Branching ratios of Hg 5*d* and Cd 4*d*: Dirac-Fock calculations

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Dirac-Fock (DF) and Dirac-Slater (DS) calculations of the photoionization of Hg 5*d* and Cd 4*d* have been performed in an effort to assess the utility of such calculations for the prediction of subshell cross sections and branching ratios as well as to attempt to elucidate the effects of relativistic (especially spin-orbit) interactions. Our results indicate that in both cases, the subshell cross section is predicted rather well by the DF results, while the DS is too large (by a factor of ~ 2) and peaks too close to threshold. For the Hg 5*d* branching ratio, the DF values are in excellent agreement with experiment and the DS results are in pretty fair agreement as well. For Cd 4*d*, on the other hand, neither calculation is entirely satisfactory; away from threshold the DF result, however, is reasonably good. The possible origin and implications of these results are discussed.

I. INTRODUCTION

The role of relativistic effects in the photoionization of intermediate- and high-Z atoms in the near-threshold region has been only slightly explored. A significant tool in the study of these interactions is examination of the branching ratios for photoionization of the $j = l \pm \frac{1}{2}$ states of a particular nl atomic subshell. These have differing binding energies so that they can be separated experimentally via photoelectron spectroscopy.

In this paper we consider the photoionization of Hg 5*d*, as representative of a high-Z case, and Cd 4*d*, representing intermediate Z. The choice of the outer d states was dictated by the largeness of the cross section which minimizes the effect(s) of interchannel interactions. The particular elements were chosen over others owing to the body of experimental data available for these cases. The photoionization of Hg 5*d* has been the subject of a number of experimental[1-5] and theoretical[6-8] studies. Cd 4*d* has also been studied both experimentally[1,5,9,10] and theoretically.[7,11]

We have performed our calculations in two approximations, both based on the single-particle Dirac equation. The first was the relativistic generalization of Hartree-Slater which employs a central-field approximation to exchange known as Dirac-Slater (DS). The other was the relativistic generalization of Hartree-Fock, where exchange is considered exactly within the framework of single-particle wave functions, known as Dirac-Fock (DF).

In addition to assessing the importance of relativistic and exchange interactions and their interplay, we have performed these calculations to get at least a qualitative idea of the shape of the branching ratios of atomic 4*d* and 5*d* subshells. This is of importance since measurements have recently been made in the solid state.[12-15] Thus, to identify the effects of the solid-state environment, an assessment of atomic effects must first be made.

II. METHOD OF CALCULATION

The details of the method of calculation employed in this paper have been given elsewhere.[16] We briefly point out some of the more important features.

In this work, neither interchannel coupling nor any other sort of correlation effects have been included. Our Dirac-Slater (DS) calculation differs from that of Walker and Waber[7] in one important respect. As in Ref. 7, we used the computer code developed by Lieberman, Cromer, and Waber[17] to generate discrete wave functions and potentials. We used, however, the potential (and resultant initial and final continuum state) appropriate to the initial atomic state, while in Ref. 7 the potential due to a completely relaxed ionic core was employed. Our method is in keeping with the great body of photoionization done using nonrelativistic Hartree-Slater wave functions.[18]

In our Dirac-Fock (DF) calculation, the discrete wave functions were generated by the code of Desclaux.[19] The initial-state wave functions were atomic wave functions, while a completely relaxed DF ionic core was used to generate the wave functions of the final continuum states of the photoelectron. Off-diagonal Lagrange multipliers were used to insure orthogonality of the continuum orbitals to the bound states and the coefficients of the direct and exchange Slater integrals were obtained from Grant[20] and Smith and Johnson.[21] The entire

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DF, as well as DS, calculations were done in j-j coupling, the natural coupling scheme for solving the Dirac equation. The cross sections are calculated in Coulomb gauge which corresponds to the "velocity" form of the dipole matrix element.[22] We note parenthetically that, in our experience, DF velocity results most nearly equal to the Hartree-Fock (HF) "length" cross sections.[16]

III. RESULTS AND DISCUSSION

Dirac-Slater (DS) and Dirac-Fock (DF) calculations have been performed for the cross sections and branching ratios of the 5d subshell of Hg and the 4d subshell of Cd. The calculations have been carried out from threshold to about 150 eV above threshold in each case.

Fig. 1 shows a selection of theoretical and experimental results for the photoionization cross section of the 5d subshell of Hg. The experimental results of Cairns *et al.*[12] are modified by the renormalization due to Dehmer and Berkowitz,[3] while the theoretical curves include the DS and DF results of this paper as well as the Hartree-Fock (HF) result.[8] None of the calculated cross sections include any interchannel coupling or other correlation effects. The DS curve, resulting from the present work, differs from the results of Ref. 7 (not shown) in both the initial-state wave function and slightly in the potential, as discussed in the previous section. Specifically, the use in Ref. 7 of an *ionic* orbital, as opposed to the use of a less compact *atomic* orbital, for the initial discrete state results in a higher, sharper peak in the photoionization cross section which is closer to threshold. The qualitative features of the two DS cross-section results are, however, the same.

It is further seen that the agreement of our DS result with experiment is only qualitative. It is apparent from the above discussion that the DS result of Ref. 7 is in even poorer agreement with experiment. The HF result[8] is in better agreement with experiment than either of the DS results; however, it is still not very good. Previously, the importance of photoelectron-hole exchange interactions for 5d photoionization in heavy elements has been shown.[23] This improved agreement of HF over the DS results suggests that a DF calculation, which includes the photoelectron-hole interaction in the more appropriate j-j coupling scheme, should improve agreement still further. This is borne out well by our DF results shown in Fig. 1. It should be emphasized, however, that there is some uncertainty in the normalization of the experimental results of Cairns *et al.*[2] as discussed above, thereby rendering it premature to speculate on the relatively small difference between the DF and experimental cross sections.

In Fig. 2 are presented the results of our DS and DF calculations along with the experimental results of Shannon and Codling[5] for the branching ratio for photoionization of Hg 5d. The agreement among these is quite good. It should be pointed out that the deviation from the nonrelativistic statistical ratio of 1.5 is rather large. This is to be expected in view of the significant spin-orbit splitting of the $5d_{3/2}$ and $5d_{5/2}$ orbitals. However, the large deviation and energy dependence of the branching ratio cannot be explained solely on the basis of the kinetic energy effect, i.e., the splitting of the $d_{3/2}$ and $d_{5/2}$ thresholds. Dynamical

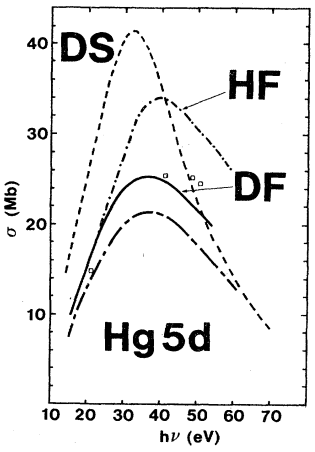

FIG. 1. Photoionization cross section of Hg 5d. The theoretical curves are the present Dirac-Slater (DS) and Dirac-Fock (DF) along with the Hartree-Fock (HF) results of Ref. 8. The experimental results are shown as squares (Ref. 4) and the (unlabeled) long dash-short dash curve (Ref. 2).

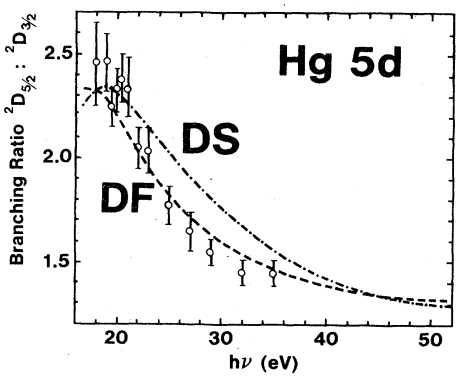

FIG. 2. $^2D_{5/2}:{}^2D_{3/2}$ photoionization branching ratios for Hg 5d. The theoretical curves are the DF (dashed) and DS (dot-dashed) results of this paper, while the experimental points are from Ref. 5.

effects on the initial- (and final-) state wave functions also play a role. This is shown in Fig. 3 where the theoretical $5d_{5/2}$ and $5d_{3/2}$ ($5d$ and $5d^*$, respectively) photoionization cross sections *per electron* are plotted versus photoelectron energy which spotlights the dynamical effects; if there were only a kinetic-energy effect, the $5d$ and $5d^*$ curves would coincide, in each case. As seen from Fig. 3, however, substantial differences exist, especially near threshold.

It is also evident from Fig. 3 that the maximum in the $5d$ cross section is below that of the $5d^*$. In the DS case, where the continuum wave functions are independent of which electron is photoionized, the shape of σ_{5d} and σ_{5d^*} are almost exactly the same, with the former being shifted slightly to lower energy. The shift is due to the $5d^*$ orbital being somewhat more compact than the $5d$ so that it is shifted inward (away) from the ϵf continuum orbitals ($d \rightarrow f$ dominates the cross section) and thus climbs more slowly and reaches its maximum at a higher energy, when the ϵf orbitals have moved in further. The situation is similar in the DF case, but here some changes in shape are evident as well, since the continuum orbitals differ depending upon which electron is photoionized. It is, nonetheless, striking that the DF and DS branching ratios are so similar, despite rather large (~50%) differences in absolute magnitudes of the cross sections in the two cases.

Our DF and DS results for the Cd $4d$ photoionization cross section are shown in Fig. 4, along with a many-body-perturbation theory (MBPT) result[11] and the experimental result.[10] The situation here is similar to the Hg $5d$ case. The DS curve is too high, by about a factor of 2, and peaks at too low an energy. The MBPT result is in much better agreement with experiment and the DF curve is still better, but only slightly. This may indicate that in the intermediate-Z region, relativistic effects as well as correlation are of importance. It must be realized, however, that the

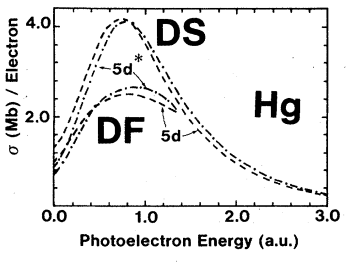

FIG. 3. Photoionization cross sections per electron for Hg $5d_{5/2}$ (labeled $5d$) and $5d_{3/2}$ (labeled $5d^*$) in DF and DS approximations plotted against photoelectron energy.

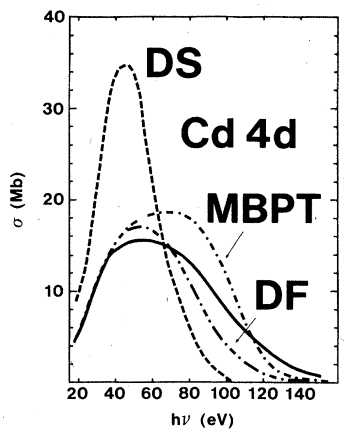

FIG. 4. Photoionization cross section of Cd $4d$. The theoretical curves are the present Dirac-Slater (DS) and Dirac-Fock (DF) along with the many-body-perturbation theory (MBPT) results of Ref. 11. The experimental results of Ref. 10 are shown as the solid curve.

model dependence of these calculations may well alter this tentative conclusion. It is interesting to note, however, that both MBPT and DF agree well with experiment (and each other) for the first 20 eV or so above threshold.

The branching ratio for Cd $4d$ is shown in Fig. 5 where our DS and DF results are given along with the extant experimental data.[5] Several points are evident from this plot. First is that the branching ratio is significantly closer to the statistical ratio of 1.5 than was the case for Hg $5d$. This is, of course, to be expected since the spin-orbit interaction, which causes this effect in the first place, is much weaker for Cd ($Z = 48$) than for Hg ($Z = 80$). Second is that the agreement between experiment[5]

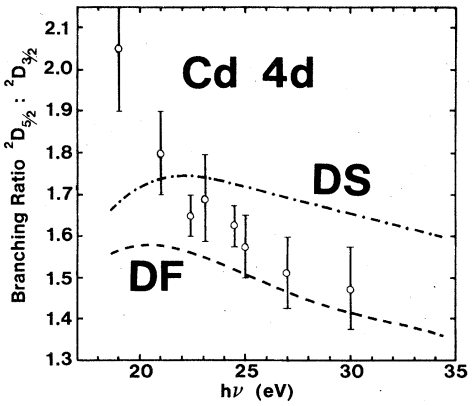

FIG. 5. $^2D_{5/2}:{}^2D_{3/2}$ photoionization branching ratios for Cd $4d$. The theoretical curves are the DF (dashed) and DS (dot-dashed) results of this paper, while the experimental points are from Ref. 5.

and theory, even DF, is not very good; extremely poor in the threshold region even as far as the qualitative shape is concerned. This is precisely the region, however, that the total subshell cross section agreed well, thus showing that the total cross section is not a good indicator of branching ratios. There is some evidence, as seen in Fig. 5, that at about 10 eV above threshold, the DF result is in fairly good agreement with experiment.

The question thus arises as to why the situation for Cd $4d$ is so different than for Hg $5d$. While we do not have a definitive answer, one strong possibility is the use of j-j coupling. This is quite well justified for Hg, but for Cd the true coupling scheme lies somewhere midway between j-j and LS and the exchange terms in the DF calculation are likely to be in error. Thus we believe that to insure quantitative accuracy in the intermediate-Z region, near threshold, the various j-j channels arising from photoionizing a $4d$ electron must be coupled. Based upon the limited experience of Cd $4d$, there is, however, some indication that the DF prediction will be reasonable starting ~10 eV above threshold.

In Fig. 6 the theoretical cross sections per electron are shown for DF and DS calculations. From these curves it is seen than the dynamical effects are rather different for DS and DF. The DS curves come together at $\epsilon \approx 0.8$ a.u., while the DF curves cross at about 0.4 a.u. and again at about 2.2 a.u. Then, since the kinetic-energy effect is so small for Cd $4d$, this indicates that the higher-energy behavior of the branching ratio is to smoothly go to the statistical ratio (1.5) from above at $h\nu \approx 40$ eV the DS approximation, while the DF prediction is that the branching ratio will continue to fall to a minimum of about 1.2 at $h\nu \approx 45$ eV, then rise to above 1.5 again at $h\nu \approx 80$ eV. It would be quite useful to have some experimental points in this energy region.

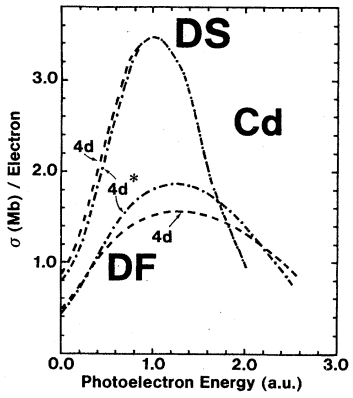

FIG. 6. Photoionization cross sections *per electron* for Cd $4d_{4/2}$ (labeled $4d$) and $4d_{3/2}$ (labeled $4d^*$) in DF and DS approximations plotted against photoelectron energy.

IV. CONCLUDING REMARKS

In this paper we have shown that the photoionization branching ratio for Hg $5d$ is predicted quite well be a DF calculation and fairly well by a DS calculation. Thus, this suggests, that these calculations can be used in other high-Z cases where no atomic experiment exists to survey the overall trends, as well as to compare with experiment on solid targets as a means of separating atomic and solid-state effects. In particular, the DS calculation may be adequate, which amounts to a significant saving in the necessary labor, particularly for open-shell atoms.

The case of Cd $4d$ was rather different since the DS result was in poor agreement throughout the energy range and the DF calculation only gave reasonable agreement at the higher energies, away from threshold. We tentatively attributed these facts to our use of j-j coupling which is not justified for an intermediate-Z atom. It would be most useful in sorting the situation out to have experimental data at higher energies, and for other atoms in this Z region.

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