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Angular Distribution of Photoelectrons from Relativistic Wave Functions

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An expression is given for the asymmetry parameter β in terms of matrix elements of relativistic wave functions. It is predicted that β will vary rapidly near the minimum of the photoionization continua of the alkali metals.

Although there has been considerable interest in the angular distribution of photoelectrons,[1,2] very little systematic experimental effort has been devoted to it. In fact, the angular distribution is often measured at only one or two photon energies. The purpose of this note is to point out that the effects of spin-orbit coupling on the angular distribution can be very important, and to suggest the part of the photoionization spectrum where it will most easily be observed. In *LS* coupling, and within the dipole approximation, the angular distribution is given by

$$d\sigma/d\Omega = (\sigma_{\text{tot}}/4\pi)[1+\beta P^2(\cos\theta)],$$

where the asymmetry parameter β is a function of the radial matrix elements and the phase shifts of the continuum orbitals. For *s* orbitals, β is always equal to 2. An exhaustive discussion of the nonrelativistic treatment and the analysis of experimental findings was recently published by Kennedy and Manson.

It has been conjectured that the angular distribution could have a different form in *jj* coupling, and we have developed the theory of the angular distribution using relativistic wave functions.[4] Taking again the dipole approximation, we find the following expression for β:

$$\beta=\left(\frac{(2j-3)(2j-1)}{48j^2}R_{j-1}{}^2-\frac{(2j-1)(2j+3)}{48j^2(j+1)^2}R_j{}^2+\frac{(2j+3)(2j+5)}{48(j+1)^2}R_{j+1}{}^2+\frac{2j-1}{8j^2(j+1)}|R_jR_{j-1}{}^*|\right.$$
$$\left.+\frac{2j+3}{8j(j+1)}|R_jR_{j+1}{}^*|+\frac{(2j-1)(2j+3)}{8j(j+1)}|R_{j-1}R_{j+1}{}^*|\right)\left(\frac{2j-1}{12j}R_{j-1}{}^2+\frac{R_j{}^2}{12j(j+1)}+\frac{2j+3}{12(j+1)}R_{j+1}{}^2\right)^{-1}, \quad (1)$$

where the radial matrix elements $R_{J'}$ are defined by

$$R_{J'}=i\left[(\kappa-\kappa'-1)\langle Q_{j'}|P_j\rangle+(\kappa-\kappa'+1)\langle P_{j'}|Q_j\rangle\right]\exp(i\delta_{J'}). \quad (2)$$

Here κ is $-(j+\frac{1}{2})a$ for $a=\pm1$, J' is one of the three values j', $j'\pm1$ for the continuum orbital, the unprimed angular momentum j of the electron being ionized is $l\pm\frac{1}{2}$, and P and Q are the real large and small radial components of the orbitals.[5]

We can obtain the nonrelativistic expression by noting that in the limit P becomes the nonrelativistic radial wave function and Q is given by

$$Q \to \frac{1}{2c}\left(\frac{d}{dr}P + \frac{K}{r}P\right).$$

The expression (1) then exactly reproduces the nonrelativistic β. It is apparent that the method of coupling the angular momenta, i.e., transition from LS to jj coupling, cannot of itself change the value of β. However, when relativistic wave functions are used, changes will occur specifically when the radial wave functions and phase shifts of the continuum functions are different for $j = l + \frac{1}{2}$ or $l - \frac{1}{2}$.

A dramatic example of this occurs when we consider s orbitals. Then Eq. (1) reduces to

$$\beta = \frac{2R_p^2 + 4R_pR_{\bar{p}}\cos(\delta_p - \delta_{\bar{p}})}{R_{\bar{p}}^2 + 2R_p^2}, \qquad (3)$$

where we have labeled $p_{1/2}$ by $\bar{p}$ and $p_{3/2}$ by p. Here δ_p and $\delta_{\bar{p}}$ are the phase shifts. When $R_p = R_{\bar{p}}$, we obtain $\beta = 2$. On the other hand, consider what happens when either of the two matrix elements $R_p, R_{\bar{p}}$ vanishes. In general, this occurs at different values of k as illustrated by the nonzero minima and spin polarization of the emitted electrons in the photoionization spectra of the alkali metals.[6-8] When $R_{\bar{p}} = 0$ one finds that $\beta = 1$, whereas when $R_p = 0$, then $\beta = 0$. Therefore, a rapid variation of β in the vicinity of the nonzero minimum should be observable. Moreover, it should be possible to determine experimentally when each matrix element becomes zero. This will provide an extra check on calculations,[9,10] which so far have been able to reproduce the position of the minimum but not its magnitude. Recent experimental results confirm that β may deviate from 2 for s electrons. Niehaus and Ruf[11] found a value of 1.68 for the 6s electron of mercury. We note that an angular-distribution formula similar to Eq. (3) is an example of the parity-unfavoredness concept discussed by Dill and Fano.[12]

It should be emphasized that since the dipole matrix elements are going to zero, it may not be reasonable to ignore higher-order terms in the multipole expansion. Certainly it may be necessary to calculate matrix elements such as

$$\langle Q|j_0(\omega r)|P\rangle \text{ rather than } \langle Q|P\rangle.$$

We are currently investigating this and have extended the theory to arbitrary multipoles. Finally, it is apparent that similar effect may occur at the Cooper minima[13] of other electrons and could lead to differences in the β values of the levels which are split by spin-orbit coupling. This could explain the very different β values for the $4d_{5/2}$ and $4d_{3/2}$ electrons of cadmium,[14] and suggests the part of the photoionization spectrum which would yield the most interesting experimental results.

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