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# Low-energy photoionization of alkali-metal atoms: Relativistic random-phase-approximation calculations

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A complete theoretical survey of low-energy photoionization cross sections, angular asymmetry, and spin-polarization parameters for the ground states of the alkali-metal atoms Li, Na, K, Rb, and Cs, including virtual core excitations in a gauge-independent relativistic random-phase approximation (RRPA) is presented and compared with length- and velocity-form Dirac-Fock results and with available experimental data. The *ab initio* RRPA formulation substantially improves the agreement of cross sections with experiment at energies above the Cooper minimum.

## INTRODUCTION

Experimental techniques involving the use of lasers as well as synchrotron light sources have opened a wide range of possibilities for measuring details of the atomic photoionization process beyond those obtained from cross-section measurements alone. Measurements of angular distributions and spin polarization are particularly important in this respect, since they place constraints on the relative phases between photoionization amplitudes that complement the information on amplitudes provided by cross-section measurements. For the alkali-metal atoms there has been substantial interest (both experimental[1–5] and theoretical[6–11]) in spin polarization, especially in the production of highly spin-polarized low-energy photoelectrons in the photoionization of cesium near the Cooper minimum just above threshold. By contrast, there has been essentially no experimental work on angular distributions. The purpose of this paper is to present the results of a systematic study of three independent low-energy photoionization parameters for alkali-metal atoms: cross sections, angular distribution asymmetry parameters, and spin-polarization parameters from the point of view of the relativistic random-phase approximation (RRPA), which we hope will provide a useful guide for future experimental and theoretical investigations.

Theoretical studies of photoabsorption by multielectron systems face two major difficulties: firstly, the strong Coulomb attraction near a heavy nucleus requires that proper account be taken of the spin-orbit interaction which is responsible for the nonzero Cooper minimum[12] and the production of spin-polarized photoelectrons[13] in the photoionization of the alkali metals except lithium. Secondly, with a growing number of core electrons, electron correlation effects play an increasingly important role in determining the properties of atoms. The relativistic Dirac-Fock (DF) formulation accounts for the spin-

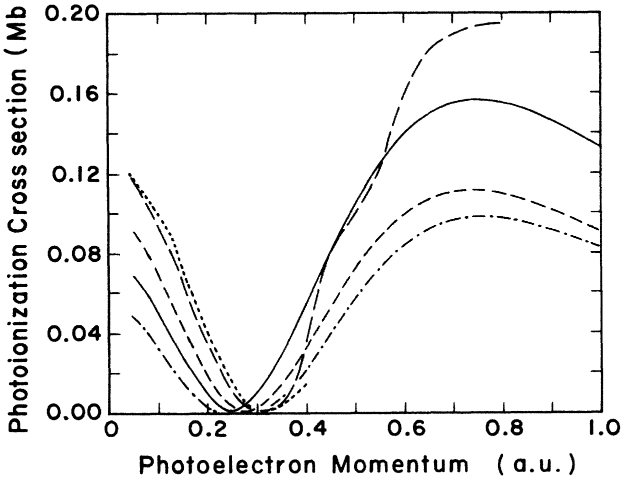

FIG. 1. Total photoionization cross section for Na ground state. ——: RRPA. — — —: DF velocity. —·—·—·: DF length. · · · · ·: experiment—best value—Marr and Creek, Ref. 19. ———: experiment—Hudson, Ref. 24; Hudson and Carter, Ref. 25.

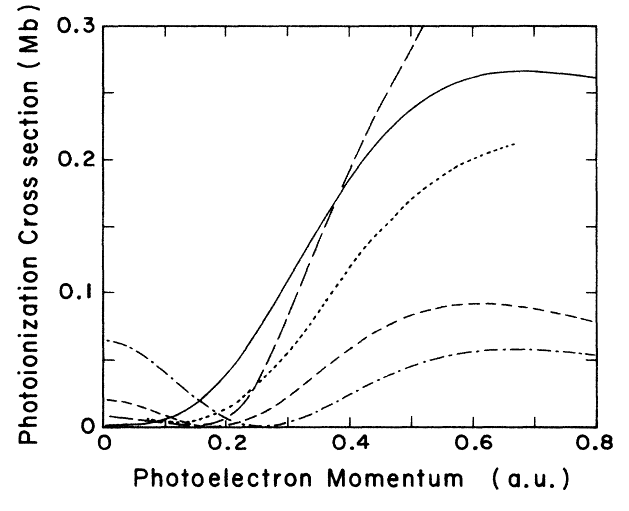

FIG. 2. Total photoionization cross section for K ground state. ——: RRPA. — — —: DF velocity. —·—·—·: DF length. · · · · ·: experiment—best value—Marr, Ref. 19. ———: experiment—Hudson and Carter, Ref. 26.

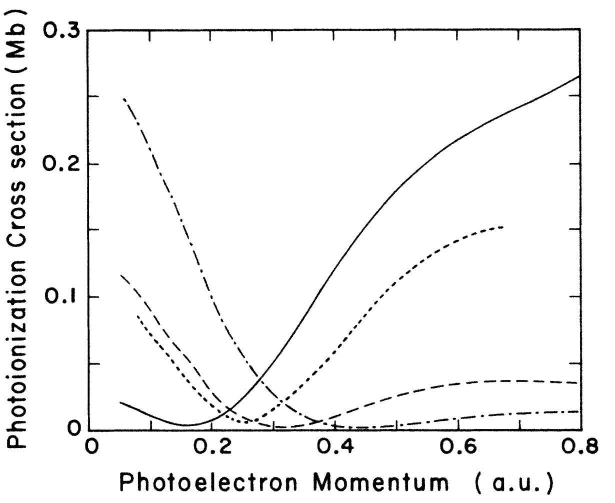

FIG. 3. Total photoionization cross section for Rb ground state. ——: RRPA. — — —: DF velocity. —·—·—·: DF length. · · · · ·: experiment—best value—Marr, Ref. 19.

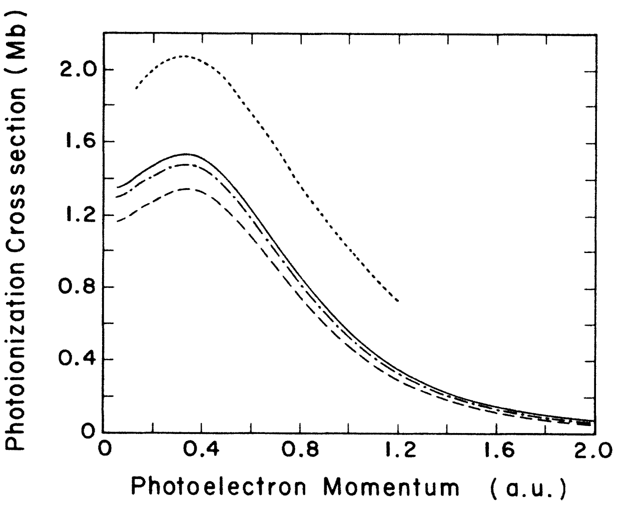

FIG. 5. Total photoionization cross section for Li ground state. ——: RRPA. — — —: DF velocity. —·—·—·: DF length. · · · · ·: experiment—Marr, Ref. 23.

orbit interaction and describes the behavior of atomic photoionization cross sections well near the threshold, but it predicts cross sections which are too small at shorter wavelengths. Moreover, the DF dipole matrix elements taken between bound and continuum states are strongly gauge dependent. The resulting ambiguity of the matrix elements and the disagreement of the cross section with experimental data at higher energies suggest that many-body effects are not negligible in the heavy alkali-metal atoms.

One of the most successful theoretical approaches to the photoionization of alkali-metals is the nonrelativistic model potential method,[9,10] which accounts for core polarization as well as for spin-orbit interaction. This approach is gauge independent but requires empirical parameters to describe the polarization potential. Nonrelativistic studies in the random-phase-approximation with exchange (RPAE), which account for core polarization in essentially the same way as the present paper, but which give no account of the spin polarization have been carried out for Li by Amusia *et al.*,[14] and for heavier alkali metals by Amusia and Cherepkov.[15] For the case of sodium, an RRPA calculation along the lines of the present work has been previously reported by Chang and Kelly.[7]

One attempt to set up a consistent *ab initio* relativistic many-body theory of photoionization including higher-order interactions between the core and valence electrons has been reported recently.[11] The method used in the calculations presented here is a modification of the approach described in Ref. 11, which includes the effects of the virtual excitations of the ionic core in the RRPA, but which

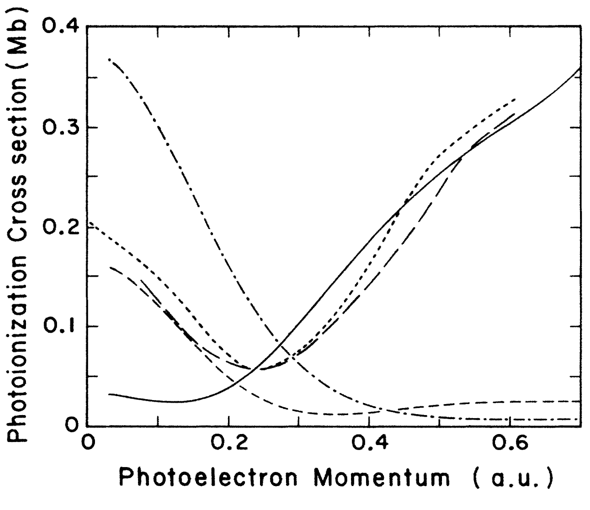

FIG. 4. Total photoionization cross section for Cs ground state. ——: RRPA. — — —: DF velocity. —·—·—·: DF length. · · · · ·: experiment—best value—Marr, Ref. 19. ———: experiment—Marr, Ref. 19.

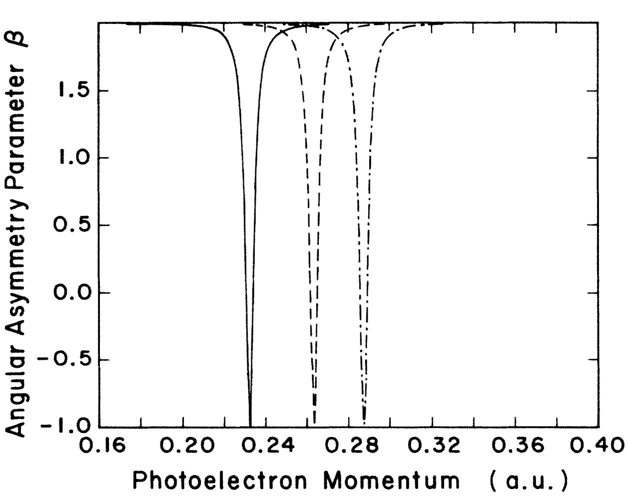

FIG. 6. Angular asymmetry parameter for photoionization of Na from ground state. ——: RRPA. — — —: DF velocity. —·—·—·: DF length.

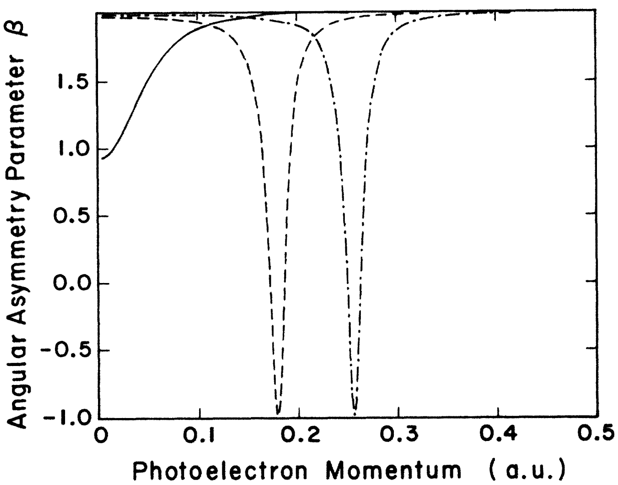

FIG. 7. Angular asymmetry parameter for photoionization of K from ground state. ——: RRPA. — — —: DF velocity. —·—·—·: DF length.

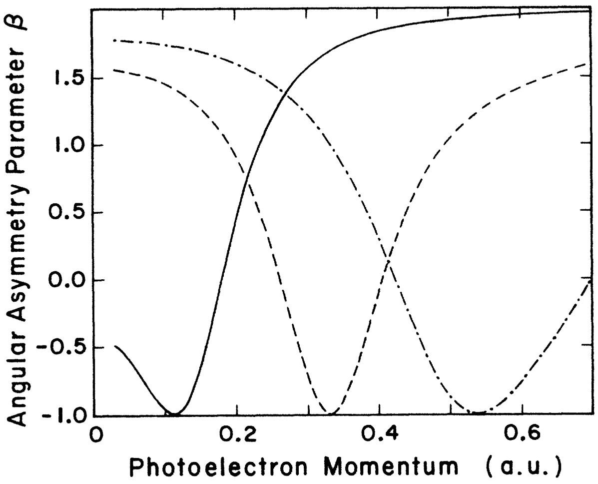

FIG. 9. Angular asymmetry parameter for photoionization of Cs from ground state. ——: RRPA. — — —: DF velocity. —·—·—·: DF length.

ignores secondary effects of the valence electron on the core. The matrix elements obtained using the present formulation have been proven to be gauge independent; in addition, they account for a major part of the virtual core excitations. A detailed theoretical description of the theory is given in Ref. 16.

The unperturbed wave functions for alkali-metal atoms are calculated by solving the relativistic *jj*-coupled Dirac-Fock equations, determining the orbital of the valence electron in the Hartree-Fock potential of the frozen ionic closed-shell core, thus neglecting the core polarization by the valence electron in absence of a radiation field. While the interaction of the atom with the radiation field is described in first-order perturbation theory, corresponding to one-photon processes, the RRPA equations when solved self-consistently account for a certain class of Coulomb matrix elements to all orders [Ref. 11, Figs. 1(a)—1(e)].

The perturbation of the core orbitals can be described from two points of view which can be proven to be formally equivalent:[17] on the one hand, the external perturbation by the radiation field can be regarded to cause virtual core excitations described by inhomogeneous RRPA equations that are driven by the dipole operator. The perturbed core orbitals give rise to a modification of the dipole field experienced by the valence electron. The matrix element of the modified dipole operator between the unperturbed valence states is added to the dipole matrix element between these states to give the total transition amplitude. Alternatively, we can drive the core RRPA equations by the Coulomb interaction with the oscillating charge distribution of the valence electron. Here the dipole matrix elements between the perturbed core states are

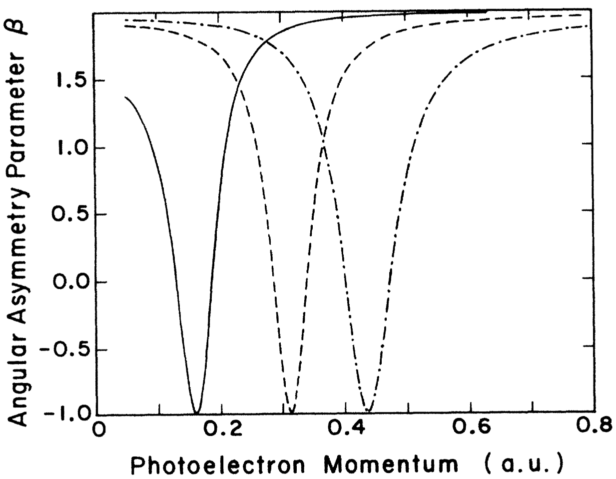

FIG. 8. Angular asymmetry parameter for photoionization of Rb from ground state. ——: RRPA. — — —: DF velocity. —·—·—·: DF length.

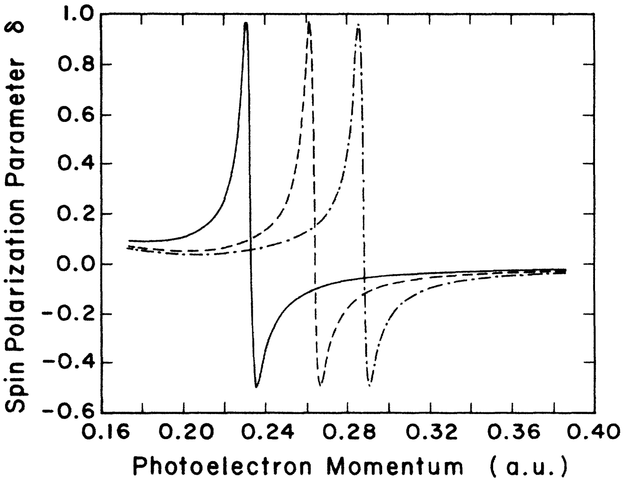

FIG. 10. Spin-polarization parameter for photoionization of Na from ground state. ——: RRPA. — — —: DF velocity. —·—·—·: DF length.

added to the zeroth-order matrix element to obtain the correlation corrections. Both versions can be derived by replacing infinite sums of terms from a perturbational expansion by solutions to differential equations. Practical considerations (the core RRPA equations are driven by the same potential in length and velocity form requiring the solution of only one set of RRPA equations) suggest the choice of the second method. Gauge independence of the dipole matrix elements leading to exact agreement between length forms and velocity forms provides a valuable check on the accuracy of the calculated wave functions. Reference 16 gives a more detailed description of the theory, including the radial RRPA equations obtained after angular decomposition.

The relation between transition matrix elements and angular distribution parameters is described in detail in Ref. 18. It should be noted that the low-energy photoionization of the $^2S_{1/2}$ ground states of the alkali metals require only two photoionization amplitudes describing the channels $^2S_{1/2} \rightarrow {}^2P_{1/2}$ and $^2S_{1/2} \rightarrow {}^2P_{3/2}$. In such cases three independent parameters suffice to describe the photoionization process completely. We choose these parameters to be the cross section ($\sigma$), the angular distribution asymmetry ($\beta$), and total spin polarization ($\delta$). Defining $D_{1/2} = \langle {}^2P_{1/2} \| d \| {}^2S_{1/2} \rangle$ and $D_{3/2} = \langle {}^2P_{3/2} \| d \| {}^2S_{1/2} \rangle$, to be the reduced matrix elements of the dipole operator $d$, it is found[18]

$$\sigma(\omega) = \frac{8\pi^4}{\omega c} \bar{\sigma}(\omega) ,$$

$$\bar{\sigma}(\omega) = ( |D_{1/2}|^2 + |D_{3/2}|^2 ) , \tag{1}$$

$$\beta(\omega) = [ |D_{3/2}|^2 + 2\sqrt{2} | \mathrm{Re}(D_{1/2} D_{3/2}^*) ] / \bar{\sigma}(\omega) , \tag{2}$$

$$\delta(\omega) = [ \tfrac{1}{3} |D_{1/2}|^2 + \tfrac{5}{6} |D_{3/2}|^2 - \tfrac{2}{3}\sqrt{2}\, \mathrm{Re}(D_{1/2} D_{3/2}^*) ] / \bar{\sigma}(\omega) . \tag{3}$$

In our calculations we integrate the RRPA equations numerically using a fixed-point eighth-order Adams method.

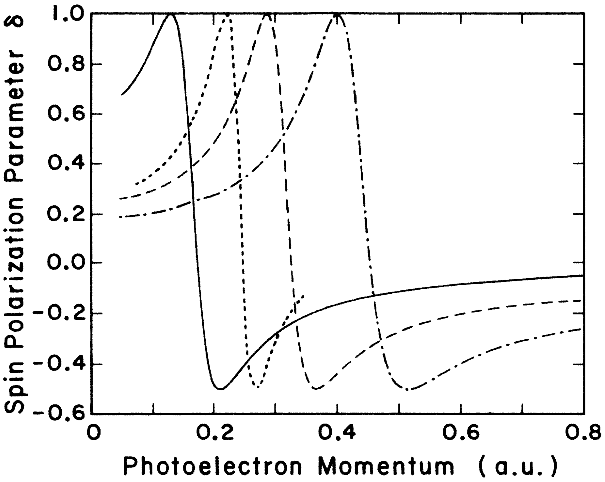

FIG. 12. Spin-polarization parameter for photoionization of Rb from ground state. ——: RRPA. — — —: DF velocity. —·—·—: DF length. · · · · ·: experiment by Baum *et al.*, Ref. 4.

It is not difficult to obtain an agreement of length and velocity forms of the matrix elements accurate to five or six significant digits, provided a sensible radial integration grid is chosen and all core excitation channels are included. Practically, the computation times for full calculations would become forbiddingly long, so such calculations were carried out only for two frequencies for the heavier atoms cesium and rubidium, whereas for other frequencies those core excitation channels contributing considerably less than 0.1% to the matrix elements in length gauge were neglected. Since the length-form matrix elements are weighted strongly for large radii, this means including only the excitations of the outer few occupied shells. We estimate that the numerical accuracy of the matrix elements is 0.1%. The matrix elements and phase shifts, which have a smoother energy dependence

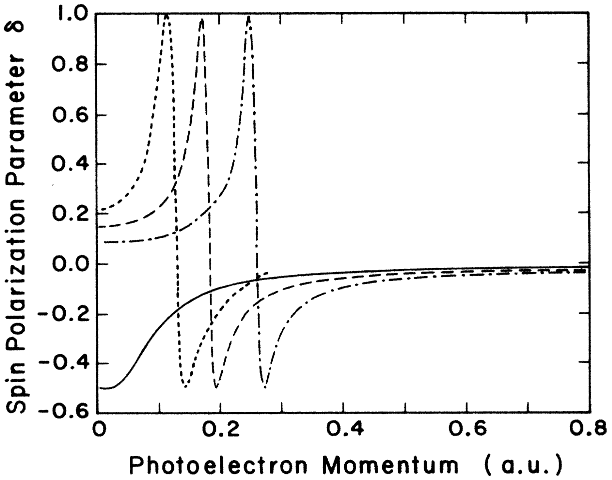

FIG. 11. Spin-polarization parameter for photoionization of K from ground state. ——: RRPA. — — —: DF velocity. —·—·—: DF length. · · · · ·: experiment by Baum *et al.*, Ref. 4.

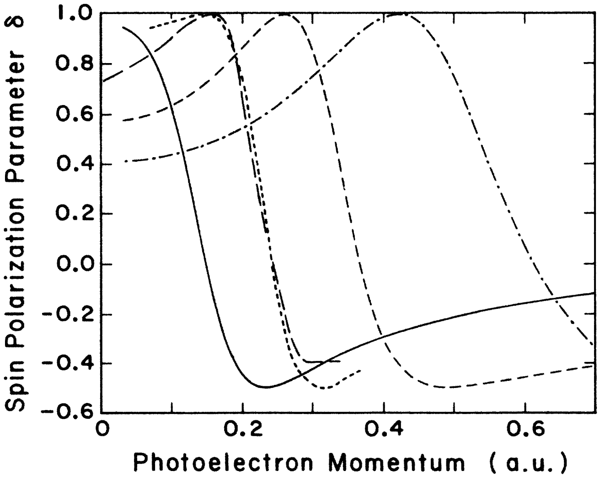

FIG. 13. Spin-polarization parameter for photoionization of Cs from ground state. ——: RRPA. — — —: DF velocity. —·—·—: DF length. · · · · ·: experiment by Baum *et al.*, Ref. 4. ————: experiment by Heinzmann *et al.*, Ref. 3.

than cross sections, asymmetry parameters, and polarization parameters, were spline interpolated before calculating these parameters. In all calculations we have used theoretical thresholds for determining the relation between photoelectron energy and radiation frequency. Although the binding energies predicted by a single-configuration approximation do not agree very well with experimental binding energies, the use of experimental energies would cause a loss of the gauge independence and of the *ab initio* character of the calculation.

## RESULTS AND DISCUSSION

There are two general tendencies observed in the calculated cross sections for all alkali metals (except lithium, which is a practically nonrelativistic few-body system).

(a) There is—in good qualitative agreement with the experimental survey done by Marr and Creek[19]—a sharp rise in the cross section towards higher frequencies. In this region cross sections predicted at the DF level are too small for heavier atoms. Quantitatively, our results agree quite well with some experiments in the higher-energy region, but are generally a bit too high compared to the *best* experimental values reported in Ref. 19 (Figs. 1–4). For lithium, as shown in Fig. 5, the RRPA gives no significant improvement over the DF; the maximum in the cross section is found at the correct energy, but the experimental cross section is much higher than our calculated values.

(b) The Cooper minimum in the cross section is consistently shifted towards lower energies as illustrated in Table I. This effect is stronger for heavier systems and pushes the minimum of potassium slightly below threshold. Compared with experimental results, calculations at the DF level predict the Cooper minimum at frequencies that are too high (the velocity form being better than the length-form results), whereas the minimum is lowered too much in the RRPA.

There is a complete lack of modern experimental data on angular distributions of photoelectrons from photoionized alkali-metal atoms. The only experiment known to us,[20] done with a nonmonochromatic light source, yields results for potassium that are not inconsistent with $\beta=2$ in a wavelength interval of 240±25 nm. Measurements of differential cross sections seem to be extremely difficult near the Cooper minimum. Our results for the DF–length-form angular asymmetry parameters agree to within graphical accuracy with the theoretical results of Ong and Manson.[21] The RRPA corrections do not change the form of the curves much but shift them towards lower frequencies as illustrated in Figs. 6–9. The flattening of the asymmetry curve for potassium seen in Fig. 7 is due to the choice of the photoelectron momentum as abscissa and would not be present if an energy scale had been used.

For spin polarization, the same general features are repeated: our theoretical values agree qualitatively with experiments but are again shifted towards lower energies. We present our results on sodium, potassium, rubidium, and cesium[3,4] in Figs. 10–13.

## CONCLUSIONS

Our results demonstrate, by substantially improving the agreement between experimental and theoretical photoionization cross sections in the higher-energy region, that core polarization corrections contribute significantly to the photoionization of alkali-metal atoms having many core electrons. In the higher-energy region, neglecting virtual core excitation processes leads to cross sections which are substantially too small.

Although the RRPA includes the effects of core polarization, from the energy dependence of the cross sections, asymmetry parameters, and spin-polarization parameters we conclude that the RRPA is still not fully satisfactory. Generally all features are shifted towards somewhat too low energies in contrast to the DF calculations. The one-configuration approximation gives—while predicting the total energy of an alkali-metal atom well—binding energies for the valence electron that are too small. This affects the relation between the photoelectron momentum and the core excitation energy and tells us that the wave functions of the valence electron are not well described. Efforts to include higher-order Coulomb interactions into the description of the unperturbed atom are underway. In addition, the RRPA method does not include all matrix elements of a full perturbational expansion. It can be expected that including the more important higher-order Coulomb interactions will improve the agreement between experiment and theory.

A straightforward extension of present calculations in

TABLE I. Minima of photoionization cross sections in Dirac-Fock length and velocity forms and in the RRPA.

| | | RRPA | DF (len) | DF (vel) | Expt.[a] |
|---|---|---|---|---|---|
| Na | $p$ (a.u.) | 0.232 | 0.287 | 0.263 | 0.311 |
| | $\sigma$ (Mb) | $10^{-5}$ | $10^{-5}$ | $10^{-5}$ | $<3\times0^{-3}$ |
| K | $p$ (a.u.) | | 0.256 | 0.180 | 0.124 |
| | $\sigma$ (Mb) | $6.65\times10^{-4}$[b] | $1.64\times10^{-4}$ | $1.72\times10^{-4}$ | $4\pm2\times10^{-3}$ |
| Rb | $p$ (a.u.) | 0.159 | 0.441 | 0.313 | 0.246 |
| | $\sigma$ (Mb) | $3.79\times10^{-3}$ | $1.73\times10^{-3}$ | $2.13\times10^{-3}$ | $8\pm3\times10^{-3}$ |
| Cs | $p$ (a.u.) | 0.124 | 0.652 | 0.349 | 0.240 |
| | $\sigma$ (Mb) | $2.42\times10^{-2}$ | $6.27\times10^{-3}$ | $1.17\times10^{-2}$ | $6\pm1\times10^{-3}$ |

[a] Marr and Creek, Ref. 19.

[b] Value at threshold.

the framework of the codes already developed is a study of the photoionization of excited states of alkali metals and other single-valence-electron systems. The existence of a sharp minimum in the photoionization cross section of the Cs $6d_{3/2}$ excited state has been of special interest, since the theoretically predicted minimum at 470 nm has not been confirmed experimentally.[22] Preliminary calculations carried out at a lower level of accuracy confirm this experimental result and predict one sharp minimum between 100 and 110 nm. At present, calculations of photoionization from excited states of alkali metals are underway using techniques essentially identical to those described in the present paper. A generalization of the present technique to the case of two-photon ionization has also been developed, but has not as yet been applied to systems of experimental interest.

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