Relativistic K-LL Auger spectra in the intermediate-coupling scheme with configuration interaction

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Theoretical K-LL Auger spectra have been calculated relativistically in intermediate coupling with configuration interaction. Results for 25 elements with $18 \leq Z \leq 96$ are listed and compared with experimental data. Relativistic effects are seen to be important above $Z \simeq 35$. Intermediate coupling with configuration interaction is necessary to describe the spectra for $Z \lesssim 60$; j-j coupling results are adequate above $Z \simeq 60$, except for the K-$L_2L_2(^1S_0)/K$-$L_1L_1(^1S_0)$ intensity ratio, which is very sensitive to correlation. The relative satellite intensity K-$L_1L_2(^3P_0)/(^1P_1)$ is found to be exceedingly sensitive to the effects of relativity; experimental data, though scant and uncertain, appear to disagree with this theoretical ratio. Otherwise, the present relativistic K-LL spectra in intermediate coupling with configuration interaction agree well with experiment over the entire range of atomic numbers from $Z = 18$ to 96.

I. INTRODUCTION

The K-LL Auger spectra of the elements have been studied extensively, both in theory and experiment,[1] because of their simplicity and high intensity.

For very light elements ($Z \leq 20$), the electrostatic interaction dominates and Russell-Saunders coupling applies. Relativistic effects are small for light elements, but the effects of electron-electron Coulomb correlation are very important in predicting relative intensities.[2-5]

For elements with atomic numbers in the range $20 \leq Z \leq 35$, the spin-orbit interaction is not negligible compared with the electrostatic interaction, and intermediate coupling is more appropriate than LS coupling to describe the spectrum.[2-5]

For $35 \leq Z \leq 60$, relativistic effects become quite important, and the K-LL spectrum must be calculated relativistically in intermediate coupling with configuration interaction.[4]

For heavy elements ($Z > 60$), relativistic effects play a major role[6,7] and the spin-orbit interaction dominates over the electrostatic interaction. In this region of atomic numbers, j-j coupling is more suitable than the LS coupling scheme.

All relativistic calculations of the transition amplitudes performed heretofore[6-8] have been carried out in the M scheme, which suppresses the total angular momentum of the coupled final two-hole configuration; hence these results are difficult to use as input for intermediate-coupling and configuration-interaction calculations. Recently, however, general relativistic Auger matrix elements have been evaluated with the two-hole final state coupled in the j-j scheme.[9] These matrix elements are arranged in such a way that intermediate-coupling and configuration-interaction calculations can easily be performed.

Here we report on theoretical K-LL Auger spectra from Dirac-Hartree-Slater (DHS) calculations in intermediate coupling with configuration interaction. Results for 25 elements with $18 \leq Z \leq 96$ are listed and compared with experimental data.

II. THEORY

From perturbation theory, in the frozen-orbital approximation, the Auger transition probability in j-j coupling is

$$T(\alpha JM \rightarrow \alpha' J'M') = |D - E|^2 , \tag{1}$$

where the direct matrix element D and the exchange matrix element E are

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

$$E = \langle j_1'(1) j_2'(2) J'M' | V_{12} | j_1(2) j_2(1) JM \rangle . \tag{3}$$

The primed quantum numbers j_1' and j_2' represent the initial hole and the hole in the continuum that is filled by the emitted Auger electron, respectively; the unprimed quantum numbers characterize the final two-hole state. The continuum wave function is normalized so as to represent one electron ejected per unit time. Atomic units are used throughout. Coupling between an outermost incomplete shell and an inner-shell vacancy is neglected in Eq. (1). No appreciable Auger-electron energy shift or splitting is introduced by such coupling in transitions discussed in this paper, whence the rates are independent of the passive electron structure.

The two-electron operator V_{12} is chosen accord-

ing to the original Møller formula,[10]

$$V_{12}=(1-\vec{\alpha}_1\cdot\vec{\alpha}_2)\exp(i\omega r_{12})/r_{12}\,, \tag{4}$$

where the $\vec{\alpha}_i$ are Dirac matrices, and ω is the wave number of the virtual photon.

The direct and exchange matrix elements can be evaluated by Racah algebra[9] or through expansions in vector spherical harmonics[11]; they can be written as a finite sum of terms that comprise the angular and radial parts. A detailed derivation is provided in Ref. 9. The total radiationless transition probability for a transition $n_1'\kappa_1'\rightarrow n_1\kappa_1 n_2\kappa_2$, in j-j coupling, is

$$T=\tau\frac{1}{2j_1'+1}\sum_{\substack{J,J'\\M,M'}}\sum_{\kappa_2}|D-E|^2\,, \tag{5}$$

where we have

$$\tau=\begin{cases}\frac{1}{2} & \text{if } n_1\kappa_1=n_2\kappa_2\\ 1 & \text{otherwise.}\end{cases} \tag{6}$$

To take into account the final-hole-state correlation and intermediate coupling, a configuration-interaction calculation for the final states involving $L_1L_1(J=0)$, $L_2L_2(J=0)$, and $L_3L_3(J=0)$ is performed. For this calculation, the j-j coupled basis states are used. The diagonal and nondiagonal electrostatic matrix elements are calculated by means of Racah algebra; they are given by the matrix

$$\begin{array}{c} \\ L_1L_1(J=0)\\ L_2L_2(J=0)\\ L_3L_3(J=0)\end{array}\begin{array}{c}\begin{array}{ccc}L_1L_1(J=0) & L_2L_2(J=0) & L_3L_3(J=0)\end{array}\\ \begin{pmatrix} E_1 & -\frac{1}{3}G^1(2s_{1/2}2p_{1/2}) & -\frac{1}{3}\sqrt{2}G^1(2s_{1/2}2p_{3/2})\\ -\frac{1}{3}G^1(2s_{1/2}2p_{1/2}) & E_2 & \frac{1}{5}\sqrt{2}G^2(2p_{1/2}2p_{3/2})\\ -\frac{1}{3}\sqrt{2}G^1(2s_{1/2}2p_{3/2}) & \frac{1}{5}\sqrt{2}G^2(2p_{1/2}2p_{3/2}) & E_3+\frac{4}{15}F^2(2p_{3/2}2p_{3/2})\end{pmatrix}\end{array}. \tag{7}$$

Here, E_1, E_2, and E_3 are the average energies of the configurations L_1L_1, L_2L_2, and L_3L_3, respectively.

The eigenfunctions and eigenvalues are obtained by diagonalizing the energy matrix. The eigenstates, with energies in descending order, are designated as $L_1L_1(^1S_0)$, $L_2L_2(^1S_0)$, and $L_3L_3(^3P_0)$. The eigenfunctions can be written as

$$\psi_i(0)=\sum_j C_{ij}(0)\phi_j\,, \tag{8}$$

with $i=1$, 2, 3 for the three eigenstates, where the $C_{ij}(0)$ are the mixing coefficients, and ϕ_1, ϕ_2, and ϕ_3 are the j-j coupled basis states of $L_1L_1(J=0)$, $L_2L_2(J=0)$, and $L_3L_3(J=0)$, respectively.

The Auger matrix element for the ith state is

$$M_i(0)=\sum_{j=1}^{3}C_{ij}(0)\langle\phi(j_1'j_2'J'M')|V_{12}|\phi_j\rangle\delta_{J'0}\delta_{M'0}\,. \tag{9}$$

The total radiationless transition rate from $n_1'\kappa_1'$ to the ith eigenstate with eigenfunction $\psi_i(0)$ is

$$T_i(0)=\frac{1}{2j_1'+1}\sum_{\substack{J'\\M',M'}}\sum_{\kappa_2}|M_i(0)|^2\,. \tag{10}$$

To use the known energy matrix, LS-coupled basis states are chosen to apply intermediate coupling to the final two-hole coupled states with angular momentum $J=1$, of the $2s2p$ configuration, and $J=2$, of the $2p^2$ configuration. The theory of intermediate coupling as applied to K-LL Auger transitions has been worked out by Asaad[2] and by Mehlhorn and Assad,[3] to whose papers the reader is referred for details. We follow Larkin's approach[12] in performing the intermediate-coupling calculations.

For the $2s2p$ configuration with $J=1$, the eigenfunctions in intermediate coupling are

$$\psi_i(1)=C_{i1}(1)\phi(^1P_1)+C_{i2}(1)\phi(^3P_1),\quad i=1,\ 2. \tag{11}$$

The higher-energy state is designated as $L_1L_2(^1P_1)$, and the lower state as $L_1L_3(^3P_1)$.

For the $J=2$ state of the $2p^2$ configuration, the eigenfunctions in intermediate coupling are

$$\psi_i(2)=C_{i1}(2)\phi(^1D_2)+C_{i2}(2)\phi(^3P_2),\quad i=1,\ 2. \tag{12}$$

The upper state is $L_2L_3(^1D_2)$, and the lower state is $L_3L_3(^3P_2)$. The $C_{ij}(J)$ are mixing coefficients due to spin-orbit interaction.

Because our relativistic Auger transition-probability calculations are carried out in j-j coupling, a coupling transformation from LS to j-j coupling is applied to the LS-coupled states in Eqs. (11) and (12). After the transformation, the eigenfunctions $\psi_i(J)$ are

$$\psi_i(J)=\sum_k C_{ik}(J)\sum_{j_1j_2}C(l_1l_2L_kS_kj_1j_2J)\phi(j_1j_2J)\,, \tag{13}$$

where the $C(l_1l_2L_kS_kj_1j_2J)$ are coefficients from the coupling transformation that can easily be ob-

TABLE I. Theoretical relativistic K-LL Auger transition rates (in milli-atomic-units [a]), in intermediate coupling with configuration interaction.

Z	K-$L_1L_1(^1S_0)$	K-$L_1L_2(^1P_1)$	K-$L_1L_2(^3P_0)$	K-$L_1L_3(^3P_1)$	K-$L_1L_3(^3P_2)$	K-$L_2L_2(^1S_0)$	K-$L_2L_3(^1D_2)$	K-$L_3L_3(^3P_0)$	K-$L_3L_3(^3P_2)$
18	1.105	3.554	0.150	0.397	0.575	1.191	10.708	0.020	0.134
20	1.205	3.807	0.169	0.442	0.610	1.247	11.369	0.047	0.274
25	1.441	4.231	0.228	0.636	0.693	1.162	12.053	0.297	1.184
30	1.683	4.414	0.306	0.930	0.773	1.081	12.392	0.487	1.944
35	1.946	4.236	0.410	1.510	0.852	0.939	12.235	0.696	2.836
36	2.004	4.177	0.435	1.648	0.871	0.920	12.214	0.726	2.986
40	2.246	3.912	0.552	2.223	0.941	0.864	12.112	0.819	3.503
42	2.380	3.800	0.622	2.495	0.980	0.842	12.086	0.853	3.710
45	2.593	3.689	0.743	2.852	1.040	0.833	12.062	0.884	3.956
47	2.746	3.652	0.837	3.062	1.086	0.829	12.079	0.903	4.100
50	2.997	3.653	0.999	3.335	1.156	0.829	12.093	0.921	4.264
52	3.179	3.689	1.123	3.493	1.206	0.831	12.106	0.929	4.352
54	3.371	3.754	1.264	3.638	1.261	0.836	12.129	0.935	4.427
56	3.578	3.843	1.419	3.769	1.317	0.844	12.162	0.941	4.494
60	4.041	4.103	1.789	4.008	1.440	0.863	12.222	0.946	4.591
63	4.435	4.373	2.127	4.171	1.545	0.881	12.280	0.948	4.647
67	5.031	4.834	2.672	4.370	1.699	0.911	12.368	0.951	4.706
70	5.541	5.271	3.168	4.514	1.829	0.936	12.432	0.951	4.737
74	6.311	5.986	3.967	4.696	2.020	0.982	12.510	0.951	4.766
80	7.743	7.423	5.543	4.958	2.355	1.048	12.646	0.951	4.805
83	8.613	8.346	6.547	5.084	2.546	1.083	12.708	0.950	4.819
88	10.340	10.291	8.650	5.289	2.910	1.150	12.816	0.948	4.843
90	11.145	11.244	9.675	5.369	3.072	1.182	12.858	0.948	4.852
92	12.032	12.314	10.822	5.447	3.242	1.214	12.922	0.947	4.871
96	14.093	14.891	13.580	5.594	3.621	1.283	13.021	0.943	4.892

[a] 1 m a.u. = 0.027 21 eV/$\hbar$ = 4.134×10^{13} $\sec^{-1}$.

tained by Racah algebra.[13]

The Auger matrix element for the final state with eigenfunction $\psi_i(J)$ is

$$M_i(J) = \sum_k C_{ik}(J) \sum_{j_1 j_2} C(l_1 l_2 L_k S_k j_1 j_2 J) \times \langle \phi(j_1' j_2' J' M') | V_{12} | \phi(j_1 j_2 J M) \rangle . \quad (14)$$

The transition rate is given by Eq. (10).

III. NUMERICAL CALCULATIONS

The relativistic Auger matrix elements in j-j coupling were calculated from DHS wave functions that correspond to the initial hole-state configuration.[9] We derived the transition energies used in the calculations from theoretical neutral-atom binding energies[14] using the "$Z+1$ rule." The consequent error in the Auger energies (~30 eV out of 2 to 80 keV) has been found to have negligible effect on the Auger matrix elements. In the configuration-interaction calculations, the average energies (E_1, E_2, and E_3) were calculated from DHS wave functions[14] with the appropriate final hole-state configurations. The electrostatic Slater integrals were computed from the initial-hole-state DHS wave functions. In the intermediate-coupling calculations we have followed Larkins' approach[12] by starting out with relativistic LS average energies, then introducing the electrostatic splitting and the spin-orbit interaction to obtain the energy matrix. Eigenvalues and eigenfunctions were obtained by diagonalizing the energy matrix. Relativistic LS average energies were computed by statistically averaging the corresponding j-j average energies.[12] The relativistic LS Slater integrals were calculated according to Larkins' recipe.[12]

We calculated the spin-orbit interaction coefficients ζ_{2p} from theoretical L_2 and L_3 binding energies,[14] using the relation[12]

$$\zeta_{2p} = \tfrac{2}{3}[E(L_2) - E(L_3)] . \quad (15)$$

The eigenfunctions obtained in diagonalizing the energy matrix were then incorporated in relativistic matrix elements to calculate the transition rates.

IV. RESULTS AND DISCUSSION

The calculated relativistic K-LL Auger transition rates in intermediate coupling with configuration interaction are listed in Table I. (It should be noted that the present DHS j-j coupling results agree with the relativistic calculations of Bhalla and Ramsdale.[6]) The relative intensities of the K-L_1L_2, K-L_2L_2, K-L_2L_3, K-L_3L_3, K-L_1L_3, and K-$L_3L_3(^3P_0)$ transitions with respect to the K-L_1L_1 transition intensity from the present calculations are compared in Figs. 1–5 with experimental data[15] and with the results of nonrelativistic calculations.[4] It should be noted, however, that disagreement at low Z between the present calculations and the nonrelativistic calculation of Ref. 4 is due to the fact that the latter is not a Hartree-Slater calcula-

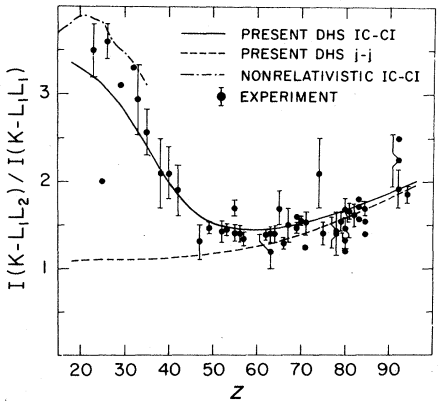

FIG. 1. K-L_1L_2/K-L_1L_1 Auger-transition intensity ratio as a function of atomic number. The present relativistic DHS calculations in intermediate coupling with configuration interaction, and in j-j coupling, are compared with results from nonrelativistic calculations in intermediate coupling with configuration interaction (Ref. 4) and with experimental data (Ref. 15).

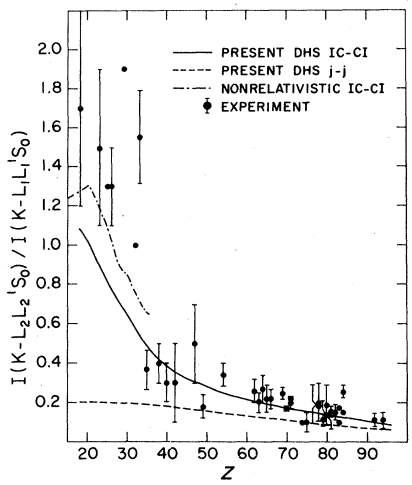

FIG. 2. K-$L_2L_2(^1S_0)/K$-$L_1L_1(^1S_0)$ Auger-transition intensity ratio as a function of atomic number. Present relativistic DHS calculations, both in intermediate coupling with configuration interaction and in j-j coupling, are compared with nonrelativistic results in intermediate coupling with configuration interaction (Ref. 4) and with experimental data (Ref. 15).

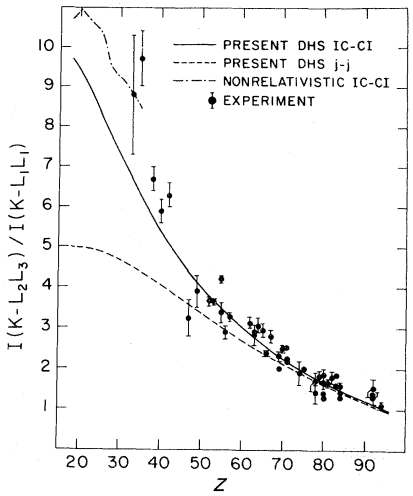

FIG. 3. K-L_2L_3/K-L_1L_1 Auger-transition intensity ratio as a function of atomic number. The present relativistic DHS results in intermediate coupling with configuration interaction, and in j-j coupling, are compared with nonrelativistic calculations in intermediate coupling with configuration interaction (Ref. 4) and with measured ratios (Ref. 15).

tion, but one based on Green's potential. Thus the wave functions are different and the discrepancy has nothing to do with the effects of relativity: the model is different.

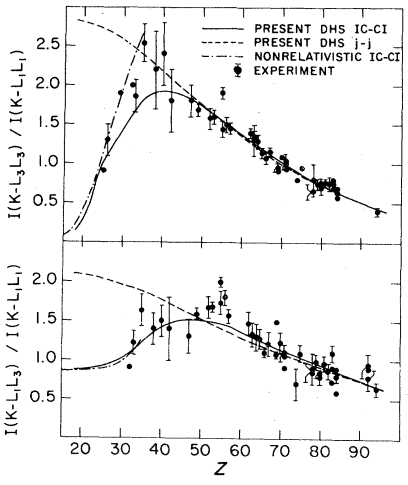

FIG. 4. K-L_1L_3 and K-L_3L_3 Auger-transition intensities, relative to the K-L_1L_1 intensity, as functions of atomic number. The present relativistic DHS results, both in intermediate coupling with configuration interaction and in j-j coupling, are compared with nonrelativistic calculations in intermediate coupling with configuration interaction (Ref. 4) and with experimental data (Ref. 15).

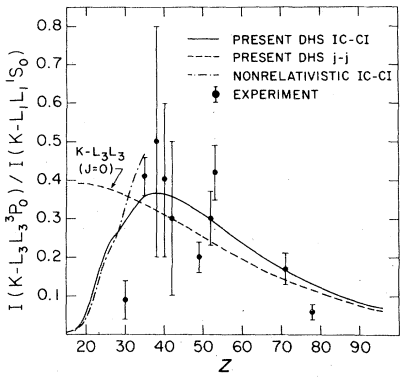

FIG. 5. K-$L_3L_3(^3P_0)/K$-$L_1L_1(^1S_0)$ Auger-transition intensity ratio as a function of atomic number. The present relativistic DHS results, in intermediate coupling with configuration interaction and in j-j coupling, are compared with nonrelativistic calculations in intermediate coupling with configuration interaction (Ref. 4) and with experimental data (Ref. 15).

The calculated intensities of K-L_1L_2, K-L_1L_3, and K-L_3L_3 satellites with respect to the main lines are compared with experiment[15] in Figs. 6 and 7.

From these systematic comparisons, the following conclusions can be drawn:

(i) The present relativistic DHS calculations of K-LL Auger transition probabilities in intermediate coupling with configuration interaction agree

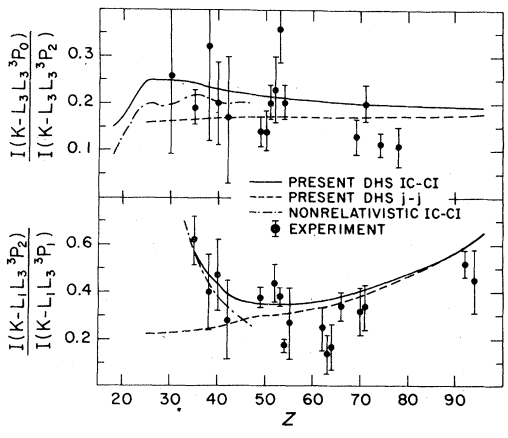

FIG. 6. K-$L_3L_3(^3P_0)/(^3P_2)$ and K-$L_1L_3(^3P_2)/(^3P_1)$ Auger satellite-to-main-line intensity ratios, as functions of atomic number. The present relativistic DHS calculations in intermediate coupling with configuration interaction, and in j-j coupling, are compared with nonrelativistic results in intermediate coupling with configuration interaction (Ref. 4) and with experiment (Ref. 15).

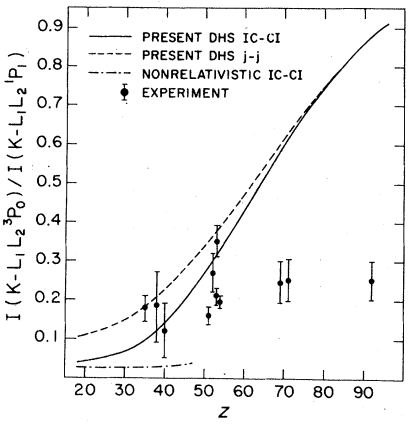

FIG. 7. K-$L_1L_2(^3P_0)/(^1P_1)$ Auger satellite-to-main-line intensity ratio, as a function of atomic number. Present relativistic DHS results in intermediate coupling with configuration interaction, and in j-j coupling, are compared with nonrelativistic calculations in intermediate coupling with configuration interaction (Ref. 4) and with experiment (Ref. 15).

well with experimental data over the whole range of atomic numbers $18 \leq Z \leq 96$.

(ii) The DHS calculations in j-j coupling are adequate to describe the relative intensities in K-LL Auger spectra for $Z > 60$, except for the K-$L_2L_2(^1S_0)/K$-$L_1L_1(^1S_0)$ intensity ratio. This particular ratio is very sensitive to electron-electron Coulomb correlation, because correlation has the effect of redistributing strength between the K-L_2L_2 and K-$L_1L_1(^1S_0)$ transitions. The correlation effect on this intensity ratio persists even for $Z > 80$.

(iii) The importance of relativistic effects on K-LL Auger transitions for $Z > 35$ has long been established.[4,6] For elements with $35 \leq Z \leq 60$, however, relativistic calculations in j-j coupling are inadequate to describe the K-LL spectrum. The importance of including configuration interaction in intermediate coupling as well as relativistic effects is clearly shown in the present work.

(iv) For light elements, some discrepancies between calculated and measured K-LL spectra remain. These differences may be due in part to the fact that measurements were made on solid targets, while the calculations are for free atoms. The importance of solid-state effects on K-LL Auger intensities has been demonstrated for sodium[16] and magnesium.[17] Furthermore, correlation effects other than those represented by the mixing of the $L_1L_1(^1S_0)$ $L_2L_2(^1S_0)$ states could be important.[18]

(v) A discrepancy appears to exist between the calculated relative satellite intensity K-$L_1L_2(^3P_0)/K$-$L_1L_2(^1P_1)$ and measured intensity ratios. The K-$L_1L_2(^3P_0)$ "satellite" intensity depends very strongly on relativistic effects. The contributions to this transition rate from the retarded current-current interaction term increase drastically with atomic number and become as large as the contribution from the retarded Coulomb term, for heavy elements. It is for this reason that the relativistic calculations predict much higher satellite intensities than nonrelativistic theory. The present relativistic calculations in intermediate coupling agree with experiment for $Z \leq 54$, but they disagree for heavier elements. At high Z, the present theory predicts that the satellite intensity should become as large as that of the main line, while measurements seem to indicate an almost constant value of 0.25 for the satellite-to-main-line ratio. Very little experimental data for heavy elements are available on this satellite ratio, however, because it is difficult to resolve the satellite from the main line; the two peaks are separated by only ~50 eV out of 73 keV for $_{92}$U, for example. More accurate experimental data on the K-$L_1L_2(^3P_0)$ satellite intensity are therefore needed to resolve this puzzling discrepancy.

Note added in proof. It has been called to our attention that W. N. Asaad and D. Petrini [Proc. R. Soc. London A 350, 381 (1976)] have also calculated relativistic K-LL spectra in intermediate coupling with configuration interaction. Using the M scheme, these authors require 158 matrix elements for the spectrum, whereas 16 matrix elements suffice for the present work. Despite the differences in approach, there is gratifying agreement in the final results. We thank Professor W. N. Asaad and Professor W. Mehlhorn for advising us of this work.

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