Validity of the independent-particle approximation in x-ray photoemission: The exception, not the rule

D.L. Hansen,[1] O. Hemmers,[1] H. Wang,[1] D.W. Lindle,[1] P. Focke,[2] I.A. Sellin,[2] C. Heske,[3] H.S. Chakraborty,[4] P.C. Deshmukh,[4] and S.T. Manson.[5]

[1]Department of Chemistry, University of Nevada, Las Vegas, Nevada 89154-4003
[2]Department of Physics and Astronomy, University of Tennessee, Knoxville, TN 37966
[3]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720
[4]Department of Physics, Indian Institute of Technology, Chennai 600036, India
[5]Department of Physics and Astronomy, Georgia State University, Atlanta, GA 30303

One fundamental assumption commonly applied to many-electron quantum systems is the one-electron or independent-particle approximation (IPA), in which effects of electron-electron interactions, i.e., electron correlation, are assumed to be negligible. Among the myriad of applications of the IPA is describing x-ray interactions with matter in all its forms; the IPA is readily used as a basis for theoretical calculations and tabulations of a variety of x-ray-interaction parameters such as total and partial cross sections, photon-scattering probabilities, and photoelectron angular distributions. With this central role in x-ray science, it is important to determine the limits of the IPA, or, equivalently, to identify the significance of electron-correlation effects to x-ray interactions. At present, it is a generally accepted axiom that the IPA is valid except in certain well-defined regimes where electron correlation is known to be important. Work at the ALS has proven this notion incorrect for x-ray photoemission; validity of the IPA is the exception, not the rule. Specifically at intermediate energies, far above outer-shell thresholds and away from inner-shell thresholds, interchannel-coupling effects are thought to be small and the IPA is reckoned to be reasonably good. A combined theoretical and experimental study of valence photoionization of argon demonstrates that this is not the case; IPA is invalid in a broad region of energy and subshell. This is of great interest owing to the upsurge in activity in the field of atomic photoionization, spurred by the development of third-generation synchrotron-radiation sources[1], along with the importance of atomic photoionization in various applications, e.g., radiation physics, astrophysical modeling[2].

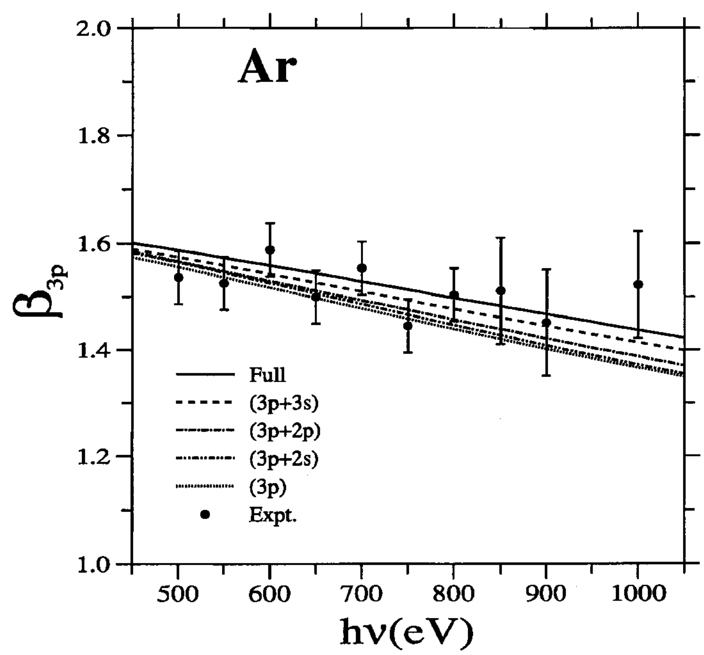

Figure 1. Beta parameter for Ar 3p. Dots represent experimental points. Dotted line represents IPA values. Solid line represents RRPA calculations with full coupling. Dashed lines represent calculations with various levels of interchannel coupling.

It was recently shown for the valence shell of neon that, owing to interchannel coupling the independent particle model is inadequate to explain photoionization of *nl* (*l*>0) electrons of atoms even at energies well above the ionization threshold [3]. New measurements of 3*p* photoionization of argon taken at ALS B.L. 8.0 confirm the earlier finding regarding the physics at high energy. Electron time-of-flight measurements were taken following photoexcitation of argon in the photon energy range of 600-850 eV. The data were analyzed to determine the angular distribution asymmetry parameter β for argon 3*p* photoionization, and the ratio of the intensities of the 3*p* and 3*s* lines. Our findings emphasize the importance of coupling for photoionization channels under consideration with channels from energetically neighboring thresholds to accurately describe the high energy *nl* (*l*>0) photoionization of atoms.

Photoemission cross sections and angular-distribution asymmetry parameters for valence 3*p* electrons of neutral argon have been calculated by the relativistic random-phase approximation (RRPA) methodology. [4-5]. Five levels of interchannel coupling scheme: all channels arising from (i) 3*p*, 3*s*, 2*p*, 2*s* and 1*s* (full RRPA); (ii) 3*p* and 3*s*; (iii)3*p* and 2*p*; (iv) 3*p* and 2*s*; and (v) only 3*p* have been considered to describe channel interactions. Note that scheme (v) should yield virtually similar results to the IPA method as the contribution of intra-shell coupling is small at high enough energy.

The experiments were performed at the ALS on beamline 8.0 during two-bunch mode, using an experimental setup described previously [6]. Briefly, four time-of-flight (TOF) electron analyzers collect spectra simultaneously at different angles. A needle serves as an effusive source for the gas under study. All analyzers are differentially pumped to avoid pressure buildup near the MCPs. The cylindrically symmetrical analyzers view the same interaction region with the 2-mm entrance apertures at a distance of about 20 mm. The apertures and needle are grounded to maintain a field-free interaction regions. A straight electron flight path provides fundamental simplicity to the TOF technique.

Results for angular-distribution asymmetry parameter, β, are shown in Fig. 1, for 3*p* photoionization up to photon energies as high as 900 eV. The branching ratios, σ_{ns}/σ_{np}, also are presented in Fig. 2. Calculations tend to fall in two groups: (a) ones in which coupling with channels from the 3*s* subshell is included and (b) ones in which it is not. Importance of *ns* coupling in *np* processes is due to (i) strong overlap between continuum wave functions of channels arising from energetically neighboring thresholds (that is largely decided by the same *n*) and (ii) faster decay of 3*p* compared to 3*s* with increasing *hν* at high enough energy [3]. The latter point is illustrated through the ratio of cross sections in Fig. 2. The experimental results for β_{3p} are in good agreement with all the calculations. For σ_{ns}/σ_{np} the situation is rather different; RRPA calculations are too large by ~20%; whereas IPA is too large by almost a factor of 2, illustrating how important interchannel-coupling effects are, even far above threshold (Fig. 2).

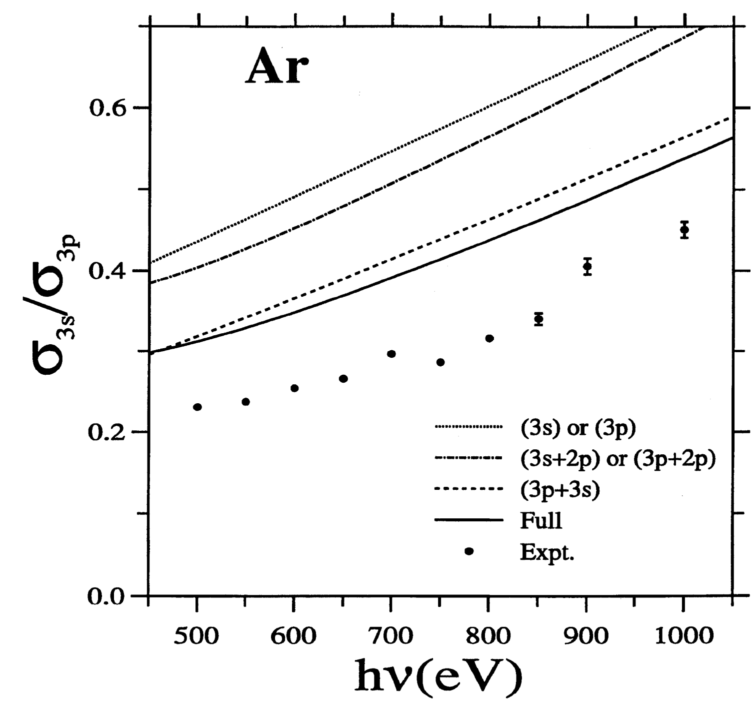

Figure 2. Cross section ratio for Ar 3s/3p. Circles give experimental values. Dotted line gives values calculated using the IPA. Solid line gives values for RRPA with full coupling taken into account. Dashed lines indicate different levels of interchannel coupling.

In conclusion, we have shown in a combined experimental and theoretical study that interchannel coupling between 3*s* and 3*p* photoionization channels in Ar dramatically alters the smaller 3*s* cross section from the predictions of the IPA, and other calculations which omit this coupling, by almost a factor of two in an energy region quite far from any thresholds. But there is nothing special about Ar, and therein lies the importance of these results. In *any* case where there are two (or more) degenerate photoionization channels emanating from subshells with similar binding energies and spatial extent, the smaller cross section(s) will be significantly affected through interchannel coupling with the stronger channel(s). Thus, calculations which omit interchannel coupling are reliable *only* for the dominant channel in such a situation; weaker channels will not be predicted reliably by Hartree-Fock or any other IPA calculation for virtually all energies. We are thus led to the inescapable conclusion that IPA is not valid for most subshells of most atoms at most energies. Finally, although the example presented was for an atom, these ideas should be equally valid for molecules, surfaces, and solids as well.

This work was supported by the NSF, Nevada DOE EPSCoR, The Research Corporation, and The Petroleum Research Fund.

[1] *New Directions in Research with Third Generation Soft X-ray Sources*, edited by A.S. Schlachter and F.J. Wuilleumier, NATO ASI Ser. E (Kluwer, Dordrect, The Netherlands, 1992), Vol. 254.

[2] *Applied Atomic collision Physics*, edited by H.S.W. Massey, E.W. McDaniel and B. Bederson (Academic Press, New York, 1983), 5 volumes.

[3] E.W.B. Dias, H.S. Chakraborty, P.C. Deshmukh, S.T. Manson, O. Hemmers, P. Glans, D.L. Hansen, H. Wang, S.B. Whitfield, D.W. Lindle, R. Wehlitz, J.C. Levin, I.A. Sellin, and R.C.C. Perera, Phys. Rev. Lett. **78**, 4553 (1997).

[4] W.R. Johnson and C.D. Lin, Phys. Rev. A **20**, 964 (1979).

[5] W.R. Johnson, C.D. Lin, K.T. Cheng and C.M. Lee, Phys. Scr. **21**, 409 (1980).

[6] O. Hemmers, S.B. Whitfield, P. Glans, H. Wang, and D.W. Lindle, Rev. Sci. Instrum. **69**, 3809, (1998).

Principal investigator: Dennis Lindle, Department of Chemistry, University of Nevada, Las Vegas. Email: lindle@nevada.edu. Telephone: 702-895-4426.