Photoionization of Mg and Ar isonuclear sequences

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Photoionization of the 2*s* inner shell of several atomic systems belonging to the Mg ($Z=12$) and Ar ($Z=18$) isonuclear sequences (Mg, Mg^{2+}, Mg^{8+}, Ar, Ar^{6+}, Ar^{8+}) is investigated using the relativistic random-phase approximation and also the relativistic random-phase approximation modified to include the relaxation of atomic core. Comparison of results obtained using these two approximations reveals an important effect of relaxation, namely, that inner-shell photoionization, particularly for neutral atoms and low-charge ions, can be quite sensitive to the removal of outer electrons, contrary to what is generally believed.

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I. INTRODUCTION

Photoionization of multiply charged ions is of interest as a test of the formalism that accounts for electron correlations and relativistic effects. Studies of atomic systems in isonuclear or isoelectronic sequences are of particular interest in this regard since they enable a systematic evaluation of the evolution of both the resonances and the background (nonresonant) cross sections [1]. Such studies are of great importance to assess theoretical data generated for their applications in fusion plasmas, in tokamaks, and in astrophysics [2–4]. Due to the ease in handling that argon offers, it has been used for magnetically controlled fusion plasmas as well as for the mitigation of tokamak plasma disruptions [5,6]. It is nevertheless difficult to produce high enough density beams of multiply charged ions, and hence only a relatively small number of experimental measurements for such systems are available [7,8]. Recently, measurements on the photoionization of the *outer shells* of isonuclear sequences have been reported for Xe [9], Cs [10], Ba [11], and Fe [12]. In addition, a number of theoretical calculations of the photoionization of *inner shells* of isonuclear sequences for O [13], Fe [14], and Hg [15], based on the Hartree-Slater and Dirac-Slater methods, as well as Mg and Ar [16] using the relativistic random-phase approximation (RRPA) have also been reported. These theoretical investigations led to the conclusion that removal of electrons from outer shells has no effect on the photoionization of inner shells except for a shift in thresholds to higher values. This is on account of the fact that the spherically averaged outer charge density exerts no force at any point in the interior region; it only changes the potential by a constant amount. Accordingly the energy dependence of the cross section, as a function of photon energy, does not change even if the ionization thresholds do of course change. This classical analysis which takes account of the time averaged static charge distribution however might break down when relaxation is taken into account; the relaxation of the atomic core that takes place when electrons are removed was not included in the earlier theoretical studies. These relaxation effects however have been shown to play an important role in the photoionization of inner shells of various neutral atoms [17,18], so it seems reasonably likely that relaxation affects ionic photoionization as well. Investigation of the relaxation effects on photodetachment cross sections of intermediate inner shells of the negative ions Cl^- and Br^- [19] using RRPA with relaxation (RRPA-R) demonstrated that for these ions, relaxation effects are of considerable importance.

In the present work, we address the following question: how do inner-shell properties vary with the removal of outer-shell electrons when the relaxation of atomic core is accounted for? Only in the case of potassium isonuclear sequence have there been reported measurements for the neutral atom [20] and the singly charged ion [21], but the errors in these measurements are rather too high to arrive at unambiguous conclusions. This experimental situation only underscores the importance of theoretical investigations.

To address this issue, in this paper we report a study of inner-shell photoionization on some members of the Mg ($Z=12$) and Ar ($Z=18$) isonuclear sequences using the RRPA-R formalism which includes both relaxation of the atomic core and significant aspects of electron correlation, along with regular RRPA for comparison. Applicability of the RRPA and the RRPA-R is unfortunately limited to closed shell systems, so we have considered only these members of the isonuclear sequences.

II. THEORY

Details of the RRPA and the RRPA-R can be found in respective works by Johnson *et al.* [22] and Radojević *et al.* [23]. In the present work, all dipole channels are included for the Mg isonuclear sequence; this insures that the length and velocity forms of the dipole matrix elements are exactly the same in the RRPA calculation. For the Ar case, the channels arising from 1*s* ionization are omitted. Since these channels are so far removed energetically from the others, the RRPA results remain gauge invariant, i.e., length and velocity forms of the dipole matrix element are equal. The RRPA-R, on the other hand, is not gauge invariant, so some disagreement between length and velocity forms is expected. The focus of

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the present work is on extracting some general features regarding the effects of relaxation, so only the geometric mean of the length and velocity forms of the RRPA-R results is presented since it has been suggested that the geometrical mean is more accurate than length or velocity form individually [24].

In the RRPA-R calculation, two sets of discrete state orbitals are used as compared to the RRPA calculation in which only one set is used. In RRPA-R, one set of orbitals consists of the ground-state self-consistent field Dirac-Fock (DF) orbitals of the atomic system and is used as the unperturbed initial state. The corrections to the matrix element arising from ground-state correlations in both RRPA and RRPA-R are calculated using these unperturbed orbitals. The second set is that of the relaxed orbitals which are also calculated self-consistently (DF) but after placing a hole in the particular subshell. The potential generated using these relaxed orbitals is used for the calculation of excited (continuum) orbital in the RRPA-R calculation [23].

We denote the transition matrix element between the ground state and an excited state as

$$\langle \Psi_f | D | \Psi_o \rangle = \gamma \langle \phi_\epsilon | d | \phi_i \rangle,$$

where Ψ_o is the N-particle initial-state wave function, Ψ_f is the excited-state (continuum) wave function constructed from $(N-1)$ core electrons and one excited (continuum) orbital ϕ_ϵ, ϕ_i is the single particle ground-state wave function of the active electron, and $D=\Sigma_{i=1}^{N} d_i$ and d_i are the many particle and single particle dipole operators, respectively. The factor γ is the overlap between the $(N-1)$-particle states constructed from unrelaxed and relaxed ground-state orbitals. In the RRPA, the overlap factor $\gamma=1$ since we use a single set of orbitals for both initial and final $(N-1)$ core electrons. On the other hand, since two sets of normalized wave functions are used in the RRPA-R, γ is always less than unity. This tends to *decrease* the RRPA-R cross section compared to that of the RRPA, but there are other factors to be considered, as discussed below. In the present work, relaxation effects arising from photoionization of the $2s$ subshell of the Mg and the Ar isonuclear sequences are considered.

Absolute values of the DF eigenvalues are the threshold energies in the RRPA calculations. For the RRPA-R calculations, the difference between the total energies calculated self-consistently for the relaxed ion with a hole in the subshell considered and the ground state of atom or ion (ΔE_{SCF} energies) is used for the thresholds. The Oxford multiconfiguration Dirac-Fock (MCDF) code [25] was used to calculate all of the unperturbed ground-state orbitals and eigenvalues. The DF, ΔE_{SCF}, and available experimental thresholds are given in Table I for the Mg sequence and in Table II for the Ar sequence. One sees that for inner shells ΔE_{SCF} energies agree substantially better with experiment than DF thresholds. The subshells for which ΔE_{SCF} energies agree better with experimental values are also the subshells where relaxation effects play an important role [18].

TABLE I. Theoretical and experimental photoionization thresholds (in a.u.) for subshells of Mg, Mg^{2+}, and Mg^{8+}.

Atom or ion	Subshell	DHF	ΔE_{SCF}	Experiment[a]
Mg	$1s_{1/2}$	49.12668	48.20395	48.174
	$2s_{1/2}$	3.78014	3.59600	3.550
	$2p_{1/2}$	2.28829	2.07972	2.126
	$2p_{3/2}$	2.27673	2.06920	2.116
	$3s_{1/2}$	0.25334	0.24320	0.281
Mg^{2+}	$1s_{1/2}$	49.86479	49.05508	
	$2s_{1/2}$	4.49649	4.39769	
	$2p_{1/2}$	3.01335	2.89667	
	$2p_{3/2}$	3.00174	2.88602	
Mg^{8+}	$1s_{1/2}$	60.59634	60.42977	
	$2s_{1/2}$	11.91711	11.90639	

[a]Reference [17].

III. RESULTS AND DISCUSSION

The results of our RRPA and RRPA-R calculations for the cross section for $2s$ photoionization of Mg, Mg^{2+}, and Mg^{8+} are shown in Fig. 1(a), with a magnified view of the region above the Mg^{8+} $2s$ threshold given in Fig. 1(b); the vertical solid lines are the DF thresholds and vertical dotted lines are the corresponding ΔE_{SCF} thresholds. It is observed that the RRPA results for Mg and Mg^{2+} are essentially equal. The removal of the $3s$ electrons has no effect on $2s$ photoioniza-

TABLE II. Theoretical and experimental photoionization thresholds (in a.u.) for subshells of Ar, Ar^{6+}, and Ar^{8+}.

Atom or ion	Subshell	DHF	ΔE_{SCF}	Experiment[a]
Ar	$1s_{1/2}$	119.1268	117.9349	117.814
	$2s_{1/2}$	12.4116	12.02490	11.944
	$2p_{1/2}$	9.6319	9.2048	9.2156
	$2p_{3/2}$	9.5471	9.1232	9.1366
	$3s_{1/2}$	1.2865	1.2285	1.0767
	$3p_{1/2}$	0.5954	0.5467	0.5857
	$3p_{3/2}$	0.5878	0.5399	0.5797
Ar^{6+}	$1s_{1/2}$	123.4968	122.6561	
	$2s_{1/2}$	16.5568	16.4259	
	$2p_{1/2}$	13.7724	13.6030	
	$2p_{3/2}$	13.6863	13.5190	
	$3s_{1/2}$	4.5008	4.4941	
Ar^{8+}	$1s_{1/2}$	125.5325	124.7761	
	$2s_{1/2}$	18.3993	18.3155	
	$2p_{1/2}$	15.6738	15.5595	
	$2p_{3/2}$	15.5868	15.4743	

[a]Reference [18].

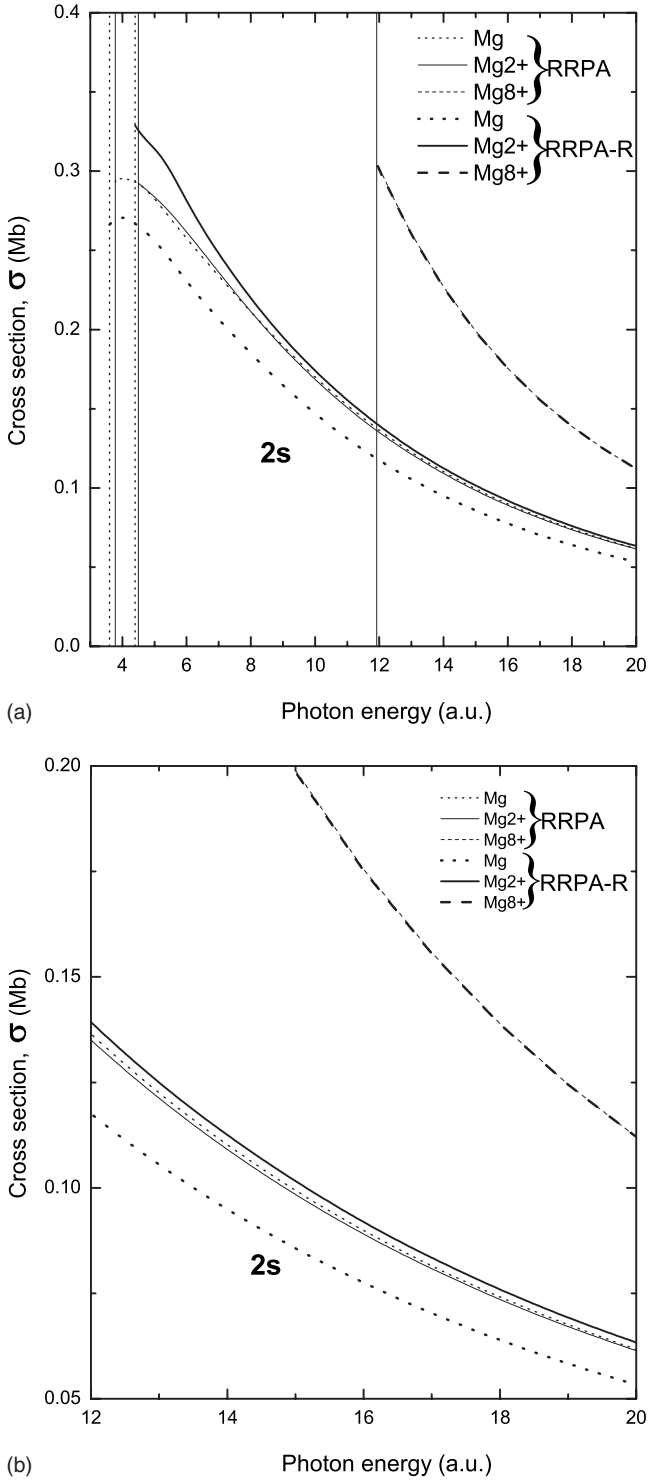

FIG. 1. (a) Photoionization cross sections for $2s$ subshell of Mg, Mg^{2+}, and Mg^{8+}: the vertical solid lines are the DF thresholds and dotted lines are the corresponding ΔE_{SCF} thresholds given in Table I. (b) Magnified view of (a).

tion at the RRPA level other than a mere shift of the threshold toward higher energy [16]. On the other hand, for Mg^{8+}, where $2p$ electrons have been removed (electrons of the same principal quantum number as the subshell of interest), aside from the shift of threshold to higher energy, the $2s$ cross section is very significantly larger than for Mg and Mg^{2+}, as discussed previously [16]. This increase is a result of the decrease in screening resulting from the removal of the $2p$ electrons so that the $2s$ electrons "see" a more attractive field, i.e., an increased effective charge. This then causes the cross section to increase, since the photoionization cross section in the threshold region increases with charge, as a simple hydrogenic argument shows [13–16].

The RRPA-R results are seen to exhibit a rather different phenomenology. First of all in the RRPA-R results, there is a significant difference between the $2s$ cross sections for Mg and Mg^{2+}, in contrast to the RRPA results. The removal of the $3s$ electrons clearly has a significant effect on $2s$ photoionization when relaxation effects are considered over and above the increase in the threshold energies. As expected, the relaxed Mg $2s$ cross section decreases compared to that of unrelaxed result because the overlap factor $\gamma<1$. There is, however, a competing effect that in fact causes an *increase* in the Mg^{2+} cross section. This competing factor arises from the relaxed orbitals which are more tightly bound than the unrelaxed orbitals which, in turn, causes the field "seen" by the photoelectron in the inner region to be more attractive than the unrelaxed orbital field, i.e., the effective charge seen by the photoelectron is larger in the relaxed case. This then causes the cross section in the relaxed case to increase for reasons discussed above. Clearly, however, for neutral Mg, the overlap effect is much more important than the field effect since the relaxed cross section decreases relative to the unrelaxed.

For Mg^{2+}, on the other hand, the relaxed cross section is seen to be larger than the unrelaxed. The overlap effect is much reduced in this case compared to neutral Mg, owing to the removal of $3s$ electrons which were the major contributors to the overlap effect for neutral Mg. The field effect is also reduced, but not nearly as much as the overlap effect so that the field effect is larger than the overlap effect in this case.

For Mg^{8+}, where the electrons from the $2p$ subshell are also removed, the RRPA-R results show clearly that removal of electrons from another subshell with the same principal quantum number changes (increases) the cross section of the given subshell significantly, just as in the RRPA result. Furthermore, for Mg and Mg^{2+}, the RRPA and the RRPA-R cross sections differ from each other, but in the case of Mg^{8+}, both methods give essentially equal values. This is due to the fact that rearrangement effects are strong only when there are spectator electrons in the same shell as the active electrons or in outer subshells so that the spectator wave functions are significantly altered by an inner-shell vacancy. For Mg^{+8} photoionization, the $2s$ vacancy is in the outermost subshell, and rearrangement effects are quite unimportant.

RRPA and RRPA-R calculations for $2s$ photoionization of Ar, Ar^{6+}, and Ar^{8+} have also been performed and are shown in Fig. 2(a) with a magnified view in Fig. 2(b). The RRPA results all lie on essentially the same curve, apart from the shift of thresholds, as shown earlier [16]; this is, of course, expected since only $n=3$ electrons ($3p$ and $3s$) are removed in these ions. For neutral argon, the RRPA-R $2s$ photoionization cross section curve is lower than the RRPA result, as in the Mg case, since $\gamma<1$ and the overlap effect is most important here. But the relaxed cross section exhibits a rather

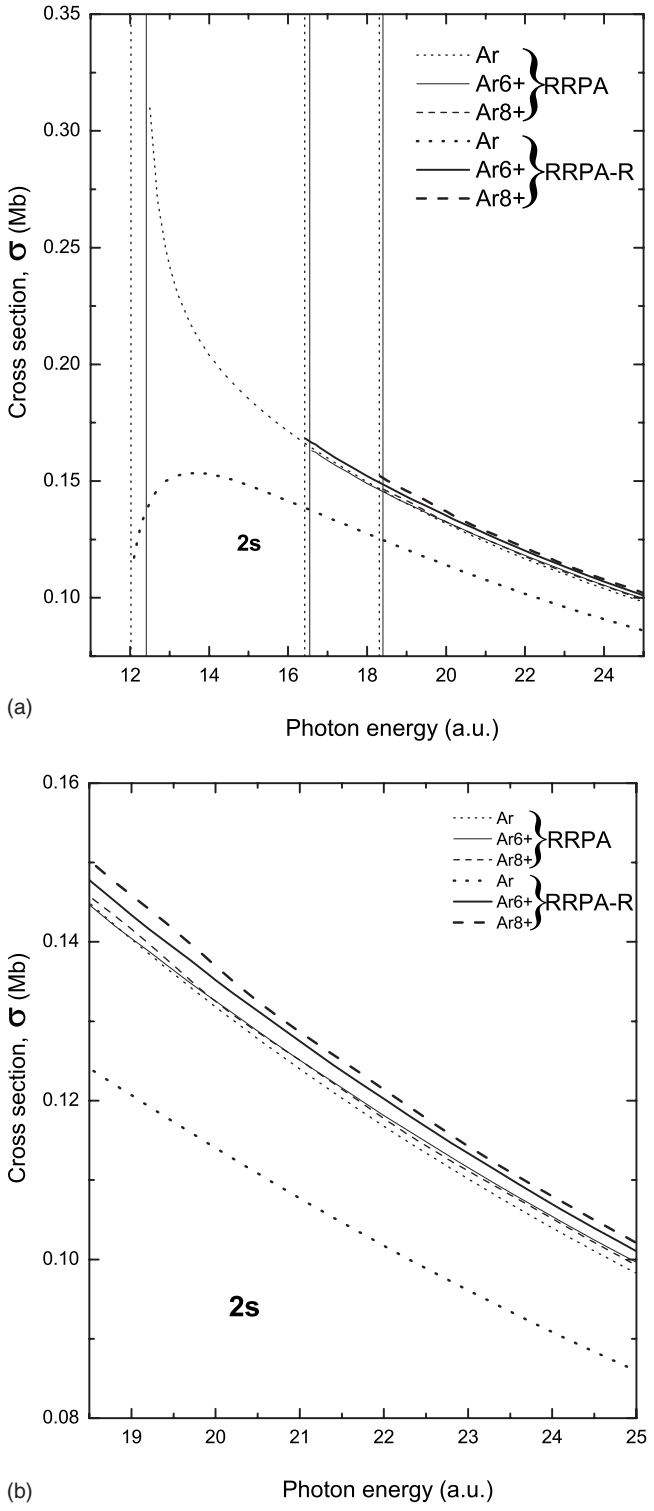

FIG. 2. (a) Photoionization cross sections for $2s$ subshell of Ar, Ar^{6+}, and Ar^{8+}: the vertical solid lines are the DF thresholds and dotted lines are the corresponding ΔE_{SCF} thresholds given in Table II. (b) Magnified view of (a).

different spectral shape near threshold, as compared to the unrelaxed cross section, indicating that field effects are important here as well. The relaxed cross section first increases little bit above the threshold, a small shape resonance, indicating that the photoelectron "sees" a rather different field than in the unrelaxed case. The fact that the spectral shapes of the relaxed and unrelaxed results are so different is a bit of an anomaly. The shape resonance is a result of the competition between the Coulomb attraction and the centrifugal repulsion so that a small change in the Coulomb attraction can lead to a large change in the effective potential [26]. This is evidently what occurs in the relaxed case.

For Ar^{6+}, the relaxed cross section is somewhat above that of the relaxed neutral $2s$ cross section; the relaxed cross section is also slightly *above* its unrelaxed counterpart. This occurs because the large $3p$ overlaps are absent and the relaxed field seen by the photoelectron is slightly stronger, as in the Mg^{2+} case. For Ar^{8+}, the pattern continues. Relaxation thus enhances the Ar^{6+} and Ar^{8+} $2s$ cross sections due to the stronger field seen by the photoelectron, as discussed earlier in the case of Mg^{2+}.

Finally, note that, if the field effect is ignored, to a good approximation the total subshell photoabsorption cross section (as opposed to photoabsorption leading to a particular final state) would not change owing to the removal of an outer-shell electron even if relaxation effects are considered. This can be understood by considering a simple case of a three-electron system such as Li in the $1s^2 2s$ state, looking at the photoionization of a $1s$ electron, and comparing with Li^+ where the $2s$ electron has been removed.

The $1s$ photoionization matrix elements, including relaxation (apart from various constants and antisymmetrization), are given by $\langle 1s|1s_f\rangle\langle 2s|2s_f\rangle\langle 1s|d|\epsilon p\rangle$ for Li, where the $2s$ shell is occupied, and by $\langle 1s|1s_f\rangle\langle 1s|d|\epsilon p\rangle$ for Li^+, where the $2s$ electron has been removed; the subscript f indicates final state relaxed orbitals. Since the overlap integral $\langle 2s|2s_f\rangle = \gamma < 1$, when relaxation effects are considered the matrix element for Li is smaller than the matrix element for Li^+ by that factor of γ. The respective cross sections are proportional to the absolute squares of the matrix elements. For Li^+ then, the cross section goes as $|\langle 1s|1s_f\rangle|^2|\langle 1s|d|\epsilon p\rangle|^2$. For Li, if the total $1s$ photoabsorption cross section is considered, this total $1s$ cross section, summed over all possible $2s$ excitations, is proportional to $|\langle 1s|1s_f\rangle|^2|\langle 1s|d|\epsilon p\rangle|^2 \Sigma_{n=2}^{\infty}|\langle 2s|ns_f\rangle|^2$. However, $\Sigma_{n=2}^{\infty}|\langle 2s|ns_f\rangle|^2 \approx \Sigma_{n=1}^{\infty}|\langle 2s|ns_f\rangle|^2 \approx 1$ since $\langle 2s|1s_f\rangle \approx 0$, so that the cross section is proportional to $|\langle 1s|1s_f\rangle|^2|\langle 1s|d|\epsilon p\rangle|^2$, exactly the result seen for Li^+. This simple example shows that, even taking relaxation into account, if the field effect can be ignored, to a good approximation the total subshell photoabsorption cross section remains constant as a function of photon energy except for the shift of threshold to higher energy.

IV. CONCLUSIONS

Using studies of the $2s$ photoionization cross section of several members of the Mg and Ar isonuclear sequences as a model, it has been revealed that inner subshell photoionization cross sections do not lie on a single curve as a result of removing outer-shell electrons when relaxation effects are considered. The deviations are particularly strong for neutral atoms and lowly charged ions, i.e., near the neutral end of the isonuclear sequence. The relaxation introduces two effects as compared to unrelaxed calculations: overlap of re-

laxed and unrelaxed orbitals which tends to lower the cross section, along with an increase in the cross section owing the fact that the escaping photoelectron experiences a more attractive field resulting from more compact final state orbitals. It is also shown that in many cases, the total subshell photoionization cross sections (summed over all excitations of the passive electrons) might lie along the same curve despite the removal of outer-shell electrons. It would be very useful to test these ideas experimentally.

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