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Relativistic Calculations of Shakeup and Shakeoff Probabilities as the Result of 1*s*-Shell Vacancy Production

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Electron shakeup and shakeoff probabilities as the result of 1*s*-shell vacancy production have been calculated relativistically for Kr and Xe by the use of Dirac-Fock-Slater wave functions in the sudden approximation. It is found that the shakeoff process is dominant for inner-shell electrons, while in the case of outer shells the shakeup process plays an important role. The calculated results are compared with the nonrelativistic calculations and the experimental data.

KEY WORDS : Shakeup probability/ Shakeoff probability/ Relativistic Hartree-Fock-Slater method/

I. INTRODUCTION

When an inner-shell vacancy is created suddenly in atoms, the atomic electrons have a small probability that they are excited to an unoccupied bound state *(shakeup)* or ionized to the continuum *(shakeoff)*. These shake processes have been extensively studied for inner-shell ionization by photoionization,[1] internal conversion,[2] and charged-particle impact.[3] The experimental and theoretical studies on the shake effect for various inner-shell ionization processes have been discussed in the recent review.[4]

Theoretically it is usual to treat the shake process in the *sudden approximation*. In this case, the shake process is considered as a two-step process, i.e. sudden creation of an inner-shell vacancy and excitation or ionization of other electrons due to presence of the vacancy. Its probability is independent of the first-step process and estimated from the electron transition probability in the second step as the imperfect overlap of electron wave functions before and after production of the inner-shell hole.

In the sudden approximation, the shake probability is independent of the mechanism of inner-shell vacancy creation and depends on the atomic number and the atomic shell. This approach corresponds to the case where the kinetic energy of the ejected electron in the primary ionization event is much larger than the binding energy of the electron to be excited or ionized in the shake process.

The validity of the sudden approximation has been studied both experimentally and

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theoretically. In the case of photoionization, Carlson and Krause[5] showed that the experimental shake probability is independent of incident energy for high-energy photons. The similar result was observed for electron-impact ionization by Carlson *et al.*[3] On the other hand, Sachenko and Burtsev[6] estimated theoretically that the sudden approximation is justified in the K- plus L-shell photoionization for photons with energy higher than 1.3 times the thereshold energy.

Using the sudden approximation, Carlson and Nestor[7] calculated the shakeup-plus-shakeoff probabilities of rare gases as the result of inner-shell vacancy production with the relativistic Hartree-Fock-Slater or Dirac-Fock-Slater (DFS) wave functions. The similar calculations for elements from He to Kr were performed by Mukoyama and Taniguchi[8] by the use of the Hartree-Fock-Slater (HFS) method. Both theoretical values for rare gases are in good agreement with each other, but about twice as large as the experimental values for the shakeup process in photoionization. The reason for the discrepancy is ascribed to the shakeoff process which was not measured in experiments.

On the other hand, the shakeup probabilities for rare gases accompanying inner-shell vacancy creation have been calculated by Martin and Shirley[9] with the multiconfiguration Hartree-Fock (MCHF) method, by Talman *et al.*[10] with the optimized-potential method, and by Bristow *et al.*[11] with the HFS method. Their results are in better agreement with the experimental shakeup probabilities in photoionization. However, they calculated only the shakeup probabilities, and no theoretical estimations for the shakeoff probabilities were made.

With recent advent of synchrotron radiation facilities, strong monoenergetic photon beams with variable energies can be easily obtained and the shake process accompanying photoionization has received a special interest. In particular, a number of experiments have been performed on multiple electron excitation processes in photoabsorption. Such processes are observed as discontinuities in x-ray absorption spectra and are important to interpret the experimental absorption spectra because they cause the background for the x-ray absorption near-edge structure (XANES) and the x-ray absorption fine structure (XFAS).[12] Recently we found that for inner-shell photoionization the multiple electron transitions in x-ray absorption spectra are mainly due to the shakeup process accompanying inner-shell photoionization and the shakeoff process plays a minor role.[13] This fact indicates that it is important to estimate the shakeup and shakeoff probabilities separately.

In order to compare the magnitude of the shakeup probability with that of the shakeoff one, theoretical calculations should be made by the use of the same atomic model, because these probabilities are very sensitive to small changes in wave functions. Mukoyama and Taniguchi[14] calculated the shakeup and shakeoff probabilities as the result of vacancy production for Ne, Ar, and Kr in the sudden approximation using the HFS wave functions. Their results indicate that the shakeoff process is dominant for inner-shell electrons, but for outermost shells the shakeup probability becomes larger. However, they used the HFS method and calculated the nonrelativistic values. It is worthwhile to perform similar calculations with the relativistic model. In the present work, we calculate the relativistic shakeup and shakeoff probabilities for Kr and Xe as the result of K-shell vacancy production. The calculations are performed in the sudden approximation using the DFS wave functions.

II. THEORY

In the sudden approximation, the shake probability is expressed as an overlap integral between the electron wave functions in the initial and final states. When an electron in the initial state i makes a transition to a final state f due to the presence of an inner-shell vacancy, the transition probability can be given by

$$p_{ij}=|\int \psi^*_f \psi_i \, d\tau|^2, \tag{1}$$

where ψ_i is the wave function of the electron in the initial state and ψ_f is that in the final state.

The initial state is a ground state of the neutral atom and the final state corresponds to a positive ion with an inner-shell vacancy. Owing to the difference in the central potentials due to the presence of the vacancy, the electron wave function in the initial state is no longer orthogonal to that in the final state and Eq. (1) becomes a small, but fiinte value.

Since the shake process has a monopole character, the selection rule allows only such transitions that the principal quantum number of the final state is different from the initial value and all other quantum numbers retain their original values. When the initial electron in the orbital with the principal quantum number n, the total angular momentum quantum number j, and the orbital angular momentum quantum number l, the shakeup probability to an $n'lj$ orbital is obtained from Eq. (1) as

$$P_{n'}=N|\int \psi'_{n'lj} \psi_{nlj} \, d\tau|^2 S^{N-1}, \tag{2}$$

where ψ_{nlj} is the single electron wave function for the nlj orbital in the initial state and $\psi'_{n'lj}$ is that for the $n'lj$ orbital in the positive ion with an inner-shell vacancy, N is the number of electrons in the initial nlj state, and S is the probability per electron that the electron remains in its initial state. The probability S can be written by

$$S=|\int \psi'^*_{n'lj} \psi_{nli} \, d\tau|^2. \tag{3}$$

From Eq. (2), the total shakeup probability is given by

$$P_{SU}=\sum_{n'>n} P_{n'}, \tag{4}$$

On the other hand, the total shakeoff probability is expressed in the manner similar to Eq. (2) as

$$P_{SO}=N\int d\varepsilon |\psi'^*_{\varepsilon lj} \psi_{nli} \, d\tau|^2 S^{N-1}, \tag{5}$$

where $\psi'_{\varepsilon lj}$ is the single electron wave function of the continuum state with the kinetic energy ε, the orbital angular momentum quantum number l and the total angular momentum quantum number j in the potential of the positive ion.

The total shake (shakeup-plus-shakeoff) probability is calculated as the sum of Eqs. (4) and (5). For this purpose, the shakeup probabilities to all possible final excited states should be taken into account and shakeoff probabilities are given by intergrating the transition probabilities involving the oscillating continuum wave function with respect to ε. These calculations are in general very tedious and time-consuming. Carlson *et al.*[15] developed a method to avoid the difficulties to calculate Rydberg states and continuum wave functions in the shake probability accompanying nuclear β decay.

The basic principle of their method is to use the completeness and orthogonality of the electron wave function. After the sudden change in the central potential, each electron has only three possibilities in the final state, i.e. it remains in the original state, is excited to an unoccupied states, or ionized to the continuum. When we calculate the possibility that all the electron remain in their original atomic orbitals in the final state and subtract this probability from unity, the shakeup-plus-shakeoff probability can be obtained. The advantage of this approach consists in the fact that we need no atomic calculation for excited states and continuum. Carlson and Nestor[7] and Mukoyama and Taniguchi[8] applied this method to shakeup-plus-shakeoff probabilities following inner-shell vacancy production.

For N-electron system, the relation among transition probabilities to three final states is expressed as

$$1=P_{SU}+P_{SO}+P_0+P_F, \tag{6}$$

where P_0 is the probability that all electrons remain in the original state and P_F is the transition probability to the occupied bound states, forbidden by the Pauli principle. The former probability is expressed as

$$P_0=S^N, \tag{7}$$

and the latter is written by

$$P_F=\frac{NN'}{2(2l+1)}\sum_{n'=1}^{x}\left|\int \psi'_{n'lj}{}^{*}\psi_{nlj}\,\mathrm{d}\tau\right|^2 S^{N-1}, \tag{8}$$

where N' is the number of electrons in the $n'lj$ orbital and x is the principal quantum number of the highest occupied orbital. Then the shakeup-plus-shakeoff probability is given by

$$P_{SUO}=1-P_0-P_F. \tag{9}$$

In the present work, we avoid to use the integrals involving the continuum wave functions and calculate P_{SU} and P_{SO} from Eqs. (4) and (9), in the manner similar to the previous work.[14] First, the shakeup-plus-shakeoff probability is obtained from Eq. (9), by the use of wave functions for ground state of the neutral atom and those of the positive ions with inner-shell vacancy. In the next step, the wave functions in excited states for the final state are evaluated by solving the Dirac equation in the self-consistent-field potential of the positive ion obtained above. The shakeup probabilities are calculated by Eq. (3), using the ground-state wave function of the neutral atom and the excited-state wave function. Then the shakeoff probability is estimated by

$$P_{SO}=P_{SUO}-P_{SU}. \tag{10}$$

III. RESULTS AND DISCUSSION

The shakeup and shakeoff probabilities accompanying 1s-shell vacancy production were computed for Kr and Xe. The wave functions for the ground state of the neutral atom and for the positive ion with the 1s-shell vacancy were calculated by the DFS method.[16] The wave functions of the excited states in the final state were obtained by solving the Dirac equation for the central potential of the positive ion with the 1s-shell vacancy. All the numerical computations in the present work were performed on the FACOM M-760/10 computer of Institute for Chemical Research, Kyoto University.

Table I. Shakeup-plus-shakeoff probabilities in Kr as the result of 1s-shell vacancy production (%).

Shell	CN[a]	MT[b]	Present
$2s$	0.060	0.057	0.058
$2p_{1/2}$	0.089		0.089
$2p_{3/2}$	0.18	0.257	0.176
$3s$	0.22	0.211	0.215
$3p_{1/2}$	0.38		0.381
$3p_{3/2}$	0.75	1.102	0.753
$3d_{3/2}$	1.43		1.431
$3d_{5/2}$	2.13	3.498	2.126
$4s$	1.80	1.843	1.798
$4p_{1/2}$	4.39		4.384
$4p_{3/2}$	9.06	12.931	9.067

[a] Carlson and Nestor (Ref. 7).
[b] Mukoyama and Taniguchi (Ref. 14).

Table II. Shakeup-plus-shakeoff probabilities in Xe as the result of 1s-shell vacancy production (%).

Shell	CN[a]	Present
$2s$	0.023	0.022
$2p_{1/2}$	0.032	0.032
$2p_{3/2}$	0.061	0.061
$3s$	0.073	0.073
$3p_{1/2}$	0.11	0.115
$3p_{3/2}$	0.22	0.223
$3d_{3/2}$	0.22	0.216
$3d_{5/2}$	0.32	0.315
$4s$	0.23	0.227
$4p_{1/2}$	0.37	0.336
$4p_{3/2}$	0.73	0.730
$4d_{3/2}$	1.65	1.651
$4d_{5/2}$	2.46	2.458
$5s$	1.67	1.668
$5p_{1/2}$	3.73	3.725
$5p_{3/2}$	8.39	8.385

[a] Carlson and Nestor (Ref. 7).

The calculated result for shakeup-plus-shakeoff probabilities for Kr are listed in Table I and compared with the DFS values of Carlson and Nester[7] and the HFS values of Mukoyama and Taniguchi.[14] The present values are in good agreement with the relativistic ones of Carlson and Nestor. Agreement with the nonrelativistic calculations of Mukoyama and Taniguchi is also good, because for Kr the relativistic effect is not large. Table II shows the comparison of the present results for the shakeup-plus-shakeoff probabilities in Xe with the DFS values of Carlson and Nestor. The results of both calculations agree well with each other.

The total shakeup probabilities, P_{SU}, were calculated from Eq. (4). The contributions up to $n'=20$ were considered. Using the P_{SU} values thus obtained and the values of P_{SUO} in Tables I and II, the shakeoff probabilities, P_{SO}, were evaluated from Eq. (10). The results for Kr are shown in Table III. For comparison, the nonrelativistic values of Mukoyama and Taniguchi[14] are also listed.

In the case of the P_{SUO} values, agreement between the relativistic and nonrelativistic calculations is good. However, the relativistic shakeup probabilities for outer-shell electrons are larger than the corresponding nonrelativistic values. It shold be noted that P_{SUO} was calculated only with the ground-state wave functions, while in the case of P_{SU} values the wave functions for the excited states were used. Due to the relativistic effect, the atomic orbitals for inner-shell electrons are contracted and there is the spin-orbit splitting for orbitals with $l \geq 1$. Because of these two effect, the central potential seen by electrons in the excited state is different between the relativistic and nonrelativistic calculations.

The shakeup and shakeoff probabilies for Xe are listed in Table IV. It is clear from Tables III and IV that for inner-shell electrons the shakeoff process is dominant and the shakeup process plays a minor role. On the other hand, the shakeup probability increases for outer shells and

Table III. Shakeup and shakeoff probabilities in Kr as the result of 1*s*-shell vacancy production (%).

Shell	Shakeup		Shakeoff	
	Present	MT[a]	Present	MT[a]
$2s$			0.057	0.057
$2p_{1/2}$			0.088	
$2p_{3/2}$	0.002	0.003	0.174	0.255
$3s$	0.015	0.014	0.200	0.197
$3p_{1/2}$	0.023		0.358	
$3p_{3/2}$	0.047	0.066	0.705	1.037
$3d_{5/2}$	0.296		1.135	
$3d_{5/2}$	0.434	0.707	1.692	2.791
$4s$	0.993	1.015	0.805	0.828
$4p_{1/2}$	2.940		1.444	
$4p_{3/2}$	6.146	8.309	2.921	4.669

[a] Nonrelativistic calculations of Mukoyama and Taniguchi (Ref. 14).

Table IV. Shakeup and shakeoff probabilities in Xe as the result of 1*s*-shell vacancy production (%).

Shell	Shakeup	Shakeoff
$2s$		0.022
$2p_{1/2}$		0.032
$2p_{3/2}$		0.060
$3s$	0.001	0.072
$3p_{1/2}$	0.002	0.113
$3p_{3/2}$	0.003	0.220
$3d_{3/2}$	0.009	0.207
$3d_{5/2}$	0.013	0.303
$4s$	0.018	0.209
$4p_{1/2}$	0.026	0.341
$4p_{3/2}$	0.055	0.675
$4d_{3/2}$	0.437	0.121
$4d_{5/2}$	0.664	0.179
$5s$	0.959	0.709
$5p_{1/2}$	2.520	1.205
$5p_{3/2}$	5.948	2.437

becomes larger than the shakeoff probability for the outermost shell. This trend has been already pointed out by the nonrelativistic calculations.[14]

In Table V the present results for shakeup probabilities in Kr and Xe are compared with the recent experimental data following 1*s*-shell photoionization. Theoretical calculations in the dipole approximation by Wark *et al.*[17] are also listed in the table. In the dipole approximation,

Table V. Comparison of calculated and measured shakeup probabilities in Kr and Xe in 1*s*-shell photoionization (%).

Shell		Theoretical		Experimental			
		Sudden[a]	Dipole[b]	Ito[c]	DH[d]	Wark[c]	DK[f]
Kr	$3s$	0.015			0.10±0.02		
	$3p$	0.070	0.07		0.24±0.02	0.1	
	$3d$	0.730	0.96	0.4	0.20±0.03	1.3	
	$4s$	0.993	1.92		0.21±0.03	2.6	
	$4p$	9.086	13.50	4.0	2.2± 0.2	18.3	
Xe	$3s$	0.001					≤0.03
	$3p$	0.005					≤0.03
	$3d$	0.022					≤0.05
	$4s$	0.018					0.12
	$4p$	0.081					0.37
	$4d$	1.101					1.4

[a] Present work.
[b] Dipole approximation (Ref. 17).
[c] Ito *et al.* (Ref. 13).
[d] Deutsch and Hart (Ref. 18).
[e] Wark*et al.* (Ref. 17).
[f] Deutsch and Kizler (Ref. 19).

the photoinization process is treated as the dipole transition and the energy dependence of the shake process is taken into account. The experimental data of Deutsch and Hart[18] and of Ito *et al.*[13] were measured by observing the discontinuties near to the K edge in x-ray absorption spectra. In this case, both shakeup and shakeoff processes are possible, but we have shown that the dominant contributions come from the shakeup process.[13] On the other hand, Wark *et al.*[17] measured electron energy spectra by 1*s*-shell photoionization and the shakeup probabilities were estimated from the intensities of satellites on the low-energy side of the main park.

In Kr, the theoretical values of Wark *et al.*[17] in the dipole approximation agree with their experimental ones. The present calculation in the sudden approximation give smaller values. However, the experimental values of Deutsch and Hart[18] and Ito *et al.*[13] for Kr are even smaller than the present theoretical values. In the case of Xe, Deutsch and Kizler[19] observed only upper limits for 3*s*, 3*p*, and 3*d* shells. For 4*s* and 4*p* shells, their values are much larger than the present values. Only the experimental value for 4*d* shell is in agreement with the theoretical one.

The discrepancy between the present results and the experimental data can be explained as follow. In x-ray absorption spectra, it is easy to determine the energies of the absorption edges for multielectron transitions, but difficult to obtain the shake probabilities accurately because of errors of subtraction of much larger contribution of the single 1*s*-shell photoionization process. Theoretically, the sudden approximation is useful where the incident photon energy is high, but it predicts smaller probabilities at energies near the 1*s*-shell absorption edge.

On the other hand, the dipole approximation of Wark *et al.* seems to give the values in agreement with their experimental data. However, the more recent study of Schaphorst *et al.*[20] on multielectron transitions in photoabsorption spectra of Kr shows that the same model cannot well reproduce the shake spectra for 3*p* and 4*p* electrons, though for 3*d* electrons the theoretical spectrum is in good agreement with the measured one. They described the reasons for the discrepancy due to neglection of configuration interaction, contributions from conjugate shakeup process and direct ionization.

IV. CONCLUSION

We have calculated the shakeup and shakeoff probabilities accompanying 1*s*-shell vacancy production of Kr and Xe, using the DFS wave functions. The calculated shakeup-plus-shakeoff probabilities are in good agreement with the similar calculations of Carlson and Nestor. For Kr, agreement with the nonrelativistic calculations of Mukoyama and Taniguchi is also good. On the other hand, the relativistic shakeup probabilities for outer-shell electrons are found to be slightly larger than the nonrelativistic ones.

As already shown by the nonrelativistic calculations, for inner-shell electrons the shakeoff process is dominant, but the shakeup probability increases for outer-shell electrons. In the case of the outermost shell, the shakeup probability is larger than the shakeoff probability.

The order-of-magnitude agreement is found between the present results for shakeup probabilities and the experimental data by x-ray absorption measurements in Kr, but the theoretical values are systematically larger. On the other hand, the present results for Kr are smaller than both calculated values in the dipole approximation and measured values by electron spectra by Wark *et al.*[17] In the case of Xe, the experimental values are larger than the present results.

Martin and Shirley[9] have already pointed out that it is important to take into account the initial- and final-state electron correlation in shakeup process accompanying photoionization for Ne. The discrepancy between theory and experiment of Schaphorst *et al.*[20] also indicates the importance of electron correlation. In orde to compare with the recent experimental data, it is hoped that theoretical calculations for shakeup probabilities including the electron correlation effect be made for other elements than Ne. More elaborate experiments for shake probabilities with high precision are needed to compare with theoretical calculations.

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