Photoionization of the excited $(6s\,6p)^{3,1}P$ states of ytterbium

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Calculations of the photoionization cross sections for the excited $(6s\,6p)^{3,1}P$ state of ytterbium have been performed at the Hartree-Fock and Hartree-Slater levels. The results for ^3P show reasonable agreement (at the edge of error bars) with a recent experiment at a single energy. Significant differences between the triplet and singlet cases exist and arise primarily due to the effects of exchange on the initial-state wave functions.

I. INTRODUCTION

Photoionization of excited states of atoms, and the inverse process of radiative recombination, are important in connection with a number of astrophysical and other applications, on the one hand. From a basic point of view, on the other hand, studies of photoionization shed light on one of the most fundamental processes in the universe, the response of a physical system to electromagnetic radiation. In addition, excited states offer a new dimension to these studies, investigation of physically large systems.

Experimentally, scrutiny of the photoionization of excited states has been spurred on by recent advances in laser technology to create the excited states along with the new synchrotron light sources to photoionize them. These twin developments have resulted in an upsurge in laboratory studies, mostly (but not exclusively) on the alkali-metal atoms.[1]

A recent experiment[2] has studied the $(6s,6p)^3P$ excited state of Yb. This experiment is of particular interest for two reasons. First Yb, having $Z=70$, represents the heaviest atom for which excited-state photoionization has been measured to date. Second, the experiment was such that the ratio of $6p\to\epsilon d$ and $6p\to\epsilon s$ cross sections was measured along with the cosine of the phase-shift difference.

It is, thus, of interest to inquire how well theory does for the photoionization of an excited state of such a heavy atom. To that end, we have performed Hartree-Fock (HF) calculations of both the ^3P and ^1P states arising from the excited $6s\,6p$ configuration of Yb along with Hartree-Slater (HS) calculations, which do not distinguish between the multiplets. In addition to giving some insight into the utility of HF and HS calculations for heavy-atom excited-state photoionization, this work allows us to assess the nature and importance of exchange effects in excited-state photoionization.

II. BRIEF REVIEW OF THEORY

Within the framework of the electric dipole approximation, which is excellent for low-energy photons,[3] the photoionization cross section for a single electron in a subshell takes a fairly simple form.[4] In particular, for a transition $(L_c S_c nl)LS\to(L_c S_c\epsilon l')L'S$, an initial nl electron coupled to a core $L_c S_c$ to give LS going to a final continuum $\epsilon l'$ coupled to a core $L_c S_c$ giving $L'S$, the cross section is given by[4]

$$\sigma_{nl}^{L_c S_c L}(\varepsilon)=\frac{4\pi\alpha a_0^2}{3}(\varepsilon+I)\sum_{l',L'}(2L'+1)l_>\begin{Bmatrix} l & L & L_c \\ L' & l' & 1 \end{Bmatrix}^2$$
$$\times(M_{nl,\epsilon l'}^{L_c S_c LL'})^2 , \qquad (1)$$

where I is the ionization potential of the nl electron in the particular state, a_0 is the Bohr radius, α is the fine-structure constant, $l_>$ is the maximum of l and l', $\begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix}$ is the Wigner $6-j$ symbol,[5] and

$$M_{nl,\epsilon l'}^{L_c S_c LL'}=\int P_{nl}^{L_c S_c L}(r)rP_{\epsilon l'}^{L_c S_c L'}(r)dr , \qquad (2)$$

where the P's are (r times) the radial wave functions for initial and final states of the electron undergoing the transition. The initial discrete wave function was obtained from a standard HF code,[6] while the final continuum HF wave function, in the field of the fully relaxed ion, was obtained from our own code.[7]

Note that the length form of the dipole matrix element, Eq. (2), may be transformed[3,8] into another form, the so-called velocity form, and these two forms must be equal for exact wave functions.[3,8] Thus equality of length and velocity results is a useful (but by no means infallible) measure of the accuracy of the HF calculation.

For the HS calculation, where a central approximation to exchange is employed,[9] the dependence of the cross section and matrix elements on $L_c S_c$, L, and L' is removed so that the HS matrix element can be factored out of the sum [Eq. (1)] over L' and the sum can be performed[10] yielding

$$\sigma_{nl}^{\rm HS}=\frac{4\pi\alpha a_0^2}{3}(\varepsilon+I)\sum_{\substack{l'=l-1 \\ l'\neq l}}^{l+1}\frac{l_>}{2l+1}(M_{nl,\epsilon l'}^{\rm HS})^2 , \qquad (3)$$

with the matrix element defined as in Eq. (2) but with HS wave functions. Note that the length and velocity forms of the matrix element must be equal in the HS formulation.[8]

III. RESULTS AND DISCUSSION

Our results for the ratio between the $6p \rightarrow \epsilon s$ and $6p \rightarrow \epsilon d$ cross sections, for the $6s6p$ ^3P initial excited state of Yb, is shown in Fig. 1 along with the experimental point of Ref. 2. From this comparison, it is clear that the length and velocity cross sections remain quite close together in the threshold region and lie at the edge of the experimental error bar. Thus, the agreement between experiment and theory is not bad.

We emphasize that the HF calculation uses the theoretical binding energy (which is extremely close to the experimental binding energy in this case) and contains no adjustable parameters. In addition, the experiment is absolute; i.e., nothing is normalized to anything else. This makes the agreement between theory and experiment more meaningful. The simple HS result (not shown in Fig. 1) lies essentially on top of the length results for low energy and on top of the velocity results above about 1 Ry. Thus, it agrees with experiment essentially as well as the HF result. But this agreement is slightly misleading. The reason is that the results in Fig. 1 are shown versus photoelectron energy. If the comparison is made versus photon energy, the HF result remains the same vis-à-vis experiment since the HF ^3P binding energy of 3.87 eV is quite close to the experimental value of 4.02 eV.[2] But the HS binding energy is 3.13 eV or almost a whole eV away. The agreement of the HS result with experiment therefore changes significantly if we compare versus photon energy.

The absolute value of the cosine of the phase-shift difference between the ϵd and ϵs continuum waves was also inferred from the measurement. The result is shown in Fig. 2, along with our HF and HS results. The theoretical curve is seen to lie just outside the experimental error bar with both HF ^3P and HS having pretty much the same value at the experimental energy. Although there are very significant differences between HS
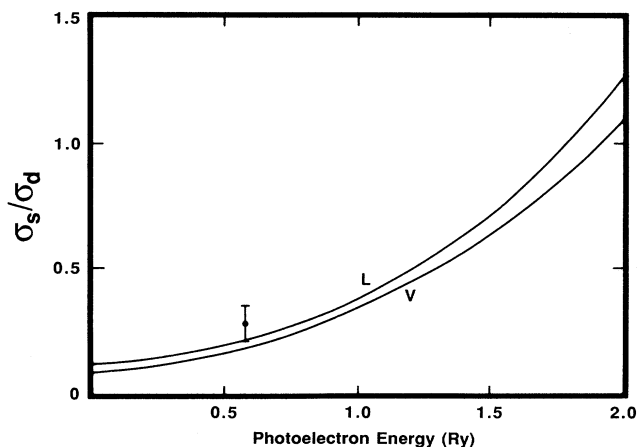
and HF ^3P values at lower energies, at the experimental energy they turn out to be about the same. In any case, it is clear that the theory does an adequate, but not outstanding, job of reproducing the experimental results.

To understand the theoretical results more adequately, we have also looked at ^1P at the HF level. A comparison of HF and HS cross sections is shown in Fig. 3, where significant differences among the formulations are seen. Note that the HS cross section, being a central-field formulation, does not distinguish between multiplets; it thus may be considered an average of the ^3P and ^1P to first approximation. The HF binding energy of the ^1P state is found to be 2.23 eV. From the binding-energy point of view, the HS result lies between ^1P and ^3P, but somewhat closer to ^3P. Thus, we might guess that the HS results will be closer to the ^3P than the ^1P.

Looking at Fig. 3, it is clear that the HS result does indeed lie between ^3P and ^1P but somewhat closer to ^3P. The outstanding feature of these results, however, is the huge difference between singlet and triplet cross sections, a factor of about an order of magnitude, over most of the energy range shown. The only difference between singlet and triplet wave functions, in both initial and final states, is the sign of the exchange between the $6s$ and $6p$ in the initial states and between $6s$ and ϵd in the dominant final states. As mentioned earlier, the HF binding energies differ considerably, the ^3P being much more tightly bound than the ^1P owing to the fact that the exchange interaction between $6s$ and $6p$ is attractive in the ^3P case and repulsive in the ^1P case. The exchange interaction is

FIG. 1. Ratio of the Yb $6s6p$ $^3P \rightarrow 6s\epsilon s$ ^3S partial cross section (σ_s) to the Yb $6s6p$ $^3P \rightarrow 6s\epsilon d$ ^3D partial cross section (σ_d) as a function of photoelectron energy in Ry (13.605 eV). The solid lines are our Hartree-Fock results in length (L) and velocity (V) formulations, and the experimental point is from Ref. 2.
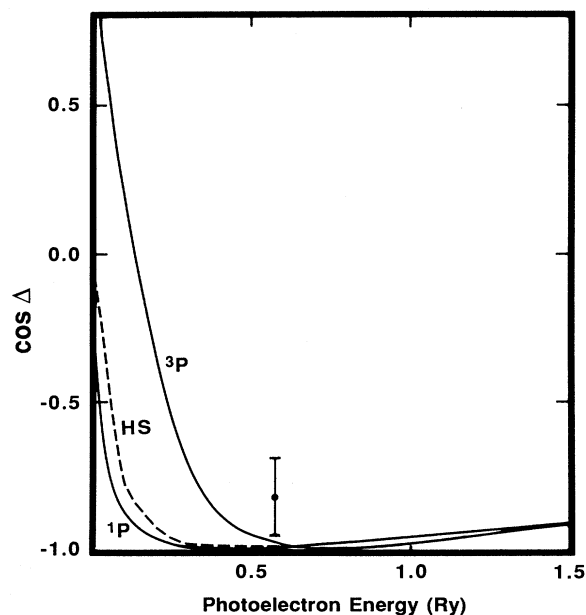
FIG. 2. Cosine of the phase-shift difference (with respect to free waves) between $6p \rightarrow \epsilon d$ and $6p \rightarrow \epsilon s$ photoionization channels as a function of photoelectron energy in Ry. The solid curves are our Hartree-Fock results for Yb $6s6p$ ^3P and ^1P initial states, the dashed curve is our Hartree-Slater result, and the point is the experimental ^3P measurement of Ref. 2.
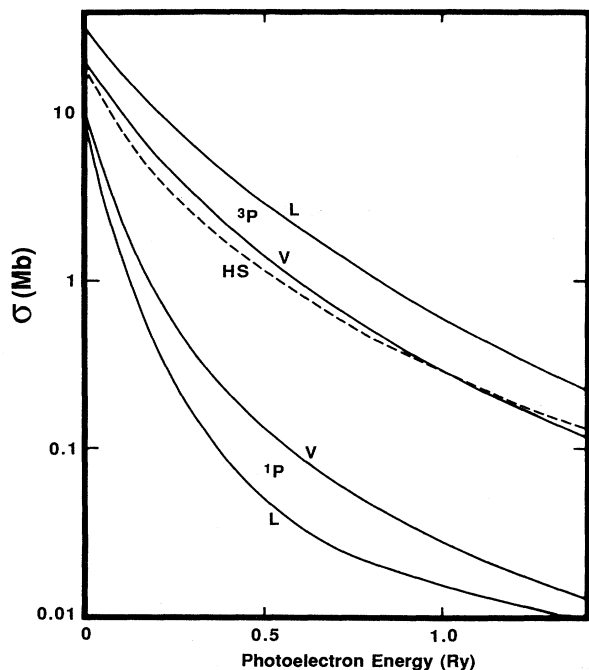
FIG. 3. Photoionization cross section of Yb $6s\,6p$ as a function of photoelectron energy. The solid curves are our Hartree-Fock ^3P and ^1P results in length (L) and velocity (V) formulations, and the dashed curve is the Hartree-Slater result.

large because the $6s$ and $6p$ have the same principal quantum number, so the overlap is large since they occupy the same region of space. Further, the HF binding energies are in good agreement with experiment,[2] suggesting that the HF initial-state wave functions realistically represent the states.

A useful manner of characterizing excited states is to use the quantum defect; the ^3P and ^1P HF value are 4.13 and 3.53, respectively, while the HS value is found to be 3.91. Since the major part of the transition strength is in the $6p \rightarrow \epsilon d$ transition, it is worthwhile to look at the threshold phase shifts in these channels. In our calculations, these phase shifts, in units of π rad, turn out to be 2.73 and 2.72 for transitions from HF ^3P and ^1P initial states, respectively, and 2.83 for the HS calculation. This points up very clearly the fact that while the ^3P and ^1P initial states differ considerably, as evidenced by their quantum defects which differ by 0.6 and their binding energy which differ by a factor of ~ 2, the final $6s\epsilon d$ $^{3,1}D$ states do not differ appreciably as seen from the near equality of the threshold phase shifts. This leads us to conclude that exchange is not important for the continuum states; the difference in ^3P and ^1P cross sections is, thus, due to the $6s$-$6p$ exchange interaction in the initial states.

But while this pinpoints the underlying cause of the differences between ^3P and ^1P cross sections, it does not tell us why they are so large (about an order of magnitude). The size of the difference can be traced to the existence of Cooper minima, in each case, in the $6p \rightarrow \epsilon d$ channels. It has been fairly well established that the loca-

tion of Cooper minima is related to the phase-shift (quantum-defect) difference between initial discrete and final continuum states at threshold.[11-14] In the present case, this difference is 1.40 for ^3P, 0.81 for ^1P and 1.08 for HS calculation. Since these differences are greater than 0.5 but less than 1.5, we expect a single change of sign in the dipole matrix element[13] for each state with ^1P, which has the smallest phase-shift difference being closest to threshold and ^3P being the furthest. This is supported by our calculations which show a ^1P Cooper minimum at about 4.9 Ry above threshold and a ^3P minimum at about 6 Ry above threshold. Since the $6p \rightarrow \epsilon d$ zeros are so widely separated, a very significant qualitative, as well as quantitative, difference appears in the cross sections; the ^1P cross section drops to its minimum at much lower energy than ^3P, leading to discrepancy between them shown in Fig. 3. This gives further evidence for the importance of Cooper minima as determinants of excited-state, oscillator-strength distributions.[13] Note that evidence for a Cooper minimum in the ϵd channel for the ^3P initial state is also shown in Fig. 1, where the ratio σ_s/σ_d is increasing as σ_d is going toward its zero, while σ_s remains slowly varying with energy.

Aside from the appeal to experiment, which in this case is limited to a single energy point, some information on the reliability of the HF calculations can be obtained by comparison of length and velocity results. Over the range shown in Fig. 3, differences in both ^3P and ^1P cross sections are as large as a factor of 2, but the ratio between $6p \rightarrow \epsilon s$ and $6p \rightarrow \epsilon d$ cross sections (shown in Fig. 1 for the ^3P case) is much closer, within $\sim 25\%$. This indicates that for more accurate calculations, correlation is required. Since the initial-state binding energies are in good agreement with experiment, it is likely that the initial-state HF wave functions are fairly accurate. In addition, the final ionic state of a single $6s$ electron outside of closed shells is likely to be represented fairly well by a HF wave function. Thus, correlation in the form of interchannel coupling is probably necessary, but such correlation is unlikely to alter the basic physics revealed by the HF results.

IV. FINAL REMARKS

The Hartree-Fock calculation of the photoionization of the excited $6s\,6p$ ^3P of Yb gives satisfactory agreement with a recent experiment.[2] Comparison of ^3P and ^1P cross sections arising from the $6s\,6p$ configuration of Yb shows very significant differences of about an order of magnitude. These cross-section differences were traced to Cooper minima, zeros in the dipole matrix elements, in the $6p \rightarrow \epsilon d$ channels; since ^3P and ^1P have Cooper minima at vastly different energies (different by more than 1 Ry), this affects the whole shape and magnitude of each cross section over a fairly broad energy range. Further, the positions of the Cooper minima were closely related to the phase-shift differences between initial and final states, confirming a previously established relationship.[11-14]

HF length and velocity results show differences of about a factor of 2 for both ^3P and ^1P cross sections. It was pointed out that interchannel coupling was the most likely candidate for bringing them closer together, although introduction of such correlation is not likely to change the physics revealed by the HF results.

Finally, it is important to note that while agreement with experiment is reasonably good, it is dangerous to generalize based on a single energy. It would be highly desirable to have some energy-dependent experiment along with measurements on excited states of other high-Z atoms.

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