CORRELATION EFFECTS IN PHOTOELECTRON SPECTROMETRY OF ATOMS*

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ABSTRACT

As intense, continuously-tunable photon sources become available throughout the vacuum-ultraviolet and soft-x-ray energy range, it is useful to survey the effects that can be studied using photoelectron spectrometry. Such a survey is presented, and examples are cited to illustrate the current state of our knowledge in this area.

Photoelectron spectrometry differs from absorption studies in that kinetic energy analysis of electrons yields information about each channel in a photoionization event, rather than yielding only the total cross-section. Electron angular distribution measurements can also provide further information about spins and multipolarities. Probably the most intriguing feature of electron spectrometry is the direct insight that it can give into electron correlation effects.

In a general description of electron correlation effects there is no necessity to consider one-electron orbitals. However, as a heuristic device it is convenient to do so, and to consider at least four "different" manifestations of electron correlation in electron spectrometry: initial-state configuration interaction (ISCI), final-ionic-state configuration interaction (FISCI), continuum-state configuration interaction (CSCI), and autoionization. There now exist

rather well-understood examples of CI satellites, which will be cited and reviewed. Future directions that further studies of these and related phenomena might take to better understand electron correlation in atoms will be discussed.

I. Introduction

Electron-electron correlation plays an important role in the electronic structure and properties of atoms. Any real improvement of our theoretical understanding of many-electron systems, beyond that afforded by the one-electron model, is possible only if correlation is taken into account. Several experimental manifestations of electron correlation have been known in optical spectroscopy for many years.¹ These include, for example, deviations of line intensities or energy interval spacing from expectations based on an independent-electron model. With the advent of tunable-energy synchrotron radiation it has become possible to extend absorption measurements into the vacuum ultraviolet and to study such manifestly correlation-dependent effects as autoionization. We may note as a good example of autoionization in the vacuum ultraviolet the absorption spectrum of atomic barium near the 5p ionization threshold, reported by Connerade, et al.²

With such an abundance of optical data available, collected over the years by many workers, a great deal of information about electron correlation in atoms is already available. We should ask, then, at the outset: what can photoelectron spectrometry tell us about correlation that is new and unique?

The answer may be given in two parts. First, photoelectron spectrometry clearly affords the possibility of obtaining much more information about an atomic system than does an absorption experiment. This point is illustrated in Fig. 1, which shows that photoelectron

spectrum of atomic barium as excited by a laboratory HeI lamp, together with the barium energy-level scheme.³⁻⁵ This detailed spectrum was obtained in large measure by the use of a single photon energy (with some contribution from electrons ejected by satellites of the main HeI α line). Each of the autoionization resonances in the absorption spectrum would presumably yield a similar electron spectrum, differing in detail. Clearly a wealth of additional information is provided by electron spectrometry.

Second, the final states reached in photoelectron spectrometry - and the intensity with which they are populated - give a very direct indication of the nature of the correlation being studied. This is particularly evident in a configuration-interaction framework. It is a consequence of the fact that electrons are being removed singly and the resultant states observed directly.

In this paper we shall review first the observation of final-ionic-state correlation (FISCI) by electron spectrometry, in Section II. The main principles are illustrated by selected examples. Initial-state correlation (ISCI) is treated next (Section III). In Section IV several cases are reviewed in which both ISCI and final-state CI play important roles. Finally, the relation between satellite structure in x-ray emission and x-ray photoelectron spectra is discussed briefly in Section V.

II. Final-Ionic-State Configuration Interaction (FISCI)

Final-state configuration interaction can be classified in the three categories of autoionization, a resonant process that actually

encompasses the other two (treated briefly in Section IV), and the non-resonant processes of final-ionic-state CI (FISCI) and continuum-state CI (CSCI), which includes the unbound electron. In this Section we discuss FISCI although CSCI is undoubtedly also present in some or all of the cases cited below.

The oldest and best-known example of FISCI is the "shake-up" phenomenon, studied particularly in rare gases by Carlson, Krause, and co-workers.⁶ Here, FISCI is manifest through weak satellites at higher binding energies accompanying the Ne 1s, etc. peaks. The origin of these peaks is shown diagrammatically in Fig. 2.^{7,8} Time evolves upward in this diagram. The first vertex corresponds to photoemission of a 1s electron from neon into a continuum p state (ϵp). Collapse of the residual valence shell to shield the 1s hole thus created is denoted by the second vertex, in which a 3p electron and a 2p hole are created. This is a useful diagram, but the mechanism must not be taken literally (as in any diagram). The final state — a $\text{Ne}^+(1s^2 2s^2 2p^5 3p)$ state — exists independently of photoemission and is reached by exactly the same mechanism as is the "main" $\text{Ne}^+(1s^2 2s^2 2p^6)$ state.⁹ Shake-up of this kind, accompanying core ionization, is often given a special designation, such as "core rearrangement".⁷ We emphasize, however, that it is operationally indistinguishable from other cases of FISCI.

The 3s shell in Mn^{3+} provides the next example of FISCI.¹⁰ In this case, as illustrated diagrammatically in Fig. 3, a 3s electron may be regarded as being photoejected into an ϵp state. The 3s hole is then converted into a 3p hole, with another 3p electron being

simultaneously excited into a 3d orbital. In the language of configuration interaction which Bagus, et al.¹¹ used to describe this case originally, the nominal primary final state configuration — $3s3p^6 3d^5; ^5S$ — is essentially degenerate with $3s^2 3p^4 3d^6; ^5S$ (which forms two levels). The latter configuration can be formed from the former by the promotion $p^2 \rightarrow sd$. The energy cost is very slight because the s orbital lies below the p orbital. Configuration interaction among the three above levels leads to three 5S peaks in the photoelectron spectrum, as observed. This case is slightly complicated by multiplet splitting, which gives rise to a 7S state as well, but that state can be ignored for the present discussion. Incidentally, a single 7P peak and several 5P peaks are also observed in the Mn^{3+} spectrum,¹² but their origin is multiplet coupling within the $p^5 d^5$ configuration.¹³

The diagram in Fig. 3 also applies as written to the well-known case of satellite structure in the 3s photoelectron spectrum of argon. The configuration is $1s^2 2s^2 2p^6 3s3p^6$ in this case, and the $p^2 \rightarrow sd$ transfer admixes configurations such as $1s^2 2s^2 2p^6 3s^2 3p^4 3d$. The first clue to this behavior was provided as early as 1965, when Bagus¹⁴ found that ASCF calculations gave an Ar(3s) binding energy about 4 eV above the experimental value. More recently, Luyken, et al.¹⁵ surmised that admixture of the configuration $3s^1 3p^6 (^2S)$ and $3s^2 3p^4 nd (^2S)$ was necessary to explain the experimental intensities in the Ar^+ optical spectrum. Spears, et al.¹⁶ found intense satellite structure in the Ar 3s,3p photoelectron spectrum, as listed in Table I. They interpreted the strongest satellite peaks, at binding energies 9.4 eV and 11.9 eV above the 3s peak as arising in this way. A less intense

shoulder at 8.1 eV was attributed to a $2P$ final state in Ar^+ , which would be a satellite of the $3p$ hole state. To test these assignments, and to understand the $L_{2,3}$ x-ray emission satellites reported by Cooper and LaVilla,¹⁷ R. L. Martin in our laboratory carried out a comprehensive configuration interaction calculation¹⁸ on Ar^+ . We summarize these results below, inasmuch as this calculation represents a serious attempt to understand the satellite structure quantitatively.

Martin used a set of Slater-type orbitals (STO) optimized by Bagus,¹⁴ to which he added optimized $3d$, $4p$, and $5p$ STO's. A number of Rydberg orbitals were also included as virtual orbitals, as well as additional $3s$ and $3p$ STO's which provided for polarization in the $n = 3$ shell. Finally eight reference configurations were selected and a configuration list was developed which consisted of the union of all single replacements of orbitals in the reference list with virtual orbitals. A total of 300 configurations were thus included in the CI calculation.

The $2P$ manifold based on the $3p$ hole state was found to be unimportant. The strongest satellite — of $3s^2 3p^4 4p$ character — was found to lie 7.3 eV above the main $3s$ hole peak, with 1.2% of its intensity. The $3s^2 3p^4 4s(^2S)$ state was calculated to lie nearby, with 2.5% intensity. Thus the shoulder reported by Spears, et al. appears to be of mixed $2P$ and $2S$ origin, as indicated in Table I.

The two main satellite peaks are calculated to arise from $3s^2 3p^4 4d; ^2S$ at 10 eV and $3s^2 3p^4 4d; ^2S$ at 12 eV. The intensity of the former is in good agreement with experiment, while that of the latter

is much too high. This follows because the $3s^2 3p^4 4d$ state interacts strongly with the shake-off continuum based on $3s^2 3p^4 ed$, as noted by Luyken, et al.¹⁵ and by Amusia, et al.¹⁹ Martin found (Table I, Basis 2) that inclusion of a 3d STO with $\xi = 3.5$ (to simulate the continuum function) reduced the 12 eV peak intensity from 25% to 18%, confirming this idea. We note that for this valence-shell case, the x-ray emission satellite intensities are about equal to those from XPS. Finally we note that inclusion of FISC1 increased the probability of "multiple excitation" from 4% to 40% while reducing the 3s binding energy by 7 eV.

From the above two examples, one might infer that FISC1 might lead to satellites on the s hole peaks of XPS spectra rather generally, because of the $sp^6 + s^2 p^4 d$ excitation. This is in fact the case.¹⁸ Table II shows the systematic variations in such satellites' energy separations for 3s, 4s, and 5s shells. The 5s shell of Xe provides a very interesting case, discussed in Paper I-27 of this Conference.²⁰ In this case, many-body techniques have been employed to account for the complex origins of satellites.

We turn now briefly to an extreme case of FISC1: the 4p spectrum of barium. Wendin and Ohno have discussed this case in detail.²¹ The reader is referred to their paper for a full discussion. We mention the Ba(4p) case here because of its importance and because of certain unique features.

Absorption²² and photoelectron spectroscopy²³ studies of the 4s,p region of xenon showed that no $4p_{1/2}$ state could be identified,

and that both the $4s$ and " $4p_{3/2}$ " states fall at energies lower than expected on the basis of Δ SCF calculations. In fact the " $4p_{3/2}$ " peak showed structure and the $4p_{1/2}$ region showed many weak peaks in the photoelectron spectrum. Wendin and Ohno showed that FISC1 accounts for all of these effects. In the $4s$ case, the $Xe^+ 4s$ unmixed hole state lies just below the $Xe^{++} 4p^5 4d^9$ ionization threshold. It mixes with the $4p^5 4d^9$ cf continuum states as well as discrete $4p^5 4d^9$ nf Rydberg states below the threshold. Wendin and Ohno describe this process as "dipole fluctuations" in the language of many-body theory. It has also been termed a "virtual Coster-Kronig" or "virtual super Coster-Kronig"²⁴ process, depending on whether the specific channel under discussion was an NNO or NNN transition, respectively (e.g., $4p^5 4d^{10} \rightarrow 4d^9 5p^5$ nd or ed, versus $4p^5 4d^{10} \rightarrow 4p^6 4d^8$ mf or ef). In the $4s$ case the $4s$ state is thus substantially admixed, and lowered in energy by 9 eV below the Δ SCF position, but is still an identifiable $4s$ state. The $4p_{1/2}$ and $4p_{3/2}$ one-electron states, on the other hand, lie above the onset of the $Xe^{2+} 4d^8$ continuum and are admixed much more strongly with configurations such as $4d^8$ nf, $4d^8$ cf, etc. The $4p_{1/2}$ state is thereby completely obliterated and admixed into many small peaks, while the main peak corresponds to the lowest state in the spectrum. It is more accurately characterized as $4d^8 4f$ than as $4p_{3/2}$ (as its structure proves), but is strongly mixed. A contributing diagram is depicted in Fig. 4. In the $Xe^+ \overline{4s}$ case FISC1 is thus very strong, and in the $\overline{4p}$ case, the one-electron picture is actually meaningless, as Wendin and Ohno have pointed out.

III. Initial-State Configuration Interaction (ISCI)

Photoelectron spectra are also strongly affected by electron correlation in the initial state. This is particularly easily understood in the CI framework. For example, the valence shells of the Groups IIA and IIB elements are nominally $ns^2, ^1S$. However, np^2, nd^2, nf^2 configurations can also mix into the ground state (in 1S coupling). Whereas ns^2 can yield only $nsep$ final states, the ionic states np, nd, nf , etc., may be reached and observed as satellites via photoemission involving the admixed configurations. A diagrammatic representation is given in Fig. 5.

To date, ISCI has been reported in the ns^2 cases Zn,²⁵ Cd,^{25,26} Hg,^{25,27} Ca,²⁵ Sr,²⁵ Ba,²⁵ Sm,⁵ Eu,⁵ and Yb.⁵ A typical spectrum - that of calcium excited by HeI radiation - is shown in Fig. 6. The ISCI peaks $4p, 3d, 5s$, and $4d$ are clearly visible. It would be valuable to interpret the intensities of these peaks quantitatively, perhaps leading to a quantitative evaluation of the ground-state admixtures of $4p^2, 3d^2$, etc. Unfortunately, this will require more knowledge of photoionization cross-sections than is presently available. Configuration-interaction calculations²⁸ by Kim and Bagus and by Hansen have shown d^2 admixtures into the s^2 ground state of Group II atoms, but with amplitudes too small to explain the observed intensities without other factors (i.e., cross-section enhancement or other channels).

ISCI effects have also been studied in the s^2p^2 case of Pb vapor²⁹ and in the s^2p^3 case of Bi vapor.³⁰ Of special interest is the predominantly $p_{1/2}$ character of the p^2 ground state in Pb. This is a

consequence of spin-orbit splitting and again well-known in optical spectroscopy.³¹ The photoelectron spectrum of Pb shows an intense $Pb^+ 2P_{1/2}$ line and only a very weak $2P_{3/2}$ line. Several ISCI satellites are present, originating from sp^2d and s^2d^2 admixtures in the ground state.

IV. Combined ISCI and Final-State Effects

Strictly speaking, a completely rigorous separation of correlation effects in the initial and final state is usually not possible. This is clear in the framework of configuration interactions because the description of configurations in terms of one-electron orbitals is always somewhat arbitrary. It is still convenient (and quite accurate), however, to classify many cases as either ISCI or FISCI; indeed this was the basis of the above Sections. In some cases initial- and final-state CI are both present to such an extent that both must be considered to obtain a description of the spectrum that is even approximately correct. Two such cases are discussed here.

The first is autoionization in the $5p^6$ shell accompanying resonant excitation in the light rare earths,⁵ together with ISCI. Among the types of final interactions, autoionization alone is a resonant process, while ISCI, of course, is not. Starting with barium ($Z=56$), in which autoionization by HeI resonant radiation is well-known (Fig. 1), the $5p^5$ ionization threshold does not increase rapidly with increasing atomic number, because the added $4f$ electrons in large measure shield the concomitant added nuclear charge. In the heavy rare earth, ytterbium ($Z=70$), there is no evidence for HeI-induced auto-

ionization, indicating that the $5p^5$ threshold is too high.⁵ Recent unpublished VUV absorption spectra by J. P. Connerade, et al. confirm this picture. As a result, the light rare earths possess $5p^5$ thresholds that lie within reach of the HeI α line or its higher-energy satellites, leading to autoionization. At the same time these elements should show ISCI in their valence s^2 configurations. In fact only - or predominantly - ISCI is present in their NeI photoelectron spectra, for which the photon energy is too low to permit autoionization.⁵ This result was found in both Sm and Eu, both of which also showed autoionization under irradiation with the HeI α lines. In some cases the same final states could be reached by both paths. For example, the $4f^6 5d$ states of Sm^+ could be reached directly by ionization of the $4f^6 5d^2$ configuration admixed into the nominally $4f^6 6s^2$ ground state of Sm. It could also be reached through the path

where the two steps denote resonant excitation of a Rydberg state followed by autoionization, with both 6s electron being lost in the second step; i.e., $6s^2 \rightarrow 5p6p$. Separation of the contributions due to autoionization and to ISCI would yield a wealth of information about electron correlations in these atoms. It will be a very complicated problem, however, which can be greatly aided by the use of monochromatic, tunable synchrotron radiation to separate the resonant and the nonresonant process.

For the second example of combined ISCI and final-state CI

effects, we return briefly to the case of shake-up in the Ne(1s) photoelectron spectrum. Gelius²³ reported a high-resolution XPS spectrum in which some 13 satellites of the main Ne(1s) hole-state peak were identified. In unpublished final-state CI calculations in 1969, P. Bagus and U. Gelius had shown that the energy separations of these satellites could be fitted rather well. The intensities remained a problem, however, until Martin⁹ found that ISCI was equally important in determining the transition strengths to these satellites. Thus a $\text{Ne}^+(1s2s^2 2p^5 3p)$ state can be reached either through FISCI, as previously believed, via the admixture of $\text{Ne}^+(1s2s^2 2p^6)$ into it, or through ISCI, via photoionization of a $1s^2 2s^2 2p^5 3p$ component in the ground state. In fact it is possible to make a fairly direct estimate of the relative importance of various configurations mixed into the ground state, from visual inspection of the intensities of the shake-up satellites. This means that shake-up spectra are of interest generally, rather than only to photoelectron spectroscopists.

V. Satellite Intensities in XES and XPS

In Section II we noted that the relative intensities of the Ar^+ (3s) satellite structure were about the same, relative to the main line, in x-ray emission spectra and x-ray photoemission. Theory and experiment were in agreement on this point, and it was also noted that the satellites were separated by several eV from the main peak in both cases. Rather general arguments can be made¹⁸ to show that this behavior should be observed whenever valence-to-core x-ray transitions are studied in conjunction with the relevant valence-shell

x-ray photoelectron spectra.

Of equal interest is the case of core-to-core x-ray emission spectra, in which the satellite intensities are usually very small, in contrast to the very intense satellites observed in XPS spectra of the same (outer) core levels. For example, Asada, et al.³² noted that in NiF_2 a strong satellite structure appears in XPS on both the $2p_{1/2}$ and the $2p_{3/2}$ lines, while the $K\alpha_{12}$ x-ray lines show no such structure. Martin, et al.⁹ have given a simple model that appears to explain this result, as shown in Fig. 7.

Let us approach this problem by considering the Ni^{2+} -ligand moiety; e.g., the cluster NiF_6^{4-} . This cluster would have a ground state and a spectrum of excited states at optical energies. If the charge on the Ni^{2+} core were increased by one unit, without changing the valence-electron configuration, there would still be a ground state and various excited states of the valence shell in this new system. Let us now focus on just two states: the ground state "g", and an excited (valence) state "e", of the same symmetry. The XPS shake-up spectra of transition-metal salts are usually explained in terms of a ground state configuration and a ligand-to-metal charge-transfer configuration, which would be our g and e. Referring to Fig. 7, we note that the valence configurations of states g and e (denoted by ψ_g and ψ_e) will be essentially the same regardless of which core electron is missing. Thus for a $\text{NiK}\alpha$ transition, $\psi_{1g} \cong \psi_{2g}$ and $\psi_{1e} \cong \psi_{2e}$, where 1 and 2 denote the 1s and 2p hole-state manifolds, respectively. Furthermore $(\psi_{ie} | \psi_{ig}) = 0$ for $i = 1, 2$ of necessity. Thus $(\psi_{ie} | \psi_{jg}) \cong 0$, where $i \neq j$. Now consider first XPS, then

XES, satellites.

In the Ni(2p) XPS spectrum, both the primary 2p state (P_2) and the secondary state S_2 will be populated. This follows because the overlap of Ψ_{2g} with the NiF_6^{4-} ground-state valence-electron configuration will be substantially less than unity as a result of polarisation toward the Ni^{3+} core. Much of this overlap is apparently taken up by the Ψ_{2e} configuration, producing large XPS satellites. The same behavior would be expected for the NiF_2 1s XPS spectrum, according to this picture.

Depopulations of the 1s-hole states would proceed almost entirely through channels A and D, in preference to channels B and C, because of the orthogonality of the g and e states. Insofar as the e-g splitting is nearly identical for the 1s and 2p manifolds, transitions A and D would be nearly degenerate in energy, and only one peak would be observed in the XES spectrum. Thus satellites would be intense in XPS but not apparent in XES.

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TABLE I. ARGON XPS AND XES SATELLITE INTENSITIES^a

Final State	XPS (I_1/I_0)			XES (I_1/I_0)	
	Exp.	Basis 1	Basis 2	Exp.	Basis 2
$3s^1 3p^6$	100%	100% (0.60)	100% (0.63)	100% (219.2, 221.4 eV)	100% (223.2 eV)
$3s^2 3p^4 4s$	$3 \pm 2\%$ (8.1 eV)	1.8% (7.4 eV)	2.5% (8.8 eV)		3.6% (8.8)
$3s^2 3p^4 3d$	$17 \pm 2\%$ (9.4)	18.1% (9.5)	14.4% (10.4)		14.7% (10.4)
$3s^2 3p^4 4d$	$6 \pm 3\%$ (11.9)	25.4% (12.3)	15.1% (13.0)	35% (11 eV)	14.8% (13.0)
$3s^2 3p^4 5s$	—	1.7% (13.3)	0.6% (14.8)		0.5% (14.8)

^a) From Ref. 18.

TABLE II. XPS CORRELATION SATELLITE SEPARATIONS (eV)^{a,b,c}

nl = 3s	(Cl ⁻) 6	(Ar) 11(25%)	(K ⁺) 14	(Ca ⁺²) 16
4s	(Br ⁻) 4	(Kr) 6.5(30%)	(Rb ⁺) 11	(Sr ⁺²) 13.5
5s	(I ⁻) 3.6	(Xe) 6.0(58%)	(Cs ⁺) 9.3	(Ba ⁺²) 9.9

a) From Ref. 18. With the exception of the rare gases, the entries in this table are taken from XPS measurements of appropriate salts. In those cases where a given ion has been studied in several salts (e.g., K⁺ in KF, KCl, and KBr), the satellite separation is an average of the observed separations. In most instances, the deviations from salt to salt are within the experimental uncertainty in the separations (~2 eV).

b) Parenthetical entries for the rare gases are the relative intensity of the correlation satellite to the primary peak.

c) S. P. Kowalczyk, "Photoelectron Spectroscopy and Auger Electron Spectroscopy of Solids and Surfaces", Ph.D. Thesis, Lawrence Berkeley Laboratory Report LBL-4319 (1976), p. 131.

FIGURE CAPTIONS

- Fig. 1 Levels in Ba and Ba^+ excited by HeI α radiation (left) and the photoelectron spectrum from this system (right).
- Fig. 2 Diagram illustrating FISC1 accompanying 1s photoemission in neon. After Chang and Poe (Ref. 7). The process depicted is 1s photoionization to the $1s2s^2p^53p$ state in Ne^+ .
- Fig. 3 Diagram illustrating FISC1 accompanying 3s photoemission from Mn^+ , Ar, other $3s^23p^6$ cases, or ns photoemission from ns^2np^6 cases.
- Fig. 4 Diagram of FISC1 processes in $Xe^+(4p)$ photoemission.
(a) virtual super Coster-Kronig processes, after Wendin and Ohno, Ref. 21. (b) a contributing diagram in which the $4d^84f$ final state is specifically recognized, to emphasize the similarity to the 3s-hole core of Fig. 3.
- Fig. 5 The ISC1 process $4p^2 + 4p$, admixed into the initial state of Ca.
- Fig. 6 The $Ca^+(HeI)$ spectrum, showing the 4s, 3d, 4p, 5s, and 4d final states, right to left.
- Fig. 7 Level diagram for core-to-core x-ray transition. Channels A and D are most intense and close in energy, as explained in text, precluding intense satellites.

Fig. 1

Fig. 2

XBL 778-1770A

Fig. 3

XBL 778-1769A

Fig. 4

XBL 778-1788

Fig. 5

XBL 778-1789

Fig. 6

XBL 778-1787

Fig. 7

XBL 778-1772