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Spin-Orbit Coupling and Photoelectron Polarization in Multiphoton Ionization of Atoms

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It is shown that multiphoton ionization of unpolarized atoms with circularly polarized light can lead to the production of highly polarized electrons. The connection of this effect with the Fano effect in single-photon ionization is discussed.

Recent[1-4] discussions of the effect of light polarization on multiphoton ionization have been based on a hydrogenlike model without spin-orbit coupling. For incident photon frequencies such that resonances with intermediate states exist, this coupling cannot always be neglected, especially when the energy splitting of the resonant intermediate state is larger than the spectral width of the incident radiation. This condition can be easily satisfied in many present-day multiphoton experiments. In that case, previously reported[1,2] differential and total cross sections change. But, perhaps more important, the emitted photoelectrons can be spin polarized to a significant degree when the incident radiation is circularly polarized. This paper presents a quantitative estimate of this effect and suggests experiments in which highly polarized and relatively intense electron beams can be produced.

For the sake of presenting specific numerical estimates, this discussion refers to the alkali atoms. Many of the general conclusions, however, would apply to other atoms as well. The results presented here are confined to two- and three-photon ionization, mainly because explicit numerical calculations of the relevant cross sections are available.[5] Again the conclusions are also valid for higher-order processes. It is assumed that the radiation intensity is low enough for perturbation theory to be valid. This would certainly be the case for all experiments that are contemplated herein.

The calculation is performed along lines similar to those of earlier papers,[1-3] except that now the atomic states have the form $|nljm_j\rangle$, where n is the principal quantum number, l the orbital angular momentum, j the total angular momentum, and m_j the projection of j on the quantization axis. For circularly polarized radiation, this axis is taken along the direction of propagation of the photon and is assumed to coincide with the positive z axis. For a one-electron atom and a given l, there are two values that j can take, namely, $l \pm \frac{1}{2}$. The states $|nljm_j\rangle$ can be expressed in terms of hydrogenlike wave functions $|nlm\rangle = R_{nl}(r)Y_{lm}(\theta, \varphi)$, the spin wave functions χ_μ ($\mu = \pm 1$), and Clebsch-Gordan coefficients. The relevant equations can be found in any book on atomic spectra as, for example, in Shore and Menzel.[6] The quantity $Y_{lm}(\theta, \varphi)$ is a spherical harmonic and (r, θ, φ) are the spherical coordinates of $\vec{r}$. The energy of the state $|nljm_j\rangle$ will be denoted by $\hbar\omega_{nlj}$. The final state of the emitted photoelectron can be written[7] as

$$f_{\vec{K}\mu}(\vec{r}) \equiv 4\pi \sum_{L=0}^{\infty} i^L \exp(-i\delta_L) F_{KL}(r) \sum_{M=-L}^{+L} Y_{LM}^*(\Theta, \Phi) Y_{LM}(\theta, \varphi) \chi_\mu, \tag{1}$$

where (K, Θ, Φ) are the spherical coordinates of the photoelectron wave vector $\vec{K}$. We will here consider radiation right circularly polarized whose polarization vector is $2^{-1/2}(\vec{\epsilon}_x + i\vec{\epsilon}_y)$ where $\epsilon_x = \epsilon_y = 1$. The cross sections and angular distributions are independent of the sense of circular polarization. The photoelectron spin orientation for left circular polarization is obtained from that for right by simply interchanging + and − in the final result. In the system of coordinates chosen here, Θ is the angle between $\vec{K}$ and the photon wave vector.

Two-photon ionization.—Since we are specifically interested in the alkalis we take the initial atomic state to be $|n0\frac{1}{2}m_{1/2}\rangle$. The possible intermediate states permitted by the selection rules are $|n'1\frac{1}{2}m_{1/2}\rangle$ and $|n'1\frac{3}{2}m_{3/2}\rangle$, while the possible final states can be written as $|K2\frac{3}{2}m_{3/2}\rangle$ and $|K2\frac{5}{2}m_{5/2}\rangle$. Note that for circular polarization, only the $L=2$ partial wave of the final state contributes. Also, because of the selection rules, only certain of the possible values of the quantum number m_j are allowed for each j state.

Using perturbation theory of the appropriate order[5] and after considerable angular momentum algebra, we obtain

$$d\hat{\sigma}_2/d\Omega = (\pi\alpha^2 mK\omega^2/2\hbar)[(R_2^2 + B_2^2)\sin^4\Theta + (R_2 - B_2)^2 \sin^2\Theta\cos^2\Theta], \tag{2}$$

where $d\hat{\sigma}_2/d\Omega$ is the differential generalized cross section (gcs) as defined in Ref. 2, and α, m, and ω are the fine structure constant, the electron mass, and the incident radiation frequency, respectively. The quantity R_2 is given by

$$R_2 = \sum_{n'} (\omega_{n'P3/2} - \omega)^{-1} R(KD\tfrac{5}{2}; n'P\tfrac{3}{2}) R(n'P\tfrac{3}{2}; nS\tfrac{1}{2}), \tag{3}$$

where, for example, $R(n'P\frac{3}{2}; nS\frac{1}{2})$ is a shorthand notation for the radial matrix element

$$\int_0^\infty R_{n'P3/2}(r) r R_{nS1/2}(r) r^2\, dr,$$

and where we have switched to the spectroscopic notation $S, P, D, F, \ldots$ instead of $l = 0, 1, 2, 3, \ldots$. In $R(KD\frac{5}{2}; n'P\frac{3}{2})$, the radial part $F_{K2}(r)$ of the $L=2$ partial wave of the final state is involved. Note that for Li, Na, and K, these radial matrix elements depend only on n', n, and the orbital angular momenta. But for Cs, and to some extent for Rb, they may also depend on the total angular momenta. This will be shown to have a significant effect on the photoelectron polarization. The quantity B_2 is given by

$$B_2 = \sum_{n'} \tfrac{1}{15} \{ 10(\omega_{n'P1/2} - \omega)^{-1} R(KD\tfrac{3}{2}; n'P\tfrac{1}{2}) R(n'P\tfrac{1}{2}; nS\tfrac{1}{2}) + (\omega_{n'P3/2} - \omega)^{-1} [2R(KD\tfrac{3}{2}; n'P\tfrac{3}{2}) R(n'P\tfrac{3}{2}; nS\tfrac{1}{2}) + 3R(KD\tfrac{5}{2}; n'P\tfrac{3}{2}) R(n'P\tfrac{3}{2}; nS\tfrac{1}{2})] \}. \tag{4}$$

The energy of the ground state has been taken as zero. As usual, the summations over n' run, in principle, over all atomic states, including the continuum.

Moreover one finds that the total spin polarization P_2 of the photoelectron is given by

$$P_2 = \frac{4(R_2^2 - B_2^2) + (R_2 - B_2)^2}{4(R_2^2 + B_2^2) + (R_2 - B_2)^2}. \tag{5}$$

The polarization $P_2(\Theta)$ as a function of angle is also obtained but will not be quoted here. From Eqs. (3) and (4) it is clear that if (a) the radial matrix elements do not depend on j, and (b) the energies of the atomic levels do not depend on j, i.e., $\omega_{n'P3/2} = \omega_{n'P1/2}$, then $B_2 = R_2$. In that case, the differential gcs reduces to the one previously reported,[1,2] and the electron polarization vanishes, as one would have expected. If either of the above conditions is not satisfied then there will in general be a nonzero polarization. From Eq. (5) and the fact that R_2 and B_2 can be taken to be real, one can deduce the inequality $-0.666 \leqslant P_2 \leqslant +1.0$. It is also obvious that P_2 attains its maximum value $+1.0$ when $B_2 = 0$. It turns out that in that case one will also have $P_2(\Theta) = P_2 = +1.0$ for all Θ which is not true for other values of B_2. Since B_2 is a rather complex function of the photon frequency ω, and of the radial matrix elements, the polarization will also be a function of ω, and will have a dispersionlike character.

From a practical standpoint, near-resonant two-photon ionization is of more interest because then the cross sections are larger and the experiments easier. In that case considerable simplification results. Only one term need be retained in the summation, namely, the term for that particular n' which is in near resonance with the photon frequency. We report here the results for two typical situations. First, assume that the radial matrix elements do not depend on j, which would be the case in Na, K, and to a large extent in Rb. The resulting polarization as a function of frequency[8] is given by curve 1 of Fig. 1. This shows that there will always be some frequency between $\omega_{n'P1/2}$ and $\omega_{n'P3/2}$ for which $P_2 = +1$, and a range of frequencies for which $P_2 > +0.9$. This range depends on the splitting $\Delta\omega_{n'P} \equiv \omega_{n'P3/2} - \omega_{n'P1/2}$, and in many cases it will be from a few wave numbers up to tens of wave numbers, as in Rb or Cs. In the second case, it has been assumed that $R(KD\frac{5}{2}; n'P\frac{3}{2}) \cong R(KD\frac{3}{2}; n'P\frac{3}{2}) \cong R(KD\frac{3}{2}; n'P\frac{1}{2})$, but that $R(n'P\frac{3}{2}; nS\frac{1}{2}) \cong 5R(n'P\frac{1}{2}; nS\frac{1}{2})$. This would be the case in Cs for about $n' = 10$ or 11. The resulting polarization is shown by curve 2 of Fig. 1. The general shape of the curve is the same as that of curve 1, with two important differences: First there is a larger range of ω over which the polarization remains high; and second, as ω moves away from the resonance, the polarization does not vanish as in the previous case, but remains finite. Its asymptotic value increases with the ratio $R(n'P\frac{3}{2}; nS\frac{1}{2})/R(n'P\frac{1}{2}; nS\frac{1}{2})$. Physically, this is due to the fact that in this case the polarization is due to the difference between the above matrix elements, as well as to the energy splitting. In curve 1, it is due solely to the energy splitting. Therefore in the latter case, as ω moves away from the resonance, the energy splitting is no longer seen and P_2 should go to zero. Of course, if one moves too far away, other P levels will become influential and the situation has to be reexamined by taking more terms of the sum into account. Space does not permit consideration of this case here.

Three-photon ionization.—In three-photon ionization, one can have two intermediate resonances, a P and a D. The possible final electron states are of the form $|KF\frac{5}{2}m_{5/2}\rangle$ and $|KF\frac{7}{2}m_{7/2}\rangle$. The resulting differential gcs is

$$d\hat{\sigma}_3/d\Omega = (\pi^2\alpha^3 mK\omega^3/2\hbar)[(R_3{}^2 + B_3{}^2)\sin^6\Theta + (R_3 - B_3)^2 \sin^4\Theta\cos^2\Theta], \qquad (6)$$

where R_3 and B_3 are now given by double sums over all atomic states. The sums involve terms consisting of triple products of radial matrix elements of the form $R(KFj; n''Dj'')R(n''Dj''; n'Pj')R(n'Pj'; nS\frac{1}{2})$, divided by resonance denominators of the form $(\omega_{n''Dj''} - 2\omega)(\omega_{n'Pj'} - \omega)$. The photoelectron polarization P_3 is given by an equation of the form of Eq. (5), with R_2 and B_2 replaced by R_3 and B_3, respectively, and the numerical factor 4 replaced by 6. One now finds the inequality $-0.75 \leqslant P_3 \leqslant +1.0$. Again, for zero spin-orbit coupling, $B_3 = R_3$ and the angular distribution reduces to the one previously reported[1,2] while P_3 vanishes. On the other hand, P_3 attains its maximum value $+1.0$ for $B_3 = 0$. Again in that case $P_3(\Theta) = P_2 = +1.0$.

We have again considered the two special cases

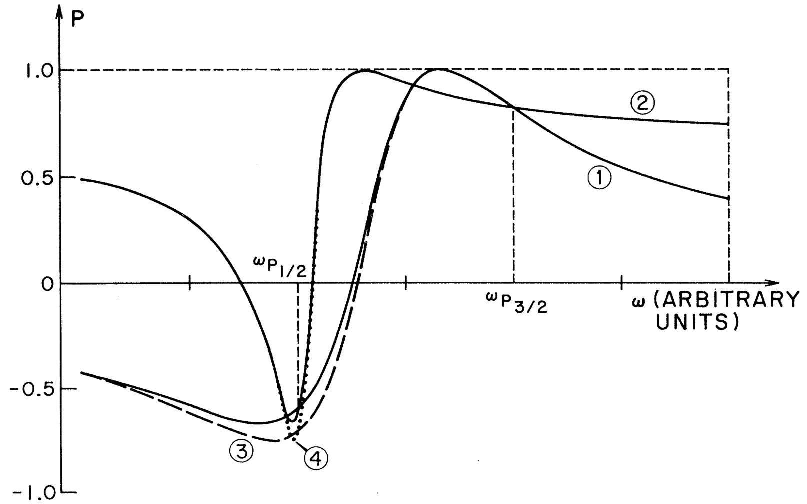

FIG. 1. Photoelectron polarization P for two- and three-photon ionization via a P near-resonance as a function of photon frequency, ω, in the vicinity of the P levels. Curve 1, two-photon ionization for $\rho \equiv R(n'P\frac{5}{2}; nS\frac{1}{2})/R(n'P\frac{1}{2}; nS\frac{1}{2}) = 1$. Curve 2, two-photon ionization for $\rho = 5$. Curve 3, three-photon ionization for $\rho = 1$. Curve 4, three-photon ionization for $\rho = 5$.

of a P near-resonance, assuming that the spin-orbit effect on the D intermediate levels is negligible. The resulting polarizations are given by curves 3 and 4 of Fig. 1. These curves do not differ much from those for two-photon ionization except near the minima. In fact this is also true for four- and five-photon ionization, and so on, as long as ω is near a P level and no other resonances occur. The minimum becomes lower but otherwise the curves remain relatively unchanged.

Of course for three-photon ionization one can also have a D intermediate resonance simultaneously with a P, or a D alone. Although D splittings are much smaller, present-day lasers are sufficiently narrow to make the observation of this case possible albeit more difficult. But space does not permit further elaboration on this case. From the viewpoint of observing these effects and producing polarized electrons, a P resonance is more favorable. We have extimated the relevant yields on the basis of Bebb's calculations[5] for the cross sections, correcting for the effect of circular polarization.[1] It turns out that, with photon fluxes of the order of $10^{26}-10^{27}$ photons/cm^2 sec, laser pulse durations from 10 to 500 nsec, and atomic densities from 10^{11} to 10^{13} atoms/cm^3 in the interaction region, one can obtain from 10^2 to 10^7 electrons per laser pulse with polarization between $+0.9$ and $+1.0$. There exist P levels in all alkalis—with the exception of Li—with splittings large enough, and with energies appropriate to achieve near-resonance conditions with presently available lasers. In fact, in some cases[5] there exist resonances for which lasers with fluxes much higher than considered here can be used (for example, ruby and Nd-glass lasers).

The present effect is analogous to a similar effect in single-photon ionization discussed by Fano[9] a few years ago and subsequently observed experimentally.[10,11] However, there are important differences between the two. The Fano effect relies on the satisfaction of a condition of the form $R(KP\frac{3}{2}; nS\frac{1}{2}) + 2R(KP\frac{1}{2}; nS\frac{1}{2}) \cong 0$. Although the present effect also requires the satisfaction of the relations $B_2 \cong 0$ or $B_3 \cong 0$, etc., the B's contain the photon frequency ω in a way that the above relations can be satisfied if ω is chosen appropriately. Thus, whereas the Fano effect is significant essentially only in Cs, the present effect, with the appropriate choice of laser frequencies, is significant in all alkalis except Li. Physically speaking, it may be said that the first photon puts the atom in a state which leads to the necessary cancelation between matrix elements; while in the Fano effect, the cancelation is solely a result of spin-orbit coupling and one does not have any control over it. Moreover, the Fano effect yields high polarization for photon frequencies for which the cross sections are low, whereas in the present case the effect is maximum where the cross sections are large. Of course, ultimately it is the availability of high-power lasers with narrow spectral width that renders the effect significant. By way of comparison, note that the experiments on the Fano effect have produced electron currents of the order of 10^{-11} A while the above estimates for the present effect are equivalent to about $10^{-10}-10^{-5}$ A. In multiphoton ionization, of course, the electrons are emitted in pulses of duration equal to that of the laser pulse.

An experimental study of the above effect in three-photon ionization is presently in progress.

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[1] P. Lambropoulos, Phys. Rev. Lett. 28, 585 (1972).

[2] P. Lambropoulos, Phys. Rev. Lett. 29, 453 (1972).

[3] S. Klarsfeld and A. Maquet, Phys. Rev. Lett. 29, 79 (1972).

[4] H. R. Reiss, Phys. Rev. Lett. 29, 1129 (1972).

[5] H. B. Bebb, Phys. Rev. 149, 25 (1966), and 153, 23 (1967).

[6] B. W. Shore and D. H. Menzel, *Principles of Atomic Spectra* (Wiley, New York, 1968), p. 322.

[7] A. Messiah, *Quantum Mechanics* (Wiley, New York, 1965), Vol. I, p. 497.

[8] The special case of $\omega = \omega_{n'P1/2}$ has also been considered by H. Zeman (private communication).

[9] U. Fano, Phys. Rev. 178, 131 (1969).

[10] G. Baum, M. S. Lubell, and W. Raith, Phys. Rev. Lett. 25, 267 (1970), and Phys. Rev. A 5, 1073 (1972).

[11] U. Heinzmann, J. Kessler, and J. Lorenz, Phys. Rev. Lett. 25, 1325 (1970), and Z. Phys. 240, 42 (1970).