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Photoelectron angular distributions: energy dependence for *s* subshells

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An overview of the theory of photoelectron angular distributions for atoms is presented. Its features, which are embodied in a single asymmetry parameter β in the electric dipole approximation, are examined within the framework of the angular momentum transfer formulation. The β parameter is in principle always energy dependent. Within the LS coupling approximation, however, there are instances, each representing a multitude of particular photoionization processes, in which β is an analytically determined constant. The energy dependence of the β parameters in such instances is due entirely to spin-orbit and other relativistic interactions. The study of the energy dependence of the β parameter in these cases is thus of interest because it spotlights weak-interaction effects which are usually overwhelmed by stronger interactions. We illustrate the general predictions by a detailed consideration of the energy dependence of the β parameter for s-subshell photoionization processes. It is shown that the asymmetry parameters for atomic s subshells are particularly suitable for distinguishing between purely geometrical effects on the photoelectron angular distribution, resulting from physical conservation laws, and dynamical effects arising from relativistic interactions and electron exchange and correlation. In general, the β parameters for s subshells vary with energy; such variation is largest near minima in the cross sections for the corresponding photoelectron channels and in the vicinity of resonances. However, a number of atomic photoionization transitions are identified for which β would be a constant (equal to one of the three values 2, 1/5, or -1) were it not for relativistic interactions and (in some cases) final-state interchannel coupling and/or initial-state electron correlations. Measurement or calculation of the β parameters for such transitions thus provides a sensitive measure of the strength of relativistic interactions as well as of electron correlations.

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I. INTRODUCTION

In all branches of modern physics, collision experiments provide a large part of our information of the interactions between particles as well as on the particles themselves. In contrast to measurements of total cross sections, differential cross-section measurements—i.e., those which measure the angular distribution of the ejected particles—provide data not only on the magnitudes of the relevant transition amplitudes but also on their relative phases. This data—suitably processed—contributes toward the goal of angular distribution studies, whether experimental or theoretical, which is to obtain static information on the initial and final states of the target as well as dynamic information on the collision process itself. The extraction of this information requires the unravelling of geometrical from dynamical effects through the use of conservation laws and angular momentum algebra and is, in general, a nontrivial task. In certain collision processes, however, this unravelling can be done with *relative* ease and clarity, thereby serving as a model for more complex collision processes. One such simpler process is the angular distribution of photoelectrons produced by low-energy (i.e., $\hbar\omega \lesssim 100$ eV) photoionization of atoms. At such low energies the electric dipole approximation is valid (i.e., the photon wavelength λ is much larger than the size of the atomic target) and the differential cross section then depends on only two dynamical parameters: the total photoionization cross section σ, which determines the intensity of photoelectrons, and the asymmetry parameter β (Yang, 1948; Cooper and Zare, 1969), which determines the an-

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gular distribution of the photoelectrons. In general, σ and β are energy dependent due to their dependence on the energy-dependent transition amplitudes. Unlike σ, however, β is expressed theoretically as a ratio which reduces to a number—independent of energy—when the scattering process under study has only a single allowed final-state channel due to geometrical considerations. In this case of constant β the photoelectron angular distribution does not depend on the incident photon energy. Furthermore, in cases where a single final-state channel may be shown to dominate all others, measurements of the deviation of β from the constant value predicted for the dominant channel alone provide a sensitive measure of the strength of the additional allowed channels. Such energy-independent β parameters never occur in principle. Within the LS coupling approximation, however, there are instances, each representing a multitude of particular photoionization processes, in which β is an analytically determined constant. The energy dependence of the β parameters in such instances is due entirely to spin-orbit and other relativistic interactions. The study of the energy dependence of the β parameter in these cases is thus of interest because it spotlights weak interactions whose influence is usually overwhelmed by stronger-interaction effects. We illustrate the general predictions by a detailed consideration of the energy dependence of the β parameter for s-subshell photoionization processes.

That the asymmetry parameter for photoelectrons from s subshells may by energy dependent at all has not always been well understood. Indeed, from a classical point of view, the angular distribution of electrons photoionized from an s subshell of an atom by linearly polarized incident radiation is expected to be proportional to $\cos^2\theta$, where θ is measured with respect to the electric vector of the incident radiation. That is, the photoelectron is expected to be ejected preferentially along the incident electric vector. In quantum mechanics this same result is obtained in the central potential model approximation, in which there is only the single $s \rightarrow p$ final-state channel, and corresponds to an angular distribution asymmetry parameter β equal to two regardless of photon energy. Recently, however, a number of experimental and theoretical studies have indicated that the asymmetry parameter β for s-subshell photoelectrons is not always equal to the energy-independent value two. Thus the β parameter for the 6s subshell of mercury (Niehaus and Ruf, 1972), the outer s subshell of the alkalis (Jacobs, 1972; Walker and Waber, 1973a, 1973b; Marr, 1974; Ong and Manson, 1978a; Huang and Starace, 1979), and the outer 5s subshell of xenon (Dehmer and Dill, 1976; Ong and Manson, 1978b; Johnson and Cheng, 1978, 1979; White *et al.*, 1979; Huang and Starace, 1980), as well as s subshells of other rare-gas atoms (Johnson and Cheng, 1979) have been found to be energy dependent. For these alkali and closed-shell atoms, this energy dependence is due to *relativistic* (mainly spin-orbit) electron-ion interactions, which permit more than one final-state channel for photoelectron escape, and is enhanced near cross-section minima, due to rapid changes in the relative magnitudes of the amplitudes for the various channels, or in the vicinity of resonances, due to configuration interaction. On the other hand it has been found theoretically that for s electrons in open-shell atoms the β parameter is, in general, energy dependent due to *nonrelativistic* anisotropic (i.e., term-dependent) electron-ion interactions, which also permit several final-state channels for photoelectron escape (Starace *et al.*, 1977). Thus calculations for the 3s subshells of chlorine (Starace *et al.*, 1977) and of aluminum (Shahabi, 1979) show significant deviations of β from the value 2, especially near cross-section minima. More recently, Chang and Taylor (1978) identified theoretically a 2s-subshell photoionization transition in carbon for which the asymmetry parameter β in *nonrelativistic* approximation differs from the classical value 2, but has the constant value -1, corresponding to a photoelectron angular distribution $\sin^2\theta$.

In this review we present a theoretical overview of the energy dependence of photoelectron angular distributions. After reviewing the general theory for photoelectron angular distributions and for the asymmetry parameter β, we show that within LS coupling there are instances in which the β parameter is an analytically known constant. In those cases in which β is energy dependent in LS coupling, we review various approximations to the photoionization scattering amplitudes and the effect of these approximations on the predicted β parameters. As s-subshell photoionization processes provide additional instances in which β would be energy independent in the absence of certain weak electron correlation effects, we study the energy dependence of s-subshell photoionization processes in detail. Specifically, we show that in *nonrelativistic* approximation the β parameter for s electrons is in general *energy dependent.* We identify, however, many cases in which β is found to equal one of the two *constant* values $+2$ or -1. Certain other cases are identified in which the energy dependence of β is due solely to final-state interchannel interactions and/or initial-state configuration mixing, in whose absence β would take the constant value $+\frac{1}{5}$. Finally, we show that when relativistic interactions are included, the β parameter for s electrons is in principle *always* energy dependent. Experimental or theoretical study of the transitions identified as having a constant value of β in the absence of relativistic interactions or of certain types of electron correlations would thus provide a very sensitive measure of the strength of these often weak interactions.

II. GENERAL FORM OF THE PHOTOELECTRON ANGULAR DISTRIBUTION

Yang (1948) has shown quite generally that when a photon interacts with an unpolarized atomic or molecular target in the electric dipole approximation (i.e., assuming the photon wavelength is much larger than the target dimensions) then the angular correlation between the incident photon and *any* ejected particle is propor-

tional to a linear combination of 1 and $\cos^2\theta$, where θ measures the ejection angle of the outgoing particle—typically an electron—with respect to the polarization vector of the incident photon. The upper limit of two on the powers of $\cos\theta$ that determine the angular distribution is fixed by the orbital angular momentum of unity imparted to the target by the absorbed photon in the electric dipole approximation. Note that the angular distribution has no term linear in $\cos\theta$ since parity is conserved in a photoabsorption process.

In general, then, the differential cross section for photoionization of an upolarized target by incident linearly polarized light in the electric dipole approximation may be written as (Cooper and Zare, 1969)

$$\left[\frac{d\sigma}{d\Omega}\right]_{\text{lin pol}} = \frac{\sigma}{4\pi}[1+\beta P_2(\cos\theta)] \ . \tag{2.1}$$

Here σ is the total photoionization cross section, β is the asymmetry parameter, $P_2(\cos\theta)\equiv\frac{1}{2}(3\cos^2\theta-1)$, and θ is measured with respect to the polarization vector of the incident light. One sees immediately from Eq. (2.1) that the angular distribution is determined completely by the asymmetry parameter β, which embodies all of the dynamical information relevant to the angular distribution. The total cross section σ determines the overall intensity of the process. Note that the requirement that $d\sigma/d\Omega$ be positive for all values of θ limits the magnitude of β to the range $-1\leq\beta\leq 2$.

It is to be emphasized that alternative polarizations of the incident light do not provide any additional dynamical information on the photoionization process. Indeed, although the form of the differential cross section may change from that in Eq. (2.1), it may always be expressed in terms of the *same* dynamical parameters σ and β appearing in Eq. (2.1). Thus, for example, one may consider unpolarized incident light as equivalent to a linear combination of two incoherent linearly polarized beams of equal intensity vibrating along orthogonal axes x and y (Born and Wolf, 1959, Sec. 10.8.2). The differential cross section is written in this case as the sum of two equally weighted differential cross sections having the form of Eq. (2.1):

$$\left[\frac{d\sigma}{d\Omega}\right]_{\text{unpol}} = \frac{1}{2}\frac{\sigma}{4\pi}[1+\beta P_2(\cos\theta_x)] + \frac{1}{2}\frac{\sigma}{4\pi}[1+\beta P_2(\cos\theta_y)] \ . \tag{2.2}$$

Taking the z axis as the direction of the incident unpolarized photon beam and using the geometric relation,

$$\cos^2\theta_x+\cos^2\theta_y+\cos^2\theta_z=1 \ , \tag{2.3}$$

one may reduce Eq. (2.2) to the form

$$\left[\frac{d\sigma}{d\Omega}\right]_{\text{unpol}} = \frac{\sigma}{4\pi}[1-\tfrac{1}{2}\beta P_2(\cos\theta_z)] \ . \tag{2.4}$$

In a similar way one may show that circularly polarized incident light gives the same photoelectron angular distribution as unpolarized incident light (Peshkin, 1970; Jacobs, 1972). Circularly polarized light may be represented as a linear combination of two *coherent* linearly polarized beams of equal intensity vibrating 90° out of phase along orghogonal axes x and y. The coherence of the two beams, however, has no effect on the photoelectron angular distribution, so that the differential cross section is represented once again by Eq. (2.4). In the case of partially linearly polarized light (Samson, 1969, 1970; Samson and Starace, 1975), one may represent the incident beam once again by two incoherent linearly polarized beams vibrating along orthogonal axes. The differential cross section then has the form of the linear superposition in Eq. (2.2) but with weighting factors (I_x/I_0) and (I_y/I_0) describing the fraction of light intensity along the x and y axes, where $I_0=I_x+I_y$. The result for the differential cross section, after application of Eq. (2.3), is

$$\left[\frac{d\sigma}{d\Omega}\right]_{\text{pp}} = \frac{\sigma}{4\pi}\{1-\tfrac{1}{2}\beta[P_2(\cos\theta_z)-\tfrac{3}{2}p(\cos^2\theta_x - \cos^2\theta_y)]\} \ , \tag{2.5}$$

where p measures the extent of polarization,

$$p\equiv\frac{I_x-I_y}{I_x+I_y} \ . \tag{2.6}$$

Lastly, when the incident light is elliptically polarized, one obtains Eq. (2.5) for the differential cross section once again (Schmidt, 1973; Samson and Starace, 1975), provided I_x and I_y are the light intensities along the major and minor axes of the ellipse characterizing the incident light polarization. This result follows since elliptically polarized light differs from partially linearly polarized light in that there is a coherence between the x and y components of the incident electric vector. This coherence, which is equivalent to a component of circular polarization in the incident elliptically polarized beam, does not affect the differential cross section and hence Eq. (2.5) may be used.

In all cases of incident light polarization, then, the dyamical information to be obtained from an experimental or theoretical study of the photoelectron angular distribution is contained in the asymmetry parameter β. Formulas for the differential cross section in the cases of linear, circular, elliptical, or partial incident light polarization as well as of unpolarized incident light have been given above and are valid provided only that the target is unpolarized and that the electric dipole approximation holds. The general angular momentum transfer formulation for β of Dill and Fano (Fano and Dill, 1972; Dill and Fano, 1972; Dill, 1973) is presented in Sec. III. Angular momentum and parity conservation laws are then used to deduce those cases in which the β parameter assumes an analytically known constant value in the electric dipole, LS coupling approximation. Further analysis is given to the occurrence of constant β parameters in the special case of s-subshell photoionization processes.

Following an examination of various approximations to the dynamical scattering amplitudes within LS coupling, detailed examples are given of energy-independent as well as energy-dependent β parameters, particularly for s-subshell photoionization processes. Modifications of these nonrelativistic predictions necessitated by spin-orbit and other relativistic interactions are indicated in Sec. IV.

III. NONRELATIVISTIC THEORY OF THE PHOTOELECTRON ANGULAR DISTRIBUTION ASYMMETRY PARAMETER β

In general, relativistic interactions have only a minor quantitative influence on the photoelectron angular distribution for elements of low to moderate atomic number Z. In those cases where nonrelativistic theory predicts a constant value for the angular distribution asymmetry parameter β, however, the effect of relativistic interactions may be detected unambiguously by deviations of β from constancy. In other cases, nonrelativistic theory provides approximate bounds (Chang and Taylor, 1978) on the variation of β that may be violated when relativistic interactions are taken into consideration. We illustrate the general predictions by a detailed consideration of s-subshell photoelectron angular distributions. For s subshells we ascertain those cases in which β is predicted to be a constant function of photon energy and also examine in some detail the behavior of those β parameters that are expected to be energy dependent. For our analysis we employ the angular momentum transfer formulation for β of Dill and Fano (Fano and Dill, 1972; Dill and Fano, 1972; Dill, 1973) in particular, as developed for the nonrelativistic case of LS coupling (Starace *et al.*, 1977; Dill *et al.*, 1974, 1975; Starace, 1982).

A. Review of the angular momentum transfer formulation for photoelectron angular distribution

Let us consider an atom (or ion) $\mathscr{A}$ initially in a state defined *in LS coupling* by the orbital angular momentum, spin angular momentum, total angular momentum, and parity quantum numbers L_0, S_0, J_0 and π_0, respectively. We are interested in low-energy photoionization processes ($\hbar\omega \lesssim 100$ eV) for which the electric dipole approximation is excellent and the incident photon, γ, can be considered to impart an angular momentum $j_\gamma=1$ and parity $\pi_\gamma=-1$ to the atom. The final state of the ion $\mathscr{A}^+$ is specified by L_c, S_c, J_c, and π_c and the photoelectron by l, s, j, $\pi_e=(-1)^l$. This general process can be schematized as

$$\mathscr{A}(L_0,S_0,J_0,\pi_0)+\gamma(j_\gamma=1,\pi_\gamma=-1) \rightarrow \mathscr{A}^+(L_c,S_c,J_c,\pi_c)+e^-(l,s,j,\pi_e=(-1)^l)\ . \tag{3.1}$$

The differential cross section for this photoionization process can be separated into contributions characterized by alternative magnitudes of the angular momentum transfer, defined by

$$\mathbf{j}_t \equiv \mathbf{j}_\gamma - \mathbf{l} = \mathbf{J}_c + \mathbf{s} - \mathbf{J}_0\ , \tag{3.2}$$

provided no measurement is made of either the photoelectron spin or the orientation of the residual ion. In LS coupling, spin angular momentum and orbital angular momentum are separately conserved. The angular momentum imparted by the photon affects only the orbital angular momentum of the system, owing to the spin independence of the electric dipole interaction. Thus

$$\mathbf{S}_0 = \mathbf{S}_c + \mathbf{s}\ , \tag{3.3}$$

and

$$\mathbf{L}_0 + \mathbf{j}_\gamma = \mathbf{L}_c + \mathbf{l}\ . \tag{3.4}$$

Equation (3.4) thus restricts the general equation (3.2) for j_t to the following LS coupling expression:

$$\mathbf{j}_t \equiv \mathbf{j}_\gamma - \mathbf{l} = \mathbf{L}_c - \mathbf{L}_0\ . \tag{3.5}$$

In either case, the constraints of parity conservation must also be considered, i.e.,

$$\pi_0 \times \pi_\gamma = \pi_c \times \pi_e\ , \tag{3.6}$$

which in the electric dipole approximation reduces to

$$\pi_0 \pi_c = (-1)^{l+1}\ . \tag{3.7}$$

In the electric dipole approximation, then, the allowed values of the angular momentum transfer j_t are determined in general by Eqs. (3.2) and (3.7) and are determined in the LS coupling approximation by Eqs. (3.5) and (3.7). In either case, once the allowed values of j_t have been determined, the asymmetry parameter β may be represented as the following weighted average (Fano and Dill, 1972; Dill and Fano, 1972; Dill, 1973):

$$\beta = \frac{\sum_{j_t} \sigma(j_t)\beta(j_t)}{\sum_{j_t} \sigma(j_t)}\ . \tag{3.8}$$

The summation in Eq. (3.8) extends over all allowed values of j_t. $\beta(j_t)$ and $\sigma(j_t)$ are the asymmetry parameter and partial photoionization cross section characteristic of a given value of j_t. Fano and Dill (Fano and Dill, 1972; Dill and Fano, 1972; Dill, 1973) have shown that when j_t is "parity favored" (i.e., when $\pi_0\pi_c=(-1)^{j_t}$), then $\beta(j_t)$ and $\sigma(j_t)$ may be written in terms of certain scattering amplitudes $S_l(j_t)$ as follows:

$$\beta_{\text{fav}}(j_t) = \frac{(j_t+2)\,|S_+(j_t)|^2 + (j_t-1)\,|S_-(j_t)|^2 - 3[j_t(j_t+1)]^{1/2}[S_+(j_t)S_-^\dagger(j_t) + \text{c.c.}]}{(2j_t+1)(\,|S_+(j_t)|^2 + |S_-(j_t)|^2)}\ , \tag{3.9a}$$

$$\sigma_{\text{fav}}(j_t) = \frac{(2j_t+1)}{2L_0+1}[\,|S_+(j_t)|^2 + |S_-(j_t)|^2]\ , \tag{3.9b}$$

On the other hand, when j_t is "parity unfavored" (i.e., when $\pi_0\pi_c=(-1)^{j_t+1}$, then $\beta(j_t)$ and $\sigma(j_t)$ assume a particularly simple form (Dill and Fano, 1972):

$$\beta_{\text{unf}}(j_t)=-1\ , \tag{3.9c}$$

$$\sigma_{\text{unf}}(j_t)=\frac{(2j_t+1)}{2L_0+1}\,|S_0(j_t)|^2\ . \tag{3.9d}$$

In Eqs. (3.9) the subscripts $\pm$ or 0 on the amplitudes $S_l(j_t)$ indicate that the photoelectron orbital angular momentum l has the value $j_t\pm1$ or j_t, respectively.

B. Occurrence of energy-independent β parameters in LS coupling

The angular momentum transfer theory expression for the asymmetry parameter β, given in Eqs. (3.8) and (3.9), is in general energy dependent due to the energy dependence of the scattering amplitudes $S_l(j_t)$, in terms of which both the cross sections $\sigma(j_t)$ and asymmetry parameters $\beta(j_t)$ are defined. Since β is defined in terms of a ratio of energy-dependent factors, the possibility exists that the energy dependence may cancel in numerator and denominator, leaving an analytically determined constant value for β. A necessary condition for this to occur is that only a single value of j_t contributes to the process under study. As shown in Sec. IV, in general there are always at least two values of j_t. In LS coupling, however, Eq. (3.5) implies that j_t will be *restricted to a single value* when either L_c or L_0 is zero, in which case j_t will have the value of the other one of this pair. When only a single value of j_t is permitted, then the cross sections in Eq. (3.8) cancel, given for the asymmetry parameter,

$$\beta=\beta(j_t)\ ,$$

where $\beta(j_t)$ is defined in Eq. (3.9a) for a favored value of j_t and in Eq. (3.9c) for an unfavored value of j_t. Whether j_t is favored or unfavored depends on whether the product of the parities of the atom and the ion, $\pi_0\pi_c$, is equal to $(-1)^{j_t}$ or $(-1)^{j_t+1}$. For an unfavored value of j_t, $\beta=-1$, and hence the angular distribution is energy independent. For a favored value of j_t, Eq. (3.9a) shows that in general β is energy dependent. This energy dependence arises since the photoelectron orbital angular momentum can usually have two allowed values, $l=j_t\pm1$, in favored photoionization processes. The interference between the scattering amplitudes $S_l(j_t)$ for these two values of l causes $\beta(j_t)$ to vary with energy. In the special case of $j_t=0$, however, l has only the single value $+1$, due to angular momentum conservation, in which case Eq. (3.9a) shows that $\beta(j_t=0)=+2$. In all other cases in which only a single value of j_t contributes to a particular photoionization process, $\beta(j_t)$ is energy dependent. These exact LS coupling predictions are summarized in Table I.

TABLE I. LS coupling predictions for $\beta(j_t)$ for photoionization transitions in which only a single j_t value is permitted. Spin-orbit and other relativistic interactions introduce additional allowed values of j_t so that β is no longer equal to a single $\beta(j_t)$ but rather to the weighted average of allowed $\beta(j_t)$'s given in Eq. (3.8). Deviation of β from constancy in the cases shown is thus a sensitive measure of these relativistic interactions.

(L_0,L_c)[a]	j_t[b]	$\pi_0\pi_c$[a]	l[a]	$\beta(j_t)$[c]
(0,0)	0(fav)	$+1$	1	$+2$
$(0,L),(L,0)$	L(fav)	$(-1)^L$	$L\pm1$	$-1\le\beta\le+2$
$(0,L),(L,0)$	L(unf)	$(-1)^{L+1}$	L	-1

[a] L_0, L_c, l, π_0, and π_c are defined for the general photoionization process in Eq. (3.1).
[b] The notation "fav" or "unf" indicates that the transition is "favored" [i.e., $\pi_0\pi_c=(-1)^{j_t}$] or "unfavored" [i.e., $\pi_0\pi_c=(-1)^{j_t+1}$].
[c] Values for $\beta(j_t)$ are obtained from Eqs. (3.9a) and (3.9c).

C. Energy-independent β parameters in s-subshell photoionization processes

From a general point of view, s-subshell photoionization processes do not present any new phenomena within LS coupling. Their study merely limits one to processes in which the initial atomic parity, π_0, and the final ionic parity, π_c, are the same, i.e., the product $\pi_0\pi_c=+1$, and thus according to Eq. (3.7) only odd values of l are allowed. Hence the general LS coupling predictions given in Table I hold, but for s subshells even values of j_t are always "favored" while odd values of j_t are always "unfavored." It is important to realize that the restriction to $\pi_0\pi_c=+1$ only limits the kinds of processes (3.1) under consideration but does not imply any approximation. Note also that these restrictions on the general photoionization process in Eq. (3.1), which are appropriate for s subshells, are appropriate also for a multitude of photoionization processes, some involving even simultaneous excitation of the ion. What is unique about s subshells is that, from an independent-particle point of view, photoionization processes result in continuum electrons with only a *single* orbital angular momentum, $l=1$. Normally, photoionization of a subshell whose electrons have angular momentum l_0 results in continuum electrons having the *pair* of orbital angular momentum values $l=l_0\pm1$. Now general angular momentum and parity conservation laws often permit other orbital angular momenta for the photoelectron, but these other values come about due to electron correlation effects in either the initial or final state and hence are expected to have a small probability. Thus if *in addition* to the LS coupling approximation one makes the approximation that photoionization of s subshells results only in photoelectrons with orbital angular momentum $l=1$, thereby ignoring other *odd* values of l which may be permitted in LS cou-

pling, then one finds some additional instances in which the β parameter is energy independent.

Before examining what new predictions this additional approximation permits, we illustrate here the kinds of electron correlation which are being ignored. Consider the photoionization of a subshell which has the predominant configuration ns^2. Photoionization of this subshell results in the expected one-electron transition,

$$ns^2+\gamma\rightarrow ns\,\varepsilon p\ .$$

In a more exact treatment, however, the initial-state wave function might have a small admixture of the excited configuration *nsnd*, among others, provided of course that the total orbital and spin angular momenta of the atom remain unchanged. Photoionization of the *nd* electron in this excited configuration results, then, in the possibility of the continuum electron's having a small *f*-wave component, i.e.,

$$nsnd+\gamma\rightarrow ns\,\varepsilon p,\varepsilon f\ .$$

In this way, initial-state correlations can introduce higher odd-l values for the continuum electron. In the final state, the electron correlation operator $\sum_{i>j} r_{ij}^{-1}$ in general has nonzero matrix elements between the final states $ns\,\varepsilon p$ and $ns\,\varepsilon l$, where l is odd. One interprets this interaction as an inelastic scattering of the continuum p electron by the ionic core, which promotes it to a state of higher, odd angular momentum. In this way, final-state interactions can introduce higher odd-l values for the continuum electron. One expects that usually both of these kinds of electron correlation effects are small. Thus, if ignoring them leads to the prediction of energy-independent β parameters, then any discrepancies between measured or calculated values for these β's and the predicted constant values provide a sensitive measure of these usually weak electron correlation effects (as well as of the spin-orbit and other relativistic interactions which are ignored in the *LS* coupling approximations).

The approximation that, in photoionization of an *s* subshell, the photoelectron can only have orbital angular momentum $l=1$ leads, then, to the following new predictions. If in the second line of Table I we insist that $l=1=L\pm1$ then $j_t=L$ can only have the "favored" values 0 and 2. The value $j_t=0$(fav) repeats the first line in Table I and actually represents no further approximation from the *LS* coupling approximation. The value $j_t=2$(fav), however, now entails the approximation that we have ignored the value $l=j_t+1=3$. From Eq. (3.9a) we find in this approximation that $\beta(j_t=2)=\frac{1}{5}$, i.e., $\beta(j_t)$ in this case is energy independent. Similarly, if in the third line of Table I we insist that $l=1$, this merely limits consideration to the unfavored values of $j_t=L=1$, but does not represent any additional approximation from the *LS* coupling approximation. These *s*-subshell results for $\beta(j_t)$ in those cases in which only a single value of j_t is permitted are summarized in Table II.

TABLE II. *LS* coupling predictions for $\beta(j_t)$ for *s*-subshell photoionization transitions in which only a single j_t value is permitted. Relativistic interactions introduce additional allowed values of j_t so that β is no longer equal to a single $\beta(j_t)$ but rather to the weighted average of allowed $\beta(j_t)$'s given in Eq. (3.8). Deviation of β from constancy in the cases shown is thus a sensitive measure of these relativistic interactions.

L_0[a]	L_c[a]	j_t[b]	l[a]	$\beta(j_t)$[c]
0	0	0(fav)	1	2
0	1	1(unf)	1	-1
0	2	2(fav)	1	$\frac{1}{5}$[d]
1	0	1(unf)	1	-1
2	0	2(fav)	1	$\frac{1}{5}$[d]

[a] L_0, L_c, and l are defined for the general photoionization process in Eq. (3.1).
[b] For *s* subshells, even values of j_t are "favored" and odd values of j_t are "unfavored."
[c] Values for $\beta(j_t)$ are obtained from Eqs. (3.9a) and (3.9c).
[d] Ground-state configuration mixing and final-state interchannel interactions may permit l to assume the value three also, which would make $\beta(j_t)$ energy dependent. Deviation of $\beta(j_t)$ from constancy is thus a sensitive measure of these electron correlations.

D. Calculation of the scattering amplitudes

When the photoelectron angular distribution is predicted to be energy dependent in *LS* coupling, then one must calculate $\beta(j_t)$ and $\sigma(j_t)$ in terms of the scattering amplitudes $S_l(j_t)$ for the photoionization process in Eq. (3.1). The scattering amplitudes $S_l(j_t)$ may be expressed in the *LS* coupling approximation in terms of reduced dipole matrix elements as follows (Starace, 1982):

$$S_l(j_t)=\left[\frac{4}{3}\frac{\pi}{c}\omega\right]^{1/2} i^l\exp(-i\sigma_l)\sum_L(2L+1)^{1/2}\begin{Bmatrix}L_c & l & L\\ 1 & L_0 & j_t\end{Bmatrix}\left\langle L_0S_0E_0\left|\left|\sum_{j=1}^{N} r_j^{(1)}\right|\right|\Psi^-_{L_cS_clLE}\right\rangle . \tag{3.10}$$

In Eq. (3.10), ω is the photon energy, the initial state is indicated by its energy E_0 and term level L_0S_0, and the energy normalized channel function $\Psi^-_{L_cS_clLE}$ describes the *N*-particle final state of energy $E=E_0+\omega$. The phase factors $i^l\exp(-i\sigma_l)$, where σ_l is the Coulomb phase shift, as well as the minus sign on the final-state wave function, indicate that incoming wave boundary conditions have been imposed on the final state: namely, at large separation, i.e., $r\rightarrow\infty$, where r is the photoelectron radial coordinate, the photoelectron has angular momentum l, the core has L_c, and the two are coupled to form the total angular momentum L. For smaller

separations r between the photoelectron and the ionic core, $\Psi_{L_c S_c lLE}^{-}$ represents a multichannel wave function, having nonzero components in all allowed final-state channels having the same total orbital and spin angular momentum L and S_0. The initial state correspondingly is described by a multiconfiguration wave function, all of whose components have the same total orbital and spin angular momenta L_0 and S_0. We reiterate that the only approximations used in Eq. (3.10) are the LS coupling approximation and the electric dipole approximation.

It is of interest to examine how Eq. (3.10) reduces when further approximations are made and what effect these additional approximations have on the β parameters. In general, the reduced dipole amplitude in Eq. (3.10) contains contributions from all open and closed channels which may be populated from the ground state and which are then scattered by electron-electron interactions into the final state indicated, namely, that labeled by the quantum numbers L_c, S_c, l, and L. When such interchannel scattering is not treated, and in addition when the initial state is represented by a single-configuration rather then by a multiconfiguration wave function, one has a single-channel Hartree-Fock (HF) calculation, and the reduced dipole amplitude, as well as the scattering amplitude, may then be written in a simplified form, as follows:

$$S_l^{\mathrm{HF}}(j_t) \propto i^l \exp(-i\sigma_l)(-1)^{l_0-l_>} l_>^{1/2} \times \sum_L \exp(-i\delta_{\varepsilon l}^{L_c S_c L}) R_{\varepsilon l}^{L_c S_c L}(2L+1) \times \left| \begin{Bmatrix} L_c & l & L \\ 1 & L_0 & j_t \end{Bmatrix} \begin{Bmatrix} L_c & l & L \\ 1 & L_0 & l_0 \end{Bmatrix} \right| . \quad (3.11)$$

In Eq. (3.11) the constant of proportionality is not given, as this factor depends only on the quantum numbers of the initial and the ionic state and hence cancels in the numerator and denominator of Eqs. (3.8) and (3.9a); $l_> \equiv \max(l_0,l)$; $\delta_{\varepsilon l}^{L_c S_c L}$ is the photoelectron's phase shift in the channel $L_c S_c l L$; and $R_{\varepsilon l}^{L_c S_c L}$ is the radial dipole integral,

$$R_{\varepsilon l}^{L_c S_c L} \equiv \int_0^\infty P_{nl_0}(r) r P_{\varepsilon l}^{L_c S_c L}(r) dr , \quad (3.12)$$

where $P_{n_0 l_0}$ and $P_{\varepsilon l}^{L_c S_c L}$ are radial wave functions for the initial and final orbitals of the photoelectron, where ε is the photoelectron's kinetic energy in the final state. Equation (3.11), then, is appropriate for a calculation which ignores interchannel final-state interactions as well as initial-state correlations. Note, however, that Eq. (3.11) does take account of the multiplet structure of the final state and of the initial state. In particular, the photoelectron's final-state wave function and phase shift usually depends upon both the ionic quantum numbers L_c and S_c of the core and the total orbital and spin angular momenta L and S_0 of the final state, which means that the electron-ion interactions are *anisotropic,* i.e., noncentral. Note also that the approximations made in deriving Eq. (3.11) are precisely those made in Table II for $j_t=2$(fav) which resulted in making $\beta(j_t=2)$ have the energy-independent value $\frac{1}{5}$. Thus, when Eq. (3.11) is substituted in Eq. (3.9a) to obtain $\beta(j_t=2)$ for the photoionization process considered in Table II, then $\beta(j_t=2)=\frac{1}{5}$. If the exact LS coupling expression in Eq. (3.10) had been used instead, then $\beta(j_t=2)$ would be energy dependent, as predicted in Table I for $j_t=2$(fav).

A further simplifying approximation for the scattering amplitudes $S_l(j_t)$ is to ignore the multiplet structure of the photoionization transition, as is done in the central-potential model approximation. In this approximation the phase shifts and the radial wave functions (and hence the radial dipole integrals) are assumed to depend only on the configuration, i.e., on n_0, l_0, and l, and are assumed to be independent of the term quantum numbers L_c, S_c, and L. One says thus that the central-potential model ignores "anisotropic electron-ion interactions" (Dill *et al.*, 1974, 1975) whose effect is to induce such a dependence of the phase shifts and the radial dipole integrals on L_c, S_c, and L. In short, Eq. (3.11) reduces to the central-potential model in the limit of isotropic electron-ion interactions, i.e.,

$$\exp(-i\delta_{\varepsilon l}^{L_c S_c L}) R_{\varepsilon l}^{L_c S_c L} \underset{\substack{\text{isotropic}\\ \text{interactions}}}{\longrightarrow} \exp(-i\delta_{\varepsilon l}) R_{\varepsilon l} . \quad (3.13)$$

In the limit of Eq. (3.13), the summation over L in Eq. (3.11) may be carried out analytically to get

$$S_l^{\mathrm{CP}}(j_t) \propto \delta(j_t,l_0) i^l \exp(-i\sigma_l)(-1)^{l_0-l_>} l_>^{1/2}(2l_0+1)^{-1} \exp(-i\delta_{\varepsilon l}) R_{\varepsilon l} , \quad (3.14)$$

where CP indicates this is the central-potential model result. Substituting Eq. (3.14) into Eqs. (3.8) and (3.9a) gives the well-known Cooper-Zare (1969) result:

$$\beta^{\mathrm{CZ}} = \frac{l_0(l_0-1)R_{l_0-1}^2 + (l_0+1)(l_0+2)R_{l_0+1}^2 - 6l_0(l_0+1)R_{l_0-1}R_{l_0+1}\cos(\sigma_{l_0+1}+\delta_{l_0+1}-\sigma_{l_0-1}-\delta_{l_0-1})}{(2l_0+1)[l_0 R_{l_0-1}^2 + (l_0+1)R_{l_0+1}^2]} . \quad (3.15)$$

Note that in Eq. (3.15) the explicit dependence of the phase shifts and radial dipole matrix elements on energy ε has been omitted for simplicity.

Two points concerning the Cooper-Zare (CZ) central-potential model result β^{CZ} are worth noting. First, from Eq. (3.14) one sees that there is only a single value of $j_t=l_0$ allowed. This is the value for j_t that one would expect from Eq. (3.2) in the central-potential model ap-

proximation, since in a one-electron picture

$$\mathbf{l}_0+\mathbf{j}_\gamma=\mathbf{l}\ , \tag{3.16}$$

and hence

$$\mathbf{j}_t=\mathbf{j}_\gamma-\mathbf{l}=-\mathbf{l}_0\ . \tag{3.17}$$

This model treats only the first stage of the photoionization process—the one-electron photoabsorption process—and ignores the second stage of the scattering of the photoelectron in the field of the ion during its escape to inifinity. Since the only good quantum number in the second stage is the total orbital angular momentum L, the ionic and photoelectron orbital angular momenta may change either their orientation or their magnitude, provided only $\mathbf{L}=\mathbf{L}_c+\mathbf{l}$. In this way, angular momentum transfers other than $j_t=l_0$ become possible once one goes beyond the central-potential model approximation to consider the second stage of the photoionization process. We note that even a simple rotation of $\mathbf{L}_c+\mathbf{l}$ about $\mathbf{L}$ which preserves the magnitudes $|\mathbf{L}_c|$ and $|\mathbf{l}|$ is sometimes sufficient to permit alternative values of j_t (see Dill *et al.*, 1975). For the special case of s-subshell photoionization,

$$j_t=l_0=0 \tag{3.18}$$

is the only angular momentum transfer permitted in the central-potential model. Hence, from either Table I or Table II, we see that the asymmetry parameter β is predicted to be an energy-independent constant, $\beta=2$, in the central-potential model approximation. The other energy-independent β parameters predicted in Table II for j_t values of 1 and 2 in s-subshell photoionization processes are simply not permitted in the central-potential model.

A second point concerning the Cooper-Zare expression β^{CZ} in Eq. (3.15) is that it has the same *form* as the exact LS coupling result, given by Eqs. (3.8)–(3.10), in the case of closed-shell atoms. This is seen by comparing the exact LS coupling result for the scattering amplitudes $S_l(j_t)$ in Eq. (3.10) with the central-potential model result in Eq. (3.14). Setting $L_0=0$ in Eq. (3.10) results, from the properties of the $6j$ coefficients, in j_t having the single value L_c. For closed-shell atoms the ionic orbital angular momentum L_c, however, is equal to the initial orbital angular momentum l_0 of the photoelectron. Hence, for closed-shell atoms, $j_t=l_0$ and the exact LS coupling formulas (3.8)–(3.10) give an expression for β similar in *form* to Eq. (3.15) but in which the reduced dipole amplitudes in Eq. (3.10) still take into account the interchannel coupling between final-state channels and the configuration mixing in the initial state.

E. Applications to specific processes

1. s-subshell photoionization processes

In order to provide concrete examples of some of the general transitions indicated in Table II, we present in Table III all final-state channels, and we indicate the energy-dependent behavior of the β parameter for s-subshell photoionization in atoms having the configuration $\mathscr{A}s^2p^q$, where $0\le q\le 6$. That is, we consider the following transitions[1]:

$$\mathscr{A}s^2p^q(^{2S_0+1}L_0)+\gamma\rightarrow\mathscr{A}^+sp^q(^{2S_c+1}L_c)\varepsilon l(^{2S+1}L)\ . \tag{3.19}$$

Note that the specific configurations indicated are given for concreteness only. These configurations may be thought of as the leading terms in a mulitconfiguration expansion of the initial and final states. Furthermore, with only a few exceptions, the β-parameter behavior indicated in Table III is based entirely on the values of L_0 and L_c and on the fact that for s-subshell transitions $\pi_0\pi_c=+1$, where π_0 and π_c are the parities of the atom and the ionic core, respectively. Thus these predictions are exact within LS coupling and do not require the specification of initial or final configurations. The exceptions, indicated by footnotes b and c, depend on the additional assumption that odd photoelectron orbital angular momenta $l\ge 3$ can be neglected. As discussed in Sec. II.C above, such higher odd-l values may occur due to initial-state or final-state configuration mixing.

a. *Energy-independent β parameters*

Table III indicates a number of specific s-subshell photoionization transitions which illustrate the general predictions in Table II for the occurrence of energy-independent β parameters. A particularly interesting case shown in Table III is that of $\mathscr{A}s^2p^3(^4S)$. In LS coupling, each of the three transitions leading to the three allowed term levels of the corresponding ion, $\mathscr{A}^+sp^3(^{2S_c+1}L_c)$, has an energy-independent β parameter for the photoelectron. For the transitions having $j_t=0$ and $j_t=1$, respectively, the geometry of the situation precludes the inference of dynamical information from the photoelectron angular distribution except for deviations from LS coupling. For the third transition, having $j_t=2$, β is constant within LS coupling only in the dynamical approximation that the $l=3$ photoelectron orbital angular momentum is ignored. Deviation of the actual β for this latter transition from constancy is thus a measure of both this dynamical approximation and of the LS coupling approximation.

b. *Energy-dependent β parameters*

Table III also indicates for the transitions in Eq. (3.19) those β parameters which are expected to be energy

[1]In LS coupling the configuration sp^q differs from s^2p^q only in the spin angular momentum. Thus for given values of L_0 and L_c the configuration sp^q has the same predicted β parameter as given in Table II for s^2p^q.

TABLE III. Dependence on photon energy of the asymmetry parameter $\beta(^{2S_0+1}L_0 \rightarrow {}^{2S_c+1}L_c)$ corresponding to s-subshell photoionization transitions of the type $\mathscr{A}s^2p^q(^{2S_0+1}L_0) + \gamma \rightarrow \mathscr{A}^+sp^q(^{2S_c+1}L_c)\varepsilon l(^{2S+1}L)$. Underlined entries occur due to either interchannel electron correlation or ground-state configuration mixing.

q	$^{2S_0+1}L_0$	$^{2S_c+1}L_c$	l	^{2S+1}L	j_t	$\beta(^{2S_0+1}L_0 \rightarrow {}^{2S_c+1}L_c)$[a]
0 or 6	^1S	^2S	p	^1P	0	$+2$
1 or 5	^2P	^1P or ^3P	p	$^2S,^2P,^2D$	0,1,2	$-1 \le \beta \le 2$
			$\underline{f}$	$^2\underline{D}$	$\underline{2}$	
2 or 4	^3P	^2P or ^4P	p	$^3S,^3P,^3D$	0,1,2	$-1 \le \beta \le 2$
			$\underline{f}$	$^3\underline{D}$	$\underline{2}$	
		^2D	p	$^3P,^3D$	1,2	$-1 \le \beta \le \frac{1}{5}$[b]
			$\underline{f}$	$^3\underline{P},^3\underline{D}$	$\underline{2,3}$	
		^2S	p	^3P	1	-1
	^1D	^2P	p	$^1P,^1D$	1,2	$-1 \le \beta \le \frac{1}{5}$[b]
			$\underline{f}$	$^1\underline{D},^1\underline{F}$	$\underline{2,3}$	
		^2D	p	$^1P,^1D,^1F$	0,1,2	$-1 \le \beta \le 2$
			$\underline{f}$	$^1\underline{P},^1\underline{D},^1\underline{F}$	$\underline{2,3,4}$	
			$\underline{h}$	$^1\underline{F}$	$\underline{4}$	
		^2S	p	^1P	2	$\frac{1}{5}$[c]
			$\underline{f}$	$^1\underline{F}$	$\underline{2}$	
	^1S	^2P	p	^1P	1	-1
		^2D	p	^1P	2	$\frac{1}{5}$[c]
			$\underline{f}$	$^1\underline{P}$	$\underline{2}$	
		^2S	p	^1P	0	2
3	^4S	^3S or ^5S	p	^4P	0	2
		^3P	p	^4P	1	-1
		^3D	p	^4P	2	$\frac{1}{5}$[c]
			$\underline{f}$	$^2\underline{D}$	$\underline{2}$	
	^2P	^3S	p	^2P	1	-1
		^1P or ^3P	p	$^2S,^2P,^2D$	0,1,2	$-1 \le \beta \le 2$
			$\underline{f}$	$^2\underline{D}$	$\underline{2}$	

TABLE III. *(Continued).*

q	$^{2S_0+1}L_0$	$^{2S_c+1}L_c$	l	^{2S+1}L	j_t	$\beta(^{2S_0+1}L_0 \rightarrow {}^{2S_c+1}L_c)$[a]
		^1D or ^3D	p	$^2P,^2D$	1,2	$-1 \leq \beta \leq \frac{1}{5}$[b]
			$\underline{f}$	$^2\underline{P},^2\underline{D}$	$\underline{2,3}$	
	^2D	^3S	p	^2P	2	$\frac{1}{5}$[c]
			$\underline{f}$	$^2\underline{F}$	$\underline{2}$	
		^1P or ^3P	p	$^2P,^2D$	1,2	$-1 \leq \beta \leq \frac{1}{5}$[b]
			$\underline{f}$	$^2\underline{D},^2\underline{F}$	$\underline{2,3}$	
		^1D or ^3D	p	$^2P,^2D,^2F$	0,1,2	
			$\underline{f}$	$^2\underline{P},^2\underline{D},^2\underline{F}$	$\underline{2,3,4}$	$-1 \leq \beta \leq 2$
			$\underline{h}$	$^2\underline{F}$	$\underline{4}$	

[a]Nonrelativistic predictions. Relativistic interactions introduce in principle an energy-dependent variation in β within the range $-1 \leq \beta \leq 2$.
[b]The upper limit applies only if the f channels are ignored, i.e., if interchannel interactions and/or ground-state configuration mixing is negligible.
[c]In princple the β parameter is energy dependent, but in the absence of interchannel interactions or ground-state configuration mixing (i.e., ignoring the f channel) β would be constant with value $+\frac{1}{5}$.

dependent. As noted in Sec. II, this energy dependence is bounded in range $-1 \leq \beta \leq 2$. However, in certain cases a more restrictive, although approximate, upper bound may be placed on the energy variation of β. In all cases, the energy variation of β may be shown to be most rapid in the vicinity of zeros in the radial dipole matrix elements. We discuss each of these points in turn. The fact that β varies rapidly in the vicinity of resonances is now well known (Dill, 1973; Chang and Taylor, 1978) and will not discussed.

Table III indicates four cases where the upper bound on the variation of β is $\frac{1}{5}$ instead of 2. This more restrictive upper bound, first pointed out for a transition in carbon by Chang and Taylor (1978), hinges on the neglect of the f-electron channels. The analysis is as follows: In each of the four cases j_t may only assume the values 1, 2, and 3, i.e., $j_t=0$ is not allowed. As shown above, $j_t=1$ and $j_t=3$ are parity unfavored transitions, so that $\beta(j_t=1)=\beta(j_t=3)=-1$. On the other hand, $j_t=2$ is parity favored and hence $\beta(j_t=2)$ is given by Eq. (3.9a). In general, a dynamical calculation must be performed to evaluate Eq. (3.9a). However, if interchannel interactions and/or ground-state configuration mixing are neglected, then the photoelectron's orbital angular momentum can only be $l=1$, i.e., $l=3$ is not allowed. In this approximation, then, $S_+(j_t=2)=0$ and only $S_-(j_t=2)$ contributes to Eq. (3.9a), which thus gives $\beta(j_t=2)=\frac{1}{5}$. Equation (3.8) gives for the total asymmetry parameter:

$$\beta=\frac{-\sigma(1)+\frac{1}{5}\sigma(2)}{\sigma(1)+\sigma(2)} . \tag{3.20}$$

Since the partial cross sections are positive, Eq. (3.20) shows that β is restricted to the range $-1 \leq \beta \leq 1/5$. Put another way, Eq. (3.20) shows β to be a weighted average of -1 and $+\frac{1}{5}$; hence it must lie between these two values. In their calculations for carbon, Chang and Taylor (1978) found that the partial cross sections for the f-electron channels were an order of magnitude smaller than for the p-electron channels. Thus Eq. (3.20) is a reasonable approximation for β. On the other hand, a measurement of β which finds that $\beta > \frac{1}{5}$ in one of the four cases in Table III for which $\frac{1}{5}$ is an approximate upper bound would give a measure of the strength of interchannel and/or ground-state interactions (as well as of relativistic interactions, as shown below).

In all cases where β is energy dependent one may show that β varies rapidly in the vicinity of zeros in the radial dipole matrix elements. These zeros may be detected as minima in experimental partial cross-section measurements. We illustrate the influence of such zeros with two recent calculations for Cl and Al in which final-state interchannel interactions and ground-state configuration mixing were ignored.

c. *Illustrative numerical calculations for Cl and Al*

Calculations have been performed (Starace *et al.*, 1977) within the framework of LS coupling and HF single-

particle wave functions (using methods described by Kennedy and Manson, 1972) for the photoionization cross section of the 3*s* subshell of ground-state Cl, i.e.,

$$\mathrm{Cl}\,3s^2 3p^5(^2P)+\gamma\rightarrow \mathrm{Cl}^+ 3s\,3p^5(^{1,3}P)\varepsilon p\,(^2S,^2P,^2D)\ . \qquad (3.21)$$

As seen in Table III, the process in Eq. (3.21) is an *energy-dependent* case with three possible values of $j_t=0,1,2$. In these calculations the approximate Eq. (3.11) was used to calculate the scattering amplitudes $S_l(j_t)$, which for the processes in Eq. (3.21) have the following expressions in terms of the HF phase shifts, $\delta_{\varepsilon p}^{L_c S_c L}$, and the radial dipole matrix elements $R_{\varepsilon p}^{L_c S_c L}$ (Starace *et al.*, 1977):

$$S_1(0)=\frac{C}{3}[\exp(-i\delta_{\varepsilon p}^{1S_c0})R_{\varepsilon p}^{1S_c0}+3\exp(-i\delta_{\varepsilon p}^{1S_c1})R_{\varepsilon p}^{1S_c1}+5\exp(-i\delta_{\varepsilon p}^{1S_c2})R_{\varepsilon p}^{1S_c2}]\ , \qquad (3.22a)$$

$$S_1(1)=\frac{C}{6}[2\exp(-i\delta_{\varepsilon p}^{1S_c0})R_{\varepsilon p}^{1S_c0}+3\exp(-i\delta_{\varepsilon p}^{1S_c1})R_{\varepsilon p}^{1S_c1}-5\exp(-i\delta_{\varepsilon p}^{1S_c2})R_{\varepsilon p}^{1S_c2}]\ , \qquad (3.22b)$$

$$S_1(2)=\frac{C}{6}[2\exp(-i\delta_{\varepsilon p}^{1S_c0})R_{\varepsilon p}^{1S_c0}-3\exp(-i\delta_{\varepsilon p}^{1S_c1})R_{\varepsilon p}^{1S_c1}+\exp(-i\delta_{\varepsilon p}^{1S_c2})R_{\varepsilon p}^{1S_c2}]\ , \qquad (3.22c)$$

with C a common factor. If we ignore the possibility of $l=3$ photoelectrons in the case $j_t=2$, then according to Eq. (3.8) and Table II the asymmetry parameter is given by

$$\beta(^2P\rightarrow{}^{1,3}P)=\frac{2\sigma(0)-\sigma(1)+\frac{1}{5}\sigma(2)}{\sigma(0)+\sigma(1)+\sigma(2)}\ . \qquad (3.23)$$

The results of these calculations for $\beta(^1P)$ and $\beta(^3P)$ are given in Fig. 1, using both HF-length and HF-velocity electric dipole formulas.[2] The strong dependence on energy and the deviations from the central potential model value $\beta=2$ are clearly seen. Note that the central-potential model value for β would obtain in the absence of anisotropic interactions, i.e., when the radial dipole matrix elements and phase shifts are independent of the final-state term level L. In this case one sees from Eqs. (3.22b) and (3.22c) that $S_1(1)$ and $S_1(2)$ vanish and hence so do $\sigma(1)$ and $\sigma(2)$. The result is that in this limit $\beta=2$ [cf. Eq. (3.23)], since only $\sigma(0)$ is nonvanishing. Our calculations indicate, however, that the anisotropic electron-ion interactions are far from negligible.

To emphasize the importance of the anisotropic interactions, consider the ratio

$$\frac{\sigma-\sigma(0)}{\sigma}\ , \qquad (3.24)$$

which vanishes in their absence. Our results for this ratio are given for the ^{3}P term of the ion in Fig. 2. Near threshold this ratio is not small, and in fact it goes to unity at one point, indicating that $\sigma(0)$, the *only* contribution in a central-potential model calculation, *gives no contribution at all!* The behavior of the ratio in Eq. (3.24) can be understood by considering the energy dependence of the radial dipole matrix elements for the ^{3}P ionic term. From Fig. 3 it is seen that all of the matrix elements change sign at continuum photoelectron energies. At a particular energy (indicated by the arrow) between the zeros in the matrix elements, the positive and negative contributions to $S_1(0)$ just cancel so that $S_1(0)\rightarrow 0$ and thus $\sigma(0)\rightarrow 0$. (We note parenthetically that from the positions of the zeros in the matrix elements one can immediately conclude that the anisotropic exchange interaction is most attractive for the ^2D channel and least attractive for the ^2S.) The effects of the anisotropic interactions are thus greatest in the neighborhood of the zeros in the matrix elements corresponding to the minima in the cross sections, although their effects are still evident, but small, at the highest energies considered. The above analysis shows that this will be a general phenomenon for open-shell atoms.

As a contrasting example, calculated results (Shahabi, 1979) for

$$\mathrm{Al}\,3s^2 3p\,(^2P)+\gamma\rightarrow \mathrm{Al}^+ 3s\,3p\,(^{1,3}P)\varepsilon p\,(^2S,^2P,^2D) \qquad (3.25)$$

are shown in Fig. 4. *Qualitatively,* the β's for the 3*s* subshell of Al are much the same as for Cl. *Quantitatively,* the differerence is substantial. The β's for Al (in the HF-length formulation) only go as low as ≈ 1.93, which is not a large deviation from the value two. This can be understood by noting that the zeros in the transition matrix elements in this case lie in the discrete energy region, so, as discussed above, the cancellation effects, which may occur between the zeros, cannot occur in this case. Thus the very significant influence of these zeros on the β parameter is evident by comparison of the angular distributions for processes (3.21) and (3.25).

We reiterate that correlation is entirely ignored in these calculations except to the extent that for Cl a relaxed ionic core was used. It is likely that inclusion of final-state interchannel electron correlations would shift

[2]The length and velocity formulas are two alternative expressions for the electric dipole interaction matrix elements. They give equal numerical values when exact atomic wave functions are used, but not necessarily when approximate wave functions are used. Thus in HF approximation the formulas generally do not agree, whereas in the central potential model approximation they do agree. See Bethe and Salpeter (1957), Sec. 59β, as well as Kennedy and Manson (1972) and Starace (1982), Sec. 5.

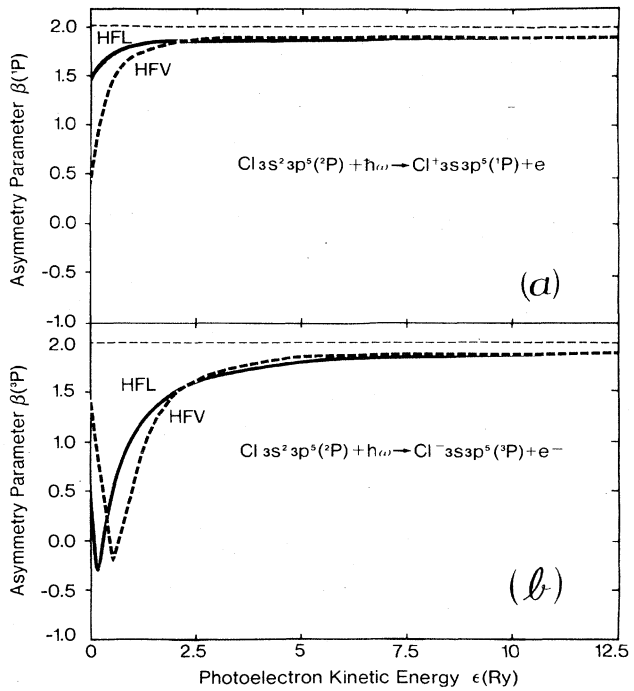

FIG. 1. Asymmetry parameters $\beta(^1P)$ and $\beta(^3P)$ versus photoelectron kinetic energy for Cl 3s photoionization. The solid (dashed) curves employ the length (velocity) form for the radial dipole matrix elements. The horizontal dashed curves indicate the value $\beta=2$ that would apply in the approximation of isotropic electron-ion interactions, as in a central-potential model calculation based upon the theory of Cooper and Zare (1969).

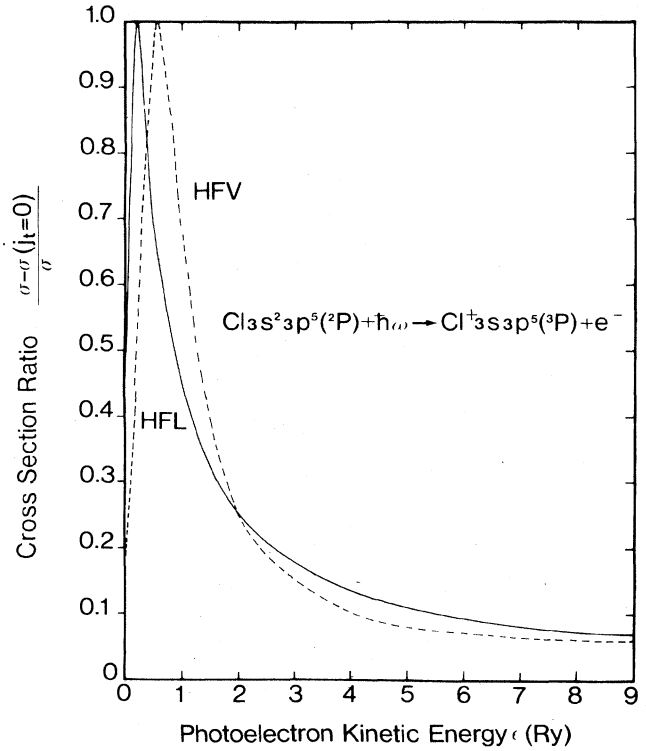

FIG. 2. The cross-section ratio $[\sigma-\sigma(j_t=0)]/\sigma$ plotted versus photoelectron kinetic energy for Cl 3s ionization to the ^3P term of the ion. The solid (dashed) curves employ the length (velocity) form of the radial dipole matrix element.

the locations of the matrix element zeros somewhat. The main effect of these shifts would be to shift the positions and to alter the depths of the minima in the β's. Qualitatively, however, the main features of the energy dependence of β illustrated by these calculations for Cl and Al are not expected to change markedly.

2. Other photoionization processes having energy-independent β parameters

To emphasize that s-subshell photoionization processes are not the only ones for which the photoelectron angular distribution may be energy independent in LS coupling, we provide here a few additional examples involving p-subshell transitions. Table I is our guide to the occurrence of such transitions; we have merely to find particular instances where L_0, L_c, and $\pi_0\pi_c$ have the values shown in Table I which imply a constant value of β.

Consider first the direct photoionization of the p^3 subshell of an atom $\mathscr{A}$ having any number of other subshells. If the atom is initially in an $L_0=2$ state, and the ion is in an $L_c=0$ state, then the only allowed photoionization transition is

$$\mathscr{A}\,p^3(^2D)+\gamma\rightarrow\mathscr{A}^+p^2(^1S)\varepsilon d(^2D)\ ,$$

and for this transition $j_t=2$. Furthermore, the transition is "unfavored" since $\pi_0\pi_c=-1=(-1)^{j_t+1}$. Hence, ac-

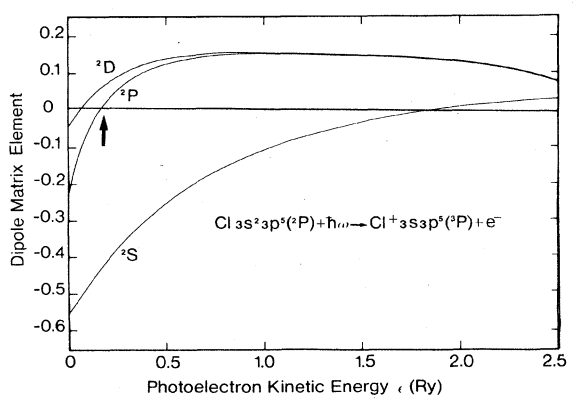

FIG. 3. The Cl 3s radial dipole matrix elements $R_{\varepsilon p}^{L_cS_cL}$ in the length form plotted versus photoelectron kinetic energy for $L_c=1$, $S_c=1$, (i.e., the ^3P level of the ion), and $L=2,1$, and 0 (i.e., the ^2D, and ^2P and ^2S final-state terms). The arrow indicates the kinetic energy at which $S_1(j_t=0)=0$, in which case only the angular momentum transfers $j_t\neq 0$ contribute to the cross section and the asymmetry parameter.

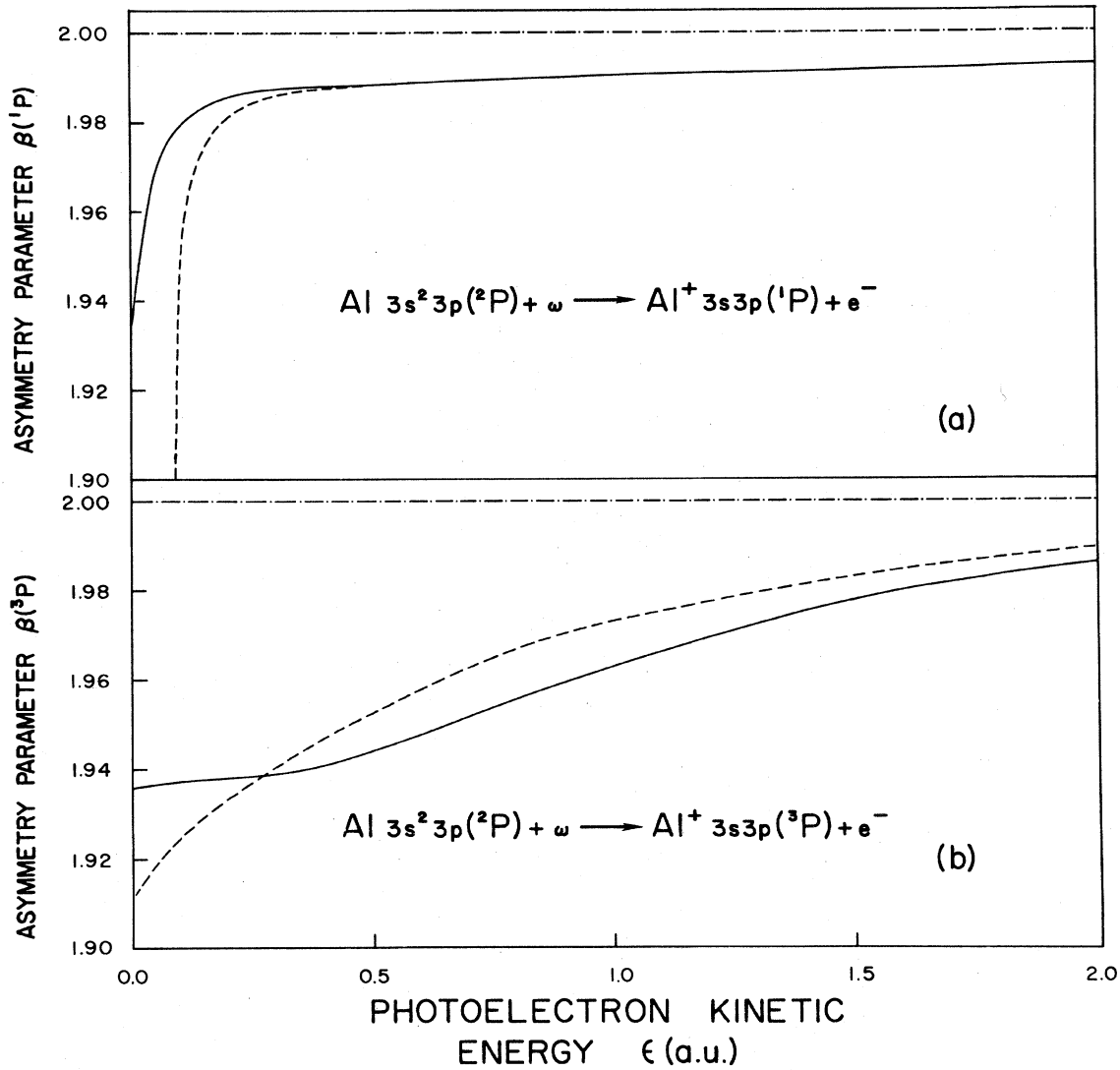

FIG. 4. Asymmetry parameters $\beta(^1P)$ and $\beta(^3P)$ versus photoelectron kinetic energy for Al 3s photoionization. The solid (dashed) curves employ the length (velocity) form for the radial dipole matrix elements. The horizontal dot-dashed curves indicate the value $\beta=2$ that would apply in the approximation of isotropic electron-ion interactions, as in a central-potential model calculation based upon the theory of Cooper and Zare (1969).

cording to the third line of Table I, β for this transition has the constant value -1 in LS coupling.

Consider next the photoionization plus excitation of the p^2 subshell of an atom having any number of other subshells. We assume that one of the p electrons is ionized and the other is excited to a bound s state in the ion. Two such transitions lead to constant β parameters:

$$\mathscr{A}p^2(^3P)+\gamma\rightarrow\mathscr{A}^+s(^2S)\varepsilon p(^3P)$$

and

$$\mathscr{A}p^2(^1S)+\gamma\rightarrow\mathscr{A}^+s(^2S)\varepsilon p(^1P)\ .$$

In the first transition, for which $L_0=1$, the angular momentum transfer is $j_t=1$. This is an "unfavored" transition since $\pi_0\pi_c=+1=(-1)^{j_t+1}$. Hence according to the third line of Table I, β must be -1 in LS coupling. In the second transition, for which $L_0=0$, we have $j_t=0$. Furthermore this is a favored transition and hence β must have the constant value $+2$ in LS coupling.

We stress that while we have given only a few examples of non-s-subshell photoionization processes having energy-independent β parameters, many other examples exist. The processes above are representative and not exhaustive.

IV. RELATIVISTIC THEORETICAL PREDICTIONS FOR *s*-SUBSHELL PHOTOELECTRON ANGULAR DISTRIBUTIONS

The occurence of energy-independent β parameters, discussed in the previous section, hinges on the neglect of spin-orbit and other relativistic interactions. When these relativistic interactions are included, the general electric dipole photoionization process in Eq. (3.1) can only be characterized by the parities and total angular momenta as the orbital and spin angular momenta are no longer separately conserved:

$$\mathscr{A}(J_0,\pi_0)+\gamma(j_\gamma=1,\pi_\gamma=-1) \rightarrow \mathscr{A}^+(J_c,\pi_c)+e^-(l,s,j,\pi_e=(-1)^l)\ . \tag{4.1}$$

The allowed values of the angular momentum transfer j_t are determined by Eq. (3.2), i.e.,

$$\mathbf{j}_t=\mathbf{j}_\gamma-\mathbf{l}=\mathbf{J}_c+\mathbf{s}-\mathbf{J}_0, \tag{4.2}$$

where $\mathbf{s}$ is the spin of the phototelectron, with magnitude $s=\frac{1}{2}$. Formulas (3.8)–(3.9) for determining β as an expansion in j_t hold as before, only now the scattering amplitudes $S_l(j_t)$ in Eq. (3.10) will have a different form since the dipole matrix elements will now depend dynamically on the total angular momenta J_0, J_c, and j rather than only geometrically.

One can see, however, from Eq. (4.2) that for the processes (4.1) it is not possible to have only a single value of j_t, and thus β is in principle always energy dependent in a relativistic formulation. Consider the second equality in Eq. (4.2). Since the sum $\mathbf{J}_c+\mathbf{s}-\mathbf{J}_0$ must equal $\mathbf{j}_\gamma-\mathbf{l}$, which is always a whole integer, $\mathbf{J}_c$ and $\mathbf{J}_0$ cannot be simultaneously zero. Thus even if either J_0 or J_c is zero, $\mathbf{s}$ can add in two ways to the other, resulting in a least two values for j_t. This possibility of flipping the photoelectron's spin due to spin-orbit and other relativistic interactions thus guarantees a minimum of two values of j_t for any photoionization process in the general case.

The relation of the general Eq. (4.2) to the nonrelativistic Eq. (3.5) may be seen more clearly by replacing in Eq. (4.2) $\mathbf{J}_c$ by $\mathbf{L}_c+\mathbf{S}_c$ and $\mathbf{J}_0$ by $\mathbf{L}_0+\mathbf{S}_0$ to obtain

$$\mathbf{j}_t=\mathbf{j}_\gamma-\mathbf{l}=(\mathbf{L}_c-\mathbf{L}_0)+(\mathbf{S}_c+\mathbf{s}-\mathbf{S}_0)\ . \tag{4.3}$$

In nonrelativistic approximation the spins are unaffected by the photoionization process. Hence the spins after ionization, i.e., $\mathbf{S}_c+\mathbf{s}$, always equal exactly $\mathbf{S}_0$, so that the second quantity on the right in Eq. (4.3) is always identically zero. When relativistic interactions are considered, $(\mathbf{S}_c+\mathbf{s}-\mathbf{S}_0)$ may take nonzero values, and thus additional values of j_t may be allowed. In particular, even if in nonrelativistic approximation only a single value of j_t is permitted, relativistic interactions will *always* permit additional values of j_t.

In order to show how the relativistic case reduces to the nonrelativistic case in the limit of vanishing spin-dependent interactions, we consider the most common examples of transitions that in nonrelativistic approximation have an energy-independent β parameter.

A. Photoionization of *H* and of the outer *s* electron in the alkalis

Consider specifically the alkali atom cesium,

$$\mathrm{Cs}\,6s(^2S_{1/2})+\gamma\rightarrow\mathrm{Cs}^+(^1S_0)\varepsilon p(^2P_{3/2,1/2})\ . \tag{4.4}$$

According to Eq. (4.2), j_t may have the values 0 or 1, and hence the β parameter in this case is given according to Eq. (3.8) by

$$\beta=\frac{2\sigma(0)-\sigma(1)}{\sigma(0)+\sigma(1)}\ . \tag{4.5}$$

According to nonrelativistic theory (cf. Table I), only $j_t=0$ is allowed and hence $\beta=2$. Thus deviations of β from the energy-independent value two are a measure of the strength of $\sigma(1)$, which is due entirely to relativistic effects.

As an example of the effect of relativistic interactions, we present in Fig. 5 the results of relativistic theoretical calculations for the outer s subshell of the alkali-metal atoms. The solid lines indicate the Dirac-Fock results of Ong and Manson (1979b) and show a sharp drop in β from $+2$ to -1 in the vicinity of the zeros, indicated by the arrows, in the $j=\frac{1}{2}$ and $j=\frac{3}{2}$ transition matrix elements; that is, β varies rapidly in the region of the near-threshold cross-section minimum. The width of the variation in β increases as the atomic number, and hence the strength of relativistic interactions, increases. In the case of Cs, in which relativistic interactions are strongest, the frozen-core dipole length result for β of Huang and Starace (1979) is also shown. In their calculation the effect of final-state spin-orbit interactions in the Breit-Pauli approximation is treated exactly within a basis of nonrelativistic HF wave functions. Their length and velocity results (note that their velocity result is not shown in Fig. 5) bracket the semiempirically determined value of β for Cs $6s$ of Marr (1974). Only one experimental measurement of the alkali β parameters have been published, that of Chaffee (1931) for K, which indicates clearly that β does drop below the nonrelativistic theoretical value of two.

B. Photoionization of an *s* subshell in a closed-shell atom

Consider the alkaline-earth atom barium, which is also a prototype for other closed-shell atoms:

$$\mathrm{Ba}\,6s^2(^1S_0)+\gamma\rightarrow\mathrm{Ba}^+6s(^2S_{1/2})\varepsilon p(^{1,3}P_1)\ , \tag{4.6}$$

According to Eq. (4.2), j_t may again have the values 0 and 1 and hence the β parameter in this case is given according to Eq. (3.8) once again by Eq. (4.5). Nonrelativistically only $j_t=0$ is allowed, and this corresponds to the $^1P_1$ final state. Thus deviations of β from the energy-independent value two are again a measure of $\sigma(1)$, which corresponds here to the $^3P_1$ final-state channel.

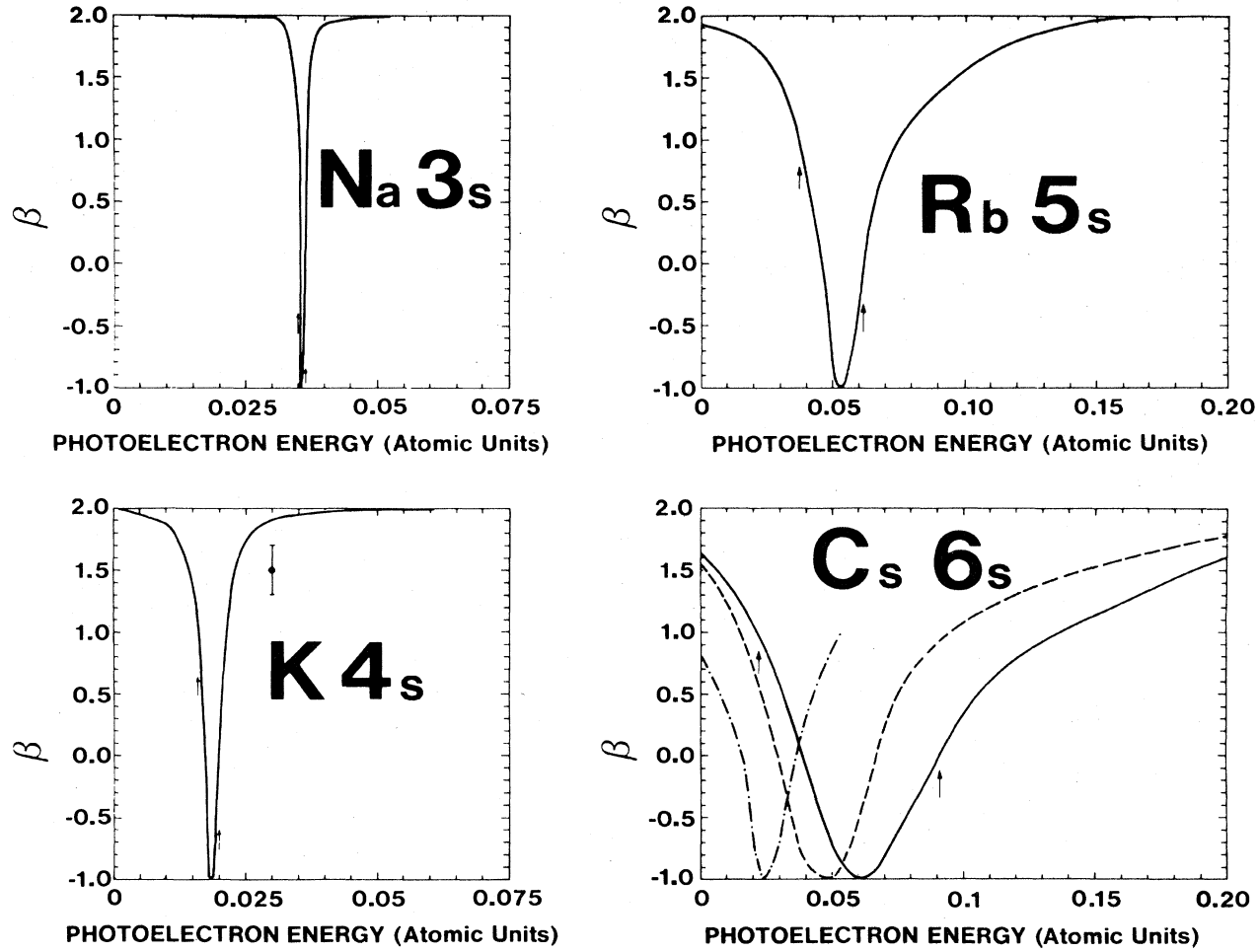

FIG. 5. Asymmetry parameters for photoionization of the outer *ns* subshell of the alkali-metal atoms Na through Cs. *Solid Curves*: Dirac-Fock calculations of Ong and Manson (1979b). Note that the lower- and higher-energy vertical arrows on each curve are the energies at which the $j=\frac{1}{2}$ and $j=\frac{3}{2}$ radial dipole integrals, respectively, vanish. *Solid Dot* (*K* 4*s*): Experimental measurement of Chaffee (1931). *Dashed Curve* (Cs 6*s*): Frozen-core dipole length result of Huang and Starace (1979) treating final-state spin-orbit interactions in the Breit-Pauli approximation within a basis of nonrelativistic HF wave functions. *Dash-Dot Curve* (Cs 6*s*): Semiempirically derived results of Marr (1974).

As a particularly striking example of the effect of relativistic interactions on the angular distribution of *s*-subshell photoelectrons in the case of closed-shell atoms, we show theoretical and experimental results for the 5*s* subshell of xenon in Fig. 6. The first experimental measurement reported by Dehmer and Dill (1976), which found that β had the value 1.4, stimulated much theoretical work to account for this deviation from the nonrelativistically predicted value of two. The Dirac-Fock (DF) result of Ong and Manson (1978a, 1979a) as well as the two relativistic random-phase approximation (RRPA) results of Johnson and Cheng (1978, 1979), which included coupling between the 5*s*- and 5*p*-subshell channels and between the 4*d*-, 5*s*-, and 5*p*-subshell channels, respectively, all passed close to the single experimentally measured point. These three calculations made very different predictions, however, for the location of the minimum in β, which is apparently very sensitive to the electron correlations included in the calculation. Only the most detailed calculation, the RRPA ($4d+5s+5p$) one, is in agreement with the most recently measured experimental points at lower energy of White *et al.* (1979). The *K*-matrix results of Huang and Starace (1980), which treat the effect of final-state spin-orbit interactions in the Breit-Pauli approximation within a basis of HF nonrelativistic wave functions, do not give nearly so large a drop in β as do the other, purely relativistic calculations. The size of this drop in β depends on the magnitude of the nonrelativistically forbidden $^3P_1$ channel. Apparently it is not possible to calculate the correct magnitude for this forbidden transition by treating only final-state spin-orbit interactions; other relativistic interactions appear to be crucial.

C. Photoionization of an *s* subshell in an open-shell atom

Consider the carbon transition first pointed out by Chang and Taylor (1978):

$$C\,2s^2 2p^2(^3P_{2,1,0})+\gamma \rightarrow C^+ 2s\,2p^2(^2S_{1/2})\varepsilon p(^1P_1,{}^3P_{2,1,0})\ . \tag{4.7}$$

According to Eq. (4.2), when the initial-state total angular momentum has the value of $J_0=2$, then the angular momentum transfer has the values $j_t=1,2$; when $J_0=1$, $j_t=0,1,2$; and when $J_0=0$, $j_t=0,1$. According to Tables I and II, nonrelativistically only $j_t=1$ is permissible. Thus a measurment of β for the transitions in Eq. (4.7) that finds deviations from the nonrelativistic value $\beta=-1$ provides a measure of the relativistically allowed angular momentum transfers $j_t=0,2$ and of their partial cross sections $\sigma(0)$ and $\sigma(2)$:

$$\beta(J_0=2)=\frac{-\sigma(1)+\frac{1}{5}\sigma(2)}{\sigma(1)+\sigma(2)}\ , \tag{4.8a}$$

$$\beta(J_0=1)=\frac{2\sigma(0)-\sigma(1)+\frac{1}{5}\sigma(2)}{\sigma(0)+\sigma(1)+\sigma(2)}\ , \tag{4.8b}$$

$$\beta(J_0=0)=\frac{2\sigma(0)-\sigma(1)}{\sigma(0)+\sigma(1)}\ . \tag{4.8c}$$

V. CONCLUSIONS

Following a review of the theory of photoelectron angular distributions and an examination of the possibility of energy-independent angular distributions within the electric dipole, *LS* coupling approximation, we have illustrated the theory by a general discussion of the energy dependence of the angular distribution asymmetry parameters β for *s*-subshell electrons in both nonrelativistic and relativistic cases. The *s*-subshell photoelectron angular distributions have been shown to be particularly good examples for disentangling purely geometrical effects from the dynamical effects of various weak interactions. When relativistic interactions (i.e., spin-dependent interactions) are taken into consideration, β has been shown to be always energy dependent in principle. We have pointed out, however, many cases which in nonrelativistic approximation have constant β with one of the values 2 or -1. Experimental measurements of β in these cases which find deviations of β from constancy thus provide a measure of the strength of relativistic in-

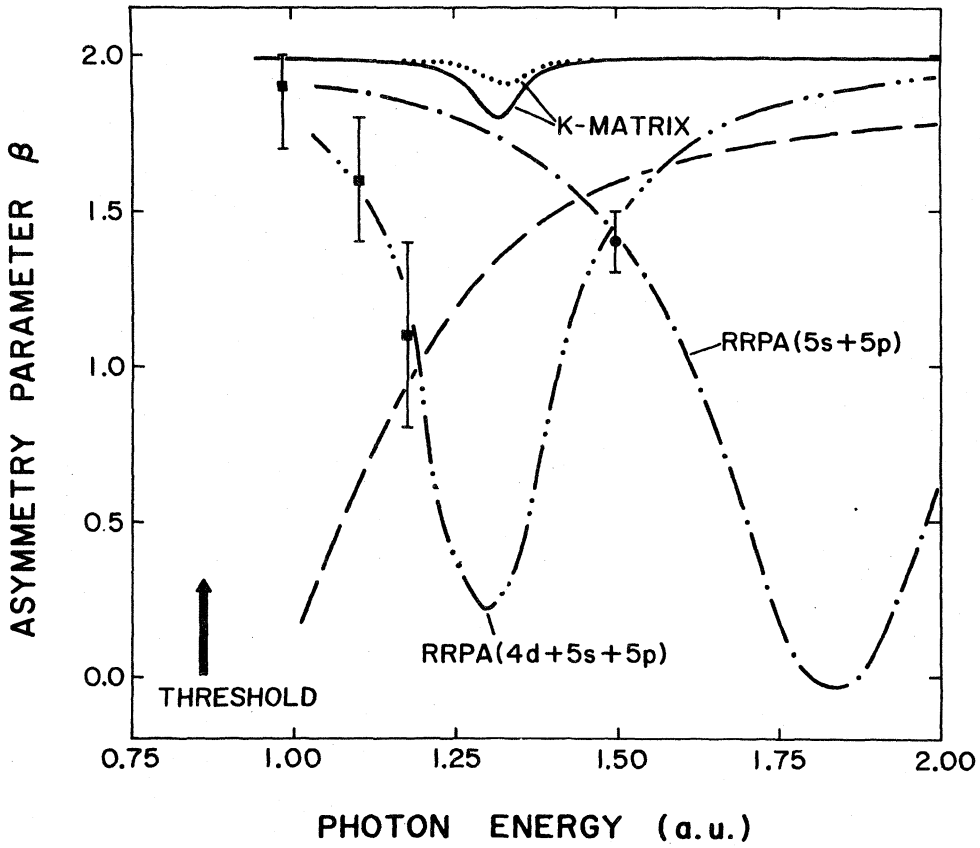

FIG. 6. Photoelectron angular distribution asymmetry parameter β for the 5*s* subshell of xenon. DF: Dirac-Fock results of Ong and Manson (1978a, 1979a). RRPA: relativistic random-phase approximation results of Johnson and Cheng (1978, 1979) including interchannel correlations between the 5*s*- and 5*p*-subshell channels (dash-dot line) and between the 4*d*-, 5*s*-, and 5*p*-subshell channels (dash-double dot line). *K-matrix*: results of Huang and Starace (1980) including final-state spin-orbit interactions and coupling between the 5*s*-, and 5*p*-subshell channels in dipole length (dotted line) and dipole velocity (solid line) approximation. *Solid Circle*: Experimental result of Dehmer and Dill (1976). *Solid Squares*: Experimental results of White *et al.* (1979).

teractions. Other cases are pointed out in which β has the constant value $\frac{1}{5}$ in the absence of interchannel interactions or ground-state configuration mixing (which permit the photoelectron to have orbital angular momentum $l=3$). Experimental measurements of the deviations of β from constancy in these cases thus provide a measure of the strength of these generally weak correlations (as well as of relativistic interactions). Still other cases are pointed out where β, while energy dependent, is bounded from above with the value $\frac{1}{5}$ when $l=3$ photoelectron orbital angular momenta are neglected. In addition, numerical examples have been presented of energy-dependent β parameters to show the influence of cross-section minima on the rapidity of the energy variation of β.

In conclusion, we reiterate that the separation of geometry and dynamics in angular distribution studies allows one to obtain the maximum amount of information from experimental data. In our examples of atomic s-subshell photoelectron angular distributions, for instance, it was shown that small effects could be spotlighted by the deviation of β from approximate geometrically determined values. These general ideas should have utility in other branches of physics as well.

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