Relativistic Effects on Low-Energy $5s \rightarrow \epsilon p$ Photoionization for Xenon

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Under suitable conditions, relativistic corrections to the interaction of a photoelectron with its parent ion are enhanced, giving rise to large anisotropic final-state effects which can be observed in the photoelectron angular distribution. The particular example of $5s \rightarrow \epsilon p$ photoionization of Xe is considered in detail. It is shown that the angular asymmetry parameter β is reduced by a factor of 9 from its nonrelativistic value of 2 near the $5s$ "Cooper minimum," so that the energy dependence of β becomes a sensitive test of atomic correlation theories.

In recent years a great deal of evidence has been accumulated illustrating the importance of both correlation[1,2] and relativity[3] in low-energy photoionization. In this Letter, we concentrate on a striking example of the influence of such effects on the photoionization of a $5s$ electron from xenon. Specifically, we consider the angular-distribution asymmetry parameter β [defined in Eq. (1) below] for low-energy $5s \rightarrow \epsilon p$ transitions. Nonrelativistically, this parameter is predicted to be 2,[4] whereas relativistically it can depart from 2 because of final-state spin-orbit interactions between the continuum p electron and the Xe^+ ion.[3] The parameter β has been measured at one photon energy ($\lambda = 304$ Å) by Dehmer and Dill,[5] and found to have the value $\beta = 1.4 \pm 0.1$. Such a large departure of β from its nonrelativistic value is difficult to understand on the basis of relativity alone because of the low energies involved in the interaction. We emphasize here that very large relativistic modifications of β are expected near a Cooper minimum and that the experimental value of $\beta = 1.4 \pm 0.1$ mentioned above can be understood quantitatively in terms of the location of the observed minimum of the xenon $5s \rightarrow \epsilon p$ cross section. Moreover, we predict that very near the cross-section minimum, the parameter β itself has a sharp minimum value of $\beta \simeq 0.22$. Since the location of the cross-section minimum is crucial to a quantitative understanding of the β parameter, one must be prepared to carry out a more or less elaborate relativistic calculation including the important correlation effects to make accurate predictions of the photoelectron angular distribution.

In the dipole approximation, the photoionization differential cross section is given by

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi}\left[1 - \tfrac{1}{2}\beta P_2(\cos\theta)\right], \qquad (1)$$

where θ is the angle of the emitted electron with respect to the incident photon direction, where σ is the integrated cross section, and where β is the asymmetry parameter. A nonrelativistic calculation of $s \rightarrow \epsilon p$ photoionization gives[4]

$$\sigma_{\mathrm{nr}} = |A(\omega)|^2, \quad \beta_{\mathrm{nr}} = 2, \qquad (2)$$

where $A(\omega)$ is the photoionization amplitude, which is a function of the photon frequency ω. Relativistically, let $A_1(\omega)$ and $A_2(\omega)$ designate the corresponding amplitudes for $s \rightarrow \epsilon p_{1/2}$ and $s \rightarrow \epsilon p_{3/2}$, respectively. One then finds the relativistic generalization of Eq. (2) to be[3]

$$\sigma_{\mathrm{rel}} = \tfrac{1}{3}|A_1|^2 + \tfrac{2}{3}|A_2|^2,$$

$$\beta_{\mathrm{rel}} = 2 - 2\left[|A_1 - A_2|^2 / (|A_1|^2 + 2|A_2|^2)\right]. \qquad (3)$$

In the nonrelativistic limit, $A_1 = A_2 = A$ and Eq. (3) reduces to Eq. (2).

For nonrelativistic single-particle theories (such as the Hartree-Fock theory of Kennedy and Manson[6]), the amplitude $A(\omega)$ is real and may have zeros. At such a zero of $A(\omega)$ (the "Cooper minimum"), the nonrelativistic cross section vanishes. In relativistic single-particle theories (such as those of Walker and Waber,[3] or Ong and Manson[7]), the amplitudes $A_1(\omega)$ and $A_2(\omega)$ pass through zero at slightly different energies because of the different final-state interactions of $\epsilon p_{1/2}$ and $\epsilon p_{3/2}$ waves. It follows from Eq. (3) that $\beta = 1$ at a zero of $A_1(\omega)$ and $\beta = 0$ at a zero of $A_2(\omega)$; thus, in the neighborhood of a Cooper

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minimum, one expects (and indeed finds) significant departures of β from the nonrelativistic value of 2.

In the single-particle Dirac-Slater (DS) calculations of Walker and Waber,[3] a value of $\beta = 1.7$ was predicted for Xe $5s \rightarrow \epsilon p$ at $\lambda = 304$ Å, whereas Ong and Manson[7] are able to get closer agreement of β with experiment using a Dirac-Fock (DF) calculation. In these single-particle calculations, the Cooper minimum occurs below the $5s$ thresholds, so that β has its minimum at the threshold and increases to ~ 2 at high energy.

Experimentally, the $5s$ cross section has its minimum at about 10 eV above the $5s$ threshold; the location of this minimum and the absolute magnitude of the cross section near the minimum have both been established in recent measurements using line sources[8] and synchrotron radiation.[9] The difference between the predictions of the single-particle calculations and experimental observations are shown by Amusia and co-worker[2] to be due to the screening of the external electromagnetic field by the $5p$ shell which raises the $5s$ Cooper minimum above its threshold; furthermore, the $4d$ correlations are shown to be important in establishing the correct position of this minimum. In Amusia's nonrelativistic random-phase-approximation calculation (RPAE) the location of the minimum is well determined and in close agreement with experiment. Because of interchannel coupling, the RPAE amplitude $A(\omega)$ is not zero at the Cooper minimum in contrast to the single-particle situation. However, the RPAE $5s$ cross section is much smaller than the measured value of 0.04 Mb[9] at the minimum. Since Amusia's calculation is nonrelativistic, he, of course, has $\beta = 2$. An alternative multichannel calculation which includes relativistic effects in the Pauli approximation by Huang and Starace[10] gives a minimum value of β of about 1.8, which is above the measured value of 1.4 ± 0.1 mentioned before.

On the basis of Eq. (3), it is clear that a reliable prediction of the angular distribution requires a relativistic theory which includes all of the correlations needed to establish the position of the Cooper minimum. To this end, we employ a relativistic version of the random-phase approximation (RRPA) which has previously been used to study oscillator strengths along various isoelectronic sequences,[11] and to study photoionization for He and Be.[12] The details of the present RRPA calculations will be described in a subsequent paper. For the present, we just point out that correlations between the shells $5s$, $5p$, and $4d$ are all included, and that the remaining core electrons are "frozen."

For a first approximation to RRPA solutions we employ intermediate-coupling Dirac-Fock (ICDF) wave functions which are the counterpart of Amusia's $V^{N-1,\,(LS)}$ wave functions.[2] These ICDF wave functions are different from the single-particle j-j coupling DS or DF wave functions used in Refs. 3 and 7 in that final-state correlations are included. Starting with the ICDF wave functions, we solve the RRPA equations numerically using an iteration scheme.

The photoionization amplitudes depend, of course, on the gauge of the photon field. Thus, if we use a Coulomb gauge we obtain "velocity-form" amplitudes, whereas we must use a different gauge to obtain "length-form" results.[13] This gauge dependence of relativistic calculations is the counterpart of the length-velocity problem of nonrelativistic calculations. The RRPA theory gives amplitudes which are independent of the gauge of the photon field, just as nonrelativistic RPAE gives identical length and velocity results.[2] In practice, we include only some of the RRPA correlations ($5s$, $5p$, $4d$) and omit others; thus, our amplitudes are slightly gauge dependent but the difference between length and velocity values is less than 5% for the results presented here.

In Fig. 1, we summarize our results for the xenon $5s \rightarrow \epsilon p$ cross sections at low energies. The curve labeled RRPA($5s + 5p$) is the result of a two-shell correlation calculation; it shows a minimum at $\omega \simeq 1.9$ a.u., which is somewhat higher than the measured position. The initial approximation in the three-shell correlation calculation is determined by the ICDF wave functions which give the cross sections labeled ICDF-L (length gauge) and ICDF-V (velocity gauge) in Fig. 1. Because of the gauge problem mentioned previously, these ICDF results are not identical. The final three-shell correlation result labeled RRPA($5s + 5p + 4d$) lies between the ICDF-L and ICDF-V values. This calculated RRPA cross section is found to be smallest at the frequency of the experimental minimum (36 ± 2 eV),[9] and agrees well with the measured absolute cross sections over the entire low-energy region. In particular, the value of σ at the minimum is 0.03 Mb, which is substantially larger than the nonrelativistic RPAE value for reasons discussed below. We are therefore confident that our amplitudes $A_1(\omega)$ and $A_2(\omega)$ are suitable for a quantitative understanding of the β parameter.

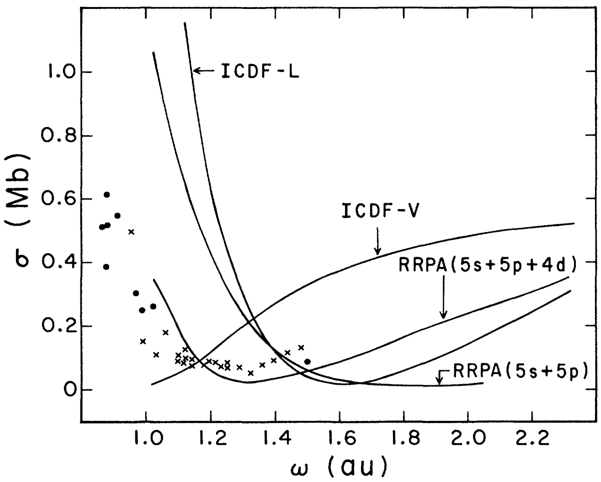

FIG. 1. The xenon $5s \rightarrow \epsilon p$ photoionization cross section σ(Mb) is plotted against photon energy ω(a.u.). The curves labeled RRPA($5s+5p$) and RRPA($5s+5p+4d$) are the two- and three-shell correlation calculations respectively. The curves ICDF-L and ICDF-V are the ICDF length and velocity calculations. The dots are experimental values from Samson and Gardner (Ref. 8) and the crosses are the measurements of Gustafsson (Ref. 9).

It should be mentioned here that A_1 and A_2 are appropriate to a j-j coupling description of the final state, whereas in a nonrelativistic context it is more convenient to deal with LS coupling. If we designate the amplitudes for ${}^1P_1$ and ${}^3P_1$ final states by A_S and A_T, respectively, we can then rewrite Eq. (3) as

$$\sigma_{\mathrm{rel}} = |A_S|^2 + |A_T|^2,$$
$$\beta_{\mathrm{rel}} = 2 - 3[\,|A_T|^2/(|A_S|^2 + |A_T|^2)]. \tag{4}$$

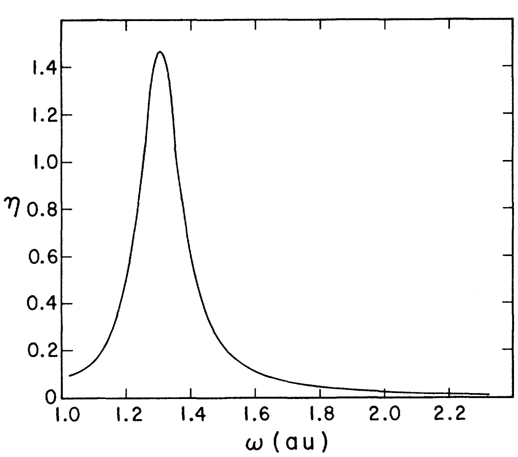

FIG. 2. The ratio η of the $(5s^2)^1S_0 \rightarrow (5s\epsilon p)^3P_1$ to ${}^1P_1$ cross sections as a function of photon energy ω.

From Eq. (4) we see that β is a measure of the branching ratio between the final triplet and singlet states, and it is clear that β is most sensitive near a nonrelativistic cross-section minimum where $|A_S|^2$ is small. Measurements of β thus provide direct tests of the triplet-to-singlet admixture in atomic final states. In Fig. 2, we plot the ratio $|A_T|^2/|A_S|^2$ over the energy range considered, and note the very sharp rise as the singlet amplitude becomes small near the Cooper minimum; the triplet amplitude is slowly varying over this entire energy range. The size of the RRPA cross section is substantially larger than the RPAE value near the Cooper minimum since both the (large) triplet amplitude and the (small) singlet amplitude contribute to the RRPA cross section [Eq. (4)], while only the singlet term is presented in RPAE [Eq. (2)].

Finally, in Fig. 3, we present our results for the asymmetry parameter $\beta(\omega)$. The curve labeled RRPA($5s+5p$) is the two-shell correlation result, while the one labeled RRPA($5s+5p+4d$) is the complete three-shell correlation calculation. The ICDF values are from the preliminary calculations mentioned before. Comparison with Fig. 1 shows that the minima of these various calculated β parameters indeed occur at the respective Cooper minima of the cross sections. It is entertaining to note that both RRPA($5s+5p$) and RRPA($5s+5p+4d$) give β values which agree well with the single experimental determination at $\lambda = 304$ Å. It should be clear, however, on the basis of the

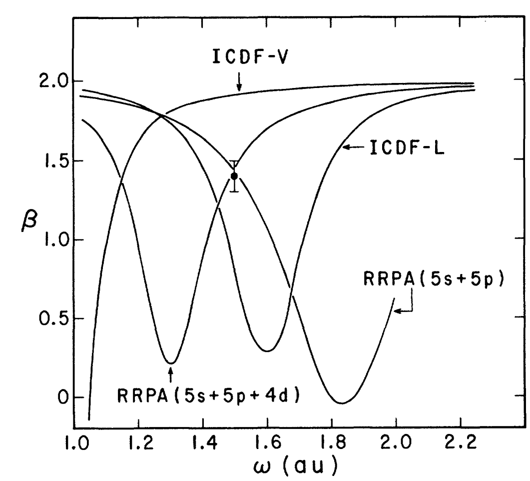

FIG. 3. The xenon $5s \rightarrow \epsilon p$ angular-asymmetry parameter $\beta(\omega)$ is given as a function of photon energy ω. The curves are labeled as in Fig. 1. The experimental datum at $\omega \simeq 1.5$ a.u. is the measurement of Dehmer and Dill (Ref. 5).

preceding discussion that the two-shell predictions are inadequate. An experimental determination of β over the entire energy range from the 5s threshold to $\omega \simeq 2$ a.u. will provide a sensitive guide to relativistic atomic-structure theories.

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Anomalous Behavior in the Vibrational Raman Spectrum of Oxygen under Near-Critical Conditions

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The isothermal density dependence of both the shift and width of the Raman Q branch in oxygen gas have been found to exhibit anomalous behavior under near-critical conditions. The observed effects are interpretable in terms of moleuclar-cluster formation, and it is concluded that the Raman effect is a potentially valuable probe of density fluctuations in the critical region.

The density-dependent effects of intermolecular forces upon the vibrational Raman spectra of gases have been the subject of extensive experimental and theoretical work.[1] As a result, these effects are now fairly well understood for values of reduced temperature (T/T_c) greater than about 2. In the present context the essential points are (i) that at low densities the resolved structure of the pure vibrational Raman spectrum is characterized by frequency shifts which are predominantly linear in the density,[2] and (ii) that at sufficiently high densities this polarized Q branch is subject to a narrowing process where the width varies as the inverse of the density.[3] In this Letter we present new experimental results for O_2 gas in the neighborhood of its critical point where the influence of density fluctuations may be responsible for departures in the behavior of the polarized spectrum from that expected on the basis of previous work. As a consequence we suggest that such experiments are capable of providing significant information regarding the nature of these fluctuations.

The data, which are presented graphically in Fig. 1, were obtained using previously described interferometric techniques.[4] The experimental errors in the determination of the relative frequency shift and the width are estimated to be ± 2% and ± 7%, respectively. Gas densities were determined using published PVT data,[5] the absolute temperature and pressure being measured within limits of ± 0.02 K and ± 0.07 bar, respectively. It is recognized that the resulting uncertainty in the density may be considerable in the neighborhood of the critical density[6] (304 amagat). However, in this preliminary report we wish to emphasize the qualitative features of the observations, it being considered highly improbable that experimental errors could account for the anomalous, and quite reproducible, behavior which oc-

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