ELECTRON CORRELATION IN ATOMS FROM PHOTOELECTRON SPECTROSCOPY

D. A. Shirley, S.-T. Lee, S. Süzer, R. L. Martin,
E. Matthias, and R. A. Rosenberg
Materials & Molecular Research Division, LBL and
Dept. of Chem., U. of California, Berkeley, CA 94720

ABSTRACT

The photoelectron spectrum of an atom A yields the eigenenergies of the ion A^+ . Additional satellite peaks arise because of electron correlation effects. Peaks observed in spectra from Ca, Sr, Zn, Cd, and Hg have been attributed to initial-state configuration interaction, while final-state configuration interaction gives satellite peaks in a Ba spectrum. The neon 1s "shakeup" spectrum is a result of both effects.

I. INTRODUCTION

The photoelectric effect has been known since approximately the turn of the century. Einstein¹ explained it in 1905 in the work that was to be noted in his Nobel Prize citation. Nevertheless, for over a half century thereafter this effect was known mainly as a threshold phenomenon manifested as the work function in metals or as the ionization potential in molecules.

Only in the 1960's was photoelectron spectroscopy exploited as an experimental method of practical use in many laboratories. Its popularization followed the development of high-resolution electron spectrometers together with convenient line sources.^{2,3} For its first decade, photoelectron spectroscopy was divided into two rather distinct subdisciplines--ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS or ESCA). With the advent of intense variable-energy photon beams from electron storage rings, this artificial separation is now

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

disappearing, and the generic term photoelectron spectroscopy (PES) can be applied to the entire field.

The essential elements of a PES experiment are few and simple. A monochromatic photon beam of energy $h\nu$ impinges on a sample, ejecting electrons of kinetic energy

$$T = h\nu - E_B \quad (1)$$

Analysis of the electron intensity $N(T)$ yields peaks that can be associated with binding energies E_B of various orbitals. In this way the complete one-electron orbital spectrum of a given element can be studied, and the Aufbanprinzip can be illustrated rather directly, a feature of particular appeal in atomic physics. Thus for example PES studies on the rare gas neon ($1s^2 2s^2 2p^6; 1S$) will yield the positions of the following states of Ne^+ :

$$(1s^2 2s^2 2p^5; ^2P_{3/2})$$

$$(1s^2 2s^2 2p^5; ^2P_{1/2})$$

$$(1s^2 2s 2p^6; ^2S)$$

$$(1s 2s^2 2p^6; ^2S)$$

among others. Note that the 2S states are reached, as well as 2P states, from the $1S$ ground states. We shall return to this point.

At this point one might well ask whether the PES method can yield any information not already available from X-ray physics. After all, can one not simply build up these one-electron hole levels by comparing optical and X-ray data, as has been done in various tabulations of core electron binding energies?

The answer is (surprisingly) "No". The optical data were obtained on free atoms, while X-ray spectra were taken using various condensed-phase anode materials, usually metals. It is now well-known⁴ that core-electron binding energies are systematically lower in metals than in free atoms. This follows from a combination of effects, the most important of which is usually "extra-atomic relaxation" or mobile valence electrons to shield the holes formed on photoemission from core orbitals in metals. Table I illustrates the magnitude of this effect for the elements Na, Ni, and Zn, taken from a new tabulation.⁵ The difference,

$$E = E_B^A - E_B^M \quad (2)$$

Table I. Binding energies of electronic orbitals in atoms and metals.

	Nl	E_B^A	E_B^M	ΔE
Element		(eV)		
Na	1s	1070	1074	5
	2s	71	66	5
	3s	5.1	3.5	1.6
Ni	2p _{3/2}	869	859	10
	3p	83	72	11
Zn	2p _{3/2}	1029	1026	3
	3p	96	93	3

between atomic and metallic core-level binding energies, runs from 3 to 11 eV in these elements, a substantial effect indeed. Thus we must conclude that all previous tabulations of core-level binding energies which did not distinguish between atomic and metallic samples are systematically in error.

Let us now compare and contrast PES with photon spectroscopy, referring to Fig. 1. We consider an atom that has S symmetry in a ground state, and we work in the electric dipole approximation. In the presence of a radiation field represented by the vector potential $A(t)$, the electron momenta are replaced by $p - eA/c$. Standard time-dependent perturbation theory with conventional approximations yields a transition probability governed by the matrix element

$$M.E. \propto \langle \psi_f | A \cdot p | \psi_i \rangle \quad (3)$$

Only states of P-symmetry are excited. For low-energy photons this means that P bound states of the N-electron (atomic) system can be found (sharp lines, Fig. 1). Above the photoionization threshold, P-symmetry N-electron states are also formed, thus satisfying the electric dipole selection rule. These give absorption edges rather than sharp lines. Further, each of these P states consists of a state of the (N - 1) electron (ionic) system, of arbitrary orbital angular momenta L' , plus a continuum electron in a state of orbital angular momentum l that satisfies the triangle condition

XBL768-3885

FIG. 1. ILLUSTRATION OF THE WAY IN WHICH THE ELECTRIC DIPOLE SELECTION RULES APPLIED TO AN ATOM IN AN S STATE YIELDS ONLY P BOUND STATES BUT IONIC STATES OF ANY SYMMETRY.

$$L' + L = L \quad (4)$$

with $|L| = 1$ for the P state. Thus in effect there is no absolute selection rule for photoemission and all states are populated.

We now turn from one-electron properties (or apparent one electron properties) to a phenomenon that is manifestly multi-electronic in nature, namely electron-electron correlation. For simplicity initial-state correlation effects are treated in the next section using the configuration-interaction formalism. Final-state correlations are the subject of Section III. In Section IV the neon 1s satellites, in which both initial- and final-state correlations are important, are discussed briefly.

II. INITIAL STATE CONFIGURATION INTERACTION

A one-electron atom or ion can be treated exactly, but any multi- (even two-) electron system must be dealt with using approximate methods. Thus the ground state of He can be described only roughly by the configuration $1s^2$. The e^2/r_{12} electron-electron repulsion term in the Hamiltonian may be regarded as leading to an explicit dependence of the electronic wavefunction on r_{12} . It is computationally most convenient to treat correlation through configuration interaction,⁷ in which eigenstates are described by adding excited configurations with the correct amplitude and phase relations. Thus the $1S$ ground state of He is

$$(^1S) = a(1s^2) + b(2s^2) + c(2p^2) + \dots \quad (5)$$

In the alkaline-earth, or Group IIA, atoms, the valence configuration may be represented as (for example)

$$\Psi(\text{Ca}) = a(4s^2) + b(4p^2) + c(3d^2) + \dots \quad (6)$$

and similarly for Sr and Ba.

Photoemission from these ground states would yield only the $4s^1;^2S$ state of Ca^+ , etc., by one-electron processes, if there were no electron correlation. The admixed configurations $4p^2$, $3d^2$, etc., lead directly to observable $4p^1;^2P$ and $3d^1;^2D$ final states on photoemission, with the line intensities being related to admixture coefficients in the initial states. Thus photoemission spectra can give a rather direct measure of initial-state configuration interaction (ISCI). Such spectra have now been observed in Ca, Sr, Ba, Zn, Cd, and Hg.⁸⁻¹⁰ The HeI resonance line at 21.2 eV was used to induce photoemission in every case except Ba, for which the NeI lines (16.7, 16.9 eV) were employed.

Table II lists the prominent satellites that were identified in the photoelectron spectra of these atoms.

Comparisons with theory are still in a rather crude stage. A quantitative analysis of these spectra requires both configuration interaction calculations on the initial states and estimates of the relative cross-sections for 4s, 4p, 3d, etc., photoemission. The latter are not yet available. Multiconfiguration Hartree-Fock calculations were done by Kim and Bagus¹¹ and by Hansen.¹² The admixture coefficients that were obtained would predict the satellite intensities to be too weak by factors between 2 and 20 before cross-section effects are taken into account. It will be interesting to learn whether the cross-section variation will resolve this discrepancy.

Because the configuration-interaction formalism is just one approach to the electron correlation problem, the reality of the configuration admixtures can be questioned. After all, one need not in principle even use the CI picture. The satellites would still be observed: what would they then mean? The answer is that operationally the one-electron states in Ca^+ (for example), together with the continuum final states are projected onto the initial state of Ca, through the dipole transition operator. This is a general statement of the process. A more specific statement, in terms of ISCI, requires care in selecting the basis functions. Once a particular set of functions is chosen, however, there exists a unique answer as to how much a given function is admixed into the initial state.

We conclude this section by pointing out a special case of ISCI involving spin-orbit coupling. The ground state of atomic Pb is normally $6s^2 6p^2$. In strong spin-orbit coupling this becomes¹³ mainly $6s^2 6p_{1/2}^2$ with a small admixture of $6s^2 6p_{3/2}^2$. Sözer¹⁴ has shown that the photoemission spectrum of atomic Pb indeed shows a very intense ($6s^2 6p_{1/2}; ^2P_{1/2}$) peak and a much less (7%) intense ($6s^2 6p_{3/2}; ^2P_{3/2}$) peak, as expected. Also present were all the peaks expected to arise from admixtures of sp^2d and s^2d^2 into the ground state.

III. FINAL-STATE CONFIGURATION INTERACTION (FSCI)

This phenomenon is manifested as additional satellites or very unusual intensities in a photoemission spectrum. There are several known cases of FSCI. One of the most dramatic is the HeI spectrum of atomic barium, which was reported by Brehm and Höfler¹⁵ and by Hotop and Mahr.¹⁶ This spectrum was re-discovered in our laboratory in the course of ISCI studies in alkaline earths. The

Table II. Summary of satellites attributable to ISCI in photoelectron spectra of Group II elements.

Ion	Main Line	Satellites	References
Ca($4s^2$)	4s	4p, 3d, 5s, 4d	10
Sr($5s^2$)	5s	5p*, 4d, 6s, 5d, 4f	10
Ba($6s^2$)	6s	6p*, 5d*, 7s, 6d, 4f	10
Zn($3d^{10}4s^2$)	4s	4p*	10
Cd($4d^{10}5s^2$)	5s	5p*	8, 10
Hg($5d^{10}6s^2$)	6s	6p*	9, 10

* Doublet energies resolved.

essential unusual features of the BaI (HeI) spectrum are the greatly enhanced 5d and 6p peaks and a number of additional nl peaks of Ba^+ arising from resonant auto-ionization by the 21.2 eV radiation. For example, the 6f and 8p states are clearly present.

The explanation for this phenomenon is too involved to be presented in detail here, but basically the HeI radiation resonantly excites a state of Ba that is embedded in the continuum of Ba^+ . The final N-electron state ($N = 56$ in this case) can be regarded as consisting of interacting N-electron configurations, each of which is made up of an $N - 1$ electron state of Ba^+ coupled with an unbound electron in a continuum state. When the resonance condition is satisfied, the outgoing electrons carry kinetic energies $(h\nu - E_i)$, where $\{E_i\}$ are the energies of the Ba^+ states.

In Ba, autoionization occurs because of excitation of an electron from the $5p^6$ shell to an ns or nd state. Thus the total configuration of the state embedded in the continuum is $5p^5 6s^2 (ns \text{ or } nd)$. This may be loosely regarded as a Rydberg-like state below the 5p photoionization threshold in Ba. Proceeding upward in Z from Ba through the rare earths, the 5p ionization threshold does not increase dramatically, because the additional nuclear charge is in large measures shielded by the filling 4f shell, and the ion core potential changes only slowly. Thus resonant autoionization by the HeI 21.22 eV line and associated satellite radiations persists through Sm (Fig. 2) and Eu ($Z = 62, 63$). It has disappeared by Yb ($Z = 70$).

NBL 767-3238

FIG. 2. THE PHOTOELECTRON SPECTRA OF Sm VAPOR EXCITED BY HeI (21.2 eV) AND BY NeI (16.7, 16.9 eV) RADIATION. THE UNUSUAL INTENSITY RATIOS AND EXTRA PEAKS IN THE HeI SPECTRUM ARISE FROM AUTOIONIZATION FOLLOWING RESONANT EXCITATION OF THE $5p$ SHELL.

Fano and Cooper¹⁷ have discussed configuration interaction effects from a very general viewpoint. As tunable (synchrotron) radiation sources become available, many instances of these phenomena can be expected.

IV. THE Ne 1s SATELLITES: ISCI AND FSCI

As a final example, let us consider the "shakeup" spectrum of the Ne 1s, in which both initial- and final-state correlations play a role. A high-resolution photoemission spectrum of the 1s region of Ne was reported by Gelius.¹⁸ In addition to the many transition

at 870 eV, there was a large number of weak satellite lines at about 40 eV higher energy. These arise from transitions of the form

.

.

.

etc.

(It should be noted that each configuration on the right gives two final states because of exchange splitting.)

There are two ways in which these transition can be understood on the basis of FSCI alone. We note that a nonzero transition probability requires overlap between the "passive" electron configurations. Expanding the matrix element, for photoemission,

$$M. E. \propto \langle x | A \cdot p | 1s \rangle \langle \text{Ne}^+ 1s^1 2s^2 2p^5 3p | \text{Ne} 1s^2 2s^2 2p^6 \rangle ,$$

we see that the overlap product would vanish if the basis functions in Ne^+ and Ne were the same (because $\langle 3p | 2p \rangle$ would be zero). In fact they are not: the Ne^+ $n = 2$ functions are relaxed because of the added core charge, giving finite overlap. Alternatively we could imagine using the basis set in Ne^+ as in Ne, but describing the relaxation in terms of configuration mixing, again yielded finite overlap. This effect is, however, not readily separable

from the second way in which FSCI leads to satellites; namely configuration interaction that is already present irrespective of relaxation. After all, the "final" states in Ne^+ are in fact eigenstates of a Hamiltonian with no reference to photoelectron spectroscopy.

The FSCI effects in the Ne 1s spectrum have been known for some time, but calculated spectra based on FSCI alone show much lower relative intensities in the satellites than are observed experimentally. It has been pointed out by Martin¹⁹ that ISCI is also important in this case. In fact ISCI is responsible for about one-half the observed satellite intensities. There is a great deal of symmetry between the ISCI and FSCI contributions to the satellite intensities, because the Ne and Ne^+ states are basically quite similar, even at the level of electron correlations. Thus it even turns out that the satellite spectrum gives a fairly direct picture of configuration admixing in the ground state.

In conclusion, we have sought in this paper to summarize specific cases in which electron correlation has manifestly affected photoelectron spectra. It seems likely that photoelectron spectroscopy will prove increasingly useful in elucidating problems of this nature in atomic physics.

REFERENCES

1. A. Einstein, Ann. d. Physik 17, 132 (1905).
2. K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. J. Lindberg, ESCA-Atomic, Molecular, and Solid State Structure by Means of Electron Spectroscopy, Nova Acta Regiae Soc. Sci. Upsaliensis Ser. IV, vol. 20, 1967.
3. D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, Molecular Photoelectron Spectroscopy (Wiley Interscience, 1970).
4. L. Ley, S. P. Kowalczyk, F. R. McFeely, R. A. Pollak, and D. A. Shirley, Phys. Rev. B 8, 2392 (1973).
5. D. A. Shirley, Chem. Phys. Letters 16, 220 (1972).
6. This difference remains after the work function correction otherwise it would be even larger.
7. J. C. Slater, Quantum Theory of Atomic Structure (McGraw-Hill, 1960), Vol. 11, p. 40.

8. S. Süzer and D. A. Shirley, J. Chem. Phys. 61, 2481 (1974).
9. J. Berkowitz, J. L. Dehmer, Y. K. Kim, and J. P. Desclaux, J. Chem. Phys. 61, 2536 (1974).
10. S. Süzer, S.-T. Lee, and D. A. Shirley, Phys. Rev. A 13, 1842 (1976).
11. Y. K. Kim and P. S. Bagus, Phys. Rev. A 8, 1739 (1973).
12. Jørgen E. Hansen (private communication, June 1976).
13. E. U. Condon and G. N. Shortley, The Theory of Atomic Spectra (Cambridge University Press, 1935), p. 275.
14. S. Süzer, M. S. Banna, and D. A. Shirley, J. Chem. Phys. 63, 3473 (1975).
15. B. Brehm and K. Höfler, Int. J. Mass Spectrom. Ion Phys. 17, 371 (1975).
16. H. Hotop and D. Mahr, J. Phys. B: Atom. Molec. Phys. 8, L301 (1975), and private communication.
17. U. Fano and J. W. Cooper, Rev. Mod. Phys. 40, 441 (1968).
18. U. Gelius, J. Electr. Spectr. and Rel. Phenomena 5, 985 (1974).
19. R. L. Martin and D. A. Shirley, Phys. Rev. A 13, 1475 (1976).

* This work was done with support from the U. S. Energy Research and Development Administration.