Angle-resolved photoemission from the Ar 2p subshell

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The angular distribution for Ar 2p photoionization has been measured from just above threshold to 400 eV photon energy, and calculated in the same energy range using the relativistic random-phase approximation. The present experimental and theoretical results are in good agreement, but disagree somewhat with earlier Hartree-Fock (HF) calculations. The HF values are found to be significantly higher in the near-threshold region. Possible reasons for this discrepancy are discussed with relevance to the general understanding of inner-shell photoionization phenomena.

I. INTRODUCTION

Most work on angle-resolved photoemission of atoms has been devoted to outer shells, where quite extensive experimental results are now available.[1] Along with these experimental developments have come increasingly sophisticated theoretical techniques that have exhibited success in reproducing and explaining the observations.[2] Much of the extant work has been on the valence shells of the noble gases, for which excellent agreement between theory and experiment is the rule.

The situation is somewhat different for angle-resolved photoemission studies of inner shells. Not only is the experimental work less mature, but the theoretical calculations completed to date are generally at a less sophisticated level than those available for valence shells. Furthermore, where theoretical techniques, previously shown to be excellent for outer shells, have been applied to atomic inner shells, agreement between experiment and theory has not always been as good, e.g., the 4*f* and 5*d* subshells of Hg.[3] In contrast, the congruence of experiment and theory for the angular distribution of Xe 4*d* photoelectrons is in a very refined state.[4] In general, however, less work has been done in the inner-shell region, even for the noble gases.

Considering this situation for inner shells of atoms, it is of interest to study in detail one atomic core subshell both experimentally and theoretically. As a test case, we have studied the Ar 2*p* subshell, for which no previous angle-resolved photoemission experiment is available, and the most sophisticated previous calculation is at the Hartree-Fock (HF) level.[5] Experimentally, the angular-distribution asymmetry parameter for Ar 2*p* photoionization was measured at two different laboratories over a broad energy range. On the theoretical side, the relativistic random-phase approximation (RRPA), one of the more successful formulations for outer shells of the rare gases, has been applied. The present experimental and theoretical results are in good agreement over the entire energy range studied.

The experimental and theoretical techniques used in the present work are described in Secs. II and III, respectively. Results and discussion are presented in Sec. IV, and Sec. V contains concluding remarks.

II. EXPERIMENT

The present measurements were performed by the Berkeley group at the Stanford Synchrotron Radiation Laboratory (SSRL) using the double-angle time-of-flight (DATOF) method, and by the Oak Ridge National Laboratory (ORNL) group at the Synchrotron Radiation Center (SRC) at Stoughton, Wisconsin, using two spherical-sector analyzers on a rotating platform. Both of these angle-resolved photoelectron spectrometers have been described elsewhere.[6,7] and each relied on Yang's theorem for an electric dipole process,[8]

$$\frac{d\sigma(h\nu)}{d\Omega}=\frac{\sigma_0(h\nu)}{4\pi}[1+\beta(h\nu)P_2(\cos\Theta)] , \quad (1)$$

to determine the angular-distribution asymmetry parameter $\beta(h\nu)$ for Ar 2p photoionization. In Eq. (1), the differential cross section, $d\sigma/d\Omega$ is related to the photoionization cross section $\sigma_0(h\nu)$ via the β parameter and the second Legendre polynomial $P_2(\cos\Theta)$. The angle Θ is measured between the incident photon polarization vector and the direction of photoelectron ejection. For the SSRL results, the β measurements were calibrated against Ne 2p and 2s photoelectron intensities. Reference 9 provides more detailed information on this procedure.

The SRC results also relied on measurements of Ne 2p photoelectrons for calibration as was done for other studies on both photoemission and Auger processes in the rare gases as a function of photon energy. The calibration procedures have been described elsewhere.[7] Photons were energy selected by a monochromator of the grasshopper design, designated Mark V, and owned by the SRC.

III. THEORY

The calculations were performed using the relativistic random-phase-approximation (RRPA) formalism.[10] Within this framework, two different levels of approximation were considered; a 14-channel calculation that included the intershell coupling among all transitions arising from the 2s, 2p, 3s, and 3p subshells of Ar; and, for comparison, a five-channel calculation which included only the interchannel coupling among the five possible transitions from the 2p subshell ($2p_{3/2}\rightarrow\epsilon s_{1/2},\epsilon d_{3/2},\epsilon d_{5/2}$; $2p_{1/2}\rightarrow\epsilon s_{1/2},\epsilon d_{3/2}$). The details of these calculations are given elsewhere.[11]

IV. RESULTS AND DISCUSSION

The experimental results for β_{2p} of Ar are shown in Fig. 1, where we have distinguished between the SSRL and SRC data to illustrate the excellent agreement achieved by the independent experiments. As can be seen, β_{2p} gradually rises with increasing photon energy, except for a possible change in slope below 10 eV photoelectron energy. Included in Fig. 1 are curves representing a HF calculation[5] and the present RRPA calculations of β_{2p}. The HF-length and HF-velocity formulations were identical in the earlier calculation. Clearly, the RRPA results exhibit good agreement with experiment.

Unfortunately, quantitative agreement does not exist for the HF-calculated angular-distribution asymmetry parameter,[5] which exceeds the present values by as much as 0.3 near the Ar 2p threshold. This is a surprising result because HF does so well for the valence Ne 2p and Ar 3p subshells, and also because 2p photoionization dominates the Ar total cross section just above its threshold. Understanding the cause of this discrepancy with the HF calculation is important because the HF method is used widely.

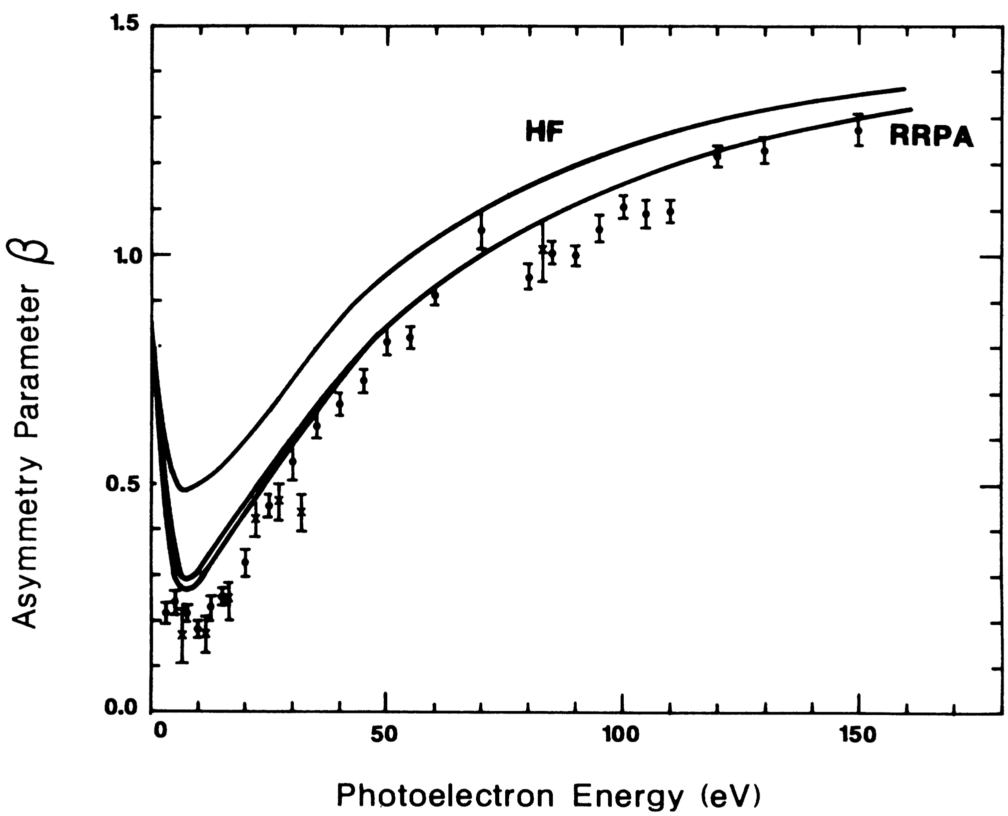

FIG. 1. Angular-distribution asymmetry parameter for Ar 2p photoionization as a function of energy above the $2p_{3/2}$ ionization threshold at 248.4 eV. All of the β_{2p} results are unresolved with respect to the 2p spin-orbit components. Experimental results are from the SSRL group (●) and the SRC group (×). Theoretical curves represent the present relativistic random-phase approximation (RRPA) 5- and 14-channel calculations (upper and lower, respectively) and HF calculations from Ref. 5.

Possible physical explanations for this discrepancy with the HF calculations are not readily obvious. One might suspect that spin-orbit or relativistic effects, which are included in the RRPA but not the HF calculations, would explain the discrepancy. To check this, we can compare similar HF calculations for β_{3d} of Kr and β_{4d} of Xe,[5] subshells for which spin-orbit and relativistic effects are at least comparable to those in the Ar 2*p* subshell. The Kr 3*d* and Xe 4*d* HF results agree well with experiment[4,12] in the near-threshold region, precisely where the Ar 2*p* HF results seem to do worst. Thus we tentatively look beyond spin-orbit and relativistic effects for the cause of the discrepancy between the HF calculations and the present results for the Ar 2*p* angular distribution.

Another possible theoretical inadequacy is the neglect of *inter*shell coupling, which is not included in a calculation such as HF, but can be included in an RRPA calculation. Intershell coupling may manifest itself in several ways. For example, coupling between different subshells may induce significant effects on cross sections and angular distributions for photoionization. Perhaps the best-known case of this phenomenon is the perturbation on the Xe 5*s* and 5*p* subshells produced by the Xe 4*d* subshell at photon energies near the $(4d \rightarrow \epsilon f)$-shape resonance.[13] The strength of the Xe 4*d* channel permits it to influence the cross sections and angular distributions of the other channels in this energy range. However, transitions from the Ar 2*p* subshell dominate the cross section just above the 2*p* threshold, suggesting that intershell coupling is not the answer. Nevertheless, to test the possibility of intershell coupling, we performed RRPA calculations with both 5 and 14 channels included. The five-channel calculation involves only 2*p* photoionization channels, i.e., *intra*shell coupling, whereas the 14-channel calculation includes intershell coupling with the 2*s*, 3*s*, and 3*p* subshells. Figure 1 shows no significant difference between these two RRPA treatments, illustrating that intershell coupling is not very important.

Similar effects to those produced by intershell coupling also may occur if strong multielectron effects are present in a single subshell. Such effects have been observed in Xe near the 5*s* Cooper minimum.[14] To check this possibility, the SSRL time-of-flight photoelectron spectra, in which nearly all photoelectron energies are recorded simultaneously, were examined for strong satellite transitions. We found that the strongest satellite channels, $3p \rightarrow np$ shakeup of the 2*p* main line, contribute an approximately constant intensity of 15(2)% of σ_{2p}. This low intensity is probably not sufficient to perturb the stronger 2*p* main-line channels. Furthermore, the onset of these satellite transitions is roughly 30 eV above the 2*p* ionization thresholds at 248.4 and 250.6 eV.

On a more fundamental level, the HF β parameter for a one-electron photoionization process depends on the ratio of dipole matrix elements for the two allowed channels (i.e., $2p \rightarrow \epsilon s, \epsilon d$ for Ar), and on their relative phase shifts. Shortcomings of the HF method that produce errors in the theoretically determined matrix-element ratio or phase shift might explain the discrepancy with experiment. Judging from the results of the present RRPA calculations, we believe this to be a likely hypothesis. The congruence of the 5- and 14-channel RRPA calculations was used above to rule out *inter*shell coupling as a possibility, but in both RRPA treatments, *intra*shell coupling among the five 2*p* photoionization channels is included. We propose that intrashell coupling, which is not included in the HF calculation, is the most probable cause of the difference between the HF results and the present experimental and theoretical results. In this picture, the $2p \rightarrow \epsilon s$ channels, which are relatively weak near threshold, are perturbed by the stronger $2p \rightarrow \epsilon d$ channels, affecting the $2p \rightarrow \epsilon s$ matrix elements or phase shifts or both, and ultimately shifting β_{2p} as a result. Further above threshold, as the $2p \rightarrow \epsilon s$ channels strengthen relative to the $2p \rightarrow \epsilon d$ channels, the intrashell coupling effect will diminish, and the HF calculation should be closer to experiment, as we observe.

Our RRPA calculations show that the strength of the $2p \rightarrow \epsilon d$ transitions is about a factor of 5 larger than the strength of the $2p \rightarrow \epsilon s$ channels, a ratio which gradually decreases with increasing energy. Thus the possibilities for coupling among these channels, and the associated modification of the weaker $(2p \rightarrow \epsilon s)$ channels, are evident. Furthermore, it is interesting to note that the situation for Ne 2*p* photoionization is rather different; both HF and RRPA calculations agree with each other and with experiment.[15] To understand this, we have also performed RRPA calculations for the Ne 2*p* case and found that, in the threshold region, the strengths of the $2p \rightarrow \epsilon d$ and $2p \rightarrow \epsilon s$ channels are approximately equal. Therefore there are no weaker channels to be modified by *intra*shell coupling, and the coupling does not alter significantly the HF matrix elements. The comparison of Ne 2*p* and Ar 2*p* shows very clearly that as an outer shell becomes an inner shell with increasing atomic number, the effects of correlation on the photoionization process do not necessarily diminish.

Finally, we note that recent work on the Ar-K edge has revealed that including relaxation into a HF calculation affects the Ar $1s \rightarrow \epsilon p$ section significantly.[16] In contrast, the Ar 2*p* HF calculation[5] did not include relaxation effects. Because Ar 2*p* is a core subshell, relaxation also might be important in the present case. Further theoretical work at a more detailed level is needed to check the importance of relaxation to β_{2p} of Ar.

V. CONCLUDING REMARKS

In summary, we have measured and calculated the photon-energy dependence of the Ar 2*p* angular-distribution asymmetry parameter in the near-threshold region. The quantitative difference between the present β_{2p} values and previous HF calculations is troubling, given the good agreement for Ne. Such a discrepancy with HF calculations is important to understand, if for no other reason than that HF is used so widely to obtain qualitative and quantitative descriptions of physical phenomena. By looking at various possibilities for this discrepancy, we suggested that the source of the problem is likely in the HF treatment of the $2p \rightarrow \epsilon s$ transition matrix elements. Based on the present RRPA calculations, we concluded that *intra*shell coupling between the

$2p \rightarrow \epsilon s$ and $2p \rightarrow \epsilon d$ photoionization channels produces a demonstrable effect on β_{2p} of Ar.

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