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Relativistic M-shell radiationless transitions

Mau Hsiung Chen and Bernd Crasemann
Department of Physics, University of Oregon, Eugene, Oregon 97403

Hans Mark
Department of the Air Force, Washington, D. C. 20330
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The first relativistic calculations of radiationless transition probabilities for the filling of vacancies in atomic M shells are reported. For eight elements with atomic numbers $70 \leq Z \leq 100$, radiationless M_4- and M_5-subshell transition rates, M-subshell fluorescence and Coster-Kronig yields, and $L\alpha_{1,2}$ and $L\beta_1$ x-ray linewidths were computed with Dirac-Hartree-Slater wave functions using the Møller two-electron operator. The inclusion of relativity is found to affect strong Auger transitions by 10–20%, and weak transitions by as much as a factor of 2, mostly because of the difference between relativistic and nonrelativistic wave functions. The new theoretical results agree substantially better with experimental data than the results of older, nonrelativistic calculations.

I. INTRODUCTION

The effect of relativity on K- and L-shell radiationless transitions has been found to be important for medium-Z and heavy atoms.[1-3] Although several calculations of M-shell radiationless transitions have been carried out,[4,5] no relativistic computations of these transitions have been performed heretofore. In the present paper, the fifth of a series of studies[1-3] of the effects of relativity on Auger transitions, we report on relativistic calculations of M_4- and M_5-subshell radiationless transition rates for eight elements with $70 \leq Z \leq 100$. The results are compared with those from nonrelativistic Hartree-Slater calculations in order to establish the effect of relativity on M-shell Auger decay.

II. THEORY

The Auger rates are calculated from perturbation theory, in j-j coupling, under the frozen-orbitals approximation. The total rate for a transition $n_1'\kappa_1' \rightarrow n_1\kappa_1 n_2\kappa_2$ is

$$T=\tau(2j_1'+1)^{-1}\sum_{\substack{J,J'\\M,M'}}\sum_{\kappa_2'}\left|\langle j_1'(1)j_2'(2)J'M'\,|\,V_{12}\,|\,j_1(1)j_2(2)JM\rangle-\langle j_1'(1)j_2'(2)J'M'\,|\,V_{12}\,|\,j_1(2)j_2(1)JM\rangle\right|^2, \quad (1)$$

where

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

The primed quantum numbers j_1' and j_2' pertain to the wave functions of the initial hole and of the hole in the continuum, respectively. The unprimed quantum numbers 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.

Equation (1) does not take account of coupling with open outer shells (if any). This introduces no error if the coupling does not significantly affect the Auger-electron energy; then one can sum over final states and the resultant rate is independent of the passive-electron structure.[6] In all cases covered by the present work, unfilled outer shells cannot produce appreciable energy shifts or splitting, so that Eq. (1) is fully applicable.

We use the Møller formula[7] for the two-electron interaction:

$$V_{12}=(1-\vec{\alpha}_1\cdot\vec{\alpha}_2)\exp(i\omega r_{12})/r_{12}. \quad (3)$$

Here the $\vec{\alpha}_i$ are Dirac matrices and ω is the wave number of the virtual photon. The Møller form of V_{12} is suitable for electron orbitals in a local potential,[8] as in our Dirac-Hartree-Slater (DHS) model.

Detailed derivations of the relativistic Auger matrix elements are given in Ref. 1. The present numerical work proves the equivalence of the Auger transition rates based on Møller's operator [Eq. (3)] and rates derived from the generalized Breit interaction [Eq. (3) of Ref. 9] in the DHS model. The Auger rates from these two operators agree to better than one part in 10^4.

III. NUMERICAL CALCULATIONS

DHS wave functions are used to describe the initial hole state. The M_4- and M_5-subshell radia-

TABLE I. M_4- and M_5-subshell Auger widths $\Gamma_A(M_i)$ and total widths $\Gamma(M_i)$, in eV, Coster-Kronig yields $f_{4,5}$, and fluorescence yields ω_i.

Element	$\Gamma_A(M_4)$	$\Gamma(M_4)$	$f_{4,5}$	ω_4	$\Gamma_A(M_5)$	$\Gamma(M_5)$	ω_5
$_{70}$Yb	1.408	2.468	0.420	0.0094	1.460	1.482	0.015
$_{74}$W	1.758	1.868	0.039	0.020	1.795	1.830	0.019
$_{80}$Hg	2.259	2.450	0.049	0.028	2.386	2.452	0.027
$_{83}$Bi	2.512	2.761	0.057	0.033	2.668	2.753	0.031
$_{88}$Ra	2.923	3.266	0.062	0.043	3.129	3.253	0.038
$_{92}$U	3.203	3.714	0.088	0.050	3.450	3.611	0.045
$_{96}$Cm	3.646	4.327	0.103	0.055	3.872	4.075	0.050
$_{100}$Fm	4.000	4.785	0.102	0.062	4.333	4.583	0.055

tionless transitions are computed with the general relativistic Auger program developed in our previous work.[1-3] The Auger energies were derived by applying the "$Z+1$ rule" to theoretical relativistic neutral-atom binding energies.[10] The transition energies from the $Z+1$ rule agree to better than 10 eV with energies from relativistic relaxed-orbital calculations that include QED corrections.[11] For the much lower Coster-Kronig transition energies, we use the relativistic relaxed-orbital values from Ref. 11.

The relativistic x-ray transition rates needed to find fluorescence yields were taken from Bhalla's work.[12] For elements not included in Ref. 12, the x-ray rates were determined by Lagrange interpolation.

IV. RESULTS AND DISCUSSION

The M_4- and M_5-subshell Auger and total widths and Coster-Kronig and fluorescence yields from the present work are listed in Table I. To establish the effect of relativity on individual M-shell Auger transitions, results from the present DHS calculations are compared in Figs. 1–4 with nonrelativistic Hartree-Slater (HS) results[13] based on the same transition energies, and with McGuire's approximate Herman-Skillman results.[5] The structure seen in McGuire's rates is due to his approximation to the Herman-Skillman potential, made through piecewise straight-line fitting[5]; the structure is therefore an artifact without physical significance.

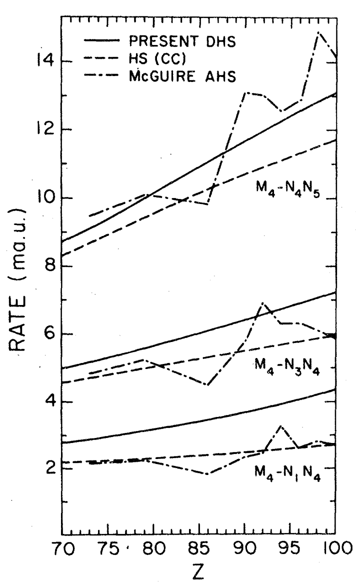

FIG. 1. Relativistic DHS rates of M_4-N_4N_5, M_4-N_3N_4, and M_4-N_1N_4 Auger transitions, in milli-atomic-units, as a function of atomic number Z. For comparison, the nonrelativistic HS results of Ref. 13 and the approximate HS results of McGuire (Ref. 5) are also shown.

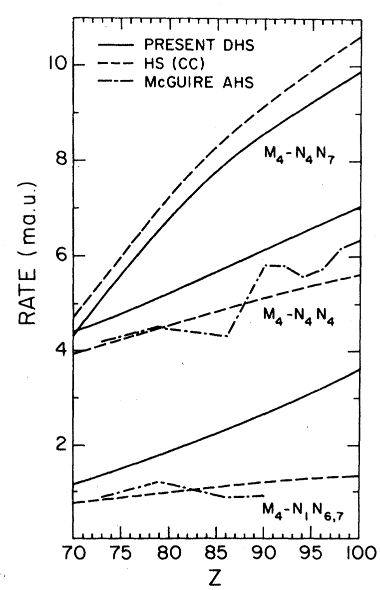

FIG. 2. Relativistic DHS M_4-N_4N_7, M_4-N_4N_4, and M_4-$N_1N_{6,7}$ Auger transition probabilities, in milli-atomic-units, as a function of atomic number Z. For comparison, the nonrelativistic HS rates of Chen and Crasemann (Ref. 13) and the approximate Hartree-Slater (AHS) results of McGuire (Ref. 5) are also shown.

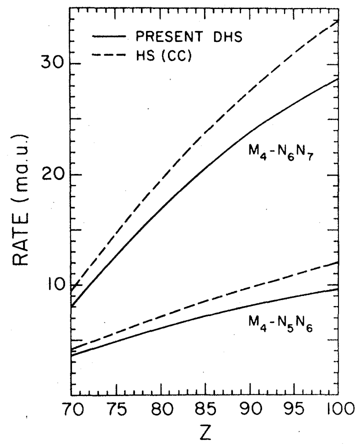

FIG. 3. Relativistic DHS M_4-N_6N_7 and M_4-N_5N_6 Auger rates, in milli-atomic-units, as a function of atomic number Z. The relativistic rates are compared with nonrelativistic HS results according to Ref. 13.

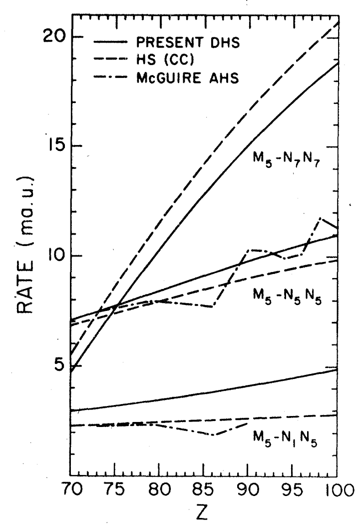

FIG. 4. Relativistic DHS M_5-N_7N_7, M_5-N_5N_5, and M_5-N_1N_5 Auger transition probabilities, in milli-atomic-units, compared with nonrelativistic HS results (Ref. 13) and AHS results (Ref. 5).

It is apparent that strong transitions ($M_{4,5}$-$N_{6,7}N_{6,7}$) are affected by 10–20% if relativity is taken into account, while weak transitions ($M_{4,5}$-$N_1N_{6,7}$) are affected by as much as a factor of 2. There appears to be no simple general principle underlying this curious effect, because the matrix elements involving four different orbitals are very complex. We can discern three physical reasons, however, that in some situations can lead to the observed sensitivity of weak Auger transitions and the insensitivity of strong transitions to the effects of relativity: (i) Weak transitions are often weak because of severe accidental cancellations in the matrix elements. Such matrix elements are particularly sensitive to the details of the wave functions, and hence to the differences between the potentials produced by nonrelativistic and relativistic electron distributions. (ii) The low intensity of some weak transitions is caused by the fact that transitions from outer orbitals are involved. The wave functions of the more loosely bound outer electrons are more sensitive to the atomic model than inner-electron wave functions. (iii) The effect of relativity on wave-function overlap in the matrix element is less pronounced when the two final holes are in nearly the same state (as in the M_4-N_4N_4 and M_4-N_4N_7 transitions shown in Fig. 2). In transitions for which the final vacancies are in very different states (e.g., $4s$ and $4f$ in the M_4-$N_1N_{6,7}$ transition in Fig. 2), the wave-function overlap in the matrix element is small and the intensity is low; this small overlap can be affected much more when the electrons are taken to move in the potential of a relativistic, rather than nonrelativistic, charge distribution.

For most of the $M_{4,5}$ Auger transitions, the difference between relativistic and nonrelativistic wave functions is found to be the dominant factor through which relativity influences the transitions. Contributions from retardation and from the current-current interaction are small. Relativity enhances some of the transition rates (M_4-N_4N_5, M_4-N_3N_4), while others are decreased (M_4-N_5N_6, M_4-N_6N_7). Consequently, intensity ratios are affected in a disparate manner (Fig. 5), and the effect of relativity on total Auger rates is much reduced by cancellations. In Figs. 6 and 7, the total M_4 and M_5 radiationless widths from the present work are compared with McGuire's[5] nonrelativistic Herman-Skillman results. The large discrepancy

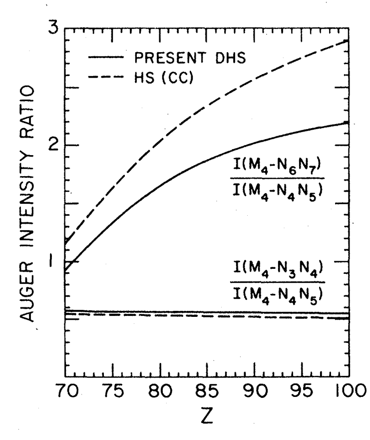

FIG. 5. Ratios of M_4-N_6N_7 to M_4-N_4N_5 and of M_4-N_3N_4 to M_4-N_4N_5 Auger transition probabilities, as a function of atomic number Z. Relativistic DHS results are compared with nonrelativistic HS ratios (Ref. 13).

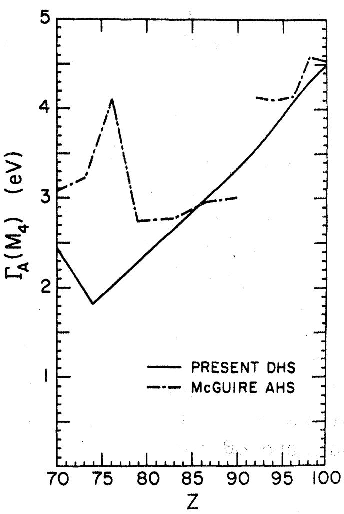

FIG. 6. M_4-subshell Auger widths, in eV, as a function of atomic number Z. The present relativistic DHS results are compared with nonrelativistic AHS widths (Ref. 5).

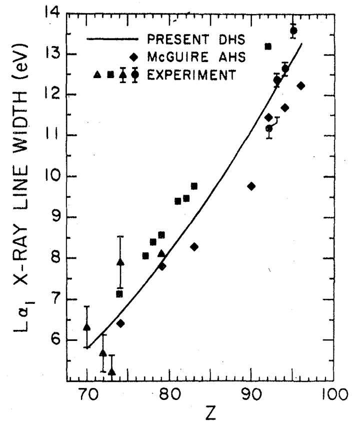

FIG. 8. Theoretical $L\alpha_1$ x-ray linewidths, in eV, from the present relativistic DHS calculations, compared with nonrelativistic AHS results (Refs. 5 and 14) and with experimental data: triangles, with error bars, Ref. 15; circles, with error bars, Ref. 16; squares, Ref. 17; circles without error bars, Ref. 18; triangles without error bars, Ref. 19.

in the M_4 Auger width below $Z = 80$ arises from the energetics of the strong M_4 Coster-Kronig transitions. In our relativistic energy calculations,[11] we find that the strong M_4-$M_5N_{6,7}$ transitions become energetically impossible for $Z \geq 74$. In McGuire's calculation, by contrast, these transitions are energetically possible up to $Z = 77$. In addition to this difference, the discontinuities in the slope of McGuire's Auger widths make it difficult to assess the effect of relativity on these widths by comparing the results of Ref. 5 with the present DHS calculations.

The abrupt change in M_4 level widths and Coster-Kronig and fluorescence yields predicted by our calculations at $Z = 74$ is due to the energy cutoff of the strong M_4-$M_5N_{6,7}$ Coster-Kronig transition.

Theoretical x-ray linewidths for $L\alpha_1$ (L_3-M_5), $L\alpha_2$ (L_3-M_4), and $L\beta_1$ (L_2-M_4) radiative transitions were calculated by adding the corresponding L- and and M-shell level widths. Results are compared in Figs. 8–10 with McGuire's values[5,14] and experimental data.[15-19] The present relativistic x-ray

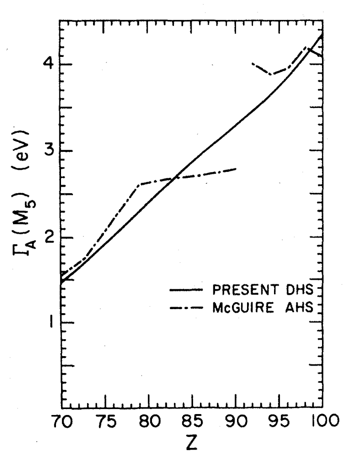

FIG. 7. M_5-subshell Auger widths, in eV, as a function of atomic number Z. Present relativistic DHS results are compared with nonrelativistic AHS widths (Ref. 5).

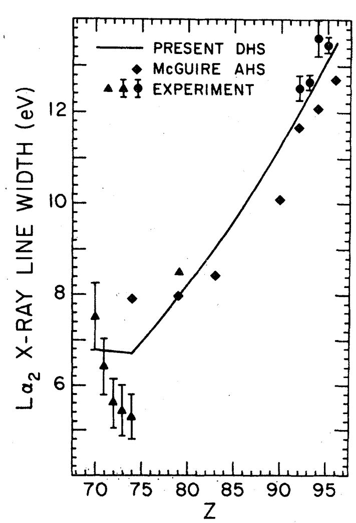

FIG. 9. Theoretical $L\alpha_2$ x-ray linewidths, in eV, from the present relativistic DHS calculations, compared with nonrelativistic AHS results from Refs. 5 and 14, and with experimental data (see Fig. 8 caption for identification).

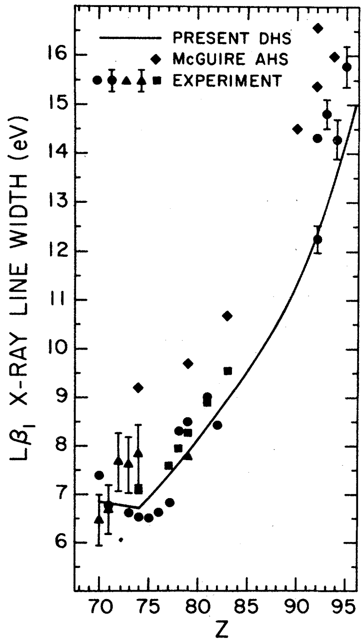

FIG. 10. Theoretical $L\beta_1$ x-ray linewidths, in eV, as a function of atomic number Z. The nonrelativistic AHS widths from Refs. 5 and 14 are shown for comparison, as are experimental data (see Fig. 8 caption for identification).

linewidths are seen to agree much better with experiment than nonrelativistic results.

V. CONCLUSIONS

The effect of relativity on M_4 and M_5 radiationless transitions has been found to be important, amounting to 10–20% for strong transitions and as much as a factor of 2 for weak transitions. The effect on total $M_{4,5}$ Auger rates and widths is greatly reduced by cancellations. For most of the $M_{4,5}$ radiationless transitions, the difference between nonrelativistic and relativistic wave functions is found to be the dominant factor through which the inclusion of relativity affects the rates. For $L\alpha_1$, $L\alpha_2$, and $L\beta_1$ x-ray linewidths, fair agreement (to within 10%) is obtained between the present theoretical DHS results and experimental data, while earlier nonrelativistic calculations agree less well with experiment.

ACKNOWLEDGMENTS

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