Ab initio determination of satellite intensities in transition-metal photoemission spectroscopy using a multiconfiguration framework

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Following atomic photoionization, the abrupt change in potential can lead to secondary ionization of an outer-shell electron in a phenomenon known as shake-off, a process which gives rise to the asymmetric $K\alpha$ profile and satellite lines. Investigation of chemical effects and relativistic quantum mechanics requires a theoretical determination of these satellite intensities; however, existing theoretical predictions are inconsistent with experimental results by up to an order of magnitude. Previously theoretical modeling required up to 12 fitting parameters to account for transition widths, energy corrections, spectator intensities, and spectator broadening. Using a multiconfiguration atomic model to account for electron-electron correlation, we provide here the first *ab initio* calculations of shake-off probabilities which are in agreement with experimental results (except for copper), an important step toward a complete theoretical profile.

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Photoemission spectroscopy is a widely used technique for investigation of atoms and molecules. These investigations range from the structural evolution of nanopowders [1] to orbital filling in organic matrices [2] to synchrotron investigations of the active centers of metalloproteins [3]. Not only can the technique be used to identify atoms by means of their characteristic radiation, but high-accuracy studies can also produce information regarding the atom's chemical environment and local structure [4,5].

In typical experiments, a core or valence electron is ionized by photon or electron impact. The ionized species then decay to a lower energy state, emitting a photon in the process. Since the initial and final energy states of the decaying electron depend on the electronic environment, this process is sensitive to changes in valence configuration or binding structure. The resulting photoemission spectra display irregularities or asymmetries that can then be understood through comparison to theory [6].

In order to isolate chemical effects, an accurate description of the atomic spectra must first be obtained. When the ionized electron comes from a core subshell, additional electrons may be excited or ionized in what are known as shake processes. Atoms exposed to intense laser fields are prone to correlated multiple ionizations, and the shake processes are some of the key contributors [7–9]. Shake processes are also responsible for the satellite peaks observed in x-ray photoemission spectra and must be properly accounted for in high-accuracy x-ray protein studies [10]. Furthermore, theoretical determination of satellite intensities is crucial for the development of x-ray calibration standards used in high-accuracy and fundamental experiments, such as tests of QED [11–13]. Despite this wide need for accurate determination of shake-off probabilities, *ab initio* calculations show poor agreement with experimental results, especially in complex atoms.

A number of models have been put forth to explain the shake processes. In the two-step model, either the outgoing ionized electron or, in the case of electron ionization, the incoming electron perturbs the atom, resulting in excitation or ejection of an additional electron. In the shake model, the sudden removal of an atomic electron leaves the atom in an excited state, and as the electronic wave function relaxes there is a probability for excitation or ionization. At the high energy limit (the sudden approximation), the initial ionization takes place in a time frame much shorter than orbital relaxation, and the shake-off probability can be expressed as the overlap integral between the initial- and final-state wave functions. For low energies, there are numerous theoretical approaches [14–16], but all require fitting parameters describing the probability of shake-off in the sudden approximation limit.

There have been dozens of experimental and theoretical investigations into the shake processes [17–29], and several advanced relativistic quantum mechanical techniques have been applied to characteristic diagram lines [30] or few-electron scattering [31,32], though only Mukoyama [22] and Kochur [24] have performed *ab initio* calculations for the difficult transition metals. Due to both the experimental and computational difficulties involved in identifying satellite intensities empirically, there has been little comparison with experimental results in open-shell atoms. Where experimental data exist, agreement with theoretical results is poor; $K\alpha$ spectra from scandium, titanium, and copper have all exhibited $3d$ satellites of much greater intensity than those predicted theoretically. Explanation of these discrepancies is the subject of this paper.

Both Mukoyama and Kochur used single-configuration wave functions in their calculations. Multiconfiguration methods (described below) have previously been applied in a limited fashion to the noble gases [20], but until now the methods have not been transferable to open-shell atoms, most likely due to the difficulty of obtaining well-converged wave functions in these systems. In the present work, we consider the

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application of the multiconfiguration method to the calculation of shake-off intensities in the transition metals. The results obtained are in far better agreement with experimental results than any previous work.

Prior to ionization, the neutral atom is in an eigenstate of the $N + 1$ electron Hamiltonian, $H(N + 1)$, with an atomic wave function $\Psi(N + 1)$. Within the sudden approximation, the removal of an electron occurs adiabatically, and so the atomic wave function undergoes the transformation

$$\Psi(N + 1) \rightarrow \Psi^*(N), \qquad (1)$$

where $\Psi^*(N)$ is formed by simply removing a core electron from $\Psi(N + 1)$ (the asterisk, $*$, is used to denote wave functions that are unrelaxed in the ionized Hamiltonian). $\Psi^*(N)$ is no longer an eigenstate of the new atomic Hamiltonian $H(N)$ and can instead be represented as a linear combination of eigenstates

$$|\Psi^*(N)\rangle = \sum_i \langle \Psi(N)^i | \Psi^*(N) \rangle | \Psi(N)^i \rangle, \qquad (2)$$

where $\Psi(N)^i$ are the eigenstates of $H(N)$. The quantity

$$P = 1 - \langle \Psi(N) | \Psi^*(N) \rangle \qquad (3)$$

is the probability for the system, initially in state $|\Psi^*(N)\rangle$, to be discovered in any state other than $|\Psi(N)\rangle$, where both $|\Psi^*(N)\rangle$ and $|\Psi(N)\rangle$ are N electron wave functions with the same set of quantum numbers. In other words, P is the probability of either a shake-up or shake-off event occurring.

In a multielectron atom, the atomic wave function is the antisymmetrized product of N independent electron wave functions

$$|\Psi^*(N)\rangle = \mathcal{A} \prod_{n,\kappa}^{N} |\chi^*(N)_{n,\kappa}\rangle, \qquad (4)$$

where $\chi(N)_{n,\kappa}$ represents the wave function of an electron with quantum numbers n, κ.

In the single-configuration description of the atom, where the total atomic wave function is a single Slater determinant, the probability of at least one electron being shaken from shell $n_1 \kappa_1$ is

$$P_{n_1 \kappa_1} = 1 - \langle \chi(N)_{n_1 \kappa_1} | \chi^*(N)_{n_1, \kappa_1} \rangle^{M_{n_1 \kappa_1}}, \qquad (5)$$

where $M_{n_1 \kappa_1}$ is the occupation number of shell $n_1 \kappa_1$, and we ignore the overlap between shells differing in primary quantum number.

In the multiconfiguration framework, we can represent the atomic wave function as the linear combination of Slater determinants. Within this description, the overlap integral in Eq. (3) becomes

$$\langle \Psi(N) | \Psi^*(N) \rangle = \sum_j \sum_k c_j d_k \langle \phi(N)_j | \phi^*(N)_k \rangle, \qquad (6)$$

where $|\Psi(N)\rangle$ and $|\Psi^*(N)\rangle$ are the initial and final atomic wave functions, c_j and d_k are mixing coefficients, and $|\phi(N)_j\rangle$ and $|\phi^*(N)_j\rangle$ are Slater determinants corresponding to some electron configuration state function (CSF) with parity and total atomic angular momentum equal to that of $|\Psi(N)\rangle$ (see [33] for details on the multiconfiguration method).

In accounting for electron-electron interactions beyond those included in the central field approximation, we break the symmetry of the atom. Instead of individual electrons being in angular momentum eigenstates, only the atom as a whole has well-defined quantum numbers. There is, therefore, no direct analog to Eq. (5) in the multiconfiguration framework. This can be understood by considering that the sets $|\phi(N)_j\rangle$ and $|\phi^*(N)_k\rangle$ consist of CSFs with differing occupation numbers and the atomic state is a combination of a number of electron configurations. Shake-off probabilities may be assigned to the atom but not to individual shells or subshells.

In practice, however, it is useful to assign probabilities to a set of quantum numbers, as calculation of satellite energies generally proceeds by assuming the shake-off electron can be localized to a particular subshell [34–37]. To this end, we adopt the following procedure for assigning shake-off probabilities to subshells:

(1) Where the CSF is generated by a single excitation, the shake-off probability of the excited electron is assigned to the subshell from which it was removed.

(2) Where multiple electrons are excited and each excited electron can be paired to a vacancy with the same angular quantum numbers, the probabilities are assigned to the subshell with the matching vacancy.

(3) Where neither of these cases apply, the total probability from all excited electrons is distributed evenly among all subshells with vacancies.

States under consideration were dominated by the first two cases. For example, if a CSF is generated by exciting a $3p$ electron to the $4p$ subshell and a $3d$ electron to the $4d$ subshell ($3p^{-1}3d^{-1}4p^1 4d^1$), then the calculated probability of shake-off from the $4p$ subshell is nominally assigned to the $3p$ subshell, and that from the $4d$ subshell is nominally assigned to the $3d$ subshell. This is in line with the observation that the most significant correlation effects for the systems under investigation are of the type $nl \rightarrow n'l$.

The number of configurations included for any particular element exceeded 10^5, with the total number of configurations contributing to this work running to several million. In order to reduce the problem to manageable dimensions and reduce computation time, we make two simplifying assumptions. First, we reduce the double sum in Eq. (6) to a single sum by assuming the mixing coefficients remain the same between initial and final states. For the data presented here, the initial mixing coefficients were used (i.e., we let $c_j = \delta_{j,k} d_k$). Choosing to use the final coefficients produces near identical results.

Second, we ignore the overlap integral between shells with the same quantum number κ and differing quantum number n. In other words, we assume a pure shake-off process. These assumptions will be valid as long as the relaxation of orbitals is small and as long as ionization is dominant over excitation, which has been demonstrated both theoretically and experimentally [40–42].

The GRASP2K [43] package was used to solve the Dirac-Hartree-Fock equations. Basic details of our new approach are given elsewhere [36,37]. The Breit interaction and first-order QED effects were included perturbatively. In generating the CSF basis, single and double excitations were allowed from the $3p$, $3d$, and $4s$ subshells to virtual orbitals up to the $n = 5$
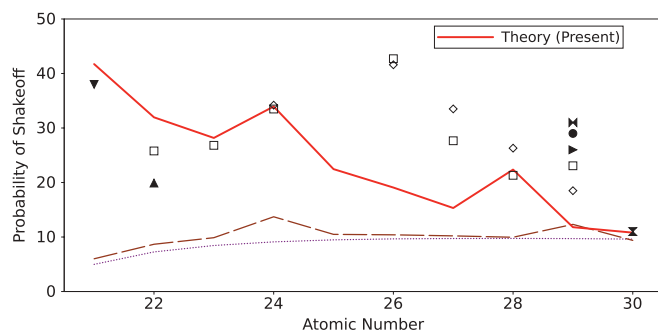
FIG. 1. (Color online) Current theoretical probability of shake-off from $3d$ subshell (solid line) compared to prior theory (dotted line) [22], (dashed line) [24], and experimental results (points). Symbols ◇ [38], □ [28], ▼ [35], ● [39], ▲ [36], ▶ [37], ▶◀ [34], and **x** [28] denote probability of shake-off from $3d$ subshell following $1s$ ionization. Two types of experimental results are presented: Multiconfiguration fits (solid points) use atomic calculations to deconvolve the raw experimental spectrum, while phenomenological fits (hollow points) use a series of arbitrary Lorentzians. The former is a more accurate method. Reference [38] reports a Lorentzian parametrization but does not infer that this represents the $3d$ shake-off probability, as in [28]. We include the results here for completeness. The present results (solid line) are in much better agreement with experimental results than earlier work which fails to account for electron correlation.

layer. Preliminary calculations indicated that core-core and core-valence contributions were negligible. Wave functions were individually optimized for initial and final states, and separate wave functions were optimized for each angular momentum eigenstate in order to maximize accuracy.

Since we are only interested in the high-energy region and since the energy separation between the $3d$ and $4s$ shells is typically less than fine structure splitting, and in many cases reverses sign after ionization, we considered all possible distributions of electrons among the $3d$ and $4s$ shells, and all angular momentum eigenstates, giving each its statistical weighting. Our results were consistent with previous approaches [22,24] for all shells excluding the anomalous $3d$ subshell, for which our results provide much better agreement with experimental spectra. The results of our calculation for the $3d$ subshell are presented in Fig. 1.

Empirical satellite intensities are not observed directly. Rather, they must be inferred from an experimental spectra through the use of fitting procedures. The most accurate means of deconvolving the experimental spectrum is to fit the results of a self-consistent atomic structure calculation to them. To date this has only been accomplished for scandium [35], titanium [36], copper [37], and zinc [28]. An approximation to

this method is to simply fit a series of Lorentzians and assume that the largest Lorentzian on the low-energy side of the main peak is representative of the $3d$ spectator. Results using this method are available for $22 \leqslant Z \leqslant 29$. We present two sets of such results, those of Ito *et al.* [28] and Hölzer *et al.* [38]. In order to obtain a value from Hölzer's measurement, we take the ratio of all Lorentzians on the low-energy side of the main peak to the total intensity.

The results of our calculation display a very different trend from the single-configuration results and are in much better agreement with experimental results, especially for the early members of the series. We calculate the highest shake-off probability for scandium at 42%. Shake-off probabilities decrease with increasing atomic number, with irregularities at chromium and nickel. We might expect to observe the second irregularity at copper, as in the results of Mukoyama [22], due to the discontinuity in the order of subshell filling. We note, though, that the energy ordering of the subshells in many of the species changes following ionization.

Our results go far toward explaining the discrepancy between existing self-consistent field calculations and the observed experimental satellite intensities. The results presented here are close to experimental results for all $3d$ transition-metal spectra besides copper, for which a significant discrepancy still remains. Our results converge on existing results for the closed-shell atom zinc, highlighting the need to include multiconfiguration effects in open-shell atoms. This necessity is already well established for the calculation of transition energies. There remains a distinct discrepancy between theoretical and experimental results for copper, and further developments are needed to understand other residual discrepancies. We note that atomic structure calculations for copper are notoriously difficult, with the $3d$ and $4s$ subshell energy ordering overlapping or swapping depending on the core configuration. This may be cause for the discrepancy.

Further comparison with experiment will require advances in the multiconfiguration method to allow accurate fitting of the remaining transition metals. Numerous experimental spectra exist in the literature, yet the self-consistent calculations necessary to analyze the results have not yet been performed.

This work has shown that multiconfiguration self-consistent field calculations can explain the magnitude of shake-off intensities in $3d$ transition metals. This represents the first *ab initio* determination of the anomalous $3d$ satellite intensity in scandium to be in good agreement with experimental results. These results illustrate the importance of electron correlation in open-shell atoms and represent a vital step toward complete *ab initio* spectra calculations of complex and open-shell systems.

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