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APPLICATION OF NEAR-RESONANT TWO-PHOTON IONIZATION TO MEASURE NON-COULOMB PHASE SHIFTS OF PHOTOELECTRON PARTIAL WAVES*

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Within the fine-structure energy scheme, photoelectron angular distributions in two-photon ionization of unpolarized ground state alkali atoms with two different light beams, the one exciting and the other ionizing, are studied theoretically applying second-order time-dependent perturbation method. Relevant formulae are proposed in a form directly applicable in experiment to measure the difference between non-Coulomb phase shifts for the S and D partial waves of the photoelectron. Emphasis is laid on disclosing analogies between the distributions for two- and one-quantum atomic photoeffect. The pioneering experiment of Duncanson et al. on Na atoms ionized resonantly via either the $3P_{1/2}$ or $3P_{3/2}$ state is commented.

1. *Introduction*

Experiments on near-resonant two-photon ionization of alkalis are known [1, 2] to provide valuable knowledge on two dynamical atomic parameters, namely the appropriate bound-free radial integral ratio and the difference between non-Coulomb phase shifts of the partial photoelectron waves involved, which are by no means easily calculable. Explicitly, if a ground state alkali atom is assumed to undergo ionization via the nearly resonant intermediate state nP_j, the parameters accessible to measurement are $d_j = R(nP_j, KS)/R(nP_j, KD)$ and $\cos(\delta_D - \delta_S)$, with $R(nP_j, KS(D))$ the usual electric dipole radial integral connecting the state nP_j with the S and D continuum state, respectively, and $\delta_{S,D}$ the non-Coulomb phase shift of those final electron states. The required near-resonance with some nP doublet level can be produced [3] with the help of e.g. a tunable dye laser, whereas ionization from the excited state can proceed due to the light beam of another laser. In such two light beam experiment, information on the parameter d_j alone can be

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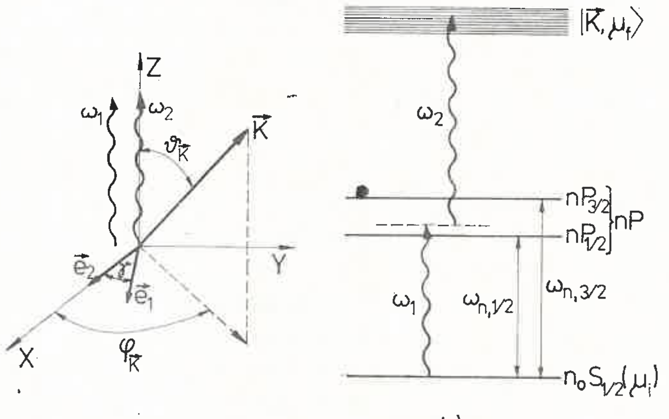
extracted from various measurable total characteristics e.g. the rate of ionization, photoelectron polarization and yield asymmetry. The relevant formulae required to this purpose have recently been derived by us and extensively discussed elsewhere [4–8]. However, to gain information on the parameter $\cos(\delta_D - \delta_S)$, strictly calculable for the hydrogen atom only, angular distributions have to be measured. To my knowledge, only one measurement of this type by Duncanson et al. [3] has hitherto been reported; thus, further experiments in this field are necessary. Obviously, it is desirable to have appropriate analytical equations for the distributions in question to this practical aim. Some have already been mentioned by us [9], permitting the measurement of the troublesome parameter $\cos(\delta_D - \delta_S)$ from the spin-depolarization degree of photoelectrons produced from polarized target atoms by linearly polarized light. In the present paper other formulae are proposed, more convenient in applications, since neither polarized targets nor photoelectron polarization measurements are required in the cases to be considered in this paper.

2. *Method of calculation*

2.1. Assumptions and geometry of the process

Let the alkali atom be unpolarized in its ground state $n_0S_{1/2}$ and occupy the origin of the Cartesian system XYZ. In the $+Z$ direction two different photon beams are propagating, the one exciting (labelled 1) with the frequency ω_1, intensity I_1 and polarization $\vec{e}_1$, and the other, ionizing (labelled 2) with the parameters ω_2, I_2 and $\vec{e}_2$. The frequency ω_1, contrary to ω_2, is assumed to be tuned to the vicinity of some nP doublet allowable by the selection rules for the $E1$ transition. However, the detuning from exact resonance with the component $nP_{1/2}$ or $nP_{3/2}$ of the nP doublet is assumed to exceed the hyperfine splitting of the components so that the fine structure energy scheme of the ionized atom



a) b)

Fig. 1. Geometry of the problem (a) and reduced energy spectrum of the ionized atom (b) used in the calculations. For explanations, see text

is fully justified in our subsequent considerations. Furthermore, the intensities of the incident beams 1 and 2 are chosen so that the predominant way of ionization is by successive absorption of the energy $\hbar\omega_1 + \hbar\omega_2$ i.e. first a photon from beam 1 and then a photon from beam 2 in an elementary two-photon event. As regards the polarizations of the incoming light beams, these are assumed to be elliptical but, in general, with different ellipticities $0 \leqslant \kappa_1 \leqslant 1$ and $0 \leqslant \kappa_2 \leqslant 1$, respectively. By assumption, the major semiaxis of the polarization ellipse of the ionizing beam 2 coincides with the X-axis, while the major semiaxis of the exciting beam 1 is tilted at an angle γ with respect to the X-axis (Fig. 1).

2.2. Transition amplitudes

The quantity most fundamental to the description of the entire physics of the process in question is the transition amplitude, to be henceforth denoted by $M^{(2)}_{\mu_f,\mu_i}$, for two-photon ionization from the ground state $n_0S_{1/2}(\mu_i)$, where the Z-component of the valence electron spin is μ_i, to the continuum $|\vec{K}, \mu_f\rangle$ with momentum $\hbar\vec{K}$ and spin projection onto the Z-axis equal to μ_f. Under the above assumed condition of near-resonance with the nP doublet and within the standard second-order time-dependent perturbation approach and fine-structure energy scheme, the following approximation

$$M^{(2)}_{\mu_f,\mu_i} = \sum_{j=1/2,3/2} \frac{\langle \vec{K}, \mu_f | \vec{e}_2 \cdot \vec{r} | nP_j \rangle \langle nP_j | \vec{e}_1 \cdot \vec{r} | n_0S_{1/2}(\mu_i) \rangle}{\omega_{n,j} - \omega_1} \tag{1}$$

holds for the transition amplitude, with $\vec{e}_1 \cdot \vec{r}$ and $\vec{e}_2 \cdot \vec{r}$ operators specific for the electric dipole coupling between atoms and photons, and $\hbar\omega_{n,j}$ the energy of the intermediate state nP_j measured with respect to the ground state. We emphasize that in Eq. (1) all off-near-resonant terms have been neglected in the summation over intermediate states of the atom (Fig. 1). Such a simplification is known [10] to be quite good in the majority of near-resonant cases.

In our previous papers [5, 8], angular momentum algebra has been carried out strictly to reduce the definition Eq. (1) to a form including, as unknowns, only the appropriate radial parameters and phase shifts $\delta_{S,D}$. The equations derived there are valid for polarized as well as unpolarized ground state alkali atoms, all conceivable experimental geometries of the process with two light beams and all practically important combinations of polarization states of the exciting and ionizing beams. Accordingly, referring the Reader to those papers, we shall restrict ourselves to give only the final equations for $M^{(2)}_{\mu_f,\mu_i}$ adapted to the geometry and light polarizations assumed above (Fig. 1). For the four possible combinations of initial and final electron spin projections onto the Z-axis, the equations are:

$$M^{(2)}_{+1/2,+1/2} = -\frac{4\pi}{9} e^{i\delta_S}(S_4 - S_3)\{[(z-1)a^{(1)}_{-1}a^{(2)}_{+1} + (z+1)a^{(1)}_{+1}a^{(2)}_{-1}]dY_{0,0}(\vartheta_{\vec{K}}, \varphi_{\vec{K}})$$

$$+ \frac{1}{\sqrt{5}}[(y-1)a^{(1)}_{-1}a^{(2)}_{+1} + (y+1)a^{(1)}_{+1}a^{(2)}_{-1}]e^{i(\delta_D - \delta_S)}Y_{2,0}(\vartheta_{\vec{K}}, \varphi_{\vec{K}})$$

$$+\sqrt{\tfrac{6}{5}}\,(y-1)a_{-1}^{(1)}a_{-1}^{(2)}e^{i(\delta_D-\delta_S)}Y_{2,-2}(\vartheta_{\vec{K}},\varphi_{\vec{K}})$$

$$+\sqrt{\tfrac{6}{5}}\,(y+1)a_{+1}^{(1)}a_{+1}^{(2)}e^{i(\delta_D-\delta_S)}Y_{2,+2}(\vartheta_{\vec{K}},\varphi_{\vec{K}})\}\,, \tag{2}$$

$$M_{+1/2,-1/2}^{(2)} = -\frac{4\pi}{9}\sqrt{\tfrac{6}{5}}\,(S_4-S_3)e^{i\delta_D}[a_{+1}^{(1)}a_{-1}^{(2)}Y_{2,-1}(\vartheta_{\vec{K}},\varphi_{\vec{K}})+a_{+1}^{(1)}a_{+1}^{(2)}Y_{2,+1}(\vartheta_{\vec{K}},\varphi_{\vec{K}})], \tag{3}$$

with $\vartheta_{\vec{K}}$ and $\varphi_{\vec{K}}$ the polar angle and azimuth describing the trajectory of the photoelectron (Fig. 1) in spherical coordinates, whereas $a_\varrho^{(\nu)}$ are the polarizational-geometrical factors [4] attached to the ν-th light beam ($\nu = 1, 2$) equal to

$$a_{-1}^{(\nu)} = (1\mp\kappa_\nu)\,[2(1+\kappa_\nu^2)]^{-1/2}e^{2i(1-\nu/2)\gamma},$$

$$a_{+1}^{(\nu)} = -(1\pm\kappa_\nu)\,[2(1+\kappa_\nu^2)]^{-1/2}e^{-2i(1-\nu/2)\gamma}, \tag{4}$$

where the double sign at the ellipticity κ_ν corresponds to the two possible senses of elliptical polarization of the ν-th light beam. If the sense of polarization is defined according to the angular momentum convention, the upper sign denotes right-hand and the lower sign left-hand elliptical polarization. Obviously, circular and linear polarizations are explicitly included in Eq. (4) as two different limiting cases for $\kappa_\nu = 1$ and $\kappa_\nu = 0$, respectively. Furthermore, y, z and d are atomic purely radial parameters, defined as

$$y = \frac{2S_4+S_3}{S_4-S_3}, \qquad z = \frac{2S_2+S_1}{S_2-S_1}, \qquad d = \frac{S_2-S_1}{S_4-S_3}, \tag{5}$$

with

$$S_1 = R(n_0S, nP_{1/2})R(nP_{1/2}, KS)\,(\omega_{n,1/2}-\omega_1)^{-1}, \tag{6}$$

$$S_2 = R(n_0S, nP_{3/2})R(nP_{3/2}, KS)\,(\omega_{n,3/2}-\omega_1)^{-1}, \tag{7}$$

$$S_3 = R(n_0S, nP_{1/2})R(nP_{1/2}, KD)\,(\omega_{n,1/2}-\omega_1)^{-1}, \tag{8}$$

$$S_4 = R(n_0S, nP_{3/2})R(nP_{3/2}, KD)\,(\omega_{n,3/2}-\omega_1)^{-1} \tag{9}$$

the radial matrix elements of near-resonant two-photon ionization with spin-orbit effects in the D-continuum being disregarded. We note that the two remaining amplitudes, namely $M_{-1/2,-1/2}^{(2)}$ and $M_{-1/2,+1/2}^{(2)}$ are obtainable from Eqs (2) and (3), respectively, by the simultaneous interchange $a_\varrho^{(\nu)} \to a_{-\varrho}^{(\nu)}$ and $Y_{l,m} \to Y_{l,-m}$.

As seen from Eqs (2) and (3), four unknowns (y, z, d and $\cos(\delta_D-\delta_S)$) are in general inherent in the equation for any angular distribution. Fortunately, the number of unknown parameters reduces to two only, namely those mentioned earlier and denoted as $d_j = R(nP_j, KS)/R(nP_j, KD)$ and $\cos(\delta_D-\delta_S)$, respectively, if the frequency ω_1 of the exciting beam 1 is near to a resonance with the component $nP_{1/2}$ or $nP_{3/2}$ of the nP doublet and, simultaneously, the detuning from that component (by assumption exceeding its hyperfine structure) is much smaller than the fine-structure splitting of the doublet under consideration. With those conditions, the following approximations are reliable:

$$y = z = -1 \quad \text{and} \quad d = d_{1/2} \quad \text{if} \quad \omega_1 \simeq \omega_{n,1/2},$$

$$y = z = +2 \quad \text{and} \quad d = d_{3/2} \quad \text{if} \quad \omega_1 \simeq \omega_{n,3/2}, \tag{10}$$

permitting the determination of d_j and, particularly, $\cos(\delta_D - \delta_S)$ by fitting the relevant theoretical equation to the experimental curve of distributions.

Finally, we would like to emphasize that, for the light alkalis, near-resonance with either the $nP_{1/2}$ or $nP_{3/2}$ state is not required in order to measure the term $\cos(\delta_D - \delta_S)$, since in the light alkalis the j-dependence of the radial wavefunctions of P discrete states is neglegible [11] entailing $d = d_0 = R(nP, KS)/R(nP, KD)$ and

$$y = z = \frac{2[(\omega_{n,1/2} - \omega_1)/(\omega_{n,3/2} - \omega_1)] + 1}{[(\omega_{n,1/2} - \omega_1)/(\omega_{n,3/2} - \omega_1)] - 1}, \tag{11}$$

which is always known at a fixed ω_1-value.

2.3. Rate of ionization in a $\vartheta_{\vec{K}}$, $\varphi_{\vec{K}}$-direction

With the transition amplitudes $M^{(2)}_{\mu_f,\mu_i}$ available, the angular distributions of photoelectrons ejected from unpolarized atoms can be calculated by having recourse to the standard formula of two-photon ionization theory [10]:

$$\sigma^{(2)}(\vartheta_{\vec{K}}, \varphi_{\vec{K}}) = \tfrac{1}{2} \frac{\hbar}{\mathrm{Ry}} \left(\frac{\varepsilon}{\mathrm{Ry}}\right)^{1/2} (\alpha r_0^2)^2 \omega_1 \omega_2 \, \tfrac{1}{2} \sum_{\mu_f,\mu_i} |M^{(2)}_{\mu_f,\mu_i}|^2, \tag{12}$$

where $\sigma^{(2)}(\vartheta_{\vec{K}}, \varphi_{\vec{K}})$ is the so-called generalized differential cross-section, in the sense introduced by Lambropoulos and Teague [10], for photoemission of an electron in a $\vartheta_{\vec{K}}$, $\varphi_{\vec{K}}$-direction; while $\alpha \simeq 1/137$; $r_0 \simeq 5.29 \times 10^{-9}$ cm; ε is the kinetic energy of the photoelectron; and Ry the Rydberg energy.

3. *Results and discussion*

Though light with elliptical polarization has been proved [6] to be more useful than light with other polarizations in some two-photon ionization experiments, nonetheless circular and linear polarizations are usually preferred by experimentators. Thus, we intentionally restrict our discussion to those two light polarizations only.

3.1. Both light beams circularly polarized with the same helicity

Such a combination of light polarizations is the simplest to theoretical description but, at the same time, inappropriate to the aims stated at the beginning of the present paper. This is closely related with the fact that if two circularly polarized photons propagating in the $+Z$-direction with the same helicity, say $+1$, are successively absorbed, the magnetic quantum number of the absorbing electron has to increase by 2. Consequently, in the final electron state, the possible magnetic quantum numbers are $+3/2$ and $+5/2$. Accordingly, from two partial waves, S and D, in general accessible in the continuum, only the latter contributes to the transition amplitudes $M^{(2)}_{\mu_f,\mu_i}$. This unavoidably leads to distributions independent of the term $\cos(\delta_D-\delta_S)$ specific for the interference between S and D photoelectron partial waves. Since the combination of polarization states of the exciting and ionizing light beams assumed here is inapplicable to measure the term $\cos(\delta_D-\delta_S)$, we refrain from analysing this case.

3.2. Both light beams circularly polarized with opposite helicity

It is of our aim to point out in this subsection that collinear light beams with circular polarizations can be used to measure the parameter $\cos(\delta_D-\delta_S)$ provided that they have opposite helicities. If this is the case then the magnetic quantum numbers of the final electron states have to be the same as in the ground state i.e. to amount to $\pm 1/2$. Accordingly, in the present case the S-continuum partial wave is allowable as well in the transition amplitudes and, consequently, the interference between S and D waves, specifically leading to the desirable term $\cos(\delta_D-\delta_S)$, is expected to appear in the formulae for the angular distributions. For an unpolarized atomic target interacting with a right-hand circularly polarized exciting and left-hand circularly polarized ionizing beam, both propagating in the same direction, the relevant formula pointing to this fact is

$$\sigma^{(2)}(\vartheta_{\vec{K}}) = \frac{\sigma^{(2)}}{4\pi}\left[1+\beta_2 P_2(\cos\vartheta_{\vec{K}})+\beta_4 P_4(\cos\vartheta_{\vec{K}})\right], \tag{13}$$

with $\sigma^{(2)}$ the generalized total cross-section for the geometry and light polarizations in question:

$$\begin{aligned}\sigma^{(2)} &= \int_0^{2\pi} d\varphi_{\vec{K}} \int_0^{\pi} d\vartheta_{\vec{K}}\,\sigma^{(2)}(\vartheta_{\vec{K}}) \\ &= \frac{8\pi^2}{405}\,\frac{\hbar}{\mathrm{Ry}}\left(\frac{\varepsilon}{\mathrm{Ry}}\right)^{1/2}(\alpha r_0^2)^2\omega_1\omega_2(S_4-S_3)^2\left[5d^2(z^2+1)+y^2+4\right],\end{aligned} \tag{14}$$

whereas β_2 and β_4 are two asymmetry parameters, both dependent on details of the atomic potential, given by

$$\beta_2 = \tfrac{5}{7}\,\frac{2y^2+14(yz+1)d\cos(\delta_D-\delta_S)+5}{5d^2(z^2+1)+y^2+4}, \tag{15}$$

$$\beta_4 = \tfrac{18}{7}\,\frac{y^2-1}{5d^2(z^2+1)+y^2+4}, \tag{16}$$

and $P_2(x)$ and $P_4(x)$ are Legendre polynomials of second and fourth rank, respectively:

$$P_2(x) = \tfrac{1}{2}(3x^2-1), \quad P_4(x) = \tfrac{1}{8}(35x^4-30x^2+3). \tag{17}$$

In our opinion, in order when applying the above equations to measure the term $\cos(\delta_D-\delta_S)$, two cases should be distinguished: (*i*) the case when the j-dependence of the radial wavefunctions in P discrete states is negligible (the light alkalis) and (*ii*) the case when this j-dependence has to be strictly taken into account (higher excited doublets of the heavier alkalis, particularly caesium [12]).

In the case (*i*), d goes over into $d_0 = R(nP, KS)/R(nP, KD)$, whereas the parameters y and z become identical and, for a fixed ω_1-value, non-necessarily resonant; they can be calculated from Eq. (11) without difficulty. Accordingly, in the case (*i*) the asymmetry parameter β_4 depends on one unknown d_0 only, while β_2 is dependent on d_0 as well as on $\cos(\delta_D - \delta_S)$. By fitting Eq. (13) to the curve $\sigma^{(2)}(\vartheta_{\vec{K}})$, measured in experiment, both β_2 and β_4 can be determined. In the next step, the parameter d_0^2 can be calculated from Eq. (16). Once d_0^2 is known then, having recourse to Eq. (15) for β_2, we determine the terms $\cos(\delta_D - \delta_S)$ with accuracy to its sign.

In the case (*ii*) near-resonance with the component nP_j of the nP doublet is required in order to measure first d_j and then the more embarrasing term $\cos(\delta_D - \delta_S)$. To this aim near-resonance with the state $nP_{3/2}$, instead of $nP_{1/2}$, is more favourable since now, in conformity with the approximations (10) for y and z, both β_2 and β_4 are nonzero and, in practice, we can proceed exactly in the same way as described above for the case (*i*). Near-resonance with the state $nP_{1/2}$ is not recommended since then $\beta_4 = 0$ and only one equation for β_2, namely (15), is available with two independent unknowns $d_{1/2}$ and $\cos(\delta_D - \delta_S)$, unfortunately. Thus, under near-resonant conditions with the state $nP_{1/2}$, a complementary measurement of $d_{1/2}$ has to be carried out in a separate experiment in order that the term $\cos(\delta_D - \delta_S)$ can be found. The parameter $d_{1/2}$ can be determined e.g. from the measured value of the ratio of two generalized total cross-sections $\sigma^{(2)}$ for two different combinations of polarization states of the exciting and ionizing light beams. The formulae required to measure the parameter $d_{1/2}$ alone have recently been proposed and discussed by us elsewhere [4].

Finally, we note that from symmetry considerations it follows that Eqs (13)–(16) are also valid for light beams circularly polarized in the same sense, provided that they are counterpropagating.

3.3 Both light beams linearly polarized in different directions

The distributions considered in the previous subsection are isotropic in the XY-plane due to rotational symmetry about the wave vector of the circularly polarized light beams and thus only one angle $\vartheta_{\vec{K}}$ is sufficient to their complete description. Since in light linearly polarized this symmetry is broken thus, in general, an additional azimuthal angle $\varphi_{\vec{K}}$ is expected to be needed to describe angular distributions generated by two collinear light beams linearly polarized with polarization vectors tilted at an angle γ (Fig. 1), on which the distributions should be in general dependent as well. However, the values of the internal atomic parameters of interest to us, namely, d_j and $\cos(\delta_D - \delta_S)$ extracted from the experimental data have to be the same for different angles γ. This can provide an additional check of the internal consistency (or discrepancy) of the results obtained experimentally. Thus, it seems that values of d_j and $\cos(\delta_D - \delta_S)$ found in experiments with two light beams linearly polarized in different directions should be more reliable than values obtained with other combinations of light polarizations.

Two collinear light beams, both polarized linearly but in different directions, produce angular distributions described by the following general formula:

$$\sigma^{(2)}(\vartheta_{\vec{K}}, \varphi_{\vec{K}}) = \frac{2\pi}{81}\,\frac{\hbar}{\mathrm{Ry}}\left(\frac{\varepsilon}{\mathrm{Ry}}\right)^{1/2} (\alpha r_0^2)^2\omega_1\omega_2(S_4-S_3)^2$$

$$\times[a_0(\gamma)+a_2(\gamma, \varphi_{\vec{K}})\sin^2\vartheta_{\vec{K}}+a_4(\gamma, \varphi_{\vec{K}})\sin^4\vartheta_{\vec{K}}], \tag{18}$$

with:

$$a_0(\gamma) = 1+(y^2-1)\cos^2\gamma+[1+(z^2-1)\cos^2\gamma]d^2$$

$$+2[1+(yz-1)\cos^2\gamma]d\cos(\delta_D-\delta_S), \tag{19}$$

$$a_2(\gamma, \varphi_{\vec{K}}) = \tfrac{3}{2}-3(y^2-1)\cos^2\gamma-3[1+(yz-1)\cos^2\gamma]d\cos(\delta_D-\delta_S)$$

$$+\tfrac{3}{2}\{1-2(y^2-1)\cos^2\gamma-2[1+(yz-1)\cos^2\gamma]d\cos(\delta_D-\delta_S)\}\cos 2\varphi_{\vec{K}}$$

$$-\tfrac{3}{2}[y^2-1+(yz-1)d\cos(\delta_D-\delta_S)]\sin 2\gamma\sin 2\varphi_{\vec{K}}, \tag{20}$$

$$a_4(\gamma, \varphi_{\vec{K}}) = \tfrac{9}{8}(y^2-1)(1+2\cos^2\gamma+4\cos^2\gamma\cos 2\varphi_{\vec{K}}$$

$$+2\sin 2\gamma\sin 2\varphi_{\vec{K}}+\cos 2\gamma\cos 4\varphi_{\vec{K}}+\sin 2\gamma\sin 4\varphi_{\vec{K}}), \tag{21}$$

where, in accordance with Fig. 1, the azimuth $\varphi_{\vec{K}}$ is measured with respect to the polarization of the ionizing light beam 2.

Let us first consider briefly the case when the polarization directions of beams 1 and 2 are identical; mathematically, this is equivalent to $\gamma = 0$. Then, with θ denoting the angle of emission of the photoelectron measured with respect to the common polarization direction of both light beams, Eq. (18) reduces to:

$$\sigma^{(2)}(\theta) = \frac{\sigma^{(2)}}{4\pi}[1+\beta_2 P_2(\cos\theta)+\beta_4 P_4(\cos\theta)], \tag{22}$$

where:

$$\sigma^{(2)} = \frac{8\pi^2}{405}\,\frac{\hbar}{\mathrm{Ry}}\left(\frac{\varepsilon}{\mathrm{Ry}}\right)^{1/2}(\alpha r_0^2)^2\omega_1\omega_2(S_4-S_3)^2(4y^2+5d^2z^2+6), \tag{23}$$

$$\beta_2 = \tfrac{10}{7}\,\frac{4y^2-14dyz\cos(\delta_D-\delta_S)+3}{4y^2+5d^2z^2+6}, \tag{24}$$

$$\beta_4 = \tfrac{72}{7}\,\frac{y^2-1}{4y^2+5d^2z^2+6}. \tag{25}$$

Since Eq. (22) is formally analogous to (13), all indications following after Eq. (17) and concerning the method of determination of the term $\cos(\delta_\mathrm{D}-\delta_\mathrm{S})$ from the experimental data are also valid in reference to formulae (22)–(25). Furthermore, although the above formulae hold for near-resonant two-photon ionization with two different (as to their frequencies and intensities) light beams, they are easily adaptable to the proces with one off-resonant light beam at frequency ω. To this aim it suffices to put $\omega_1 = \omega_2 = \omega$ and, additionally, the sign of summation over all bound and free P states has to appear on the right-hand side of the definition equations (6)–(9) for the radial matrix elements $S_1 - S_4$. Further, neglecting in the next step spin-orbit effects in P states (independence of the energy levels and radial wavefunctions on j), one is easily convinced that with the help of our Eq. (22) the previous formula of Zernik [13] and Arnous et al. [14] for the hydrogen atom can be reproduced exactly.

The general Eq. (18) leaves the experimentator considerable freedom as to the choice of the plane of observation of the photoelectron angular distributions. However, in order to take up an attitude towards the pioneering experiment of Duncanson et al. [3], we now adapt Eq. (18) to observation in the XY-plane in which both polarization vectors $\vec{e}_1$ and $\vec{e}_2$ are lying. In this plane the distributions are analytically described by:

$$\begin{aligned} \sigma^{(2)}(\varphi_{\vec{K}}) = {} & c_1 + c_2 \cos 2\varphi_{\vec{K}} + c_3 \sin 2\varphi_{\vec{K}} \\ & + c_4 \cos 4\varphi_{\vec{K}} + c_5 \sin 4\varphi_{\vec{K}}, \end{aligned} \tag{26}$$

with $c_n = c_0 c'_n$, where $n = 1, 2, \ldots, 5$, and

$$c_0 = \frac{2\pi}{81} \frac{\hbar}{\mathrm{Ry}} \left(\frac{\varepsilon}{\mathrm{Ry}}\right)^{1/2} (\alpha r_0^2)^2 \omega_1 \omega_2 (S_4 - S_3)^2, \tag{27}$$

$$\begin{aligned} c'_1 = {} & \tfrac{9}{8}(y^2+1) + \tfrac{1}{4}[1+(y^2-1)\cos^2\gamma] + [1+(z^2-1)\cos^2\gamma]d^2 \\ & - [1+(yz-1)\cos^2\gamma]d \cos(\delta_D - \delta_S), \end{aligned} \tag{28}$$

$$c'_2 = \tfrac{3}{2}\{1+(y^2-1)\cos^2\gamma - 2[1+(yz-1)\cos^2\gamma]d\cos(\delta_D-\delta_S)\}, \tag{29}$$

$$c'_3 = \tfrac{3}{4}[y^2-1-2(yz-1)d\cos(\delta_D-\delta_S)]\sin 2\gamma, \tag{30}$$

$$c'_4 = \tfrac{9}{8}(y^2-1)\cos 2\gamma, \tag{31}$$

$$c'_5 = \tfrac{9}{8}(y^2-1)\sin 2\gamma. \tag{32}$$

Formally, Eq. (26) is identical with that used by Duncanson et al. in their measurement of the angular distributions of electrons from resonant two-photon ionization of unpolarized sodium atoms via either the $3P_{1/2}(y = z = -1$ and $d = d_{1/2})$ or $3P_{3/2}(y = z = +2$ and $d = d_{3/2})$ level. Of particular interest are their results for resonance with the $3P_{3/2}$ state. For this case, Duncanson et al. have found the coefficients c_1, c_2, c_3, c_4 and c_5 at three different angles γ by least-squares fits of Eq. (26) with the experimental curve $\sigma^{(2)}(\varphi_{\vec{K}})$ normalized to 1 at $\varphi_{\vec{K}} = 0$. In the next step, having available (but unfortunately unreported in their paper) analytical expressions for $c_1, \ldots, c_5$ they determined the parameters $d_{3/2}$ and $\cos(\delta_D-\delta_S)$. Their final conclusion is that the best fit is at $d_{3/2} = +2$ and $\cos(\delta_D-\delta_S) = +1$. For the above best-fit values of the parameters $d_{3/2}$ and $\cos(\delta_D-\delta_S)$ they further present in their Table II theoretical values of the coefficients $c_1, \ldots, c_5$ found on the basis of their equations for those coefficients. Obviously, if their equation for $c_1, \ldots, c_5$, not presented in [3], and ours given by (27)–(32) are identical, it should be feasible to reproduce their Table II with the help of our Eqs (27)–(32), in which $y = z = +2$, $d = d_{3/2} = +2$ and $\cos(\delta_D-\delta_S) = +1$ should be put to this aim. Unfortunately, this is not possible unless we change the sign at the interference term $d\cos(\delta_D-\delta_S)$ in our Eqs (28)–(30). However, if this is done, the formula of Zernik [13] and Arnous et al. [14] for hydrogen cannot be obtained from our equations modified in such a way. This suggests that there may be some mistake concerning the sign at the term $d\cos(\delta_D-\delta_S)$ in the formulae of Duncanson et al. for the coefficients $c_1, \ldots, c_5$. If our supposition is true, the parameters $d_{3/2}$ and $\cos(\delta_D-\delta_S)$ have to be of opposite signs and the best fit is achievable either at $d_{3/2} = +2$ and $\cos(\delta_D-\delta_S) = -1$ or at $d_{3/2} = -2$ and $\cos(\delta_D-\delta_S) = +1$, but not at $d_{3/2} = +2$ and $\cos(\delta_D-\delta_S) = +1$, as reported by Duncanson et al.

3.4. Analogies to one-quantum photoeffect

Eqs (13) and (22) of the present paper are consistent with the general theorems of Yang [15] concerning the form of angular distributions of products of nuclear reactions and disintegrations based only on the invariance properties of the physical processes under space rotation and under inversion. As seen from (13) and (22) in two-photon process the angular distributions are in general described by two asymmetry parameters β_2 and β_4, as distinct from the usual one-quantum photoeffect, where only one asymmetry parameter is sufficient [16]. In fact, the term $\beta_4 P_4$, inherent in Eqs (13) and (22), is specific to the two-photon nature of the process. However, in particular, at both $y = -1$ and $+1$ this term is ruled out from these equations and the distributions become similar to those for the one-photon process with the obvious restriction that for one-quantum photoeffect both the total cross-sections and asymmetry parameters are described by other equations than those marked as (14), (15) and (23), (24), respectively. With regard to Eq. (10), the condition $y = -1$ is tantamount to a near-resonance with the state $nP_{1/2}$, whereas in order to assign the corresponding frequency to the condition $y = +1$, let us assume for the moment that the j-dependence of radial wave-functions in P discrete states can be disregarded, as for all doublets in the light alkalis and the first excited doublet in the heavy alkalis. In that case the approximation (11) for y is in force, whence it follows that $y = +1$ is equivalent to $\omega_1 = \omega_{n,1/2}+\frac{2}{3}(\omega_{n,3/2}-\omega_{n,1/2})$ i.e. to observe the cancellation of the term $\beta_4 P_4$, specific for the two-photon process, it is recommended to detune the frequency ω_1 of the exciting beam 1 by about 1/3 of the fine splitting interval from the $nP_{3/2}$ doublet component towards lower frequencies. In addition, just at $\omega_1 = \omega_{n,1/2} +\frac{2}{3}(\omega_{n,3/2}-\omega_{n,1/2})$ the distributions (18) cease to depend on relative orientation of polarization vectors $\vec{e}_1$ and $\vec{e}_2$ of collinear linearly polarized light beams 1 and 2, if the light alkalis are ionized. The last result is complementary to the result of Duncanson et al. who have previously found that the γ-independence and, consequently, the analogy to one-quantum photoeffect occurs at $\omega_1 = \omega_{n,1/2}$.

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