

Atomic Excitation and Ionization as the Result of Vacancy Production

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The excitation and ionization probabilities of atoms as a result of vacancy production have been calculated in the sudden approximation using the Hartree-Fock-Slater wave functions. It is found that the ionization process is dominant for inner-shell electrons, while for outermost shells the excitation probability is comparable with or larger than the ionization probability. Comparison with other theoretical calculations and with the experimental results is made.

KEYWORDS : Shakeup process/Shakeoff process/Vacancy production/

I. INTRODUCTION

When there is a sudden change in atomic potential, atomic electrons in the same atom have a small probability that they are excited to an unoccupied bound state (*shakeup*) or ionized to the continuum (*shakeoff*). In the case of radioactive decays, such as α or β decay, the change in the nuclear charge causes shake processes¹⁾. On the other hand, in photoionization and impact ionization by charged particles the central potential of the atom changes due to the loss of an atomic electron and another electron in the same atom is excited during rearrangement of electron cloud.

The experimental evidence of shake processes can be established by observing satellite peaks or satellite continuum in the low-energy side of the main peak in the electron spectra for photoionization²⁾ and internal conversion³⁾, by measuring satellites or hypersatellites in x-ray emission spectra⁴⁾, and by detecting discontinuities in x-ray absorption spectra⁵⁾. With recent progress of synchrotron radiation facilities, photoionization becomes very powerful tools to study the shake process, especially for its dependence on incident x-ray energy⁶⁾.

The theoretical calculations on the shakeup and shakeoff probabilities have been usually performed in the *sudden approximation*⁷⁾. In this approach, the shake process is considered as a two-step process, i. e. creation of a vacancy in an atom and atomic excitation due to the presence of the vacancy, and its probability is estimated only from the second step. This fact means that the shake probability is independent of the mechanism, by which the initial vacancy is produced, and is a function of the atomic number and the atomic shell.

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The assumption of the sudden approximation is valid when the energy of the ejected electron in the initial ionization process is large compared to the binding energy of the electron to be excited. In practice, Carlson and Krause⁸⁾ found that the shakeoff probability in photoionization becomes constant for incident photons with energy higher than three times the threshold energy for double-electron emission. The similar results were also observed by Carlson *et al*⁹⁾ in the case of electron impact ionization. Sachenko and Burtsev¹⁰⁾ showed theoretically that in K-plus L-shell photoionization the sudden approximation is justified when the photon energy is higher than 1.3 times the threshold energy.

Carlson and Nestor¹¹⁾ calculated the atomic excitation plus ionization probabilities for rare gases in the sudden approximation with the relativistic Hartree-Fock-Slater (RHFS) wave functions. Recently we have made the similar calculations for elements from He ($Z=2$) to Kr ($Z=36$) by the use of the Hartree-Fock-Slater (HFS) wave functions¹²⁾. We compared the results with the measured intensities of shakeup satellite peaks from the outermost p -shell electrons in photoionization of Ne and Ar. Our calculated intensities are in good agreement with the theoretical values of Carlson and Nestor, but about twice as large as the experimental data. This discrepancy was explained due to the contributions from the shakeoff process included in both theoretical models.

On the other hand, the $2p \rightarrow np$ shakeup probabilities accompanying K-shell photoionization of Ne have been calculated by Martin and Shirley¹³⁾. They used the multiconfiguration Hartree-Fock (MCHF) method and showed that the electron correlation is important to predict intensities of the shakeup satellites. The shakeup intensities in photoionization have also been calculated for rare gases, i. e. on Ne, Ar, Kr, and Xe, by Talman *et al*¹⁴⁾ using an optimized potential method, and by Bristow *et al*¹⁵⁾ using the HFS method.

All theoretical calculations described above have been made either for shakeup process only or for shakeup plus shakeoff process, and no separate calculations of shakeup and shakeoff probabilities using the same wave functions for both processes have been reported. This is related to the experimental method to observe of the shake process. In x-ray emission and absorption spectra, only shakeup plus shakeoff intensities can be measured, while in electron spectra the shakeup satellites are easily observed, but it is very difficult to estimate the shakeoff probability because of the continuous energy distribution of ejected electrons. However, it is interesting to study relative importance of the shakeup and shakeoff probabilities in atomic excitation process for various atomic shells in various elements. Since the shake probability depends on the imperfect-overlap of atomic wave functions, it is important to calculate both probabilities with the electron wave functions based on the same atomic potential.

In the present work, we have computed the atomic excitation and ionization probabilities separately for Ne, Ar, and Kr using the HFS wave functions. For this purpose, the atomic excitation and ionization (shakeup plus shakeoff) probability is calculated in the manner similar to our previous work¹²⁾. Then shakeup probabilities to various higher shells are estimated using the same atomic potential and initial-state wave functions. The shakeoff probability is obtained by subtracting the sum of shakeup probabilities from the shakeup plus shakeoff probability. The calculated results for shakeup probabilities are compared with other theoretical calculations and the experimental data.

II. THEORY

In the sudden approximation, the probability that an electron in the initial state i makes a transition to a final state f with the presence of an inner-shell vacancy can be expressed as the overlap integral :

$$p_{if} = \left| \int \phi_f^* \phi_i d\tau \right|^2, \quad (1)$$

where ϕ_i is the electron wave function in the initial state and ϕ_f is that in the final state.

The initial state corresponds to the ground state of the neutral atom. On the other hand, for the shakeup process the final state is a Rydberg state of the positive ion with an inner-shell vacancy, while for the shakeoff process it is a continuum state in the same central potential. Owing to the difference in atomic potentials for the initial and final states, two wave functions with the same symmetry are no longer orthogonal and the integral in Eq. (1) for these wave functions has a finite value.

Due to the monopole character of the shakeup and shakeoff processes, the selection rule allows such transition that there is a change only in the principal quantum number (or energy) and all other quantum numbers should retain their original values. We shall neglect multi-electron shake processes and consider that only single electron is excited or ionized. When the initial electron in the orbital nl , where n is the principal quantum number and l is the orbital quantum number, the shakeup probability to an $n'l$ state accompanying vacancy production is written from the single electron transition probability, Eq. (1), by

$$P_{n'} = N \left| \int \phi_{n'l}^* \phi_{nl} d\tau \right|^2 S^{N-1}. \quad (2)$$

Here ϕ_{nl} represents the electron wave function for the nl orbital in the neutral atom, $\phi_{n'l}$ is that for the $n'l$ orbital in the positive ion with an inner-shell vacancy, N is the number of electrons in the initial nl orbital, and S is the probability per electron that the electron remains in its original orbital :

$$S = \left| \int \phi_{nl}^* \phi_{nl} dr \right|^2. \quad (3)$$

The factor S^{N-1} in Eq. (2) means that other $N-1$ electrons are neither excited nor ionized. The total shakeup probability is given by

$$P_{SU} = \sum_{n' > n} P_{n'}, \quad (4)$$

The shakeoff probability is expressed in the similar manner as

$$P_{SO} = N \int d\varepsilon \left| \int \phi_{\varepsilon l}^* \phi_{nl} d\tau \right|^2 S^{N-1}, \quad (5)$$

where $\phi_{\varepsilon l}$ is the electron wave function of the continuum state with the kinetic energy ε and the orbital angular momentum l in the potential of the positive ion with the inner-shell vacancy.

In order to calculate the total atomic excitation and ionization probabilities, all possible transitions to excited and ionized states should be considered. However, the calculations for Rydberg states are in general more difficult than for the ground state, and especially the evaluation of overlap integrals involving continuum wave functions and integration over kinetic energy are tedious and time-consuming. Carlson *et al*¹⁶⁾ proposed a method to avoid this difficulty and computed the atomic excitation plus ionization probabilities accompanying β decay. Carlson and Nestor¹¹⁾ applied this method for the case of inner-shell vacancy production in rare gases by the use of the RHFS wave functions. The same method has also been used in our previous work¹²⁾ with the HFS wave functions.

This approach is based on the completeness and orthonormal property of the electron wave function. For N -electron system, the relation among the excitation, ionization, and remaining probabilities can be written as

$$1 = P_{SU} + P_{SO} + P_0 + P_F \quad (6)$$

where P_0 denotes the probability that all electrons remain in the original states and P_F is the electron transfer probability to occupied bound states, forbidden by the Pauli principle. These two probabilities are given by¹⁷⁾

$$P_0 = S^N, \quad (7)$$

$$P_F = \frac{NN'}{2(2l+1)} \sum_{n=1}^x \left| \int \phi_n^* \phi_{n'} d\tau \right|^2 S^{N-1}, \quad (8)$$

where N' is the number of electrons in the $n' l$ orbital and x is the principal quantum number of the highest occupied orbital. From Eq. (6), the shakeup plus shakeoff probability is obtained as

$$P_{SUO} = 1 - P_0 - P_F. \quad (9)$$

In Eq. (9), the probability is expressed by the overlap integrals between the ground-state wave functions for the neutral atom and those for the positive ion, and therefore one can bypass the calculations for Rydberg and continuum states. This method is very useful to estimate the shakeup plus shakeoff probability, but both probabilities are not obtained separately.

In the present work, first we calculate the shakeup plus shakeoff probability by Eq. (9), using the ground-state wave functions for the neutral atom and for the positive ion. Then the calculations of the wave functions for Rydberg states in the positive ion are made and the total shakeup probability is evaluated by Eq. (4). The shakeoff probability is obtained from the relation

$$P_{SO} = P_{SUO} - P_{SU}. \quad (10)$$

III. RESULTS AND DISCUSSION

The atomic excitation and ionization probabilities as the result of vacancy production

have been computed in the sudden approximation. We calculated the HFS wave functions for the neutral atom and the positive ion with the Herman-Skillman program¹⁸⁾. The wave functions for Rydberg states were obtained by solving the Schrödinger equation in the atomic potential for the positive ion. All numerical computations in the present work were performed on the FACOM VP-30E computer in Information Science Center of Osaka Electro-Communication University and on the FACOM M-760/10 computer in Institute for Chemical Research, Kyoto University.

In Figs. 1 and 2, the calculated results for the shakeup and shakeoff probabilities, P_{SVO} , from various shells as the result of vacancy production in $2s$ and $2p$ shells are plotted as a function of atomic number Z . The similar figure accompanying $1s$ vacancy is shown in our previous paper¹²⁾. As has already been pointed out, the probability per electron generally decreases with Z , but there are small bends at the atomic numbers where the nl shells are filled.

Using the method described above, the shakeup and shakeoff probabilities were obtained separately from P_{SVO} . The results for Ne, Ar, and Kr are listed in Table I. It is clear from the table that for inner-shell electrons the shakeoff probability is dominant and the excitation process is almost negligible. On the other hand, the shakeup probability increases with principal quantum number n and in the case of the outermost s and p shells of rare gases, the excitation probability is higher than the ionization probability. It is also seen that the shakeup and shakeoff probabilities depend on n of the initial vacancy, but dependence on l is weak.

In Table II, comparison between calculated and measured values of intensities of shakeup satellite peaks originated from the outermost p shell accompanying the inner-shell photoioniza-

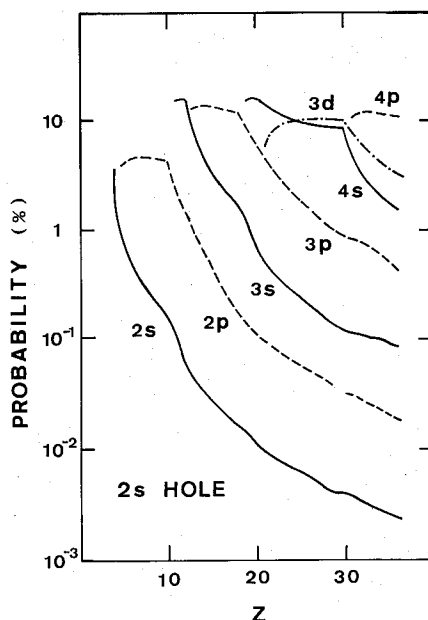


Fig. 1. Total atomic excitation plus ionization probabilities (%) from various shells as the result of a sudden $2s$ vacancy production.

Table II. Comparison between theory and experiment for intensities of shakeup satellite peaks for the outermost p shell accompanying the inner-shell photoionization of rare gases.

Element	Initial vacancy	Photon energy (eV)	Theory ^a					Experiment	Reference
			MT ^b	CN ^c	MS ^d	BTB ^e	Present		
Ne	1s	930	18.3	19.6	8.94 ^f	13.95 ^f	9.62 ^g	5.5 ^g	19
		1254	18.3	19.6	8.94 ^f	13.95 ^f	10.7	9.6±0.7	20
		1487	18.3	19.6	8.94 ^f	13.95 ^f	10.4 ^f	10.4 ^f	21
		1487	18.3	19.6	8.94 ^f	13.95 ^f	10.7	8.7±0.7	20
		1487	18.3	19.6	8.94 ^f	13.95 ^f	10.7	11.1	22
Ar	2s	930	13.8	14.6		12.65 ^f	8.99	8±2	23
		1254	13.8	14.6		12.65 ^f	8.99	8±1	20
	2p	930	14.5	15.4		12.65 ^f	9.32	7±2	23
		1254	14.5	15.4		12.65 ^f	9.32	7±1	20
		1254	14.5	15.4		12.65 ^f	8.89 ^f	12.5 ^f	15
		1487	14.5	15.4		12.65 ^f	9.32	7±1	20

^aRelative to *normal* photoelectron peak, which is equal to 100.^bMukoyama and Taniguchi, shakeup plus shakeoff (Ref. 12).^cCarlson and Nestor, shakeup plus shakeoff (Ref. 11).^dMartin and Shirley (Ref. 13).^eBristow *et al.* (Ref. 15).^fExcitation up to $6p$ state.^gExcitation to $3p$ and $4p$ states only.

tion of rare gases is shown. The theoretical values in the table are normalized so that the intensity of the *normal* photoelectron peak is equal to 100. When comparison of the calculated values with the experimental data is made, it should be noted that all theoretical calculations in the table are based on the sudden approximation, i. e. the energy of incident photons is assumed to be high enough. The experimental value of Kobrin *et al.*¹⁹⁾ for low-energy photoos is about 40% smaller than other experimental values. This suggests that the sudden approximation is invalid in the energy region used by them and it is inadequate to compare their value with the theoretical values in the table.

The shakeup plus shakeoff probabilities by Carlson and Nestor¹¹⁾ and by Mukoyama and Taniguchi¹²⁾ are about twice as large as the experimental data. We have pointed out in the previous work¹²⁾ that this discrepancy is ascribed to the contribution from the shakeoff process. As can be seen in Table I, the relative importance of the shakeoff process becomes smaller for outer-shell electrons, but is still appreciable in the outermost shells.

Martin and Shirley¹³⁾ calculated the shakeup probabilities for Ne including the electron correlation in the MCHF method. Their results are in good agreement with the experimental values for high-energy photons. The present values are slightly larger than their values, but agree well with the measured ones. On the other hand, the HFS values of Bristow *et al.*¹⁵⁾ are larger than the experimental data, except for their experimental value for Ar $2p$ shell.

Table III shows the calculated and measures shakeup satellite intensities for $2s$ - and $2p$ -shell electrons accompanying photoionization of Ne $1s$ shell. The results of Martin and Shirley¹³⁾ in the MCHF method are in agreement with the measured values. In other three theoretical models, the electron correlation effect is neglected. The values of the variationally

Table III. Comparison between theory and experiment for shakeup intensities relative to the main Ne 1s line (%).

Transition	Theory				Experiment	
	MS ^a	TBJ ^b	BTB ^c	Present	G ^d	S ^e
2s → 3s		0.79		0.66	1.06	~1.1
2s → 4s				0.12		~0.3
2s → 5s				0.05		~0.07
2s → 6s				0.02		~0.02
2p → 3p	5.07	9.3	11.77	8.21	6.30	6.42
2p → 4p	2.18	1.5	1.50	1.41	2.98	3.2
2p → 5p	0.54	0.54	0.47	0.52	0.59	~0.9
2p → 6p	0.15		0.21	0.25	0.5	~0.5

^aMartin and Shirley (Ref. 13).^bTalman *et al.* (Ref. 14).^cBristow *et al.* (Ref. 15).^dGelius (Ref. 21).^eSvensson *et al.* (Ref. 22).

Table IV. Comparison between theory and experiment for shakeup intensities relative to the Ar 2s and Kr 3d lines (%).

Element	Transition	Theory			Experiment ^b
		TBJ ^a	BTB ^b	Present	
Ar	3s → 4s	1.02	1.12	0.75	2.1
	3s → 5s		0.17	0.15	1.0
	3p → 4p	8.63	10.91	7.21	6.0
	3p → 5p	1.24	1.34	1.22	4.2
	3p → 6p	0.45	0.40	0.45	2.3
Kr	4s → 5s	0.82	0.87	0.58	1.9
	4p → 5p	7.3	9.20	5.96	8.1
	4p → 6p	1.0	1.11	0.97	2.4
	4p → 7p	0.37	0.32	0.36	1.2

^aTalman *et al.* (Ref. 14).^bBristow *et al.* (Ref. 15).

optimized effective potential model by Talman *et al.*¹⁴⁾ and of the HFS model by Bristow *et al.*¹⁵⁾ agree with each other, but agreement with the experimental data is poor. The present results are in better agreement with the experimental values than the values of Talman *et al.* and of Bristow *et al.*

The similar comparison between theory and experiment for shakeup satellites in the Ar 2p and Kr 3d lines is made in Table IV. It is clear from the tables that the present model underpredicts the intensities of the lowest-energy satellite for *ns* electrons and overestimates those for *np* electrons, except for the case of 4p → 5p transition in Kr. For higher-energy

satellites, the present values are always smaller than the experimental ones. As shown by Martin and Shirley¹³⁾, the electron correlation effect is important in multi-electron transition process in photoionization. The reason for the discrepancy in satellite line intensities between the present values and the measured ones can be attributed to neglect of this effect.

In conclusion, we have calculated the shakeup and shakeoff probabilities as the result of vacancy production in the sudden approximation, using the HFS wave functions. It is found that for inner-shell electrons the shakeoff process is dominant, while the shakeup process is larger for outermost shells. The total shakeup probabilities for the outermost p shells accompanying the inner-shell photoionization in rare gases are in agreement with the experimental data. However, the measured intensity of individual satellite line is not well reproduced, because of neglect of the electron correlation effect. It is hoped to estimate satellite intensities due to the shakeup process by the theoretical approaches including the electron correlation effect, because such calculations have been made only for Ne. Elaborate experimental measurements of the shakeoff probabilities in vacancy production are also interesting.

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