>1</sup> two main theories have been advanced: Firstly, Theodosiou and Armstrong<sup>34</sup> introduce time dependence by using a



sudden coupling between the atomic states and the field, an assumption that is not fulfilled by the experimental conditions described by Morellec *et al.*<sup>4</sup>. Secondly, Armstrong and Eberly<sup>35</sup> studied the effects of laser bandwidth in the case that only two distinct near-resonant channels of ionization exist as intermediate unperturbed states, but this has not been found at all and thus this last explanation seems to be irrelevant.

In the present work, we obtain the essential features of the experiment,<sup>4</sup> i. e., the existence of the interference destructive effects and the deep minimum. Good agreement has been found for the value corresponding to the minimum of the generalized cross section for linearly polarized light. On one hand, the examination of Fig. 2 shows that the theoretical curve related to the deep minimum region is displaced about  $500 \text{ cm}^{-1}$  (less than 0.1 eV), but on the other hand, a very good agreement is found far from this minimum region with respect to the experimental results<sup>4</sup> on the low incident-photon-energy side. For instance, for the wavelength value  $\lambda = 528 \text{ nm}$  (2.348 eV) the measured values of  $W_L^{(2)}/F^2$  for the second harmonic of a single mode linearly polarized Nd<sup>3+</sup> glass la-

ser were, respectively,  $(6.2 \pm 2.6)$  and  $(7.1 \pm 3) \times 10^{50} \text{ cm}^4 \text{ s photon}^{-2}$  for a cylindrical and spherical focusing, while the predicted value obtained in the present work is  $6.598 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-2}$ . A possible explanation of the previously indicated difference may be due to the fact that we have not introduced higher-order effects. On one hand, it is well known<sup>36</sup> that these effects are very important on the resonant region for a few number of dressed states which are strongly mixed. On the other hand, far from resonances, the shift and broadening of the coupled atom-field states are weak, but in this case all these states occur with the same weight in the expression of the generalized cross section, thus leading to a cumulative correction which may become important. This then suggests possible research on the influence of higher-order effects in the off-resonance region.

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<sup>24</sup>In our problem, we shall consider  $E > 0$  relatively small (because  $E \leq E_I/2$  for the two-photon ionization,  $E \leq E_I/3$  for the three-photon ionization and so on,  $E_I$  being the ionization energy of the studied atom) so the wave number  $k$  will be equally small. Therefore to establish expression (2.17) we have neglected the quantity  $\exp(-2\pi/k)$  beside unity which appears in the course of calculation. From relation (2.8) we note that this assumption is equivalent to considering  $\delta_l = \pi\mu_l$  as it will be used in the next section of this text.

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