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THE CALCULATION OF PHOTOIONIZATION CROSS SECTIONS

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1. INTRODUCTION

Photoionization is a sensitive probe of many-body and spin-dependent interactions. One can test our understanding of these interactions and the role they play in atomic dynamics by comparing the results of theoretical calculations with corresponding experimental measurements. One finds from such comparisons that our understanding of the photoionization process in atoms is excellent in many cases, imperfect in many others, and inadequate in still others. One finds in general also that the kinds of many-body and spin-dependent interactions included in a calculation is, in many cases, a more important consideration than the particular calculational method employed.

In this brief report we sketch those aspects of the photoionization process which are well understood as well as those which are not. We then comment on recent calculations for an eclectic assortment of atoms from throughout the periodic table. We close with remarks on some recent theoretical developments. No attempt at a definitive review of this growing field is made here. However, the situation up to about 1982 has been reviewed by the author elsewhere. (1)-(4)

2. GENERAL FEATURES OF PHOTOIONIZATION CROSS SECTIONS

Particular electronic interactions have characteristic effects on photoionization cross sections. These may be outlined as follows:

2.1 Effective Potential Effects

A characteristic feature of VUV photoionization cross sections of the outer subshells of heavier atoms (i.e., $Z \geq 18$) is a delayed maximum above the ionization threshold.[5] This is due to an effective potential barrier seen by $\ell = 2$ and $\ell = 3$ photoelectrons in the region of the outer edge of the atom which lowers the probability of their escape until they have enough excess energy to surmount the barrier. Such behavior is non-hydrogenic. Furthermore, in cases where an inner subshell with $\ell = 2$ or 3 is being filled as Z increases (as in the transition metals, the lanthanides, and the actinides) there is a double well potential. This double well has profound effects on the 3p-subshell spectra of the transition metals, the 4d-subshell spectra of the lanthanides, and the 5d-subshell spectra of the actinides, as well as on atoms with Z just below those of these series of elements. [6],[7]

The nature of cross section minima has long been of theoretical interest. These minima arise due to a change in sign of the radial dipole transition matrix element in a particular channel.[8],[9] Rules for predicting their occurrence have been developed.[10] Studies of their occurrence in photoionization from excited states,[11] in high Z atoms,[12] and in relativistic approximation[13] have been carried out. Only recently, has a proof been given[14] that such minimum do not occur in atomic hydrogen spectra. For other elements, theory has recently provided further rules on when and how many minima may occur.[15]

2.2 Particle - Hole Interaction Effects

The experimental photoionization cross sections for the outer subshells of the rare gases near the ionization thresholds can be understood theoretically in terms of certain kinds of interactions (between the photoelectron, the residual ion, and the photon field) which are called in many-body theory language, "particle-hole" interactions. These have been discussed in some detail elsewhere.[1],[2],[4] We discuss here very briefly the three major kinds of particle-hole interactions.

Intrachannel interaction effects are taken into account automatically when the correct Hartree-Fock (HF) basis set is employed. This is the HF basis in which the photoelectron sees a net Coulomb field due to the residual ion and is coupled to the ion to form the appropriate total orbital, L, and spin, S, angular momenta. Any other basis set requires explicit treatment of intrachannel interactions. Such interactions tend to broaden cross section maxima and push them to higher photon energies (as compared to central potential model calculations).

Ground state correlation effects are necessary to bring HF-level calculations into agreement with experimental measurements in the case of photoionization cross sections for the rare gases. The most important ground state correlations are those involving the excitation of a virtual pair of electrons out of the closed-shell, ground configuration. The incoming photon may then de-excite one of these virtually-excited electrons back to its initial state, leaving the other electron to go off with the appropriate kinetic energy. Such interactions imply that atoms are more diffuse than is the case in the HF model. They tend to reduce the HF-predicted photon energy at which the cross section has a maximum to values in agreement with experiment.

Interchannel interaction effects are usually very conspicuous features of photoionization cross sections. When the interacting channels have partial photoionization cross sections which differ greatly in magnitude, one finds theoretically that the calculated cross section for the weaker channel is completely dominated by the effect on it of its interaction with the stronger channel. At the same time, it is often a safe approximation to ignore the effect of weak channels on stronger channels. In addition, when the interacting channels have differing binding energies, then their interchannel interactions lead to resonance structure in the channel with lower binding energy (arising from its coupling to the Rydberg series in the channel with higher binding energy).

2.3 Discussion of Ab Initio Theoretical Methods for Photoionization

Most of the ab initio theoretical methods for the calculation of photoionization cross sections (e.g., The Many-Body Perturbation Theory (MBPT) Method,[16] The Close-Coupling (CC) Method,[17] The R-Matrix Method, [18] The Random Phase Approximation (RPA) Method,[19] The Relativistic RPA Method,[20] The Transition Matrix Method,[21] The Multi-Configuration Hartree-Fock (MCHF) Method,[22] etc.) have successfully calculated outer p-subshell photoionization cross sections of the rare gases by treating in their alternative ways the key interactions described above, i.e., the particle-hole interactions. In general, these methods all treat both intrachannel and interchannel interactions to infinite order and differ only in their treatment of ground state correlations. (The exception is MBPT, which often treats interchannel interactions between weak and strong channels only to 1st or 2nd order.) These methods therefore stand in contrast to Central Potential Model Calculations, which do not treat any of the particle-hole interactions, and single-channel Term-Dependent HF calculations, which treat only the intrachannel interactions.

The fact that the widely different treatments of ground state correlations in these ab initio theoretical methods do not lead to significantly different calculated photoionization cross sections is an indication of the perturbative nature of these ground state correlations. Indeed, the MBPT treats ground state correlations only to first or second order, the CC, R-Matrix, and MCHF methods treat them by configuration interaction, and the RPA and RRPA methods treat them to infinite order (violating the Pauli Principle in the process[23]). Furthermore, the ground state correlations found to be most important are those in which a <u>pair</u> of electrons in the ground configuration subshell $n\ell^q$ is excited to states having angular momenta $\ell + 1$, e.g., as in $3p^6 \rightarrow 3p^4$ nd n'd in argon.

One may conclude therefore that on the basis of our collective experience with the calculation of photoionization cross sections for closed-shell atoms, <u>any</u> theoretical method for the calculation of photoionization cross sections which includes the key particle-hole interactions discussed

above is to be preferred over theoretical methods which do not include these interactions. This rule of thumb separates those simpler calculational methods as well as those which treat correlation effects in only the initial or in only the final state from the more sophisticated ab initio theoretical methods mentioned above which attempt a more systematic treatment of electron correlation effects. Distinguishing among these latter theoretical methods is a much more difficult task that is highly dependent on the atom (and even the subshell!) under consideration and on the treatment of additional interaction effects which are often prominent in only particular energy regions. Some of these additional interactions are described in the next section.

2.4 Additional Interaction Effects

A number of interactions, not of the particle-hole type, lead to conspicuous effects in localized energy regions. Among these are the following:

(a) **Relativistic and Spin-Dependent Interactions.** The fact that $j = \ell - 1/2$ electrons are contracted more than $j = \ell + 1/2$ electrons at small distances has an enormous effect on the location of cross section minima in heavy elements.[13],[24] It may explain the large experimentally observed differences in the resonance profiles of a resonance decaying to final states that differ only in the fine structure quantum numbers.[25]

(b) **Inner-Shell Vacancy Rearrangement.** Inner-shell vacancies often result in significant production of satellite structures in photoelectron spectra. Theoretical calculations for inner subshell partial photoionization cross sections are often substantially larger that experimental photoelectron measurements.[26] It is thought that this difference is due to such satellite production.

(c) **Polarization and Relaxation Effects.** It is well known that negative ion photodetachment cross sections often exhibit strong effects of core polarization near threshold. These effects can be treated semiemperically, resulting in excellent agreement between theory and experiment.[27] Less well known is the fact that even for inner shell photoionization cross sections of heavy elements, ab initio theories do not reproduce experimental measurements near threshold without the inclu-

sion in the theory of polarization and relaxation effects. [28]-[29] Note, however, that for the outer p^6 subshells of the negative halogen ions (which have the same configuration as the rare gases), RRPA calculations of the photodetachment cross section have provided results in good agreement with experiment without the inclusion of polarization effects (just as they do for the outer subshells of the rare gases).[30]

(d) **An Example.** The calculation of the energy dependence of the photoelectron angular distribution asymmetry parameter, β, for the 5s subshell of xenon appears to require the theoretical treatment of all of the above effects. In the absence of relativistic interactions, β in this case would have the energy-independent value of 2. Deviations of β from 2 are therefore an indication of the presence of these relativistic interactions. Not surprisingly, the greatest deviation of β from 2 occurs in the localized energy region where the partial photoionization cross section for the 5s subshell has a minimum. In this region, however, relativistic theoretical calculations show larger deviations from 2 than are observed experimentally. It is thought that inner shell rearrangement and relaxation effects play an important role here.[31]

3. PARTIAL SURVEY OF THE ELEMENTS

It is frequently instructive to study together elements having common characteristics in order to understand the role of electron correlations on their photoionization spectra. We comment briefly on some recent findings for four groups of elements:

3.1 Open p-subshell Atoms

The 3p-subshell photoionization cross section of atomic chlorine has been studied extensively by various theoretical methods.[32] One reason for this interest is its proximity in the periodic table to argon, a very well understood atom. In contrast to argon, however, one finds that the relative strengths of the different particle-hole interactions are different. Where-

as in argon the final-state, interchannel interaction is weak and the ground state, virtual-electron-pair interaction is strong, in chlorine the final-state, interchannel interactions are strong and the ground state, virtual-electron-pair interactions are weak. Thus there appears to be a significant difference between closed and open subshells for the theoretical treatment of electron correlation effects. This difference seems to hold also for inner subshells of open-shell atoms.[33]

Samson, et. al., have recently obtained absolute experimental measurements for the photoionization cross sections of two open p-subshell atoms: atomic chlorine[34] and atomic oxygen.[35] In the energy region starting several electron volts above the lowest three ionization thresholds (in LS-coupling) and beyond, agreement of experiment with theory is quite good. There are significant differences between theory and experiment, however, in the vicinity of the $C\ell^+3p^4(^1S)$ ionization threshold and the $O^+2p^3(^2P)$ ionization threshold.[34],[35] In each of these cases experiment is significantly larger than theory. This near threshold effect is not understood theoretically at present.

3.2 Transition Metal and Lanthanide Atoms

Recent experimental photoelectron spectra of the transition metal[36] and lanthanide metal[37] atoms have provided a fairly detailed picture of the extent of inner-shell vacancy rearrangement processes occurring during photoionization. One finds in particular that the relative strength of alternative inner vacancy decay mechanisms is highly dependent on atomic number. Recent theoretical calculations[38] appear to agree with experiment in describing some of the most important features of the spectra, in particular, the dominance of super Coster-Kronig transitions on the 3p-subshell transition metal spectra.[38a]

3.3 "Two-Electron" Atoms

The atoms having outer s^2 subshells (i.e., He, Be, Mg, Ca, Sr, and Ba) have been frequently studied theoretically because of the strong electron correlation effects exhibited in their photoionization spectra. For He it is

well known from hyperspherical coordinate studies that final states having so-called "+" character dominate the observed spectra.[4] Calculations for Be[39],[40] as well as for the heavier elements Mg[40] and Ca[41] find similarly that "+" type states dominate, at least for radial distances near the origin. Whereas ab initio theoretical calculations for Ca[42] and Ba[43] have given reasonable agreement with experiment, calculations for Mg[40], Ca[41], and Sr[44] using Greene's eigenchannel R-matrix method have produced theoretical results that are in excellent agreement with experiment. Among the reasons for the success of Greene's method are, firstly, that he focuses at small radial distances on two-electron interactions by diagonalizing the Hamiltonian within an over-complete two-electron basis of orbitals; secondly, the atomic core electrons are represented by a semi-empirically--determined model potential; and lastly, for large radial distances the photoelectron wave function is represented analytically by means of quantum defect theory.

4. SOME NEW THEORETICAL DEVELOPMENTS

Two of the most successful theoretical methods for describing atomic collision processes, the quantum defect theory[45] and the R-matrix theory,[18] were developed in Britain and have been adopted and extended by groups elsewhere. We mention here two recent extensions which are particularly noteworthy.

The quantum defect theory (QDT) was developed to describe analytically the rapid energy variation of atomic collision cross sections in the vicinity of thresholds for escape of an electron in a Coulomb field.[45] The key point is that such an analytic description of rapidly varying quantities frees theory to concentrate on the numerical calculations of dynamical quantities which vary only slowly with energy. These benefits have now been extended by Greene et. al. [46] to long-range potentials other than Coulomb ($1/r$), i.e., to dipole potentials ($1/r^2$) and polarization potentials ($1/r^4$).

The R-matrix theory's rationale is to restrict the heavy numerical computation of many-electron interaction effects to a small sphere of radius r_0 about the nucleus of the atom or ion.[18] Beyond r_0, the numerical wave functions may be matched onto wave functions whose form is given by QDT or its generalizations. The recent calculations[40],[41],[44] using Greene's eigenchannel R-Matrix approach have shown that, for the alkaline earth elements at least, a good description of two-electron interactions inside r_0 is essential. Indeed, these calculations represent all but the outer two electrons by a semi-empirical potential. At the same time, Burke, Nobel, and Scott[47] have proposed a completely ab initio approach in which the region inside r_0 is further subdivided into two regions: An inner region, $r \leq r_1 < r_0$, in which interactions among all electrons are treated, and an outer region, $r_1 \leq r \leq r_0$, in which two-electron interactions are treated explicitly. Both of these approaches and their future extensions promise to provide accurate theoretical predictions of the detailed experimental results for heavier atoms that are becoming increasingly common nowadays.

5. CONCLUSIONS

For all but the lightest elements, a minimum requirement for reliable theoretical calculations of photoionization cross sections is that they treat explicitly the particle-hole interactions known to be important for the rare gases. For heavier atoms or for inner shells, particularly in the vicinity of cross section minima, additional interactions (e.g., relativistic and spin-dependent interactions, core rearrangement processes, polarization effects, etc.) must often be treated to achieve good agreement with experiment, at least in localized energy regions. Applications of advanced theoretical approaches to photoionization processes for atoms other than the rare gases are providing much new information on the specific many-body interactions which govern atomic dynamics.

6. ACKNOWLEDGEMENT

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