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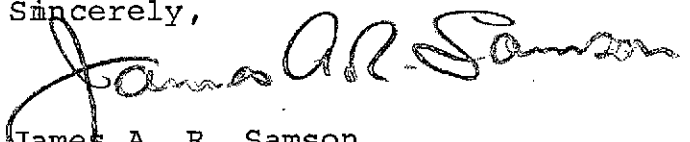College Park, Maryland 20740

RE: Grant NGR 28-004-021

Dear Sirs:

   Please find enclosed the material prepared for
Grant NGR 28-004-021.

   Thank you.

Sincerely,

James A. R. Samson
Professor of Physics

JAR/le

PHOTOELECTRON ANGULAR DISTRIBUTIONS
AS A PROBE OF ANISOTROPIC ELECTRON-ION INTERACTIONS*

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ABSTRACT

Expressions are given for atomic photoelectron angular distributions in
LS coupling in which the role of anisotropic final state electron-ion inter-
actions emerges explicitly. Calculations of photoelectron angular distribu-
tions for atomic sulfur are presented ·in which these anisotropic interactions
produce pronounced deviations from the predictions of the Cooper-Zare model.
Such effects are expected to be a general feature of photoelectron angular
distributions for most open-shell atoms.

We report here expressions for atomic photoelectron angular distributions in LS coupling which exhibit clearly the influence of anisotropic electron-ion interactions. To illustrate these effects we have calculated the angular distributions of electrons photoionized from atomic sulfur, for which these anisotropic final state interactions are large. These effects take the form of pronounced differences between the distributions of photoelectron groups corresponding to alternative LS term levels of the residual ion. This result is to be contrasted with that of the Cooper-Zare model,[1] in which the role of final state interactions is not considered: no dependence on the ionic term level is predicted. The past success of the Cooper-Zare model in confirming measurements[2,3] is due to the fortuitous circumstance that the measurements have dealt with closed-shell atoms, for which we show angular momentum and parity conservation impose severe restrictions on the effects of any anisotropic interactions.

Our results are aimed on the one hand at theorists engaged in photoionization cross section calculations that include electron correlation. The criteria for assessing the importance of anisotropic interactions are given in terms of interaction parameters provided by such calculations. On the other hand, we wish to emphasize to experimentalists this new dynamical information on final state interactions that can emerge through the study of open-shell atoms.

Our analysis is based on the resolution of the angular distribution into separate contributions characterized by the alternative values j_t of the angular momentum transferred in the photoionization process.[4] Consider the following schematic photoionization process:

$$A(J_o\pi_o) + \gamma(j_\gamma=1, \pi_\gamma=-1) \rightarrow A^+(J_c\pi_c) + e^-[\ell s j, \pi_e=(-1)^\ell] \tag{1}$$

If no measurements are made of the orientation of the ion or of the polariza-
tion of the electron's spin, then the amplitudes for photoionization with
alternative values of the angular momentum transfer $\vec{j}_t = \vec{J}_c + \vec{s} - \vec{J}_o = \vec{j}_\gamma - \vec{\ell}$
superpose incoherently in the differential cross section.[5] The allowed val-
ues of j_t are those consistent with the conservation of total angular momen-
tum $\vec{J} = \vec{J}_o + \vec{j}_\gamma = \vec{J}_c + \vec{s} + \vec{\ell}$ and parity $\pi = \pi_o \pi_\gamma = \pi_c \pi_e$. In the absence of
all anisotropic interactions between the departing electron and the ion, how-
ever, j_t is restricted to the single value ℓ_o, the photoelectron's initial
orbital momentum, and the resulting angular distribution is that given by the
Cooper-Zare (CZ) model.[4] Consequently, contributions to reaction (1) by an-
gular momentum transfers $j_t \neq \ell_o$ are a measure of both anisotropic interaction
strength and the breakdown of the CZ model. This consideration motivated
our analysis.

The angular momentum transfer expansion of the differential cross sec-
tion is[4]

$$\frac{d\sigma}{d\Omega} = \sum_{j_t} \frac{\sigma(j_t)}{4\pi} [1 + \beta(j_t) P_2 (\cos \theta)] \ . \tag{2}$$

Explicit expressions for the partial cross sections $\sigma(j_t)$ and asymmetry para-
meters $\beta(j_t)$ are given in Ref. (4) in terms of scattering amplitudes $S_\ell(j_t)$,
whose form in LS coupling is a main result of this paper. Using these ingre-
dients, the measured asymmetry parameter is given by the following weighted
average:[4]

$$\beta = \left\{ \sum_{j_t} \sigma(j_t) \beta(j_t) \right\} / \sum_{j_t} \sigma(j_t) \tag{3}$$

To consider in detail the influence of anisotropic interactions on angu-
lar distributions we now analyze specifically atomic photoionization in the

LS coupling scheme:

$$A[(\ell_o^n L_o S_o)J_o\pi_o] + \gamma(j_\gamma = 1,\ \pi_\gamma = -1)$$

$$\rightarrow A^+[(\ell_o^{n-1} L_c S_c)J_c\pi_c] + e^-[\ell s j, \pi_e = (-1)^\ell] \tag{4}$$

In particular, we are concerned with the dependence of the angular distribution on different ionic term levels, $L_c S_c$, for the usual circumstance where the separation between such levels is far greater than the separations between the fine-structure levels J_c of a given term. For this situation the scattering amplitude for transfer of j_t units of angular momentum is[6]

$$S_\ell(j_t) = \frac{4\pi}{\lambda}\left(\frac{\pi\alpha h\nu}{3}\right)^{\frac{1}{2}} i^{-\ell}\ \exp(i\sigma_{\varepsilon\ell})\,\hat{J}_o\,\hat{\ell}\hat{\ell}_o \begin{Bmatrix} \ell & 1 & \ell_o \\ o & o & o \end{Bmatrix} (\ell_o^n L_o S_o \{|\ell_o^{n-1} L_c S_c)$$

$$\times \sum_L \exp\left[i\delta_{\varepsilon\ell}^{L_c S_c L}\right] R_{\varepsilon\ell}^{L_c S_c L}\ \hat{L}^2 \begin{Bmatrix} L_o & L_c & j_t \\ \ell & 1 & L \end{Bmatrix} \begin{Bmatrix} L_o & L_c & \ell_o \\ \ell & 1 & L \end{Bmatrix}. \tag{5}$$

Here $\sigma_{\varepsilon\ell}$ is the Coulomb phase shift, dependent on the photoelectron orbital momentum ℓ and kinetic energy ε, $\hat{x} \equiv (2x+1)^{\frac{1}{2}}$, $\nu\lambda = c$, $R_{\varepsilon\ell}^{L_c S_c L}$ is the radial dipole matrix element, and $\delta_{\varepsilon\ell}^{L_c S_c L}$ is the photoelectron phase shift relative to Coulomb waves.

The dependence of the phase shift $\delta_{\varepsilon\ell}^{L_c S_c L}$ and dipole matrix element $R_{\varepsilon\ell}^{L_c S_c L}$ on the term level of the residual ion arises through the dynamical coupling of the orbital motion of the electron to the net orbital motion of the residual ion. This coupling determines dynamical weights with which transition amplitudes for alternative values of the total orbital momentum $\vec{L} = \vec{L}_c + \vec{\ell}$ superpose in Eq. (5). When there is no dynamical coupling, the weights become independent of L, and hence of L_c:

$$\exp\left[i\delta_{\varepsilon\ell}^{L_c S_c L}\right] R_{\varepsilon\ell}^{L_c S_c L} \xrightarrow[\text{interaction}]{\text{no}} \exp(i\delta_{\varepsilon\ell})R_{\varepsilon\ell} \tag{6}$$

The remaining statistical weights can then be summed analytically:

$$\sum_L \hat{L}^2 \begin{Bmatrix} L_o & L_c & J_t \\ \ell & 1 & L \end{Bmatrix} \begin{Bmatrix} L_o & L_c & \ell_o \\ \ell & 1 & L \end{Bmatrix} = \hat{\ell}_o^{-2} \, \delta(J_t, \ell_o) \quad . \tag{7}$$

That is, only in the limit of vanishing anisotropic electron-ion interaction is the motion of the photoelectron independent of the term level of the ion; j_t is restricted to the single value $j_t = \ell_o$ and upon using Eqs. (5), (6), and (7), the asymmetry parameter (3) reduces to the CZ formula.[4]

The scattering amplitudes enter into the expression for β as $|S_+(j_t)|^2$, $|S_-(j_t)|^2$, and $[S_+(j_t)S^\dagger_-(j_t) + c.c.]$, where the subscripts $\pm$ denote $\ell = j_t \pm 1$. While only the third of these terms will depend on the Coulomb phase shift difference $\sigma_+ - \sigma_-$, all three terms depend on the interference between the different terms of (5), i.e., on the phase shift differences of alternative pairs of electron-ion LS-coupled channels $(L_o \ell)L$. In contrast, the CZ formula has only the single interference, in the third term, depending on the total phase shift difference $(\sigma_+ + \delta_+) - (\sigma_- + \delta_-)$ between the two independent particle model channels $\ell = \ell_o \pm 1$. Thus, the differences between the phase shifts $\delta_{\varepsilon\ell}^{L_c S_c L}$ for alternative channels $(L_c \ell)L$ measure the extent of anisotropic interactions and thus the validity of the CZ model.

The anisotropic electron-ion coupling thus results in an angular distribution which differs from the CZ result in two respects: (1) The asymmetry parameter depends on interference of ionization amplitudes characterized not only by alternative values of $\vec{\ell}$, but also by alternative values of the total orbital momentum $\vec{L}$. (2) All allowed values of the angular momentum transfer can be expected to contribute to the ionization process.

However, both of these factors are inoperative in the special case of ionization from a closed shell. For then $L_o = 0$ and the sum over L in Eq. (5) collapses to the single term with $L = j_\gamma = 1$ and j_t is restricted to the single value $j_t = \ell_o$. Thus purely geometrical factors impose severe restrictions,

consistent with the CZ model, on the angular distribution of photoelectrons ejected from closed shells, and it is for this reason that the CZ model has been generally successful when applied to such systems.[2,3]

To illustrate these ideas consider the photoionization of a typical open-shell atom such as sulfur:

$$S(3p^4 \; {}^3P) + \gamma \longrightarrow S^+(3p^3 \; L_cS_c) + e^-(\ell = 0,2) \tag{8}$$
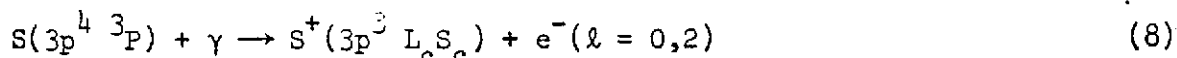
The allowed values of L_cS_c are ${}^4S^o$, ${}^2D^o$, and ${}^2P^o$. Ionization to each of these terms can proceed with $j_t = \ell_o = 1$, both for $\ell=0$ and $\ell=2$. In addition, when $\ell=2$, the ${}^2P^o$ term can also result from the transfer of $j_t=2$ units of angular momentum, and the ${}^2D^o$ term has both $j_t=2$ and $j_t=3$ allowed. In Fig. 1 we plot the Hartree-Fock phase shifts $\delta_{\varepsilon d}^{L_cS_cL}$ as a function of photoelectron kinetic energy ε for the ${}^2D^o$ ion term and for alternative allowed values of the total L. Because of the differences in these phase shifts we expect the predictions of the CZ model to be quite erroneous for sulfur.

Fig. 2 shows our calculated asymmetry parameters for the three photoelectron groups belonging to the alternative ionic term levels as a function of ε. The length formula for the dipole matrix elements has been used since this is the correct one for Hartree-Fock calculations.[7] As expected, contrary to the CZ model, these asymmetry parameters are found to be quite different from one another, particularly in the region of the Cooper minimum[8] in the total cross section (which is due to the sign change in the $3p \rightarrow \varepsilon d$ radial dipole matrix elements in the region $\varepsilon \simeq 2$ Rydbergs).

Fig. 3 shows the dependence of β and of the total cross section σ on angular momentum transfers $j_t \neq \ell_o$, which do not occur in the CZ model. The solid line presents the same β for the ${}^2D^o$ ion level as in Fig. 2. The dashed line, however, is a plot of $\beta(j_t=1)$ for the ${}^2D^o$ level, which would equal β only if

$\sigma(j_t \neq 1) = 0$. We see that the difference $\beta - \beta(j_t = 1)$ can be as large as 0.2. The dot-dash line in Fig. 3 is a plot of the percentage contribution of angular momentum transfers $j_t \neq 1$ to the total cross section. This percentage reaches a maximum of more than 8% for the $^2D^o$ ion level.
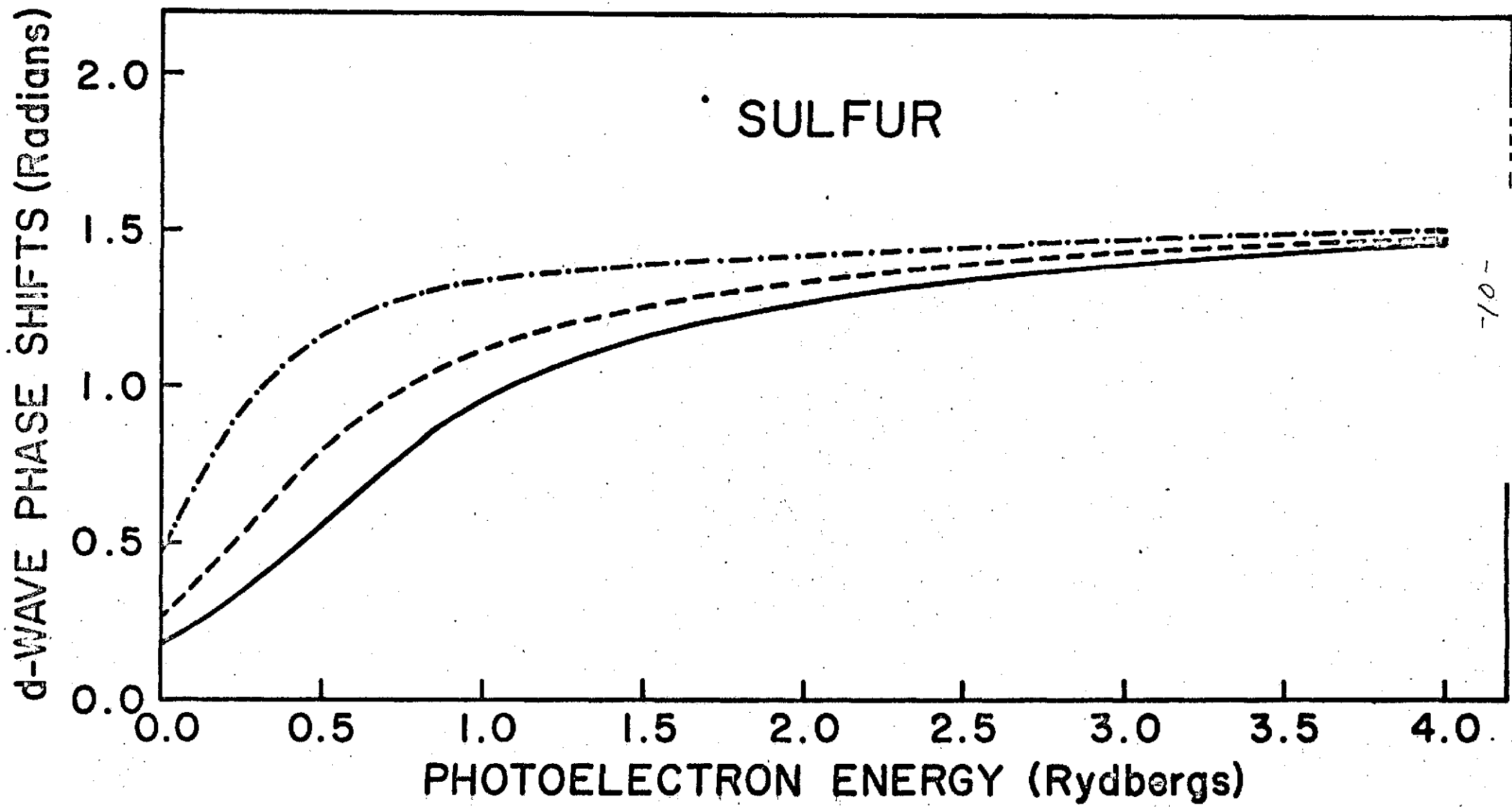
In conclusion, we have presented criteria for determining both the importance of anisotropic electron-ion interactions and equivalently for establishing the validity of the CZ formula for the asymmetry parameter β. Namely, for most open-shell atoms we expect anisotropic interactions to exert substantial effects, and therefore the CZ formula to give poor predictions, whenever the phase shifts for different total angular momenta L differ significantly from one another. Atomic sulfur has been presented as a typical example. Detailed theoretical and numerical analyses of our results will be given elsewhere.[6]

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FIGURE CAPTIONS

1. Hartree-Fock d-wave phase shifts $\delta_{\epsilon d}^{L_c S_c L}$ for the $^2D^o$ ion term vs. photo-electron kinetic energy ϵ for alternative allowed values of L. Solid line corresponds to L=0 (i.e., the state $3p^3(^2D)\epsilon d\ ^3S$), dashed line to L=1 (^3P), dot-dash to L=2 (^3D).

2. Asymmetry parameters for the photoionization transitions $3p^4(^3P) \rightarrow 3p^3(L_c S_c) + e^-$ in sulfur vs. photoelectron kinetic energy. Solid line corresponds to ^4S ionic term, dashed line to ^2D, dot-dash to ^2P.

3. Dependence of asymmetry parameter β and cross section σ for the ^2D ion term on angular momentum transfers $j_t \neq \ell_o$ as a function of photoelectron kinetic energy. Left-hand scale refers to (1) the solid line denoting β and (2) the dashed line denoting $\beta(j_t=\ell_o=1)$. Right-hand scale refers to the dot-dash line which denotes the ratio $[\sigma - \sigma(j_t=1)]/\sigma$.

SULFUR

SULFUR

ASYMMETRY PARAMETER (y-axis left): 2.0, 1.5, 1.0, 0.5, 0.0, -0.5, -1.0

(right axis): 30.0%, 25.0%, 20.0%, 15.0%, 10.0%, 5.0%, 0.0%

PHOTOELECTRON ENERGY (Rydbergs)

SULFUR