Atomic excitation as the result of inner-shell vacancy production

Takeshi Mukoyama
Institute for Chemical Research, Kyoto University, Kyoto 606, Japan

Kazuo Taniguchi
Department of Solid State Electronics, Osaka Electro-Communication University, Hatsu-Machi, Neyagawa, Osaka 572, Japan
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The probabilities of atomic excitation as a result of vacancy production in the 1*s*, 2*s*, and 2*p* shells have been calculated for elements with Z between 2 and 36 in the sudden approximation. Calculations were made with the Hartree-Fock-Slater wave functions. For rare gases, our results are in good agreement with those obtained by Carlson and Nestor [Phys. Rev. A **8**, 2887 (1973)] with relativistic wave functions. The validity of the prediction of Carlson and Krause [Phys. Rev. **137**, A1655 (1965)] by means of effective charge is discussed. Comparison with other theoretical calculations and the experimental data is made.

I. INTRODUCTION

When there is a sudden change in atomic potential, an atomic electron has a small probability to be excited to an unoccupied bound state (shakeup) or ejected into the continuum (shakeoff). In the case of nuclear decay, such as α decay, β decay, and electron capture, the atomic electron is excited as a result of a sudden change in the nuclear charge. Extensive studies of these processes have been performed both theoretically and experimentally.[1]

Atomic excitation is also possible in the case of inner-shell vacancy production following photoionization, electron impact ionization, and internal conversion. In this case, the excitation takes place because of the change in the central potential as a result of removal of the inner-shell electron. The experimental evidence for this process has been established by observing satellite peaks or a satellite continuum on the low-energy side of the main peak in photoelectron and conversion-electron spectra.[2,3]

Carlson and Nestor[4] have performed theoretical calculations for atomic excitation probabilities of rare gases as a result of inner-shell vacancy production. Their model is based on the so-called *sudden approximation,* in which the atomic excitation is treated separately from the initial vacancy-production process. The calculations have been performed using the relativistic Hartree-Fock-Slater (RHFS) wave functions.

The sudden approximation is valid when the incident energy of the photons or charged particles which produce the inner-shell vacancy is high. Carlson and Krause[5] found that the atomic excitation probability accompanying photoionization is constant when the incident photon energy is higher than three times the threshold energy for double electron ejection. Similar experimental results were obtained by Carlson *et al.*[6] for electron impact ionization. Theoretically, Sachenko and Burtsev[7] showed that the sudden approximation is justified in K- and L-shell double photoionization for photons with energy higher than 1.3 times the threshold energy. These results indicate the validity of the sudden approximation for atomic excitation following inner-shell vacancy production.

With the recent advance of high-resolution x-ray and electron spectrometers, the atomic excitation process accompanying inner-shell vacancy creation becomes more important as a source of satellites in x-ray, photoelectron, and conversion-electron spectroscopy. In particular, a number of experimental data on the shakeup structure

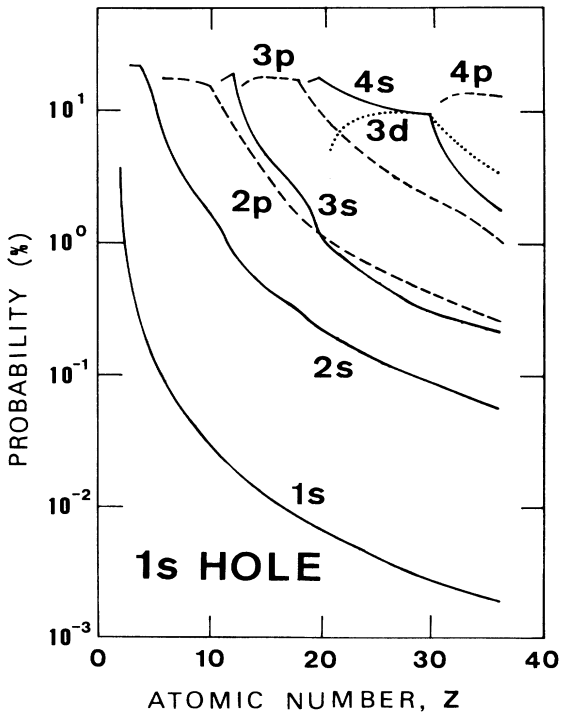

FIG. 1. Atomic excitation probabilities (%) from the various shells as the result of a sudden 1*s* vacancy production.

have been reported for photoelectron spectra.[8] Martin and Shirley[9] have shown that for the shakeup process in the K-shell photoionization of Ne, the electron correlation effect plays an important role. On the other hand, intensity calculations for shakeup satellites within the framework of the single-configuration description have been made for rare gases by Talman, Bancroft, and Johnston[10] using an optimized potential model and by Bristow, Tse, and Bancroft[11] using the Hartree-Fock-Slater (HFS) model. However, all calculations reported until now have been limited to rare gases. It is worthwhile to calculate the atomic excitation probabilities as a result of inner-shell vacancy production for other elements.

In the present work, we have computed the atomic excitation probabilities for elements from $Z=2$ to 36 as the result of $1s$, $2s$, and $2p$ vacancy production. The calculations are based on the sudden approximation following the model of Carlson and Nestor, using the nonrelativistic HFS wave functions. Such a model is considered to be realistic in the high-photon-energy range where electron correlation is of minor importance. The calculated results are compared with the values of Carlson and Nestor for rare gases and with a simplified prediction using the concept of effective nuclear charge.[12] Comparison with other theoretical calculations and with the experimental data is made for the outermost p-shell electron excitation in rare gases. Since the calculations are made in the sudden approximation, the present results are independent of initial excitation modes and can be applied to any excitation process, such as photoionization, internal conversion, and inner-shell ionization by charged-particle impact.

II. THEORY

In the sudden approximation, the probability that an orbital electron makes a transition from an initial state to a final state is given by the imperfect-wave-function overlap due to the sudden change in the atomic potential:

$$P_{if}=\left|\int \psi_f^* \psi_i d\tau\right|^2 , \tag{1}$$

TABLE I. Electron excitation probabilities (%) from the various shells as the result of a sudden $1s$ vacancy production.

Z	$1s$	$2s$	$2p$	$3s$	$3p$	$3d$	$4s$	$4p$
2	3.670							
3	0.476	21.779						
4	0.210	21.018						
5	0.125	10.250	14.824					
6	0.087	6.154	17.349					
7	0.061	4.119	17.487					
8	0.047	2.951	16.957					
9	0.036	2.205	16.245					
10	0.029	1.709	15.478					
11	0.024	1.292	10.571	17.975				
12	0.019	0.843	8.045	18.973				
13	0.017	0.671	5.943	9.791	15.381			
14	0.014	0.556	4.461	6.561	17.729			
15	0.012	0.467	3.407	4.823	17.992			
16	0.011	0.401	2.628	3.758	17.633			
17	0.009	0.349	2.036	3.016	17.097			
18	0.008	0.307	1.603	2.482	16.518			
19	0.007	0.262	1.339	1.781	12.099		16.516	
20	0.007	0.216	1.141	1.129	9.769		17.997	
21	0.006	0.194	1.016	0.936	7.759	4.983	15.158	
22	0.006	0.176	0.912	0.786	6.383	7.265	13.521	
23	0.005	0.161	0.815	0.668	5.420	8.445	12.424	
24	0.004	0.146	0.739	0.597	4.615	9.108	11.644	
25	0.004	0.134	0.669	0.519	4.003	9.478	11.062	
26	0.004	0.123	0.612	0.461	3.511	9.659	10.605	
27	0.004	0.111	0.563	0.413	3.103	9.724	10.245	
28	0.003	0.103	0.519	0.367	2.762	9.742	9.933	
29	0.003	0.097	0.465	0.335	2.464	9.707	9.673	
30	0.003	0.092	0.435	0.307	2.225	9.618	9.457	
31	0.003	0.084	0.400	0.289	2.093	7.470	5.194	11.488
32	0.002	0.077	0.366	0.272	1.895	6.127	3.804	13.152
33	0.002	0.071	0.334	0.255	1.685	5.183	3.043	13.403
34	0.002	0.066	0.306	0.240	1.478	4.480	2.523	13.340
35	0.002	0.062	0.280	0.225	1.282	3.934	2.138	13.162
36	0.002	0.057	0.257	0.211	1.102	3.498	1.843	12.931

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

The initial state corresponds to the ground state of the neutral atom, while the final state is a positive ion with an inner-shell vacancy and the atomic potential is different from that for the ground state. The shakeup and shakeoff processes correspond to the monopole transition. According to selection rules for this transition, there is a change only in the principal quantum number and all other quantum numbers should retain the original values.

In order to obtain the atomic excitation probability for a certain shell, the transition probabilities to all possible final states should be considered. This means that one must sum the probabilities given by Eq. (1) over all the unoccupied bound states and integrate over the continuum states. These calculations are, in general, not easy because excited states of ions are more difficult to calculate than the ground state. In addition, the evaluation of the matrix element containing the continuum wave functions is also a difficult problem.

Carlson *et al.*[12] have proposed a method to avoid this difficulty and estimated the atomic excitation probabilities accompanying β decay. Later, Carlson and Nestor applied the same method for atomic excitation following inner-shell vacancy production.[4] The basic principle of this method is to calculate the probability that an atomic electron remain in an orbital with the same quantum numbers in the final state and to subtract this probability from unity. Following the expression of Carlson and Nestor,[4] the probability of promoting an orbital electron designated by n and l, where n and l are the principal and orbital angular momentum quantum numbers, to a higher bound state or to the continuum, is written by

$$P_{nl}=1-\left\{\left|\int \psi'^{*}_{nl}\psi_{nl}d\tau\right|^2\right\}^N-P_F\ , \tag{2}$$

where ψ_{nl} represents the electron wave function of the orbital nl in the neutral atom, ψ'_{nl} is that in the ion with a single vacancy created in a given inner shell, and N is the number of electrons in the nl shell.

The quantity P_F represents the transition probability to occupied bound states, forbidden due to the Pauli principle. When the principal quantum number of the highest occupied state is x, this probability is[4]

TABLE II. Electron excitation probabilities (%) from the various shells as the result of a sudden 2s vacancy production.

Z	2s	2p	3s	3p	3d	4s	4p
4	3.450						
5	0.757	4.043					
6	0.471	4.690					
7	0.337	4.774					
8	0.256	4.695					
9	0.200	4.553					
10	0.160	4.395					
11	0.111	2.250	15.988				
12	0.061	1.505	16.294				
13	0.045	0.980	7.740	13.046			
14	0.035	0.668	4.915	14.395			
15	0.029	0.464	3.471	14.118			
16	0.023	0.330	2.631	13.452			
17	0.020	0.237	2.075	12.740			
18	0.017	0.167	1.668	12.099			
19	0.014	0.136	1.127	8.058		15.925	
20	0.011	0.113	0.659	6.135		17.091	
21	0.010	0.097	0.513	4.541	5.604	14.139	
22	0.009	0.085	0.408	3.511	8.100	12.449	
23	0.008	0.075	0.332	2.830	9.322	11.369	
24	0.007	0.066	0.278	2.294	9.980	10.594	
25	0.006	0.059	0.236	1.900	10.298	10.039	
26	0.006	0.053	0.202	1.601	10.419	9.613	
27	0.005	0.048	0.175	1.363	10.421	9.277	
28	0.004	0.043	0.150	1.171	10.371	8.995	
29	0.004	0.037	0.133	1.010	10.282	8.760	
30	0.004	0.034	0.120	0.885	10.137	8.570	
31	0.004	0.032	0.116	0.864	7.723	4.589	10.752
32	0.003	0.029	0.112	0.795	6.206	3.316	12.120
33	0.003	0.026	0.106	0.707	5.147	2.627	12.181
34	0.003	0.024	0.101	0.618	4.363	2.159	11.976
35	0.003	0.021	0.095	0.528	3.762	1.815	11.689
36	0.002	0.019	0.089	0.444	3.288	1.553	11.373

$$P_f = \sum_{n'=1}^{x} \frac{NN'}{2(2l+1)} \left| \int \psi'^{*}_{n'l} \psi_{nl} d\tau \right|^2 , \quad (3)$$

where $n' \neq n$ and N' is the number of electron in the $n'l$ shell. Similar to Eq. (2), a change in l is forbidden by the monopole selection rule.

III. RESULTS AND DISCUSSION

The atomic excitation probabilities accompanying formation of an inner-shell vacancy were computed for elements between $Z=2$ and 36, according to Eq. (2). For the location of the initial vacancy, 1*s*, 2*s*, and 2*p* shells were considered. The HFS wave functions were obtained with the Herman-Skillman program.[13] All the calculations were performed on the Facom M-360AP computer in the Information Science Center of Osaka Electro-Communication University.

The calculated results for the atomic excitation probabilities from various shells as the result of 1*s* hole production are listed in Table I and plotted in Fig. 1 as a function of atomic number Z. As pointed out by Carlson *et al.*, for the case of atomic excitation during β decay,[12] the relative probability per electron, i.e., the probability divided by the number of electrons in a given shell, decreases with Z.

However, it is clear from the figure that the atomic excitation probability is not a smooth function of Z, except for the case of the 1*s* shell. The probability for the *ns* shell decreases with Z after this shell is filled, but there is a small bend when the *np* shell is closed. The 4*s* curve shows a discontinuity when the 4*d* shell is filled. The *np*-shell excitation probability increases slightly with an increase of the number of electrons in the given shell until one-half of the shell is filled. Then the probability decreases gradually, but it can be said that the probability is almost constant until the shell is closed. After the point where the shell is filled, the probability decreases with Z. There is a small bend when the *nd* shell is closed. For the 3*d* shell, the probability increases until the shell is filled and then decreases with Z.

The calculated atomic excitation probabilities for various shells accompanying vacancy production in the 2*s* and 2*p* shells are listed in Tables II and III, respectively. The excitation probabilities for the 1*s*-shell electron are negligibly small and omitted from the tables. When these values are plotted against Z, the general trend is quite similar to Fig. 1, although the bend where the outer shell is closed is somewhat enhanced.

TABLE III. Electron excitation probabilities (%) from the various shells as the result of a sudden 2*p* vacancy production.

Z	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*
6	0.973	2.411					
7	0.708	3.317					
8	0.541	3.696					
9	0.425	3.840					
10	0.342	3.875					
11	0.261	2.181	15.997				
12	0.152	1.542	16.355				
13	0.118	1.055	7.842	13.242			
14	0.094	0.750	5.022	14.720			
15	0.079	0.540	3.572	14.540			
16	0.066	0.397	2.723	13.940			
17	0.057	0.294	2.159	13.274			
18	0.050	0.214	1.742	12.667			
19	0.042	0.177	1.185	8.585		16.004	
20	0.034	0.150	0.699	6.617		17.214	
21	0.030	0.131	0.547	4.960	5.627	14.221	
22	0.027	0.116	0.439	3.873	8.147	12.559	
23	0.025	0.103	0.360	3.151	9.393	11.473	
24	0.022	0.093	0.303	2.577	10.069	10.692	
25	0.020	0.084	0.258	2.152	10.402	10.132	
26	0.019	0.076	0.222	1.827	10.536	9.702	
27	0.016	0.069	0.193	1.567	10.547	9.362	
28	0.015	0.064	0.166	1.354	10.505	9.076	
29	0.014	0.055	0.149	1.177	10.421	8.838	
30	0.014	0.052	0.134	1.037	10.279	8.645	
31	0.012	0.048	0.129	1.007	7.886	4.643	10.836
32	0.011	0.043	0.124	0.926	6.377	3.362	12.244
33	0.011	0.039	0.118	0.827	5.319	2.667	12.332
34	0.010	0.036	0.112	0.724	4.535	2.196	12.149
35	0.009	0.033	0.105	0.623	3.931	1.849	11.880
36	0.008	0.030	0.099	0.528	3.452	1.584	11.579

In Table IV, the present results for Kr are compared with those of Carlson and Nestor.[4] The model used in both calculations is the same except for the method used to obtain the atomic wave function; i.e., Carlson and Nestor used the RHFS model, while we used the HFS model. The values of Carlson and Nestor for a $2p$-shell vacancy are obtained as an average of the values for $2p_{1/2}$- and $2p_{3/2}$-shell vacancies. It can be seen that the present nonrelativistic results are in good agreement with the relativistic values of Carlson and Nestor. This indicates that the relativistic effect is of minor importance in the atomic excitation probability for elements $Z \leq 36$.

There is a slight discrepancy for the outermost shell. This is probably due to the relativistic effect in the atomic potential used by Carlson and Nestor. Similar comparison has also been made for Ne and Ar. Agreement is better than for Kr because of a smaller relativistic effect. The discrepancy is less than 1% for all cases, except for the outermost shell.

Carlson and Krause[14] suggested that the atomic excitation probability of an electron in a certain shell is proportional to the square of the change in effective charge experienced by that electron as a result of the sudden change in the central potential. According to this prediction, the atomic excitation probability is expressed as[14]

$$P = (\Delta Z)^2 P_\beta \ , \tag{4}$$

TABLE IV. Comparison of the calculated electron excitation probabilities in the Kr atom as the result of inner-shell vacancy production (%).

Initial vacancy	Shell	Present work	CN[a]	CK[b]
$1s$	$1s$	0.0019	0.002	0.003
	$2s$	0.0574	0.060	0.134
	$2p$	0.257	0.27	0.256
	$3s$	0.211	0.22	0.438
	$3p$	1.102	1.130	1.298
	$3d$	3.498	3.560	3.28
	$4s$	1.842	1.80	2.39
	$4p$	12.931	13.45	13.76
$2s$	$2s$	0.0024	0.002	0.011
	$2p$	0.0193	0.021	0.043
	$3s$	0.0893	0.089	0.316
	$3p$	0.444	0.46	0.938
	$3d$	3.288	3.40	3.28
	$4s$	1.553	1.50	2.39
	$4p$	11.373	11.75	13.76
$2p$	$2s$	0.0084	0.008	0.023
	$2p$	0.0299	0.031	0.036
	$3s$	0.0992	0.098	0.316
	$3p$	0.528	0.54	0.938
	$3d$	3.452	3.55	3.28
	$4s$	1.584	1.53	2.39
	$4p$	11.579	11.97	13.76

[a]Carlson and Nestor (Ref. 4).
[b]Prediction of Carlson and Krause, $(\Delta Z)^2 P_\beta$.

where ΔZ is the change in the effective charge and P_β is the atomic excitations probability during β decay, which can be considered as $\Delta Z = 1$. The validity of this prediction has been tested numerically by Carlson and Nestor[4] for atomic excitation of the $5p_{3/2}$ subshell of Xe as a function of the inner-shell vacancy. On the other hand, Mukoyama[15] derived Eq. (4) analytically for the shakeoff process by the use of nonrelativistic hydrogenic wave functions.

In Table IV, the atomic excitation probabilities calculated according to Eq. (4) are also listed. We took the values of P_β from the RHFS calculations of Carlson *et al.*[12] and used Slater's recipe[16] to estimate ΔZ. It is clear that for *np* and *nd* shells the prediction of Carlson and Krause yields a reasonable estimate to the atomic excitation probability, unless these shells are not close to the initial vacancy. However, in the case of the *ns* shell, their prediction overestimates the probability. A similar trend has also been pointed out by Carlson *et al.*[12]

It is well known that when the atomic excitation takes place from the same shell as the shell in which the initial vacancy is created, the sudden approximation with the single-electron wave functions, such as the HFS and RHFS wave functions, underestimates the atomic excitation probability.[17] In such a case, the present results give only an order-of-magnitude estimate of the atomic excitation probability. In order to obtain more realistic values for this case, one should use the wave functions which include the effect of initial-state electron correlation explicitly.[18–20] For the shakeup process, the final-ionic-state configuration interaction is of equal importance.[9]

In Table V, comparison between the calculated and measured values of intensities of satellite peaks corresponding to the outermost p-shell excitation in the inner-shell photoionization of rare gases is shown. The calculated values are normalized so that the intensity of the *normal* photoelectron peak is equal to 100. It should be noted that the present results and the theoretical values of Carlson and Nestor[4] include the shakeup plus shakeoff process, while the experimental data contain the shakeup process only. The recent experimental value of Kobrin *et al.*[21] for photon energy near to threshold is about 40% smaller than the values in the high-energy limit. All the theoretical results are larger than their value. This can be ascribed to the fact the sudden approximation becomes invalid for photon energy close to threshold.

The shakeup probability of Martin and Shirley,[9] who included electron correlation in the multiconfiguration Hartree-Fock method, is in good agreement with the experimental data for the high-energy region. The HFS calculation of Bristow, Tse, and Bancroft[11] for the shakeup process is larger than the value of Martin and Shirley, but smaller than the present result. This discrepancy comes from the shakeoff process. On the other hand, the calculated intensities for total atomic excitation by Carlson and Nestor and from the present work are always about twice as large as the measured ones. This fact suggests that the electron shakeup process accounts for about one-half of the atomic excitation probability for the outermost-shell electrons. The importance of the shakeoff process has also been discussed by Bristow, Tse, and Bancroft.[11]

TABLE V. Comparison between theory and experiment for intensities of satellite peaks originated from the outermost p shell in the photoionization of inner shells of rare gases.

Element	Initial vacancy	Photon energy (eV)	Theory[a] Present work	CN[b]	MC[c]	BTB[d]	Experiment	Ref.
Ne	$1s$	930	18.3	19.6	8.94[e]	13.95[e]	5.5[f]	21
		1254	18.3	19.6	8.94[e]	13.95[e]	9.6±0.7	22
		1487	18.3	19.6	8.94[e]	13.95[e]	10.4[e]	2
		1487	18.3	19.6	8.94[e]	13.95[e]	8.7±0.7	22
Ar	$2s$	930	13.8	14.6			8±2	23
		1254	13.8	14.6			8±1	22
	$2p$	930	14.5	15.4		12.65[e]	7±2	23
		1254	14.5	15.4		12.65[e]	7±1	22
		1254	14.5	15.4		12.65[e]	12.5[e]	11
		1487	14.5	15.4		12.65[e]	7±1	22

[a]Relative to "normal" photoelectron peak, which is equal to 100.
[b]Carlson and Nestor (Ref. 4).
[c]Martin and Shirley (Ref. 9).
[d]Bristow, Tse, and Bancroft (Ref. 11).
[e]Excitation up to $6p$ state.
[f]Excitation to $3p$ and $4p$ states only.

In conclusion, we have calculated the atomic excitation probability for elements from $Z=2$ to 36 as the result of $1s$-, $2s$-, and $2p$-shell vacancy production. The calculations have been performed in the sudden approximation using the HFS wave functions. The obtained results are in good agreement with the RHFS calculations for rare gases. It is found that when the Slater screening constant is used the prediction of Carlson and Krause gives a good estimate for p- and d-shell electron excitation, but overestimates the s-shell excitation probability.

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