Photoionization of positive ions: Outer p subshells of the noble-gas isoelectronic sequence*

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Calculations have been performed for the photoionization of the Ne $2p$, Ar $3p$, Kr $4p$, and Xe $5p$ isoelectronic sequences using both multiconfiguration Hartree-Fock and Hartree-Slater wave functions. The results show that away from the vicinity of a Cooper minimum, which moves rapidly into the discrete in going along an isoelectronic sequence, agreement between the two calculations is quite good. Thus we conclude that for highly stripped ions, the Hartree-Slater results are an excellent approximation to the multiconfiguration Hartree-Fock photoionization cross sections.

I. INTRODUCTION

Photoionization cross sections for positive atomic ions are of interest in solar, stellar, and atmospheric physics, as well as in laboratory fusion studies. For the neutral atoms, systematic features of photoionization cross sections throughout the periodic system are fairly well-known through the interplay of theory and experiment.[1-4] For positive ions relatively few photoionization calculations have been performed.[5-7] In addition, although several experiments are in progress, no results have yet been reported on photoionization of multicharged positive atomic ions.

It is thus useful to produce theoretical estimates of the cross sections. In particular, it is highly desirable to have some *a priori* guide to the accuracy of the theoretical results. In this paper we attempt to do just that for the isoelectronic sequences of the outer np subshells of the noble gases Ne, Ar, Kr, and Xe. The noble gases were selected because the neutrals have been studied extensively,[1-4,8,9] both experimentally and theoretically. In these studies it was found that independent particle calculations give good *qualitative* agreement[3,4,10] with experiment for the outer np states but, except for neon, *quantitative* agreement is found only for more sophisticated calculations. These latter calculations (discussed in the preceding paper by Swanson and Armstrong,[11] hereafter referred to as SA) show that of critical importance for quantitative accuracy is the initial state configuration mixing of the $(p^6)\ ^1S_0$ configuration with states of the type $(p^4d^2)^1S_0$. We have thus performed calculations including this configuration mixing via a multiconfiguration Hartree-Fock method for the first few members of each isoelectronic sequence.

Furthermore, it is clear that as the nuclear charge Z is increased while the electron number (and state) remain the same, the central potential of the nucleus on each electron, $-Ze^2/r_i$, will increase in size relative to the noncentral interelectron potential, e^2/r_{ij}. Therefore, in going along an isoelectronic sequence, it is expected that a central-field calculation will improve with increasing Z. Central-field calculations have, thus, also been performed along each of the isoelectronic sequences to $Z=90$.

This paper has two major purposes. The first is to produce accurate photoionization cross sections of ions for use in other areas. The second is to understand and determine the regions of quantitative accuracy of the central-potential calculation for ionic photoionization since this model is eminently suitable for large-scale calculations owing to its simplicity.

Section II gives a description of the theory of photoionization and briefly discusses the two types of calculations performed. Section III presents our results for the isoelectronic sequences as well as a discussion of them. Finally, in Sec. IV, conclusions and a summary are given.

II. THEORY

The cross section for photoionization of an n-electron atom or ion initially in state $|i\rangle$ by unpolarized photons is given by[12]

$$\sigma(\epsilon)=\tfrac{4}{3}\pi^2\alpha a_0^2(\epsilon+I_{if})\sum_{f,\,m}|\langle f|T|i\rangle|^2, \tag{1}$$

where

$$T=\sum_{j=1}^{n}\vec{r}_j$$

in length formulation[1] and

$$T=[i(\epsilon+I_{if})]^{-1}\sum_{j=1}^{n}\vec{\nabla}_j$$

in the velocity form.[1] In Eq. (1) the final continuum state $|f\rangle$ is normalized per unit energy in rydbergs, I_{if} and ϵ (both in rydbergs) are the ionization potential and photoelectron energy ϵ, respectively ($h\nu = \epsilon + I_{if}$), α is the fine structure constant, a_0 the Bohr radius, and the sums over f and m refer to degenerate final states and magnetic substates, respectively; the matrix elements are evaluated in atomic units.

Two types of calculations have been performed. The first, as described in SA, was the multiconfiguration Hartree-Fock (MCHF) calculation which employed an initial-state wave function of the form

$$|i\rangle = a|(np^6)^1S\rangle + \sum_{S,L} d^{SL}|(np^4)SL,(n'd^2)SL;{}^1S\rangle . \tag{2}$$

The summation gives three nonvanishing terms and the wave function was calculated using the MCHF program of Froese Fischer.[13] Here, as in SA, other configurations were tested and found to have a negligible effect. The final continuum state used was a single configuration HF much the same as used in previous continuum HF calculations.[3,14] No core relaxation was included. Thus the only difference from previous HF calculations of photoionization is the addition of terms from a p^4d^2 configuration to the p^6 description of the outermost subshell of the *initial* (ground) state of the noble gases. As is shown in SA, however, this addition removes most of the discrepancies between length and velocity and between HF and experiment.[4,14]

The second type performed were central potential calculations. In this model, the photoionization cross section of an electron in an nl subshell in the dipole approximation [Eq. (1)] becomes[10]

$$\sigma(\epsilon) = \tfrac{4}{3}\pi^2\alpha a_0^2 N_{nl}\frac{\epsilon - \epsilon_{nl}}{2l+1} \times [lR_{l-1}(\epsilon)^2 + (l+1)R_{l+1}(\epsilon)]^2 , \tag{3}$$

with N_{nl} the number of electrons in the subshell, ϵ_{nl} ($=I_{if}$) the binding energy, and the radial dipole matrix elements

$$R_{l\pm1}(\epsilon) = \int_0^\infty P_{nl}(r) r P_{\epsilon,l\pm1}(r)\, dr , \tag{4}$$

where $r^{-1}P_{nl}(r)$ and $r^{-1}P_{\epsilon,l\pm1}(r)$ are the radial parts of the single-particle wave functions of the active electron in the initial (discrete) and final (continuum) states, respectively. P_{nl} is normalized to unity and $P_{\epsilon,l\pm1}$ to unit energy in Rydbergs.

Hartree-Slater (HS) central field wave functions were used for the wave functions of the discrete orbitals of the initial ionic states and were calculated using the program of Herman and Skillman.[15] For the final state the wave function of the continuum orbital was taken to be the solution to the radial Schrödinger equation with the *same* central potential as the initial state. The orbitals of the passive electrons in the residual ion core were taken to be unchanged by the photoionization process, i.e., no core relaxation. The details of the calculation and normalization of the continuum wave function are given in Ref. 10.

III. RESULTS AND DISCUSSION

In SA it was found that the MCHF calculation gave good agreement with experiment for the outermost np subshells of the noble gases. Further, agreement will improve as one goes to higher Z along an isoelectronic sequence for reasons discussed above. Thus, although no experimental data is available for the photoionization of multicharged positive ions, it is reasonable to assume that the MCHF calculation provides an excellent approximation thereto.

As shown in SA and discussed in Sec. II, the MCHF results show good agreement between the length and velocity formulations of the dipole matrix element. Owing to this agreement, we report only the MCHF length results. Parenthetically, the HS calculation is a central field model and, therefore, length and velocity must be equal as long as theoretical energies are employed.

A. Neon $2p$ sequence

In Fig. 1 comparison of our MCHF (in the length formulation) and HS photoionization cross section results is shown for $Z = 10$, 13, and 15 for the neon $2p$ sequence. The comparison shows excellent

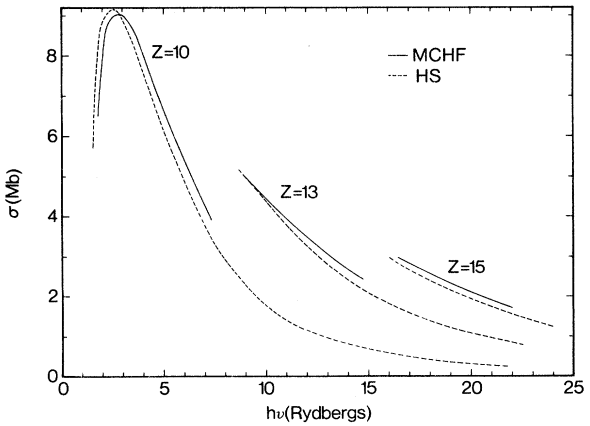

FIG. 1. Photoionization cross sections for members of the neon $2p$ isoelectronic sequence in MCHF and HS approximations.

agreement (within 10%) for all stages of ionization including the neutral. This is because the Ne $2p$ is nodeless and has no Cooper minimum[10, 16, 17] in contrast to the outermost np subshells of the higher noble gases. Thus the HS photoionization results should be excellent for all members of the Ne $2p$ isoelectronic sequence.

Figure 2 gives our HS results over a large range of Z. Here we see the delayed maximum,[1, 10, 17] which is strongly evident in the neutral, becoming much less pronounced in $Z=11$, and moving entirely into the discrete range for $Z=12$. For $Z \geq 12$ the cross sections are monotone decreasing from threshold. In addition, for $Z \geq 12$ the photoionization cross section increases monotonically with Z for a given photon energy. In fact the series of photoionization cross section curves for the various values of Z are roughly parallel and the value for each succeeding Z is increased approximately 15% over the lower Z cross section. The increase with Z at a given $h\nu$ is a consequence of the fact that the wave functions, both discrete and continuum, become more compact as Z increases along the isoelectronic sequence and their overlap becomes greater. This increases the dipole matrix element and, thus, the photoionization cross section.

It is worthwhile to point out that these calculations are nonrelativistic. For very large Z, above the rare earths, relativistic effects will be important in that binding energies and wave functions will be significantly modified, although the dipole approximation is still good. The relativistic effects probably make the wave functions even more compact, at high Z, and, thus, are likely to increase the cross sections somewhat. This applies not only to the neon $2p$ sequence, but also to all of our high Z results.

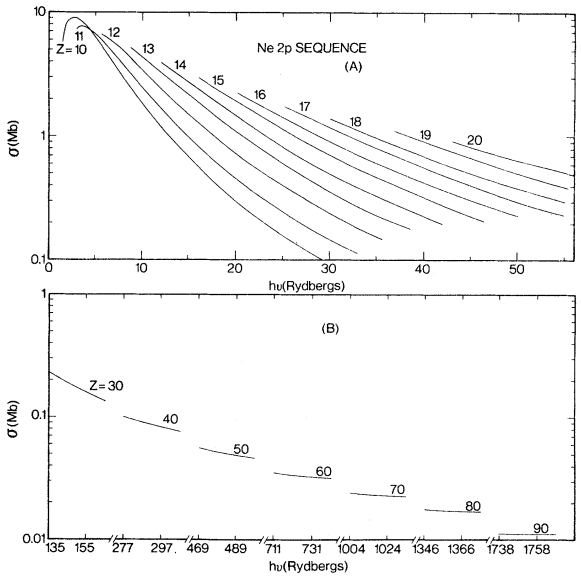

FIG. 2. Photoionization cross sections for the neon $2p$ isoelectronic sequence. Note broken scale in the lower curve.

B. Argon $3p$ sequence

Comparison between MCHF (in the length formulation) and HS photoionization results for $Z=18, 21$, and 23 for the argon $3p$ sequence is shown in Fig. 3. For neutral argon the MCHF and HS results are *qualitatively* similar but *quantitatively* quite different. Both show a maximum just above threshold followed by a Cooper minimum, but the HS maximum is a factor of 2 too large, and is at too low an energy. The HS Cooper minimum is too low in energy and does not go deep enough, compared to theMCHF result which was shown in SA to agree well with experiment. Note, however, that at $h\nu \sim 7$ Ry, (approximately 6 Ry above threshold) the two results are in good agreement. For $Z=21$ the Cooper minimum is in the discrete in both calculations, but its effects are still evident. The Cooper minimum probably occurs at lower energy and is not quite so deep (in the discrete) for the HS, as compared to the MCHF calculation, so that the HS result is considerably higher at threshold. The two results do come together at $h\nu \sim 9$ Ry which is only ~3.5 Ry above threshold. Thus the region of agreement of the HS and MCHF results is seen to be moving closer toward threshold with increasing Z along the isoelectronic sequence. For $Z=23$, the Cooper minimum has moved so far into the discrete range that its effect

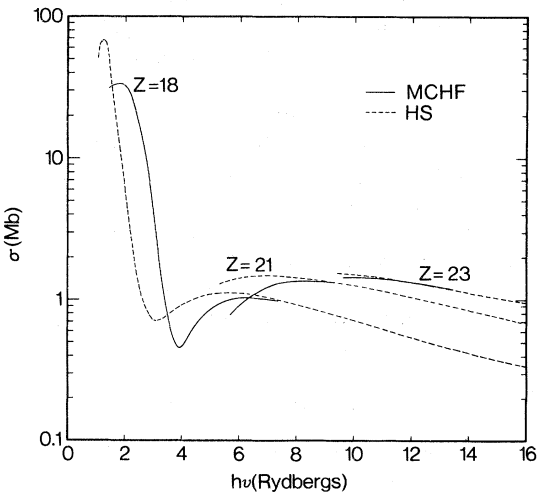

FIG. 3. Photoionization cross sections for members of the argon $3p$ isoelectronic sequence in MCHF and HS approximations.

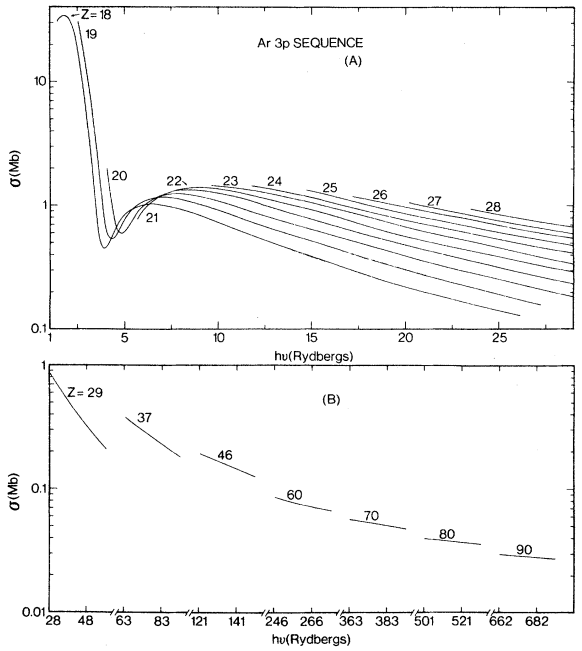

FIG. 4. Photoionization cross sections for the argon $3p$ isoelectronic sequence. Note broken scale in the lower curve.

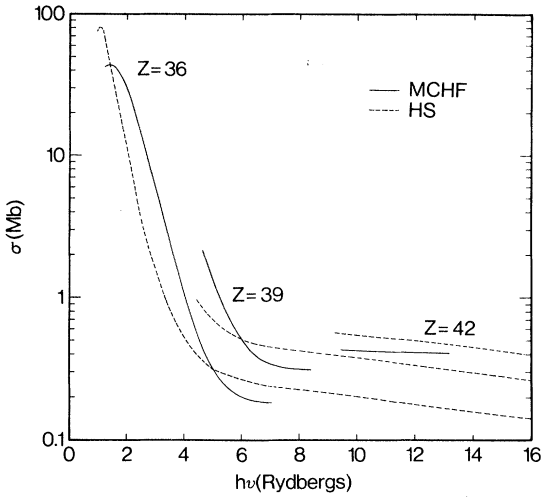

FIG. 5. Photoionization cross sections for members of the krypton $4p$ isoelectronic sequence in MCHF and HS approximations.

on the photoionization is minimal and good agreement is seen even at threshold.

In Fig. 4, our results are for a broad range of Z. For $Z=18$ to 23 the photoionization cross sections shown are from the MCHF calculation, while the higher Z results, where MCHF and HS agree well, are from the HS calculation. Here it is seen that the Cooper minimum remains at almost a constant photon energy along the isoelectronic sequence; actually it moves out very slightly with increasing Z. The maximum just above the threshold moves into the discrete by $Z=19$, and the Cooper minimum is just at threshold at $Z=20$ and in the discrete by $Z=21$. The second maximum remains just above threshold until $Z=24$, where the cross sections become monotone decreasing from threshold on out to higher Z. We also note, as in the neon $2p$ case, the increase of the cross section with increasing Z for a given photon energy, at the higher Z values. Here too the curves are roughly parallel and increase by about 15% with each succeeding Z.

C. Krypton $4p$ sequence

In Fig. 5, the MCHF (length) and the HS results are compared for $Z=36$, 39, and 42 for the photoionization cross section of the krypton $4p$ sequence. Here the situation is quite similar to the argon case discussed above. One difference is that, although a Cooper minimum exists since the $4p \rightarrow \epsilon d$ dipole matrix element changes sign, no minimum appears in the Kr $4p$ cross section. The reason is that the minimum occurs in an energy region in which the $4p \rightarrow \epsilon s$ matrix element is fairly large and rapidly decreasing so that the net effect on the total $4p$ photoionization is a dramatic change of slope, rather than a minimum. For the neutral, the HS result has a maximum just above threshold which is a factor of 2 too large and occurs at too low an energy; the HS cross section then falls off too rapidly since its Cooper minimum is at too low an energy. Above this point, the MCHF calculation Cooper minimum results in the HS result being too large again. For $Z=39$ the Cooper minimum is just above threshold but at too low an energy in the HS calculation. Thus the HS result is too small near threshold, since this is just above its Cooper minimum, while at somewhat greater energies it is too large, in the region at and just above where the MCHF calculation shows the Cooper minimum. For $Z=42$ the Cooper minimum has moved well down in the discrete and its effects above the ionization threshold are small. The HS result is still ~25% greater than the MCHF cross section at threshold since the HS Cooper minimum is lower in the discrete, but by $h\nu \sim 13$ Ry (~3.5 Ry above threshold) we find agreement to within 10%. Thus agreement should be excellent for $Z>42$ and the HS will be a good approximation in this region.

Figure 6 show our photoionization cross section results over the extent of the Kr $4p$ isoelectronic sequence. The $Z=36$ to 42 results shown are from MCHF calculations while the higher-Z results are the HS cross sections. The Cooper minimum,

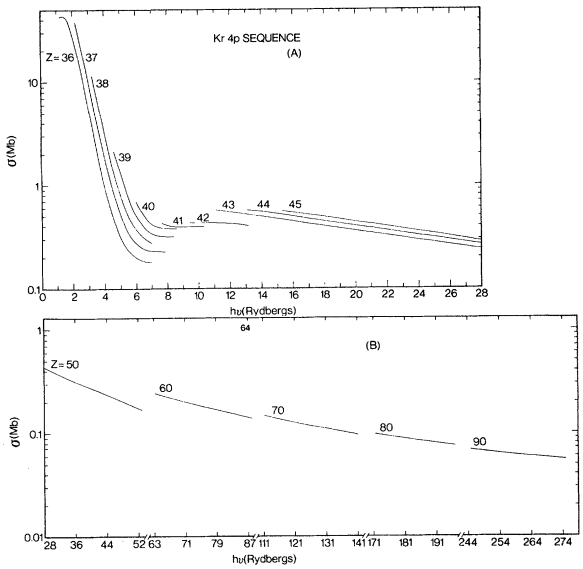

FIG. 6. Photoionization cross sections for the krypton $4p$ isoelectronic sequence. Note broken scale in the lower curve.

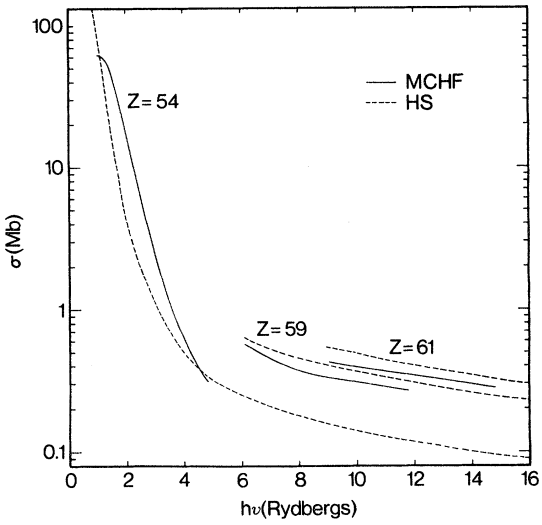

FIG. 7. Photoionization cross sections for members of the xenon $5p$ isoelectronic sequence in MCHF and HS approximations.

whose presence can be discerned by an abrupt change of slope in the cross section, again remains at roughly a constant photon energy, moving out only slightly with increasing Z along the sequence until, by $Z=41$, it is overtaken by the ionization threshold and moves into the discrete. For $Z \geq 41$ the cross section decreases monotonically from threshold. The results for the various Z values in this range are again roughly parallel, increasing with Z for a given photon energy. The increase is again about 15% per increase of Z by one.

D. Xenon $5p$ sequence

Comparison between MCHF (length) and HS results for $Z=54$, 59, and 61 is given in Fig. 7 for photoionization of the xenon $5p$ sequence. The xenon sequence is qualitatively almost identical to the krypton case discussed above The Cooper minimum in the xenon $5p \rightarrow \epsilon d$ channel is not seen as a minimum but as a change of slope of the cross section just as in the krypton $4p \rightarrow \epsilon d$ channel. The Cooper minimum occurs, however, at slightly higher energy in xenon compared to krypton. Thus it is clear that its effects will persist to a higher stage of ionization in xenon, i.e., it will move to the lower discrete region for a member of the xenon sequence more highly ionized than the corresponding member of the krypton sequence. Thus we see, from Fig. 7, that the large quantitative differences between MCHF and HS in the neutral (consisting of a factor of 2 in the maximum of the cross section, a too rapid fall off from the maximum by the HS, and a Cooper minimum at too low an energy) disappear as Z increases. The disappearance is not as rapid as in the krypton case, but by $Z=59$ one finds 25% agreement and by $Z=61$ it is 10%. The HS is approaching MCHF from above since the HS Cooper minimum is at a lower energy than the MCHF and the HS cross section "recovers" from the minimum at a lower energy. For $Z>61$, then, it seems that HS results will be good.

In Fig. 8 an overview of the photoionization cross sections of the xenon $5p$ sequence is presented. From $Z=54$–61 the results are MCHF and HS are given for greater Z. The Cooper minimum remains at about the same photon energy in all cases, moving out only slightly with increasing Z. By $Z=59$ it has just moved into the discrete as the ionization threshold energy overtakes the minimum. The higher Z cross sections are again approximately parallel and increasing (at a given $h\nu$) with Z by ~15% per Z.

IV. FINAL REMARKS

We have presented reliable results for the photoionization cross sections of the isoelectronic sequences of Ne $2p$, Ar $3p$, Kr $4p$, and Xe $5p$. The results show excellent agreement between MCHF and HS for the neon $2p$ sequence (which has no Cooper minimum) for all members of the sequence including the neutral. In the other cases, which have Cooper minima, agreement is good through-

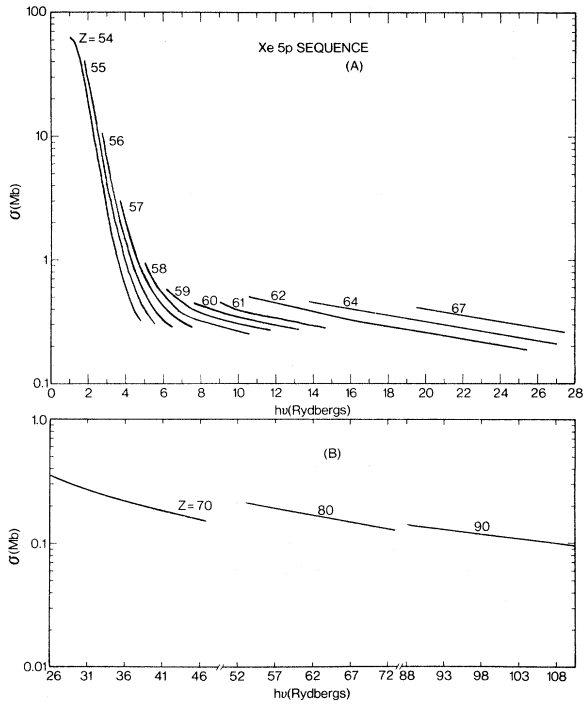

FIG. 8. Photoionization cross sections for the xenon $5p$ isoelectronic sequence. Note broken scale in the lower curve.

out the sequences only for high energies and for large enough Z such that the Cooper minima are in the lower discrete ranges. We thus conclude that, far removed from a Cooper minimum, the HS gives good results for the photoionization of positive ions. This conclusion should, however, be tested further.

It is well-known that for an isonuclear sequence[5-7,18] (ions of various stages of ionization with the same Z) an increase in stage of ionization (decrease in electron number) leads to a decrease in the total continuum oscillator strength, which is proportional to the photoionization cross section and an attendant increase in the discrete sum. For an *isoelectronic* sequence it is not clear what happens since the ionization energy increases with Z and moves some of the continuum energy range into the discrete, but the oscillator strength (cross section) in the continuum increases. Our calculations were not carried out to large enough energies to be able to find the total continuum oscillator strength, but it is an important point and should be pursued.

For high enough Z in each sequence, it was found that the cross section curves were approximately parallel and increased by ~15% per increase of Z by one. It would be very useful if this scaling law were generally true since then given the results for one member of an isoelectronic sequence, one could infer the photoionization cross sections for other members also. This point should be studied further.

In an earlier work,[19] photoionization of the first few members of the Ar $3p$ and Ne $2p$ sequence was studied using a central-field model. The results were shown vs photoelectron energy, rather than photon energy. Looking at the cross sections vs photon energy fails to spotlight the simplicity we have found in *isonuclear* sequences[6,7,20] as well as some of the features found herein for isoelectronic sequences, e.g., the fact that Cooper minima remain at about the same $h\nu$ for an isoelectronic sequence. Thus, based upon our results, it is recommended that photon energy be chosen as the independent variable to see most clearly the regularities in an isoelectronic sequence.

Finally, note that only a selection of our results have been presented. Our MCHF calculations were carried out for the first six members of the Ne $2p$ and Ar $3p$ sequences, seven for the Kr $4p$, and eight for the Xe $5p$. The HS calculation was carried out for many values of Z to $Z=90$ for each sequence. This detailed data is available to interested persons on request.

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