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Relativistic Dirac-Fock calculations of *KLL* Auger transition energies in intermediate coupling

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Multiconfiguration relativistic Dirac-Fock calculations of *KLL* Auger energies are reported for neon, argon, uranium, and americium. These selected examples demonstrate the feasibility of this method to calculate completely *ab initio*, in intermediate coupling, Auger transition energies with a precision of a few eV. Comparison of our results with semiempirical ones shows that this *ab initio* method performs at least as well as those which rely partially on experimental results.

I. INTRODUCTION

Auger transition energies have been, up to now, a challenge for completely *ab initio* calculations, since they require the simultaneous handling of the problems of intermediate coupling and relativistic and many-body effects. Therefore, besides a few definite attempts to solve this problem from first principles, only semiempirical methods were developed to reproduce experimental data over a large range of Z values. Numerous expressions, functions of Z, have been proposed by different authors for the two-electron integrals to include a relativistic correction fitted to experimental data either for a few given Z values, or for a wide range of Z values with a least-mean-square adjustment. The foregoing emphasizes the need for a complete *ab initio* calculation, avoiding any adjustable parameters.

In the present work, we calculate the *KLL* Auger transition energies and the inner-shell binding energies as the differences between the total energies of the relevant initial and final states. The total energies are calculated from the Dirac-Fock method without any approximation for the exchange terms. The higher-order relativistic corrections are included. Using the multiconfiguration technique, these *ab initio* calculations allow one to remove the J degeneracy and thus are done in the intermediate-coupling scheme. Before describing our method in more detail, we briefly review the earlier semiempirical methods.

II. EARLIER CALCULATIONS

After the introduction by Asaad and Burhop[1] of the intermediate-coupling scheme for two-hole states, which has been of prime importance for the understanding of electron Auger spectra, the general trend of Auger transition-energy calculations has mainly been to use the expressions given by these authors. These energy expressions were adjusted to the experimental data through various corrective coefficients, functions of Z, which try to take into account, among other corrections, relativistic effects.

In these expressions, Auger transition energies are given as functions of (i) the binding energies $B(nlj)$, (ii) the matrix elements of the two-electron Coulomb interaction $F^k(nl, n'l')$ and $G^k(nl, n'l')$, and (iii) the spin-orbit coupling constant $\zeta(SL)$.

In Ref. 1, the F and G integrals were calculated using screened hydrogenic wave functions, the screening parameters being adjusted to fit Hartree calculations for $Z = 80$. The observed discrepancy[2] with the experimental results for $Z = 83$ was attributed to relativistic effects and the authors proposed to approximate the F and G integrals by $A(Z-\sigma)(1-\alpha Z^2)$, where σ is the screening constant and αZ^2 ($\alpha > 0$) allows for relativistic effects. Later, Listengarten[3] proposed to add the term $1.1(80-Z)$ eV to the transition energy expressions, to give closer agreement for low-Z values.

However, comparison with earlier experimental results showed that these expressions do not give a good agreement for the whole range of Z, and Hörnfeldt[4] proposed the corrective term $1+\beta Z^3$, with $\beta > 0$, instead of $1-\alpha Z^2$, and gave a table of Auger transition energies for $Z = 20-100$. A and β were calculated by a least-mean-square adjustment with the published Auger experimental data, while the Slater screening constants σ were those of Asaad and Burhop.

Later, Asaad[5] assumed a corrective term of the form $1+aZ^2$, with $a > 0$, except for $G^1(1s, 2p)$ and $G^2(2p, 2p)$, and found that closer agreement between experimental and calculated energies is obtained with a correction of the form[6]

$$-4\times 10^{-6}(Z-3)(Z-12)^2(Z-52)^2$$

for the F^0's.

More recently, Shirley[7] improved the formulation of Asaad and Burhop by adding a relaxation-energy term. This formulation relies again, although to a lesser degree, on experimental data; (i) the binding energies, which could in principle be calculated, are the experimental ones, and (ii) the $1+aZ^2$ relativistic correcting factor to the Mann's two-electron integrals are fitted with the experimental Auger transition energies. Thus these corrective terms appear to be general fitting coefficients including also other neglected terms and the uncertainty owing to the approximation used in the relaxation-term calculation.

Compared to the above semiempirical methods, only a few *ab initio* calculations have been done. These calculations were either nonrelativistic or, when relativistic, in pure *j-j* coupling with approximate treatment of potential terms.

More details can be found in the review papers of Briançon,[8] Sevier,[9] Burhop and Asaad,[10] and Asaad.[6]

III. METHODS OF CALCULATION

For each hole state to be considered, the total energy is calculated using the multiconfiguration Dirac-Fock program written by Desclaux.[11] The total Hamiltonian of the system used in the variational principle is the sum of one-electron Dirac operators plus the classical Coulomb repulsion between the electrons. After achieving self-consistency, the full Breit operator (magnetic interaction and retardation) is included as a first-order perturbation to the total energy to partially take into account the relativistic interaction between the electrons. As the Dirac-Fock formalism has been described in various articles we will not discuss it further but rather refer the reader to, for example, the detailed review article of Grant.[12] In the relativistic case, the extension of the single-configuration approximation to the multiconfiguration scheme is quite analogous to its nonrelativistic counterpart except that, because spin-orbit interaction is included explicitly, we have to build up the total wave function on a basis of *jj* states instead of *LS* ones. Since we perform a variational calculation of each state under consideration, the relaxation energy is automatically included.

As mentioned, the wave functions are defined in *jj* coupling; if we had restricted ourselves to a single *jj* configuration per state, such a description would have been meaningless for the light atoms, which obviously are close to the *LS* limit. On the other hand, the importance of intermediate coupling for the calculation of *KLL* Auger energies has been previously demonstrated.[1-10] In all these previous works, the problem of intermediate coupling was handled in a semiempirical way by extracting the spin-orbit coupling constant from experimental results. The relativistic multiconfiguration approach we use here allows to introduce the intermediate coupling completely *ab initio* and provides the ability to handle a smooth transition from the almost pure *LS* limit exhibited by the light atoms to the almost pure *jj* limit of the very heavy atoms. To illustrate the method, consider the case of the $J=2$ states of the double-hole p^4 configuration. Because of the spin-orbit interaction, the p shell is split into the $p_{1/2}$ and $p_{3/2}$ subshells. In the pure *LS* limit we have the well-known triplet and singlet states given by[13]

$$\begin{aligned} |{}^3P_2\rangle &= (1/\sqrt{3})\,(\sqrt{2}\,|p_{1/2}^2 p_{3/2}^2\rangle + |p_{1/2}p_{3/2}^3\rangle)\,, \\ |{}^1D_2\rangle &= (1/\sqrt{3})\,(|p_{1/2}^2 p_{3/2}^2\rangle - \sqrt{2}\,|p_{1/2}p_{3/2}^3\rangle)\,, \end{aligned} \tag{1}$$

which are mixed by spin-orbit interaction. Thus we may write each state as

$$|J=2\rangle = a|p_{1/2}^2 p_{3/2}^2\rangle + (1-a^2)^{1/2}|p_{1/2}^1 p_{3/2}^3\rangle, \tag{2}$$

where the deviation of a from the values given in Eq. (1) is just the measure of the breakdown of *LS* coupling. The multiconfiguration method proceeds in the following way: Starting from a wave function as that defined in Eq. (2) (where obviously we select the $J=2$ eigenvector of the total angular momentum) the expectation value of the energy is calculated and then minimized with respect to both the radial wave functions and the coefficient a. For the example we consider, the total energy is

$$\begin{aligned} E_T = {} & a^2 E_{\mathrm{av}}(p_{1/2}^2 p_{3/2}^2) + (1-a^2)E_{\mathrm{av}}(p_{1/2}^1 p_{3/2}^3) \\ & -\tfrac{4}{75}a^2 F^2(p_{3/2}, p_{3/2}) + \tfrac{3}{50}(1-a^2)G^2(p_{1/2}, p_{3/2}) \\ & +\tfrac{8}{50}(\sqrt{2})a(1-a^2)^{1/2}R^2(p_{1/2}p_{3/2}, p_{3/2}p_{3/2}), \end{aligned}$$

where E_{av} is the average energy[12] of the configuration and F, G, and R are the usual Coulomb integrals. We perform one self-consistent calculation for each state by forcing the program to converge either to the lower or to the upper state. The method we have just described is also used for the ${}^3P_0$, ${}^1S_0$ states of the p^4 configuration and the ${}^3P_1$, ${}^1P_1$ states of the sp^5 configuration. We discuss in Sec. IV the results obtained for the a coefficients.

The total energy includes, through the Breit interaction, relativistic effects up to order $1/c^2$ (c is the speed of light). However, it is well known that for heavy atoms higher-order corrections have to be considered. The next-order terms responsible for the Lamb shift are included in the following approximate way: for $1s$ electrons the

TABLE I. *KLL* Auger energies for neon (in eV).

Final configuration	Auger line	State	Semiempirical		Present calc.	Experimental (Ref. 18)
			(Ref. 7)	(Ref. 6)		
$(2s)^0(2p)^6$	KL_1L_1	$^1S_0$	751	754.1	747.5	748.0 ±0.1
$(2s)^1(2p)^5$	KL_1L_2	$^1P_1$	774	776.1	771.6	771.4 ±0.1
		$^3P_0$	785	787.9	783.7	
	KL_1L_3	$^3P_1$	785	787.9	783.7	782.0 ±0.1
		$^3P_2$	785	787.9	783.8	
$(2s)^2(2p)^4$	KL_2L_2	$^1S_0$	802	805.4	801.8	800.4 ±0.1
	KL_2L_3	$^1D_2$	806	807.5	806.9	804.1 ±0.4
	KL_3L_3	$^3P_0$	809	810.3	810.3	
		$^3P_2$	809	810.3	810.4	

results published by Desiderio and Johnson[14] show a smooth variation as a function of the atomic number Z (roughly Z^4), and it is easy to extrapolate for uranium and americium. For $2s$ electrons, the only published value for many-electron systems is that of fermium.[15] To obtain an estimate for uranium and americium, we calculated the self-energy contribution from the recent work of Mohr,[16] using an effective value of Z reduced by 1.6 (this screening coefficient is calculated from the expectation value of r). The vacuum polarization contribution was estimated by Fricke[17] for uranium (13 eV for the $2s$ shell), using the Uehling potential. For americium, we interpolate between uranium and fermium and find 16 eV. The same procedure is applied to the $2p_{1/2}$ and $2p_{3/2}$ subshells, the latter being negligible. As we shall see in Sec. IV, our assumption seems to produce reasonable binding energies.

For the light atoms considered here (Ne and Ar), the Lamb-shift correction is not included.

IV. RESULTS AND DISCUSSION

Our method of calculating Auger transition energies was first tested on the *KLL* spectra of neon (Table I) and argon (Table II). For these elements very precise measurements[18,19] have been performed and these free-atom spectra are directly comparable with theoretical atomic calculations. As pointed out by Kelly,[20] the Hartree-Fock transition energies obtained for neon are in quite good agreement with the experimental results, the many-body effects contributing only a few eV. For these light elements we do not expect that a relativistic treatment will drastically modify the results. Nevertheless, if the relativistic correction to the $1s$ binding energy is only about 0.8 eV for neon, it already amounts to 10 eV for argon, which

TABLE II. *KLL* Auger energies for argon (in eV).

Final configuration	Auger line	State	Semiempirical		Present calc.	Experimental (Ref. 19)
			(Ref. 7)	(Ref. 6)		
$(2s)^0(2p)^6$	KL_1L_1	$^1S_0$	2524	2508.9	2511.6	2508.9 ±0.4
$(2s)^1(2p)^5$	KL_1L_2	$^1P_1$	2584	2573.8	2575.6	2575.8 ±0.3
		$^3P_0$	2607	2597.2	2599.2	
	KL_1L_3	$^3P_1$	2608	2597.9	2600.0	2599.4 ±0.3
		$^3P_2$	2609	2599.2	2601.4	
$(2s)^2(2p)^4$	KL_2L_2	$^1S_0$	2654	2649.9	2649.9	2650.6 ±1.0
	KL_2L_3	$^1D_2$	2666	2657.8	2661.8	2660.6 ±0.3
	KL_3L_3	$^3P_0$	2672	2664.2	2668.4	2666.8 ±0.4
		$^3P_2$	2674	2666.1	2670.6	2669.1 ±0.3

TABLE III. *KLL* Auger energies for uranium (in eV).

Final configuration	Auger line	State	Semiempirical (Ref. 7)	Present calc. [a]	Experimental (Ref. 8)
$(2s)^0(2p)^6$	KL_1L_1	$^1S_0$	71 748	71 749	71 745 ±20
$(2s)^1(2p)^5$	KL_1L_2	$^1P_1$	72 567	72 560	72 560 ±20
		$^3P_0$	72 615	72 614	72 620 ±20
	KL_1L_3	$^3P_1$	76 302	76 332	76 320 ±20
		$^3P_2$	76 395	76 430	76 430 ±20
$(2s)^2(2p)^4$	KL_2L_2	$^1S_0$	73 353	73 272	73 320 ±40
	KL_2L_3	$^1D_2$	77 141	77 125	77 130 ±20
	KL_3L_3	$^3P_0$	80 873	80 889	
		$^3P_2$	80 938	80 955	

[a] Corrected for the Lamb shift: $1s$, 245 eV; $2s$, 50 eV; $2p_{1/2}$, ~3 eV; $2p_{3/2}$, negligible.

is greater than the contribution from correlation effects (the Dirac-Fock result corrected for Lamb shift is 3205.6 eV, compared to the experimental value of 3205.9 eV[21]). Besides these relativistic corrections, the argon case enables us to judge the quality of our method for the intermediate coupling. From Table II it can be seen that the experimental splitting between the $^3P_2$ and $^3P_0$ states of the KL_3L_3 line is 2.3 eV, while our calculated value is 2.2 eV. As implied in the description of our method given in Sec. III, all of the contributions to the spin-orbit and spin-spin interactions are taken into account, but with different levels of approximation. The spin-same-orbit interaction is included in the variational calculation, since the associated operator belongs to the Dirac one-electron Hamiltonian. On the other hand, the spin-other-orbit and spin-spin interactions are included via the Breit operator and thus treated as first-order perturbations, the only consistent way to handle them.[12]

We now consider the results obtained for uranium (Table III) and americium (Table IV), which are the relevant part of this study. For these high-Z elements it is obvious that relativistic effects have to be carefully taken into account if a good agreement with experiment is to be achieved. Besides the inclusion of the relativistic corrections discussed in Sec. III it is also necessary to go beyond the point-charge-nucleus approximation. For mercury the change in the $1s$ binding energy is already 50 eV owing to the finite size of the nucleus.[12] The calculations we present here have been done using uniform charge distribution inside a sphere of mean radius equal to $1.2A^{1/3}$ fm where A is the nuclear mass. Because americium

TABLE IV. *KLL* Auger energies for americium (in eV).

Final configuration	Auger line	State	Semiempirical (Ref. 7)	Present calc. [a]	Experimental (Ref. 22)
$(2s)^0(2p)^6$	KL_1L_1	$^1S_0$	77 116	77 021	77 012 ±23
$(2s)^1(2p)^5$	KL_1L_2	$^1P_1$	77 956	77 878	77 895 ±12
		$^3P_0$	78 006	77 942	
	KL_1L_3	$^3P_1$	82 349	82 300	82 320 ±50
		$^3P_2$	82 446	82 414	82 470 ±50
$(2s)^2(2p)^4$	KL_2L_2	$^1S_0$	78 763	78 670	
	KL_2L_3	$^1D_2$	83 211	83 152	83 169 ±12
	KL_3L_3	$^3P_0$	87 601	87 575	87 360 ±50
		$^3P_2$	87 669	87 642	87 602 ±24

[a] Corrected for the Lamb shift: $1s$, 270 eV; $2s$, 58 eV; $2p_{1/2}$, ~4 eV; $2p_{3/2}$, negligible.

TABLE V. Binding energies for argon and americium (in eV).

	Argon		Americium	
	Experiment (Ref. 21)	Present calc.	Experiment[a] (Ref. 22)	Present calc.
$1s$	3205.9 ±0.5	3205.6	124 986 ±5	124 978
$2s$	326.3 ±0.1	327.1	23 811 ±2	23 811
$2p_{1/2}$	250.56 ± 0.07	250.3	22 955 ±3	22 951
$2p_{3/2}$	248.45 ± 0.07	248.2	18 513 ±3	18 514

[a] Values and uncertainties deduced by us from the Porter *et al.* (Ref. 22) precision electron and γ-ray measurements in $^{241}\mathrm{Cm} \rightarrow {}^{241}\mathrm{Am}$ decay (without any work-function correction).

TABLE VI. Coefficient a of the configuration with two $2p_{1/2}$ electrons [cf. Eq. (2)].

Atom \ State	$^3P_1$ [a]	$^3P_0$ [b]	$^3P_2$ [c]
Ne	0.581 07	0.586 65	0.826 54
Ar	0.613 19	0.670 87	0.884 59
U	0.999 80	0.999 97	0.999 98
Am	0.999 84	0.999 98	0.999 99

[a] Configuration sp^5: LS limit 0.577 35.
[b] Configuration p^4: LS limit 0.577 35.
[c] Configuration p^4: LS limit 0.816 50.

and uranium are well-deformed nuclei, errors of a few eV may result from this approximation. It is difficult to assess the error limits of the calculated values but we expect that they will not exceed 10 or 20 eV. To justify this value, let us consider the main uncertainties in the calculations. Many-body effects are neglected but it seems unlikely that the difference in the correlation energies of the initial and final states could exceed a few eV. This order of magnitude is supported by the semiempirical treatment of Cowan[23] based on a statistical approach. The second main uncertainty is our treatment of the Lamb-shift correction for the $2s$ electrons and the neglect of higher-order relativistic corrections. Here again the order of magnitude must not exceed a few eV, as can be seen from the comparison of theoretical and experimental binding energies given in Table V.

When comparing binding energies, it is worthwhile to point out that any error in calculation of the Lamb-shift correction is of great importance for the s shells, but less significant for the p shells. The same situation arises for the Auger transition energies and is even worse for the KL_1L_1 line, since any error in the $2s$ contribution will be counted twice. For this reason we believe that the validity of our method has to be judged with respect to the double-$2p$-hole final-state configuration. Among the various states of this configuration, the most relevant one is certainly the $^1D_2$ state of the KL_2L_3 line, which is the most intense one and the best determined, experimentally.

So far we have considered only the intrinsic errors of the calculation, but it remains for us to estimate the validity of relating the free-ion calculations to the experimental results. For light elements, it is well known that solid-state effects shift the metallic or oxide Auger spectra by as much as[24,25] 10–20 eV compared to the vapor results, while this contribution of the solid-state effect is only about 5 eV for the inner-shell binding energies. Besides the two extreme experimental situations, (i) monatomic gases and (ii) electrically conducting sources (external excitation of metals, radioactive-ion implanted sources, vaporization of metallic radioactive elements, etc.), most experiments with radioactive sources have been performed with sources of poorly known chemical states.

Nevertheless, these solid-state effects, for high Z, will be of the same order of magnitude as the experimental uncertainty, and it is not worthwhile to try to incorporate them. For intermediate- and low-Z elements, they should be included, since their contribution is of the same order of magnitude as the higher-order relativistic corrections. Preliminary work has been carried out in this direction and results will be reported in a forthcoming paper.

Finally, we give in Table VI the value of the coefficient a of Eq. (2) for the $^3P_2$ state of the p^4 final configuration, its equivalent for the $^3P_0$ state of the same configuration, and that of the $^3P_1$ state of the sp^5 configuration. For neon our value reproduces the almost pure LS limit, while for uranium and americium we reach the almost pure jj limit (results expected for the inner shells of such heavy atoms).

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[1] W. N. Asaad and E. H. S. Burhop, Proc. Phys. Soc. (Lond.) 71, 369 (1958).

[2] M. Mladjenovic and H. Slätis, Ark. Fys. 9, 41 (1954).

[3] M. A. Listengarten, Bull. Acad. Sci. USSR 24, 1050 (1960).

[4] O. Hörnfeldt, Ark. Fys. 23, 235 (1962).

[5] W. N. Asaad, Z. Phys. 203, 362 (1967).

[6] W. N. Asaad, in *Proceedings of the International Conference on Inner-Shell Ionization Phenomena and Future Applications, Atlanta, 1972,* edited by R. W. Fink *et al*. CONF-720404 (Natl. Tech. Information Service, U. S. Dept. of Commerce, Springfield, Va., p. 463, 1972).

[7] D. A. Shirley, Phys. Rev. A 7, 150 (1973).

[8] Ch. Briançon, Ann. Phys. (Paris) 5, 151 (1970).

[9] K. D. Sevier, in *Low Energy Electron Spectrometry* (Wiley, New York, 1972).

[10] E. H. S. Burhop and W. N. Asaad, in *Advances in Atomic and Molecular Physics* (Academic, New York, 1972), Vol. 8.

[11] J. P. Desclaux, Comput. Phys. Commun. 9, 31 (1975).

[12] I. P. Grant, Adv. Phys. 19, 747 (1970).

[13] E. V. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge U. P., London, 1935), p. 294.

[14] A. M. Desiderio and W. R. Johnson, Phys. Rev. A 3, 1267 (1971).

[15] B. Fricke, J. P. Desclaux, and J. T. Waber, Phys. Rev. Lett. 28, 714 (1972).

[16] P. J. Mohr, Phys. Rev. Lett. 34, 1050 (1975).

[17] B. Fricke (private communication).

[18] H. Körber and W. Mehlhorn, Z. Phys. 191, 217 (1966).

[19] M. O. Krause, Phys. Rev. Lett. 34, 633 (1975), and private communication.

[20] H. P. Kelly, Phys. Rev. A 11, 556 (1975).

[21] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werne, R. Manne, and Y. Baer, in *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969), p. 36.

[22] F. T. Porter, I. Ahmad, M. S. Freedman, J. Milsted, and A. M. Friedman, Phys. Rev. C 10, 803 (1974).

[23] R. D. Cowan, Phys. Rev. 163, 54 (1967).

[24] L. Ley, F. R. McFeely, S. P. Kowalczyk, J. G. Jenkin, and D. A. Shirley, Phys. Rev. B 11, 600 (1975).

[25] A. Barris and F. J. Street, J. Electron Spectrosc. 7, 1 (1975).