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Calculation of Electron Shake-Off for Elements from $Z=2$ to 92 with the Use of Self-Consistent-Field Wave Functions*

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Calculations of electron shake-off, based on the sudden approximation, have been made for several different processes. In particular, electron shake-off as the result of β decay has been computed for each of the shells in 15 different cases from an initial $Z=2$ to 92. An interpolation of the results has been made for the remaining elements. Calculations were made with nonrelativistic Hartree-Fock wave functions for the lighter elements, and relativistic Hartree-Fock-Slater wave functions for the heavier ones. A comparison is made with available experimental data, and satisfactory agreement is obtained. Other ionization processes amenable to the use of the sudden approximation are also discussed, viz., β^+ decay, Auger processes, photo-ionization, internal conversion, electron capture, and inner-shell ionization by electron impact.

I. INTRODUCTION

ELECTRON shake-off is the phenomenon by which an electron in a given orbital is excited into a new orbital or into the continuum as the result of a sudden change in the central potential. Since the potential seen by the electron is made up of the nuclear charge minus the shielding of the other electrons, electron shake-off may be initiated either by a sudden change in the nuclear charge, e.g., β^- or positron decay, or by a rapid alteration in the electron configuration, e.g., photo-ionization, or the Auger process.

The most successful treatment of electron shake-off has been through the use of the sudden approximation, in which the probability of shake-off is derived in terms of the square of the overlap integrals of atomic wave functions representing the initial and final states involved in a sudden change in the central potential. The earliest calculations[1–4] of electron shake-off were done on β^- decay by utilizing hydrogenic wave functions. Later Winther[5] investigated the problem in the decay of ^{6}He using Hylleras-type wave functions, and Green[6] made calculations for Kr using interpolated solutions from self-consistent-field (SCF) calculations for Rb$^+$. With the use of high-speed computers it is now possible to obtain good SCF wave functions for all the elements. A number of specific cases relating to electron shake-off following β^- decay and photo-ionization have been reported,[7–11] in which use has been made of SCF wave functions.

In this paper we shall give the results of calculations on the probability for electron shake-off following β^- decay for a wide variety of atoms from $Z=2$ to 92. In these calculations we have used nonrelativistic Hartree-Fock and relativistic Hartree-Fock-Slater wave functions. It has also been possible to interpolate the results, so that evaluation can be made of the probability for ejecting any electron from any shell of any element undergoing β^- decay up to uranium. Comparison with available experimental data in general yields favorable agreement with the calculations.

In order to give a broader base to our discussion of electron shake-off, we have also examined calculations of electron shake-off following positron decay, photo-ionization, internal conversion, electron capture, electron impact, and Auger processes. Finally, we shall discuss the limitations of the sudden approximation and the use of single-electron wave functions.

II. SUDDEN APPROXIMATION

The sudden approximation[12] rests on the assumption that if there is an instantaneous change in the Hamiltonian of an atom from H_1 (the initial state) to H_2 (the final state), the time-dependent wave function describing the electron in that atom is made up of the

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TABLE I. Comparison of calculations on the shake-off probability[a] (%) as the result of Xe $\xrightarrow{\beta^-}$ Cs$^+$.

Shell	NRHF	RH	RHFS (1.5)	RHFS (1)	Hydrogenic
$1s$	0.0314	0.0354	0.0348	0.0350	0.0231
$2s$	0.0632	0.0804	0.0791	0.0809	0.0414
$2p_{1/2}$		0.0516	0.0494	0.0502	
$2p_{3/2}$		0.0856	0.0819	0.0834	
$2p$	0.121	0.137	0.131	0.134	0.0660
$3s$	0.141	0.166	0.160	0.162	0.0950
$3p_{1/2}$		0.152	0.144	0.147	
$3p_{3/2}$		0.274	0.258	0.264	
$3p$	0.392	0.426	0.402	0.411	0.225
$3d_{3/2}$		0.228	0.205	0.213	
$3d_{5/2}$		0.333	0.300	0.311	
$3d$	0.529	0.561	0.505	0.524	0.302
$4s$	0.394	0.398	0.376	0.378	0.346
$4p_{1/2}$		0.463	0.417	0.424	
$4p_{3/2}$		0.884	0.784	0.798	
$4p$	1.31	1.35	1.20	1.22	1.00
$4d_{3/2}$		1.79	1.56	1.68	
$4d_{5/2}$		2.67	2.32	2.51	
$4d$	3.93	4.46	3.88	4.19	3.72
$5s$	2.55	2.05	2.09	2.03	4.72
$5p_{1/2}$		4.99	3.88	4.21	
$5p_{3/2}$		12.15	8.51	9.50	
$5p$	13.1	17.1	12.4	13.7	18.9

[a] From wave functions as designated below: NRHF, nonrelativistic Hartree-Fock, code of C. Froese, RH, relativistic Hartree (i.e., no exchange). RHFS (1.5), relativistic Hartree-Fock-Slater with coefficient for exchange potential = 1.5. RHFS (1), relativistic Hartree-Fock-Slater with coefficient for exchange potential = 1.0, hydrogenic, based on shake-off constants given in Ref. 16 and σ given in Ref. 13.

overlap integral of wave functions for the initial state and wave functions for the various possible final stationary states. Thus, the probability for an electron initially represented by the wave function ψ_i to be found in a given final state ψ_f is

$$P_{i\to f}=\left|\int \psi_f{}^*\psi_i d\tau\right|^2. \tag{1}$$

Electron shake-off is a monopole transition [the operator in Eq. (1) is unity]. The selection rules for such a transition require that ΔS, ΔL, and $\Delta J=0$. There is a change only in the principal quantum number. In our calculations using single-electron wave functions we have first computed P_s, the probability that a given electron will stay in the same orbital. The probability that it will not stay in the same orbital is $1-P_s$, and the probability that at least one of the N electrons in a given shell will leave due to shake-off is $1-P_s{}^N$. If the electron does not remain in the same orbital, it may go either to the continuum or to a discrete state. Nothing in the calculation has excluded the possibility for transitions to orbitals that are already filled. However, such transitions are not physically possible according to the Pauli exclusion principle. We have therefore corrected the shake-off probabilities by subtracting these contributions to filled states. The shake-off probability for removing any electron to an orbital designated by n, l, j, where n and l are the principal and angular-momentum quantum numbers and $j=l\pm\frac{1}{2}$, is given by

$$P=1-\left[\left|\int \psi_{nlj}{}^*(z+1)\psi_{nlj}(z)dr\right|^2\right]^N-P_F, \tag{2}$$

where $\psi_{nlj}(z)$ and $\psi_{nlj}(z+1)$ are the single-electron wave functions for the initial and final states of a given orbital. P_F are the contributions to filled states (from $n'=1$ to x) which equal

$$P_F=\sum_{n'=1}^{n'=x} N\left|\int \psi_{n'lj}{}^*(z+1)\psi_{nlj}(z)dr\right|^2, \tag{3}$$

where $n'\neq n$ and N is the number of electrons in the n', l, j shell. A partly filled orbital is treated the same as a filled orbital except for the difference in the number of electrons. We have also arbitrarily assigned j values to electrons in an unfilled shell, filling first the $j=l-\frac{1}{2}$ level and then the $l+\frac{1}{2}$.

III. ELECTRON SHAKE-OFF AS THE RESULT OF β^- DECAY

A. Calculation

We have utilized Eq. (2) in order to calculate the probability for electron shake-off following β^- decay for each of the shells of 15 elements from helium to uranium. The wave functions computed at Oak Ridge on the CDC 1604-A using (1) a code written by Froese[13] for nonrelativistic Hartree-Fock solutions, and (2) a code written at Oak Ridge by Nestor *et al.*[11] for relativistic Hartree-Fock-Slater solutions. For a comparison of shake-off probabilities using various SCF wave functions, see Table I. There is reasonable agreement between the results, although failure to include exchange affects the outermost shell. There is no substantial difference between using the Slater[14] correction for the exchange potential and one suggested by Dirac[15] which is in accord with statistical theory. In the former case the exchange potential is given by

$$V_{\text{exc}}(r)=1.5[3\rho(r)/\pi]^{1/3}, \tag{4}$$

where $\rho(r)$ is the local electron density. In the later case the coefficient 1.5 is replaced by 1.0. At higher Z, deviations occur between the relativistic and nonrelativistic solutions, particularly for the lower shells, and for the s subshells in general. Also serious is the failure of the nonrelativistic solutions to account for the difference in shake-off probabilities between the levels that arise from j-j coupling. Table I also includes for comparison a more approximate calculation based on hydrogenic wave functions as obtained by using shake-

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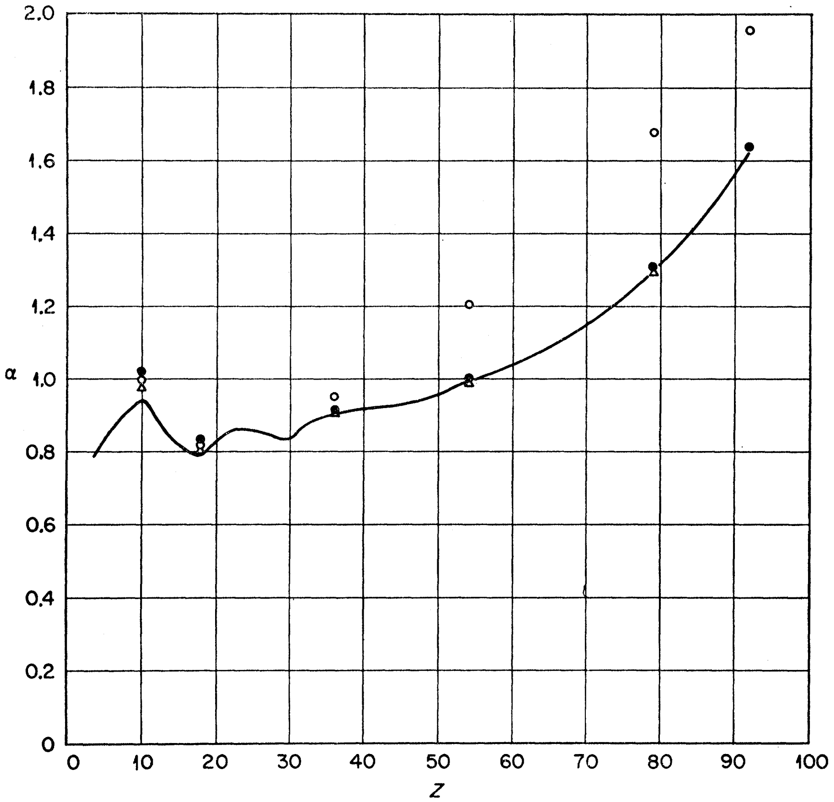

FIG. 1. Electron shake-off "constant" α, as calculated from Eq. (5) plotted against Z. Solid line has been derived using screening constants σ from nonrelativistic Hartree-Fock solutions; the points △ using σ from relativistic wave function with relativistic definitions [see Eq. (6)]; the points ○ from relativistic wave functions with nonrelativistic definition; and the points ● from Slater's recipe.

off constants derived by Skorobogatov,[16] and screening constants from Ref. 13. As with the SCF calculation we have employed the definition for electron shake-off as given by Eq. (2).

For most of the calculations reported in this paper we have used relativistic Hartree-Fock-Slater solutions (with the coefficient in the exchange potential = 1.5) with the exception of the light elements, $Z \leq 31$, in which nonrelativistic Hartree-Fock solutions were used. The calculated results for 15 elements undergoing β^- decay are shown in italics in Table II for all the possible shells. It would be desirable to interpolate these values in order to obtain the shake-off probabilities for all the elements. With this purpose in mind it is interesting to note that the use of hydrogenic wave functions gives the following simple expression[1-4]:

$$P_s = \alpha/(Z-\sigma)^2, \tag{5}$$

where P_s is the shake-off probability for a given shell n, l, j; α is a constant associated with that shell; σ is the screening number; and Z is the nuclear charge. In Fig. 1 we have plotted α for various evaluations of σ using P_s as obtained from SCF wave functions. The different values for σ have been determined from (1) nonrelativistic Hartree-Fock wave functions,[13] (2) Slater's recipe,[17] (3) relativistic Hartree solutions using the nonrelativistic definition for screening,[11] and (4) relativistic Hartree solutions using a relativistic definition for screening, viz.,

$$\sigma = Z - Z\bar{r}_H/\bar{r}_Z, \tag{6}$$

where $\bar{r}_H$ is the mean radius determined relativistically for a single electron moving in a given orbital about a nucleus of charge Z, and $\bar{r}_Z$ is the mean radius of an electron moving in the same orbital but for an atom with Z electrons as determined from relativistic SCF wave functions. It is apparent from Fig. 1 that α is not a true constant, regardless of the choice of σ. Nevertheless, such plots as shown in Fig. 1 are of use in helping to interpolate the calculated values for shake-off probabilities. We have interpolated between values of P_s for all the shells that are completely filled. These interpolated values are also given in Table II. Uncertainties arising from interpolation are smallest for the inner shells where changes in the shake-off probabilities between neighboring elements are gradual, and are largest for the outermost shells. With regard to the application of the results for the outermost shells, it should be remembered that the calculations given in Table II are for isolated atoms. For cases in which the atom is in a condensed medium or part of a molecule the shake-off probabilities, though essentially unchanged for the inner shells, may be considerably altered for the valence shells.

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Table II. Calculated electron shake-off as the result of β^- decay. Values in italic type have been calculated using SCF wave functions. Interpolated values are given in ordinary type. (Probability per shell given in %.)

Z	Element undergoing β^- decay	K $1s$	L_{I} $2s$	L_{II} $2p_{1/2}$	L_{III} $2p_{3/2}$	M_{I} $3s$	M_{II} $3p_{1/2}$	M_{III} $3p_{3/2}$	M_{IV} $3d_{3/2}$	M_{V} $3d_{5/2}$
2	He	*26.9*								
4	Be	6.10								
6	C	2.74								
8	O	1.56								
10	Ne	*1.03*	*4.77*	*5.55*	*11.10*					
12	Mg	0.673	2.76	2.66	5.35					
14	Si	0.455	1.78	1.55	3.14					
16	S	0.337	1.25	1.01	2.04					
18	Ar	*0.264*	*0.914*	*0.703*	*1.41*	*4.24*	*5.92*	*11.84*		
20	Ca	0.215	0.705	0.525	1.04	2.14	3.42	6.85		
21	Sc	*0.206*	*0.581*	*0.468*	*0.936*	*1.75*	*2.89*	*5.79*	*5.72*	
22	Ti	0.179	0.552	0.411	0.809	1.53	2.45	4.92		
24	Cr	0.153	0.447	0.334	0.659	1.21	1.79	3.54		
26	Fe	*0.132*	*0.367*	*0.273*	*0.547*	*0.981*	*1.36*	*2.69*	*6.31*	*3.21*
28	Ni	0.115	0.308	0.229	0.463	0.827	1.09	2.25		
30	Zn	0.102	0.265	0.194	0.387	0.710	0.872	1.91		
31	Ga	*0.0922*	*0.248*	*0.178*	*0.358*	*0.654*	*0.778*	*1.725*	*2.96*	*4.41*
32	Ge	0.0892	0.231	0.166	0.325	0.597	0.695	1.57	2.43	3.60
34	Se	0.0803	0.206	0.144	0.273	0.511	0.550	1.09	1.75	2.61
36	Kr	*0.0723*	*0.185*	*0.124*	*0.230*	*0.438*	*0.446*	*0.852*	*1.32*	*1.96*
38	Sr	0.0654	0.164	0.109	0.201	0.380	0.371	0.720	1.02	1.48
40	Zr	0.0593	0.148	0.0958	0.175	0.336	0.320	0.624	0.772	1.14
42	Mo	0.0539	0.133	0.0861	0.154	0.301	0.285	0.550	0.597	0.887
44	Ru	0.0496	0.121	0.0774	0.134	0.273	0.255	0.482	0.471	0.712
46	Pd	*0.0459*	*0.110*	*0.0703*	*0.124*	*0.248*	*0.231*	*0.429*	*0.387*	*0.572*
48	Cd	0.0425	0.100	0.0636	0.111	0.222	0.205	0.381	0.330	0.477
50	Sn	0.0395	0.0920	0.0583	0.100	0.199	0.179	0.336	0.275	0.403
52	Te	0.0372	0.0853	0.0537	0.0907	0.178	0.157	0.292	0.235	0.344
54	Xe	*0.0348*	*0.0791*	*0.0494*	*0.0819*	*0.160*	*0.144*	*0.258*	*0.205*	*0.300*
56	Ba	0.0330	0.0740	0.0459	0.0749	0.147	0.129	0.235	0.184	0.271
58	Ce	0.0311	0.0696	0.0430	0.0692	0.137	0.121	0.216	0.167	0.245
60	Nd	0.0296	0.0657	0.0402	0.0639	0.128	0.115	0.200	0.153	0.224
61	Pm	*0.0288*	*0.0640*	*0.0395*	*0.0616*	*0.125*	*0.112*	*0.193*	*0.146*	*0.211*
62	Sm	0.0282	0.0623	0.0380	0.0594	0.122	0.110	0.187	0.141	0.206
64	Gd	0.0270	0.0596	0.0361	0.0551	0.115	0.104	0.175	0.131	0.189
66	Dy	0.0258	0.0571	0.0345	0.0515	0.109	0.0999	0.165	0.121	0.176
68	Er	0.0247	0.0548	0.0331	0.0485	0.104	0.0954	0.156	0.113	0.164
70	Yb	*0.0240*	*0.0531*	*0.0322*	*0.0457*	*0.102*	*0.0901*	*0.147*	*0.106*	*0.151*
72	Hf	0.0232	0.0512	0.0307	0.0430	0.0954	0.0856	0.137	0.0982	0.138
74	W	0.0225	0.0493	0.0298	0.0405	0.0914	0.0814	0.128	0.0896	0.125
76	Os	0.0219	0.0474	0.0289	0.0380	0.0883	0.0777	0.119	0.0816	0.113
78	Pt	0.0214	0.0459	0.0281	0.0358	0.0846	0.0742	0.112	0.0744	0.104
79	Au	*0.0212*	*0.0453*	*0.0277*	*0.0348*	*0.0832*	*0.0721*	*0.108*	*0.0707*	*0.0992*
80	Hg	0.0210	0.0447	0.0274	0.0338	0.0814	0.0706	0.105	0.0680	0.0948
82	Pb	0.0206	0.0437	0.0266	0.0319	0.0785	0.0676	0.102	0.0629	0.0874
83	Bi	*0.0204*	*0.0432*	*0.0264*	*0.0311*	*0.0771*	*0.0658*	*0.0941*	*0.0608*	*0.0841*
84	Po	0.0203	0.0430	0.0261	0.0303	0.0758	0.0643	0.0970	0.0587	0.0809
86	Rn	0.0200	0.0429	0.0257	0.0286	0.0734	0.0623	0.0904	0.0547	0.0750
88	Ra	0.0198	0.0430	0.0254	0.0272	0.0711	0.0603	0.0836	0.0510	0.0698
90	Th	0.0197	0.0432	0.0251	0.0260	0.0691	0.0584	0.0773	0.0477	0.0666
92	U	*0.0196*	*0.0436*	*0.0250*	*0.0247*	*0.0678*	*0.0572*	*0.0721*	*0.0445*	*0.0606*

Z	Element undergoing β^- decay	N_{I} $4s$	N_{II} $4p_{1/2}$	N_{III} $4p_{3/2}$	N_{IV} $4d_{3/2}$	N_{V} $4d_{5/2}$	N_{VI} $4f_{5/2}$	N_{VII} $4f_{7/2}$	O_{I} $5s$	O_{II} $5p_{1/2}$	O_{III} $5p_{3/2}$
2	He										
4	Be										
6	C										
8	O										
10	Ne										
12	Mg										
14	Si										
16	S										
18	Ar										
20	Ca										
21	Sc	*19.3*									
22	Ti										
24	Cr										
26	Fe	*15.1*									
28	Ni										
30	Zn										
31	Ga	*7.24*	*11.2*								
32	Ge	5.22									
34	Se	3.47									
36	Kr	*2.39*	*4.53*	*9.23*							

TABLE II. (*continued*).

Z	Element undergoing β^- decay	N_{I} $4s$	N_{II} $4p_{1/2}$	N_{III} $4p_{3/2}$	N_{IV} $4d_{3/2}$	N_{V} $4d_{5/2}$	N_{VI} $4f_{5/2}$	N_{VII} $4f_{7/2}$	O_{I} $5s$	O_{II} $5p_{1/2}$	O_{III} $5p_{3/2}$
38	Sr	1.67	2.42	5.14							
40	Zr	1.32	1.70	3.52							
42	Mo	1.08	1.30	2.60							
44	Ru	0.815	1.03	2.00							
46	Pd	*0.771*	*0.849*	*1.62*	*6.30*	*10.0*					
48	Cd	0.650	0.710	1.34	4.27	6.89					
50	Sn	0.542	0.586	1.10	2.82	4.52					
52	Te	0.448	0.492	0.923	2.03	3.17					
54	Xe	*0.376*	*0.417*	*0.784*	*1.56*	*2.32*			*2.09*	*3.88*	*8.51*
56	Ba	0.325	0.360	0.672	1.23	1.80			1.11	2.29	5.04
58	Ce	0.289	0.321	0.591	1.03	1.50			0.852	1.87	4.11
60	Nd	0.262	0.288	0.522	0.871	1.28			0.694	1.61	3.43
61	Pm	*0.251*	*0.275*	*0.492*	*0.813*	*1.19*	*5.19*		*0.639*	*1.49*	*3.13*
62	Sm	0.240	0.264	0.464	0.763	1.10			0.598	1.42	2.94
64	Gd	0.225	0.244	0.420	0.664	0.964			0.531	1.28	2.61
66	Dy	0.212	0.230	0.389	0.586	0.848			0.486	1.16	2.40
68	Er	0.201	0.215	0.360	0.522	0.752			0.463	1.06	2.26
70	Yb	*0.193*	*0.204*	*0.341*	*0.468*	*0.671*	*2.56*	*3.80*	*0.432*	*0.983*	*2.18*
72	Hf	0.183	0.193	0.323	0.416	0.595	1.72	2.29	0.410	0.827	1.86
74	W	0.174	0.183	0.305	0.371	0.530	1.28	1.66	0.394	0.725	1.59
76	Os	0.165	0.174	0.288	0.330	0.478	0.996	1.30	0.376	0.650	1.35
78	Pt	0.158	0.166	0.270	0.300	0.435	0.801	1.06	0.358	0.583	1.13
79	Au	*0.155*	*0.162*	*0.262*	*0.288*	*0.416*	*0.726*	*0.970*	*0.351*	*0.560*	*1.05*
80	Hg	0.150	0.157	0.252	0.273	0.396	0.671	0.897	0.342	0.514	0.996
82	Pb	0.142	0.145	0.225	0.246	0.356	0.598	0.796	0.314	0.400	0.918
83	Bi	*0.139*	*0.138*	*0.209*	*0.236*	*0.337*	*0.572*	*0.759*	*0.301*	*0.358*	*0.883*
84	Po	0.135	0.133	0.199	0.225	0.319	0.539	0.727	0.288	0.334	0.831
86	Rn	0.129	0.125	0.184	0.206	0.291	0.469	0.652	0.264	0.299	0.700
88	Ra	0.123	0.119	0.173	0.189	0.267	0.410	0.592	0.244	0.285	0.584
90	Th	0.118	0.115	0.165	0.174	0.248	0.356	0.537	0.226	0.262	0.483
92	U	*0.113*	*0.111*	*0.158*	*0.162*	*0.230*	*0.308*	*0.488*	*0.209*	*0.242*	*0.399*

Z	Element undergoing β^- decay	O_{IV} $5d_{3/2}$	O_{V} $5d_{5/2}$	O_{VI} $5f_{5/2}$	P_{I} $6s$	P_{II} $6p_{1/2}$	P_{III} $6p_{3/2}$	P_{IV} $6d_{3/2}$	Q_{I} $7s$
54	Xe								
56	Ba								
58	Ce								
60	Nd								
61	Pm				*12.6*				
62	Sm								
64	Gd								
66	Dy								
68	Er								
70	Yb				*11.6*				
72	Hf								
74	W								
76	Os								
78	Pt								
79	Au	3.85	6.80		*3.49*				
80	Hg	3.20	5.08						
82	Pb	2.11	3.31						
83	Bi	*1.80*	*2.81*		*2.40*	*6.13*	*5.00*		
84	Po	1.56	2.43		1.89				
86	Rn	1.24	1.92		1.26				
88	Ra	1.04	1.62		0.912				
90	Th	0.881	1.34		0.690				
92	U	*0.762*	*1.21*	*3.57*	*0.539*	*1.15*	*2.55*	*4.69*	*9.43*

Z	Element undergoing β^- decay	Total shake-off
2	He	*26.9*
10	Ne	*22.5*
18	Ar	*25.3*
21	Sc	*37.7*
26	Fe	*31.0*
31	Ga	*29.7*
36	Kr	*21.8*
46	Pd	*21.8*
54	Xe	*21.3*
61	Pm	*27.1*
70	Yb	*24.2*
79	Au	*19.7*
83	Bi	*22.6*
92	U	*26.7*

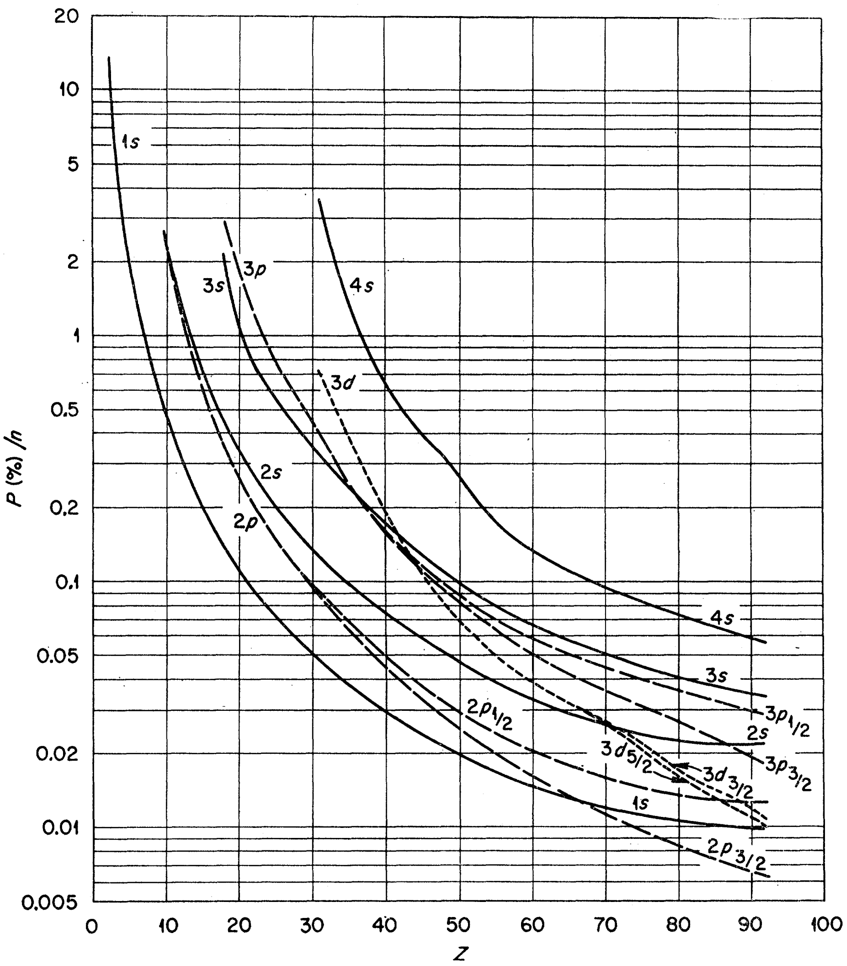

FIG. 2. Calculated percent probability for electron shake-off per shell divided by number of electrons in given shell, plotted as a function of Z for shells from 1s to 4s.

A graphical display of the dependence of electron shake-off on Z is given in Fig. 2 for all the shells from 1s to 4s. To give a better picture of the relative shake-off probability per electron, the calculations in Table II have been divided by the number of electrons in a given shell. From these plots and from Table II the following generalizations can be made: (1) For a given shell, shake-off decreases with Z. (2) For a given atom and angular momentum, shake-off increases with the principal quantum number. (3) For a given principal quantum number the shake-off per electron is greater for the higher angular momentum at low Z, but that at higher Z the roles are reversed. (4) The shake-off probability per electron becomes greater for the higher j states as Z becomes larger. (5) The total amount of electron shake-off summed over all the shells is fairly independent of Z.

B. Comparison of Electron Shake-Off Calculations with Experiment

Before a comparison is made between the calculations and experiment, the reader is reminded that the calculations are for the probability of producing a vacancy in a given shell due to electron shake-off. For the inner shells this is nearly the same as having the electron completely removed from the atom into the continuum. Simply described, if the electron has enough energy to promote itself from an inner shell to an excited state, it will probably also have the extra amount necessary for going to the continuum. For example, this can be seen from Table III, which shows the rapid decrease in the overlap integrals for filled states as one increases n, so that when n reaches a value where the shells are empty, transitions to these excited states should be negligible.

A comparison between theory and experiment is first made for electron shake-off from the innermost shells (see Table IV). The experimental data were obtained for the most part by observing the number of characteristic x rays in coincidence with the β^- particle, which gave evidence of the number of initial vacancies produced as the consequence of β^- decay. For calculations based on hydrogen wave functions, use was made of electron shake-off constants as calculated by Skorobogatov[16] and from the screening constants of Froese.[13] The agreement between calculations using hydrogenic

TABLE III. $|\psi_f{}^*\psi_i d\tau|^2$ for one electron initially in the $1s$ state of uranium as the result of β^- decay.

Final state	SCF	Hydrogenic
$1s$	0.99981017	0.99991020
$1-1s$	0.00018983	0.00008980
$2s$	0.00007637	0.00003740
$3s$	0.00001183	0.00000707
$4s$	0.00000294	0.00000264
$5s$	0.00000075	0.00000120
$6s$	0.00000016	0.00000072
$7s$	0.00000002	0.00000048
$1-\sum_{n=1}^{7} ns$	0.00009776	0.00004029

wave functions and those using SCF wave functions are in fairly good agreement for the K shell at lower Z. For higher Z and the higher shells, however, the hydrogenic wave functions give too low a value. In general, the agreement between the present calculations and experiment is satisfactory, in particular, the most recent data[18] on ^{169}Er and ^{210}Bi. The reader should, however, be warned that in the case of the K shell for the heavier elements the theory may not always hold, since the mean β^- energy may not always be in large excess of the binding energy. In fact for low-energy transitions many of the β^- particles may have energies lower than that required for K-shell ionization. For low-Z elements and for shells above the K, the requirement for the sudden approximation to be valid is nearly always met, viz., $E_\beta \gg E_B$, where E_β is the energy of the β^- particle and E_B is the binding energy of the given shell.

In Table V we have compared the results of theory and experiment for electron shake-off, primarily in the outer shells. In this case the experimental studies are based on the relative abundances of the differently charged ions resulting from the respective β^- decays. The calculated values of the outermost shell can be expected to be slightly higher than the experimental ones, since they include transitions to excited states that will not lead to ionization. In the case of Ne and Kr it has been possible in some recent experiments[19,20] to distinguish between transitions to excited states and to the continuum, and it was found that the probability for transitions to excited but bound states amounts to only a couple of percent, which is consistent with the difference between theory and experiment as listed in Table V. In the case of the β^- decay of He, transitions to bound excited states do play a very important role. However, a complete analysis, using Hylleras wave functions, of shake-off to the various bound states was made by Winther,[5] and his results were in excellent agreement with experiment. As far as it has been possible to ascertain, shake-off of the outer electrons has also been correctly predicted.

TABLE IV. Comparison of theory and experiment for electron shake-off probability ($\times 10^4$) in the inner shells as the result of β^- decay.

Isotope	Shell	Experiment[a]	Theory SCF[b]	Hydrogenic[c]
$^{32}\text{P}_{15}$	K	35[d]; 73[e]	39	35 (29)
$^{35}\text{S}_{16}$	K	22[e]; 30[f]	34	28 (23)
$^{90}\text{Y}_{39}$	K	4.7[d]; 12.7[g]	6.2	4.4 (4.3)
$^{90}\text{Y}_{39}$	L	48[d]	45	23 (17)
$^{99}\text{Tc}_{63}$	K	4.8[h]	5.2	3.6 (3.5)
$^{143}\text{Pr}_{59}$	K	4.3[i]	3.0	1.9 (1.9)
$^{143}\text{Pr}_{59}$	L	20[e]	18	8.9 (7.4)
$^{147}\text{Pm}_{61}$	K	1.3[i]; 3.8[j]; 0.9[h]	2.9	1.8 (1.7)
$^{147}\text{Pm}_{61}$	L	18[e]; 22[j]	17	8.2 (6.9)
$^{169}\text{Er}_{68}$	K	2.4[k]	2.5	1.4 (1.3)
$^{210}\text{Bi}_{83}$	K	1.2[j]; 1.4[g]; 2.0[k]	2.0	0.98 (0.95)
$^{210}\text{Bi}_{83}$	L	7[j]; 10[f]	10.1	4.1 (3.6)
$^{210}\text{Bi}_{83}$	M	40[d]	38	16 (10)

[a] Based on number of x rays and converted to total number of vacancies with the aid of atomic fluorescence yields. R. W. Fink, R. C. Jopson, H. Mark, and C. P. Swift, Rev. Mod. Phys. **38**, 513 (1966).

[b] As obtained from Table II either directly or by interpolation.

[c] As obtained from Ref. 16. Values in parentheses exclude transitions to excited states.

[d] G. Renard, J. Phys. Radium **18**, 681 (1957).

[e] F. Suzor and G. Charpak, J. Phys. Radium **21**, 465 (1960), and earlier work.

[f] W. Rubinson and J. J. Howland, Phys. Rev. **96**, 1610 (1954).

[g] A. Michalowicz and R. Bouchez, J. Phys. Radium **16**, 578 (1955).

[h] P. Stephas and B. Crasemann, Phys Rev. **164**, 1509 (1967).

[i] H. Langevin-Joliot, Ann. Phys. (Paris) **2**, 16 (1957).

[j] F. Boehm and C. S. Wu, Phys. Rev. **93**, 518 (1954).

[k] P. Erman, B. Sigfridsson, T A. Carlson, and K. Fransson, Nucl. Phys. (to be published); values include correction for β rays whose energies fall below the K binding energy.

In summary, the calculation of electron shake-off using SCF wave functions seems to be in good agreement with the existing experimental evidence. Further confirmation is, however, desirable, particularly in view of the possibility of other modes of ionization such as direct collision, which will be discussed briefly in Sec. III D.

C. Average Energy

Serber and Snyder[21] have calculated the average energy transferred to the parent atom as the result of β^- decay by determining the change in the electrostatic energy of the nucleus at the center of the electronic charge cloud. They give two formulas in Ref. 21: first,

TABLE V. Comparison between theory and experiment for electron shake-off from the outermost shell.

Parent atom	Z	Shell	Probability of removing one electron (%) Experiment[a]	Theory[b]
He	2	K	10.1	10.5
Ne	10	L	17.5	19.1
Ar	18	M	12.5	19.3
Kr	36	N	10.9	14.0
Xe	54	O	8	12.7

[a] See T. A. Carlson, Phys. Rev. **131**, 676 (1963), and earlier references cited therein.

[b] As based on Table II together with a correction for multiple shake-off. This correction, which is small, is discussed in Ref. 7. These calculations *include* possible transitions to excited states, and thus should be slightly higher than the experimental value, with the exception of He which has been calculated elsewhere and does not include transitions to the excited states [A. Winther (Ref. 5)].

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[18] P. Erman, B. Sigfridsson, T. A. Carlson, and K. Fransson, Nucl. Phys. (to be published).

[19] M. O. Krause, T. A. Carlson, and R. Dismukes, Phys. Rev. (to be published).

[20] H. J. Andra, K. Luchner, and W. Schambeck, Z. Naturforsch. **21**, 1987 (1966).

[21] R. Serber and H. S. Snyder, Phys. Rev. **87**, 152 (1952).

TABLE VI. Comparison of calculations of average energy (eV) expended in electron shake-off.

Parent atom	Z	Present paper[a]	Serber and Snyder[b] (2a)	(2b)
Ne	10	28	53	57
Ar	18	38	64	73
Kr	36	54	81	96
Xe	54	70	93	112
Yb	70	84	100	124
U	92	131	110	139

[a] Based on 1.8 $\Sigma_n P_n E_n$, where P is the probability for electron shake-off from shell n as taken from Table II, E_n is the binding energy, and 1.8 is an approximate correction factor relating binding energies to the average energy expended in electron shake-off.

[b] R. Serber and H. S. Snyder, Phys. Rev. **87**, 152 (1952); (2a) and (2b) refer to the two different equations that are given in that paper. (2a) should be better for lighter elements and (2b) for heavier.

Eq. (2a), which is designed to fit the lighter elements better; and second, Eq. (2b), which is suited for heavier elements. Results based on their formulas are given in Table VI. One may also obtain the average energy from the probabilities listed in Table II and the binding energies. These values must be amended, however, to also include the average excess energy possessed by shake-off electrons. This has been estimated from the shape of the shake-off energy spectrum given by Levinger[3] for the K shell to be 1.8 times the binding energy. A similar relationship can be expected for the other shells. Thus, the average energy $\bar{E}$ can be obtained from

$$\bar{E}=1.8\sum_{nlj} P_{nlj}E_{nlj}\,, \tag{7}$$

where P_{nlj} and E_{nlj} are the probabilities and binding energies for the various shells of a given atom. Results using Eq. (7) are also given in Table VI. There is a fair agreement between our evaluation and those of Serber and Snyder, although the present treatment gives somewhat lower values, particularly noticeable for the lighter elements.

D. Direct Collision

In addition to electron shake-off, which has been described as a monopole excitation, there is also the possibility of self-ionization by means of a direct dipole interaction between the emerging β^- particle and an electron that is part of the same atom as the decaying nucleus. The importance of direct collision to auto-ionization was appraised earlier[2] to be negligible. More recent theoretical evaluations,[22,23] however, have shown that in certain areas direct collision should not be neglected, particularly the shape of the energy spectrum for electrons resulting from auto-ionization. With regard to the total probability for direct collision relative to shake-off it can be said that when $E_\beta \gg E_B$, where E_β is the energy of the β^- particle and E_B is the binding energy of an electron in a given shell, direct collision is indeed negligible. When $E_\beta \approx E_B$, the probability for direct collision may be the same order as shake-off. However, when the energy of the β particle is close to the threshold, the simple theories for direct collision and shake-off are no longer valid. What happens near the threshold has been investigated experimentally by measuring the amount of auto-ionization in the K shell as a function of the energy of the β^- particle.[18] This study (as well as one on photo-ionization[9] in the K shell of Ne that gives rise to L-shell ionization) showed that the total probability for auto-ionization was essentially independent of the initial energy of the β^- particle (or photoelectron) as long as the energy was higher than about three times the ionization threshold, but between this point and threshold the probability dropped with decreasing energy. In summary, the probability for removing an electron from a given shell by means of direct collision is negligible compared to electron shake-off so long as the energy of the β^- particle is more than several times the binding energy of that shell; at energies near the threshold, the situation is confused, but the net result seems to be a decrease in the total probability for auto-ionization.

IV. ELECTRON SHAKE-OFF AS THE RESULT OF PROCESSES OTHER THAN β^- DECAY

Electron shake-off can arise from a variety of processes other than β^- decay. Calculations of the shake-off probabilities for these processes can be made in an analogous fashion to β^- decay, by obtaining the single-electron wave functions for the initial and final states and evaluating Eq. (2). Let us consider a few examples.

A. β^+ Decay

In positron decay the final state has the same electron configuration as in negatron decay, but the nuclear charge is $Z-1$ rather than $Z+1$. In the earlier more approximate treatment, it was assumed that positron decay of a given element would yield the same shake-off probability, as would β^- decay for the same element. In Table VII we have compared calculations using single-electron wave functions from Hartree-Fock solutions for Kr undergoing β^+ and β^- decay. The results for the inner shells are quite similar, but there is substantially

TABLE VII. Comparison of electron shake-off in β^- and β^+ decay. Probability for electron shake-off[a] (%).

Shell	$\mathrm{Kr}\xrightarrow{\beta^-}\mathrm{Rb}^+$	$\mathrm{Kr}\xrightarrow{\beta^+}\mathrm{Br}^-$
1*s*	0.070	0.074
2*s*	0.174	0.200
2*p*	0.324	0.415
3*s*	0.460	0.525
3*p*	1.41	1.70
3*d*	3.39	3.73
4*s*	2.89	10.0
4*p*	14.1	19.8

[a] Calculations based on equations using nonrelativistic Hartree-Fock wave functions.

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[22] E. L. Feinberg, J. Nucl. Phys. (USSR) **1**, 612 (1965).

[23] R. M. Weiner, Phys. Rev. **144**, 127 (1966).

more shake-off in the case of positron decay for the outer shells.

B. Photo-Ionization and Internal Conversion

In photo-ionization, electron shake-off arises from change in the effective charge that is felt by the remaining electrons as a vacancy is suddenly created in an atom. Calculations are obtained from the overlap of wave functions for the atom and for the final state, which is a singly charged ion with a hole in the shell where photo-ionization has taken place. A number of such calculations have been previously reported.[8–11] The shake-off probabilities for the outer shells of a given atom are similar to those found for β^- decay. That is, when the outer shell feels a loss of one shielding electron, an effect is produced that is very similar to the gain of one unit of nuclear charge. It was in fact suggested earlier[8,24] that for a given shell the probability for electron shake-off due to photo-ionization, P_p, is related to shake-off due to β^- decay, P_β, by the following:

$$P_p = P_\beta[\Delta Z_{\text{eff}}(p)]^2/[\Delta Z_{\text{eff}}(\beta)]^2, \tag{8}$$

where $\Delta Z_{\text{eff}}(p)$ and $\Delta Z_{\text{eff}}(\beta)$ are the changes in effective charge felt by that shell for photo-ionization and β^- decay, respectively. In Table VIII we have given shake-off probabilities for K photo-ionization of Kr, using Hartree-Fock wave functions. In the third and fourth columns we have also estimated P_p by using Eq. (8) and the effective charges as determined by (1) Slater's recipe[17] and (2) from the wave functions themselves. We see that good agreement is obtained between P_p calculated directly and calculated using ΔZ_{eff} from the wave functions. The use of Slater's recipe is also of some use but can be misleading, particularly for shells close to the initial vacancy and for s orbitals.

Probabilities for electron shake-off as the result of internal conversion can be taken directly from the results on photo-ionization. That is, if an electron is converted in shell X, then the shake-off probabilities using Eq. (2) are the same as though photo-ionization had occurred in this shell, simply because in both cases final states are identical, viz., a singly charged ion with a hole in the X shell.

TABLE VIII. Probability (%) for electron shake-off as the result of K photo-ionization in Kr.

Shell	P[a]	$P(S)$[b]	$P(\sigma)$[c]
$1s$	0.0038	0.0063	0.0022
$2s$	0.053	0.126	0.067
$2p$	0.27	0.23	0.25
$3s$	0.25	0.46	0.25
$3p$	1.22	1.41	1.28
$3d$	3.66	3.39	3.68
$4s$	2.23	2.83	2.27
$4p$	13.91	14.14	13.91

[a] Calculation of electron shake-off using Eq. (2) and nonrelativistic Hartree-Fock wave functions.
[b] Estimation of electron shake-off using Eq. (8) and σ from Slater's recipe.
[c] Estimation of electron shake-off using Eq. (8) and σ from Hartree-Fock wave functions.

TABLE IX. Electron shake-off probability (%) resulting from electron. Capture in ^{133}Cs.

Experiment[a]	Theory
0.0025±0.0002	0.0088[b] 0.0062 (0.0032)[c]

[a] N. L. Lark and M. L. Perlman, Phys. Rev. **120**, 536 (1960).
[b] From Eq. (2) using single-electron relativistic Hartree wave functions.
[c] From H. Primakoff and F. T. Porter [Phys. Rev. **89**, 920 (1953)], using a two-electron solution. The value in parentheses includes an estimated correction for transitions to filled states.

C. Auger Processes

Auger processes also can remove an inner-shell electron suddenly and thus give rise to electron shake-off. Here the initial state is the ion with a hole in the X shell, whereupon following the X-YY' Auger transition, the final state is the doubly charged ion with holes in the Y and Y' shells. Several calculations of electron shake-off have been reported for Auger processes[8,10,25] and have been most useful in helping to give a complete account of the charge spectrum arising from the atomic readjustment to inner shell vacancies. (However, see Sec. IV D for the limitation of shake-off calculations.)

D. Electron Capture and Other Cases where Electrons Are Removed from the Same Shell

As pointed out in Sec. III D, calculations based on Eq. (2) will no longer be valid when the outgoing electron which gives rise to shake-off has insufficient velocity for application of the sudden approximation. The validity of Eq. (2) also depends on being able to treat the problem with single-electron wave functions rather than as a many-body problem. Calculations based on single-electron wave functions agree with experiment so long as one considers only a change in the central potential due to a change in nuclear charge or the loss of an electron from a shell that is inside the one being considered. In cases where sudden vacancies in a given shell have promoted additional electron ejection from the same shell, the simple treatment using Eq. (2) is no longer correct and a many-body solution, explicitly containing electron correlation, must be applied. Such cases can be found in the double-electron ejection from the same shell as the result of photo-ionization,[26] Auger processes,[27,28] and electron capture.[29]

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[24] M. O. Krause, M. L. Vestal, W. H. Johnston, and T. A. Carlson, Phys. Rev. **133**, A385 (1964).

[25] M. Wolfsberg and M. L. Perlman, Phys. Rev. **99**, 1833 (1955).

[26] T. A. Carlson, Phys. Rev. **156**, 142 (1967). Also relative to this paper see the two-electron calculation of F. W. Byron, Jr., and C. J. Joachain, Phys. Letters **24A**, 616 (1967).

[27] T. A. Carlson and M. O. Krause, Phys. Rev. Letters **14**, 390 (1965).

[28] T. A. Carlson and M. O. Krause, Phys. Rev. Letters **17**, 1079 (1966).

[29] N. L. Lark and M. L. Perlman, Phys. Rev. **120**, 536 (1960).

For an example of this problem we have compared in Table IX the experimental result[29] on double K vacancies as the consequence of electron capture in Cs with calculations using relativistic single-electron wave functions. The initial configuration is the Cs atom and the final one is singly charged Xe with a hole in the K shell. The agreement is poor. Also listed in Table IX is the calculation of Primakoff and Porter,[30] who made a two-electron calculation. Their calculation does not contain a correction for contributions to filled states. From our computations we estimate that such a correction would reduce their value by about $\frac{1}{2}$ (this value is given in parentheses) which would then be in fairly good agreement with experiment.

E. Electron Impact

Double ionization by electron impact is not generally considered a simple shake-off phenomenon, and in the case of ionization in the outer shell it probably is not.[31] However, if an electron is ejected by electron impact from an inner shell, there is often the possibility that the velocities of both the bombarding electron and the knocked out electron are large compared to the velocities of the outer shell orbital electrons. If such is the case, electron shake-off for the outermost shell can be calculated from Eq. (2). In fact the initial and final states are precisely the same as would be the case of photo-ionization. It is interesting to compare the intensities for simultaneous K and L vacancies in neon due to bombardment of 5-keV electrons[32] with those obtained for photo-ionization. In both cases the probability is about 16%, which in turn agrees with electron shake-off calculations. Thus, it would appear that if an electron is ejected from one of the inner shells of an atom by means of impact with a high-energy electron, shake-off can occur from the outer shell that is amenable to calculations based on the sudden approximation. In this context the appearance of x-ray satellites has been discussed as the result of double vacancies produced in electron bombardment.[33,34]

V. CONCLUSION

The availability of good self-consistent wave functions in increasing number has now made it possible to compute fairly accurate electron shake-off probabilities in a comprehensive manner. This has been done for β^- decay. It may also be done for a number of other phenomena, of which several examples are given. In addition to offering a more extensive and accurate evaluation of electron shake-off, these calculations should also serve as a goad for more precise experiments to test the limits of the applicability of the sudden approximation.

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[30] H. Primakoff and F. T. Porter, Phys. Rev. **89**, 930 (1953).

[31] Experimental results on the excitation of argon due to ionization in the outer shell by electrons [W. R. Bennett, Jr., G. N. Mercer, P. J. Kindlmann, B. Wexler, and H. Hyman, Phys. Rev. Letters **17**, 987 (1966)] have been compared with calculations based on the sudden approximation [S. H. Koozekanani, J. Quant. Electron. **2**, 770 (1966)]. The experimental results are several times larger than theory, but there is some question as to cascade contributions.

[32] H. Korber and W. Mehlhorn, Z. Physik **191**, 217 (1966). W. Mehlhorn (private communication) gives, in a more recent analysis using 4-keV electrons, 19±2%.

[33] V. P. Sachenko and V. F. Demekhin, Zh. Eksperim. i Teor. Fiz. **49**, 765 (1965) [English transl.: Soviet Phys.—JETP **22**, 532 (1966)].

[34] T. Åberg, Phys. Rev. **156**, 35 (1967).