Relativistic K-shell Auger rates, level widths, and fluorescence yields

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Systematic relativistic (Dirac-Hartree-Slater) calculations of atomic K-shell Auger transition probabilities are reported for 25 elements with $18 \leq Z \leq 96$. K-level Auger widths are found to be enhanced by relativistic effects, while total K-level widths are reduced. Relativistic theoretical K-shell fluorescence yields are in excellent agreement with experiment. Theoretical relative intensities of K-LX Auger transitions in heavy elements, calculated in j-j coupling, agree well with measurements; for low Z, configuration interaction and intermediate coupling must apparently be included.

I. INTRODUCTION

Radiationless transitions that fill atomic 1s vacancies have been the subject of numerous theoretical studies[1] since the time when Wentzel formulated the basic ansatz for the calculation of Auger rates.[2] Systematic theoretical work on K-shell Auger transitions has to date been confined to nonrelativistic calculations. Although several relativistic calculations have been performed,[3-6] these deal with selected transitions, usually for only a few elements. None of the K-LN and only a few of the K-XY transitions have ever been calculated relativistically. These transitions account for ~10% of the 1s Auger width of Hg, for example.

In the present paper, we report on systematic relativistic calculations of K-shell Auger rates, including all possible transitions, for 25 elements with $18 \leq Z \leq 96$. These radiationless transition rates have been combined with relativistic x-ray emission probabilities[7] to derive fluorescence yields. The theoretical K-LX spectra are compared with experimental data. In a separate paper,[8] we report on relativistic K-LL Auger spectra in intermediate coupling with configuration interaction.

II. THEORY

We calculate the Auger transition probabilities from perturbation theory, in j-j coupling, assuming frozen orbitals. The total rate for a transition $n_1'\kappa_1' \rightarrow n_1\kappa_1 n_2\kappa_2$ is

$$T = \tau(2j_1'+1)^{-1} \sum_{\substack{J,J' \\ M,M'}} \sum_{\kappa_2'} |D-E|^2 , \tag{1}$$

where

$$\tau = \begin{cases} \frac{1}{2} \text{ if } n_1\kappa_1 = n_2\kappa_2 \\ 1 \text{ otherwise.} \end{cases} \tag{2}$$

The direct and exchange matrix elements are

$$D = \langle j_1'(1) j_2'(2) J'M' \mid V_{12} \mid j_1(1) j_2(2) JM \rangle , \tag{3}$$

$$E = \langle j_1'(1) j_2'(2) J'M' \mid V_{12} \mid j_1(2) j_2(1) JM \rangle . \tag{4}$$

The primed quantum numbers j_1' and j_2' pertain to the major components of the wave functions of the initial hole and of the hole in the continuum (filled by the Auger electron), respectively. The unprimed j_1 and j_2 characterize the final two-hole state. The continuum wave function is normalized to represent one ejected electron per unit time. Atomic units are used throughout this paper.

Coupling with open outer shells (if any) is not taken into account in Eq. (1). No error is introduced by this approximation because such coupling does not produce appreciable shifts or splitting in the K Auger-electron energy. One can therefore sum over final states and the resultant rate is independent of the passive-electron structure.[9]

The wave functions are solutions of the Dirac-Hartree-Slater (DHS) equations.[10] The two-electron operator V_{12} is chosen according to the original Møller formula,[11]

$$V_{12} = (1 - \alpha_1 \cdot \alpha_2) \exp(i\omega r_{12})/r_{12} , \tag{5}$$

where the α_i are Dirac matrices and ω is the wave number of the virtual photon. The form V_{12} of the interaction operator is suitable for electron orbitals in a local potential, as in the DHS model used here.

The direct and exchange matrix elements can be evaluated through standard techniques.[11,12] For details, the reader is referred to Ref. 11.

III. NUMERICAL CALCULATIONS

The wave functions were generated according to the DHS approach[10] for configurations that contain an initial 1s vacancy. A general relativistic Auger program, developed in the course of calculations of L-shell radiationless transition probabilities,[11] was used to compute the K-shell Auger transition rates. The transition energies were derived by applying the "$Z+1$ rule"[13] to theoretical neutral-atom binding energies.[10] This simplification was important, because so many transitions must be included in a complete K-shell Auger calculation. The error introduced in the Auger energies is typically ~30 eV; this has been found to have negligible effect on the Auger Matrix elements.

The total Auger rates were combined with relativistic x-ray transition rates[7] to derive K-shell fluorescence yields.

IV. RESULTS AND DISCUSSION

A. K-shell Auger level widths and fluorescence yields

Partial K-LL, K-LX, and K-XY Auger widths, the total K-shell Auger width $\Gamma_A(K)$, the total K level width $\Gamma(K)$, and the flourescence yield ω_K are listed in Table I for each of 25 elements with atomic numbers $18 \leq Z \leq 96$. The present relativistic DHS total K-shell Auger widths $\Gamma_A(K)$ are compared in Fig. 1 with nonrelativistic Hartree-Slater (HS) results.[14,15] At low Z, the DHS widths are seen to converge toward the nonrelativistic HS results of Walters and Bhalla.[14] Relativistic effects enhance the K Auger width by 4% at $Z=35$ and by 18% at $Z=54$. The nonrelativistic widths computed by McGuire[15] consistently exceed the HS results as well as the present DHS widths, except for the lowest atomic numbers. The structure displayed in McGuire's[15] widths may be due to the procedure by which they were calculated,

TABLE I. Theoretical K-shell Auger and total atomic level widths (in eV) and fluorescence yields, from relativistic calculations.

Element	Γ_{K-LL}	Γ_{K-LX}	Γ_{K-XY}	$\Gamma_A(K)$	$\Gamma(K)$	ω_K
$_{18}$Ar	0.485	0.0866	0.003 95	0.576	0.656	0.122
$_{20}$Ca	0.522	0.115	0.006 45	0.643	0.774	0.170
$_{25}$Mn	0.599	0.144	0.008 65	0.749	1.106	0.323
$_{30}$Zn	0.654	0.166	0.010 5	0.830	1.620	0.488
$_{35}$Br	0.699	0.213	0.015 9	0.928	2.488	0.627
$_{36}$Kr	0.707	0.224	0.017 3	0.948	2.714	0.651
$_{40}$Zr	0.740	0.263	0.022 6	1.025	3.825	0.732
$_{42}$Mo	0.757	0.279	0.025 0	1.061	4.52	0.765
$_{45}$Rh	0.781	0.305	0.028 6	1.114	5.77	0.808
$_{47}$Ag	0.799	0.323	0.029 8	1.151	6.76	0.830
$_{50}$Sn	0.825	0.350	0.035 6	1.211	8.53	0.858
$_{52}$Te	0.843	0.370	0.038 6	1.252	9.92	0.874
$_{54}$Xe	0.863	0.391	0.042 7	1.297	11.49	0.887
$_{56}$Ba	0.884	0.413	0.045 9	1.343	13.25	0.899
$_{60}$Nd	0.929	0.450	0.051 7	1.431	17.36	0.918
$_{63}$Eu	0.968	0.479	0.056 2	1.503	21.05	0.929
$_{67}$Ho	1.028	0.520	0.062 4	1.611	26.87	0.940
$_{70}$Yb	1.079	0.554	0.067 5	1.700	32.02	0.947
$_{74}$W	1.157	0.609	0.075 7	1.842	40.04	0.954
$_{80}$Hg	1.304	0.708	0.091 4	2.104	54.82	0.962
$_{83}$Bi	1.393	0.770	0.101	2.264	63.63	0.964
$_{88}$Ra	1.574	0.890	0.120	2.584	80.59	0.968
$_{90}$Th	1.660	0.947	0.128	2.728	88.20	0.969
$_{92}$U	1.756	1.007	0.137	2.900	96.31	0.970
$_{96}$Cm	1.979	1.146	0.158	3.282	114.09	0.971

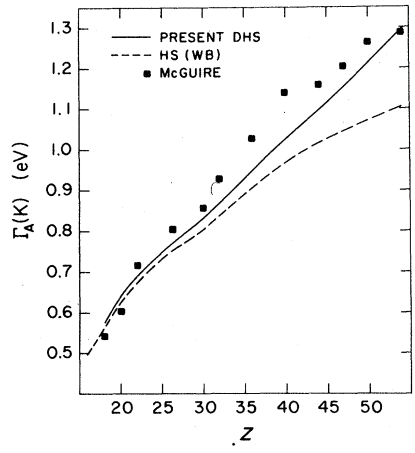

FIG. 1. Atomic K-shell Auger widths, in eV, as a function of atomic number. Results from the present relativistic DHS calculations are compared with nonrelativistic HS results of Walters and Bhalla (Ref. 14) and nonrelativistic calculations by McGuire (Ref. 15).

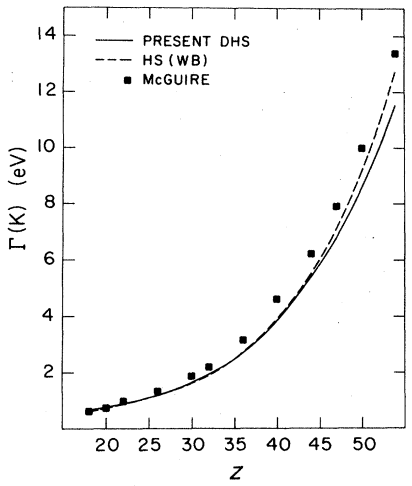

FIG. 2. Total atomic K-level widths, in eV, as a function of atomic number. The present relativistic DHS results are compared with nonrelativistic HS calculations of Walters and Bhalla (Ref. 14) and nonrelativistic results of McGuire (Ref. 15).

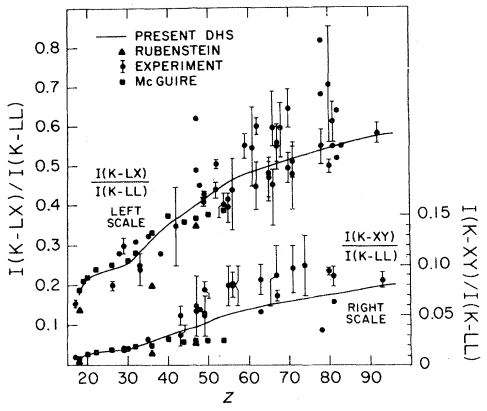

FIG. 3. $(K\text{-}LX)/(K\text{-}LL)$ and $(K\text{-}XY)/(K\text{-}LL)$ Auger-transition intensity ratios, as functions of atomic number. Theoretical ratios from the present relativistic DHS calculations are compared with nonrelativistic Hartree calculations of Rubenstein and Snyder (Ref. 17) and nonrelativistic results of McGuire (Ref. 15), and with experimental data (Ref. 16).

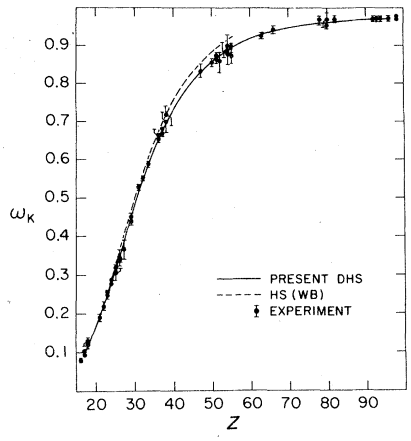

FIG. 4. Atomic K-shell fluorescence yields, as a function of atomic number. Theoretical results from the present relativistic DHS calculations are compared with nonrelativistic HS calculations of Walters and Bhalla (Ref. 14) and with experimental data selected as "most reliable" by Bambynek *et al.* (Ref. 1).

which involves the piecewise fitting of the HS atomic potential by straight lines.

In Fig. 2, we compare the total K-level widths from the present relativistic calculations with nonrelativistic HS results.[12,13] The relativistic effects enhance the K Auger rates but reduce the x-ray rates, so that the total level widths are affected less than the radiative or radiationless partial widths; they are reduced by 10% at $Z = 54$.

TABLE II. K-LX Auger spectrum of platinum.

Transition	Relative intensity [a] Experiment [b]	Present theory [c]
$K\text{-}L_1M$	0.35 ± 0.05	0.42
$K\text{-}L_1M_2$	0.32 ± 0.04	0.36
$K\text{-}L_2M_1$, $K\text{-}L_1M_3$, $K\text{-}L_2M_2$	0.47 ± 0.02	0.54
$K\text{-}L_1M_4$, $K\text{-}L_1M_5$, $K\text{-}L_2M_3$	0.35 ± 0.05	0.36
$K\text{-}L_2M_4$, $K\text{-}L_2M_5$	0.11 ± 0.05	0.07
$K\text{-}L_3M_1$	0.11 ± 0.05	0.16
$K\text{-}L_3M_2$, $K\text{-}L_1N_1$	0.44 ± 0.09	0.41
$K\text{-}L_1N_{2,3}$	0.10 ± 0.05	0.14
$K\text{-}L_3M_3$, $K\text{-}L_1N_{4,5}$	0.4 ± 0.12	0.32
$K\text{-}L_2N_1$, $K\text{-}L_1O_{1\text{-}3}$, $K\text{-}L_1N_{6,7}$	0.1 ± 0.05	0.12
$K\text{-}L_3M_4$, $K\text{-}L_1O_{4,5}$, $K\text{-}L_2N_{2,3}$, $K\text{-}L_3M_5$	0.25 ± 0.07	0.15
$K\text{-}L_3N_{1\text{-}7}$	0.18 ± 0.06	0.21

[a] Normalized to $I(K\text{-}L_1L_1) = 1.0$.
[b] Reference 18.
[c] Relative intensities for $Z = 80$.

The theoretical intensity ratios $I(K\text{-}LX)/I(K\text{-}LL)$ and $I(K\text{-}XY)/I(K\text{-}LL)$ are compared in Fig. 3 with measurements tabulated by Sevier.[16] The theoretical DHS $(K\text{-}LX)/(K\text{-}LL)$ ratios agree very well with the experimental data, while agreement of the $(K\text{-}XY)/(K\text{-}LL)$ ratios is only fair; in both cases, however, the present relativistic theory comes much closer to the data than earlier nonrelativistic calculations.[15,17]

In Fig. 4 K-shell fluorescence yields ω_K from the present relativistic work are compared with

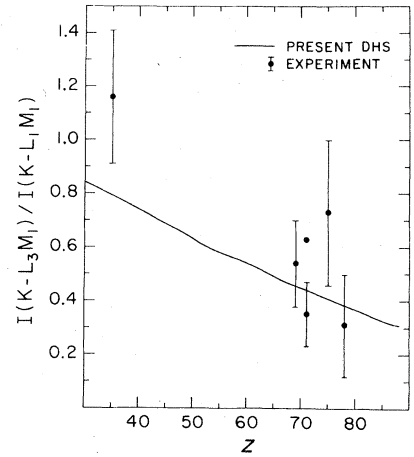

FIG. 5. $(K\text{-}L_3M_1)/(K\text{-}L_1M_1)$ Auger-transition intensity ratios, as a function of atomic number. Present relativistic DHS calculations are compared with experimental data from Ref. 16.

TABLE III. K-LX Auger spectra of thulium and lutetium.

Transition		Relative intensities [a] $_{69}$Tm [b]	$_{71}$Lu [c]	Present theory [d]	
K-L_1M_1		0.39 ± 0.04	0.40 ± 0.05	0.42	
K-L_1M_2		0.30 ± 0.03	0.31 ± 0.05	0.31	
K-L_1M_3	0.29 ± 0.05	0.53 ± 0.06	0.52 ± 0.10	0.26	0.50
K-L_2M_1	0.24 ± 0.05			0.24	
K-L_2M_2	0.05 ± 0.02			0.04	
K-L_1M_4	0.05 ± 0.02	0.63 ± 0.06	0.45 ± 0.04	0.02	0.49
K-L_1M_5	0.09 ± 0.03			0.02	
K-L_2M_3	0.44 ± 0.04			0.41	
K-L_2M_4		0.16 ± 0.07	0.09 ± 0.03	0.02	0.09
K-L_2M_5				0.07	
K-L_3M_1		0.21 ± 0.04	0.14 ± 0.03	0.19	
K-L_3M_2		0.44 ± 0.05	0.42 ± 0.05	0.39	
K-L_1N_1	0.12 ± 0.03	0.63 ± 0.07	0.55 ± 0.05	0.10	0.50
K-L_3M_3	0.50 ± 0.06			0.40	
K-L_1N_2		0.12 ± 0.05	0.05 ± 0.02	0.13	
K-L_1N_3					
K-$L_1N_{4,5}$					
K-L_3M_4		0.30 ± 0.09	0.21 ± 0.03	0.24	
K-L_3M_5					
K-L_1O					
K-L_2N_1					
K-L_2N_2		0.20 ± 0.06	0.12 ± 0.02	0.10	
K-L_2N_3					
K-$L_2N_{4,5}$			0.03 ± 0.02	0.04	
K-L_2O					
K-$L_3N_{4,5}$			0.04 ± 0.02	0.06	
K-L_3O					
K-L_3N_1			0.21 ± 0.03	0.22	
K-L_3N_2					
K-L_3N_3					

[a] Normalized to $I(K\text{-}L_1L_1) = 1.0$.
[b] Reference 20.
[c] Reference 19.
[d] Relative intensities for $Z = 70$.

nonrelativistic HS results[14] and with the selected "most reliable" experimental values compiled by Bambynek *et al.*[1] The DHS results are in excellent agreement with the data. Relativistic effects are seen to reduce ω_K by 3% at $Z = 54$. For medium-Z and heavy elements, the decay of a 1s vacancy is dominated by radiative transitions; for this reason relativistic effects do not show up strongly in K-shell fluorescence yields. If one compares instead the Auger yields $a_K = 1 - \omega_k$, the effect of relativity is clearly seen: for $Z = 54$, we have $a_K = 0.113$ from the relativistic theory, and $a_K = 0.087$ from non-relativistic HS calculations.

B. K-LX Auger spectra

Some of the $(K\text{-}LX)/(K\text{-}L_1M_1)$ relative intensities from the present DHS calculations are compared with experiment[16] in Figs. 5 and 6. Agreement between theory and experiment is seen to be good, considering the scarcity of data and large experimental error bars.

Experimental[18] and calculated relative intensities of the Auger lines in the K-LX spectrum of $_{78}$Pt are listed in Table II. Similarly, the measured relative K-LX Auger intensities of thulium[20] and lutetium[19] are compared in Table III with DHS intensities from the present calculations, in j-j coupling. In the Pt, Tm, and Lu spectra, intensities have been normalized with reference to the K-L_1L_1 transition. In Table IV, we compare experimental intensities[21] of lines in the bromine K-LX Auger spectrum with results of the relativistic DHS calculations; here, intensities are normalized with reference to the K-L_1M_1 transition.

The line identification from the original experimental work[18-21] is retained in Tables II–IV, with one exception in the Pt spectrum. Here, the K-L_1N_1 line was regrouped with the K-L_3M_2 line (Table II) on the basis of our relativistic transition-energy calculations.[10] Toburen and Albridge[18]

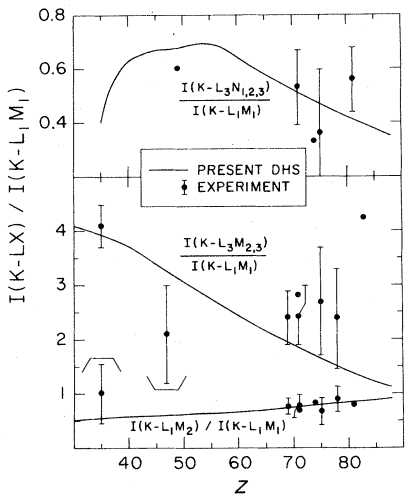

FIG. 6. Selected $(K\text{-}LX)/(K\text{-}L_1M_1)$ Auger-transition intensity ratios, as functions of atomic number. Present relativistic DHS results are compared with experimental data from Ref. 16.

had identified a peak observed at 63 694 eV as $K\text{-}L_3M_2$, and a peak observed at 63 870 eV as $K\text{-}L_1N_{1,2,3}$. The DHS energy calculations[10] show, however, that the $K\text{-}L_3M_2$ Auger-electron energy is 63 685 eV, and the $K\text{-}L_1N_{1,2,3}$ energies are 63 696, 63 812, and 63 903 eV, respectively. We conclude that the peak observed in the Pt Auger spectrum[18] at 63 694 eV is in fact due to the $K\text{-}L_3M_2$ *and* $K\text{-}L_1N_1$ transitions, and that the 63 870-eV peak is produced by the $K\text{-}L_1N_{2,3}$ transitions. This new identification leads to agreement between theoretical and observed intensities: the calculated relative intensities of the 63 694- and 63 870-eV peaks then are 0.41 and 0.14 and the observed intensities are 0.44 ± 0.09 and 0.10 ± 0.05. (With the original identification,[18] the calculated intensities would have been 0.30 and 0.25.)

With this slightly revised identification, we find good agreement between theoretical and experimental $K\text{-}LX$ Auger spectra of the heavier elements $_{69}$Tm, $_{71}$Lu, and $_{78}$Pt. Agreement is not so good for $_{35}$Br (Table IV); here the relativistic DHS $(K\text{-}LX)/(K\text{-}L_1M_1)$ relative line intensities, computed in j-j coupling, are consistently lower than the experimental results. This discrepancy could be caused by the neglect of final-state correlation (e.g., $2s3s$ and $2p3p$; $2s3p$ and $2p3s$) and intermediate coupling, as was found in the $K\text{-}LL$ spectrum.[8]

TABLE IV. $K\text{-}LX$ Auger spectrum of bromine.

Transition	Relative intensities [a] Experiment [b]	Present theory
$K\text{-}L_1M_1$	1.0	1.0
$K\text{-}L_1M_{2,3}$	1.78 ± 0.20	1.50
$K\text{-}L_1M_{4,5}$, $K\text{-}L_2M_1$	0.84 ± 0.10	0.57
$K\text{-}L_3M_1$	1.16 ± 0.25	0.79
$K\text{-}L_2M_{2,3}$	3.85 ± 0.40	2.04
$K\text{-}L_3M_{2,3}$	4.08 ± 0.40	3.93
$K\text{-}L_2M_{4,5}$	0.35 ± 0.10	0.26
$K\text{-}L_3M_{4,5}$	0.50 ± 0.15	0.48
$K\text{-}L_2N$, $K\text{-}L_3N$	0.84 ± 0.25	0.60

[a] Normalized to $I(K\text{-}L_1M_1) = 1.0$.
[b] Reference 21.

A relativistic calculation of $K\text{-}LM$ spectra in intermediate coupling with configuration interaction is in progress.

V. CONCLUSIONS

The most complete relativistic calculations to date of K-shell Auger transitions have been performed and compared with experiment. Relativistic effects are found to enhance the K-level Auger width by 18% at $Z = 54$. Simultaneously, these effects reduce the K x-ray emission rate; the total K-level width is thus reduced by 10% at $Z = 54$, because radiative transitions dominate the deexcitation of $1s$-vacancies in atoms with $Z > 30$. Relativistic theoretical K-shell fluorescence yields are in excellent agreement with experiment. Relative intensities of transitions in the $K\text{-}LX$ spectra of heavy elements agree well with theoretical relativistic intensities, calculated in j-j coupling. For low Z, discrepancies in the Br $K\text{-}LX$ spectrum suggest that configuration interaction and intermediate coupling for the final two-hole states must be included in the calculations.

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