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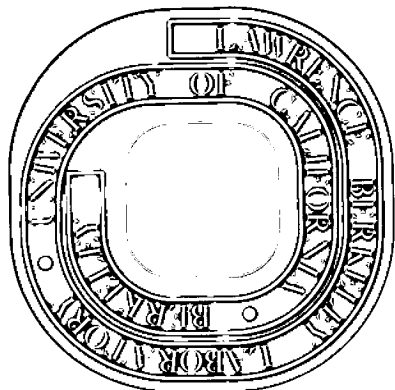
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RELAXATION EFFECTS ON AUGER ENERGIES[*]

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Abstract:

A hitherto-neglected relaxation-energy effect in

the Auger process was found, and an approximate theory for

calculating it was developed. The effect ranges from

about 6 eV in neon to about 150 eV in fermium. Theoretical

KL_IL_I energies show excellent agreement with experiment.

The relaxation term is large enough to affect seriously

the analysis of unknown Auger spectra. It appears to

have very wide application to Auger spectroscopy.

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In the course of a systematic study of the theory of Auger electron

energies, it has become clear that an important effect--outer-shell relaxation

in the final state--has been generally neglected until now. The use of three-

or four parameter semi-empirical theories to fit existing data has obscured

the significance of outer-shell relaxation, because these theories were

flexible enough to give good fits. However, the agreement deteriorates

drastically if one attempts to use calculated, rather than empirically adjusted,

Slater integrals. In this Letter a new theoretical approach that includes

relaxation is derived. It relates Auger energies to measured one-electron

binding energies (as did the semi-empirical theory) plus two-electron integrals

from Hartree-Fock calculations in the ground states of neutral atoms. One

adjustable parameter is required if the integrals employed are based on

nonrelativistic wavefunctions; none is required if the wavefunctions are

relativistic. Comparison of the predictions of this theory with experimental

KL_IL_I Auger energies of the elements shows generally excellent agreement with

experiment. The theory may be readily applied to estimate Auger energies

throughout the Periodic Table. An application to energies of MNN groups

in xenon is given, to indicate the wide applicability of the relaxation term.

For brevity let us consider the KL_IL_I Auger transition explicitly. In

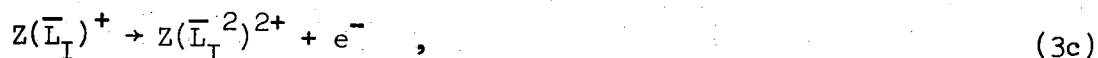an element of atomic number Z this process may be denoted by

$$Z(\overline{K})^+ \rightarrow Z(\overline{L_I}^2)^{2+} + e^- \quad , \tag{1}$$

where the atom is assumed to have its full complement of electrons excepting

those denoted by the "hole-state" notation $\overline{K}$, $\overline{L_I}$, etc. An approximate estimate

of the kinetic energy of the outgoing electron is given by

$$E(KL_IL_I) \cong E_B(K) - 2E_B(L_I) \quad , \tag{2}$$

i.e., by a combination of one-electron binding energies. In deriving Eq. (2)

one implicitly considers Eq. (1) to be obtained as a combination of the

processes

$$Z \rightarrow Z(\overline{K})^+ + e^- \tag{3a}$$

$$Z \rightarrow Z(\overline{L_I})^+ + e^- \tag{3b}$$

$$Z(\overline{L}_I)^+ \rightarrow Z(\overline{L}_I^2)^{2+} + e^- \quad , \tag{3c}$$

and the energy of step (3c) is assumed to be identical to that of (3b) in the derivation of Eq. (2). Although this is a very poor assumption, it is the only assumption, and efforts to improve theoretical estimates of KL_IL_I Auger energies can be focused on Eq. (3c).

At this point we note that empirical binding energies will be used throughout this Letter in estimating Auger energies. Accurate theoretical K and L_I binding energies are available for relatively few elements. Even in these cases the empirical binding energies are preferred because in combining them to form an Auger transition energy there is a partial cancellation of such effects as extra-atomic relaxation[1] and the work function in condensed phases; in addition, relativity and electron correlation effects are of course included in the empirical binding energies.

To improve on Eq. (2), Asaad and Burhop[2] noted that Step (3c) differs from Step (3b) in one important way; when the second electron is ejected from the L_I shell, there is no electron remaining in this shell. The binding energy will therefore be increased by the two-electron interaction energy. Neglecting the relatively small electron-correlation term, the two-electron energy for this case is given by the Slater integral $F_0(2s,2s)$. Thus Eq. (2) becomes, according to Asaad and Barhop,

$$E(KL_IL_I) = E_B(K) - 2E_B(L_I) - F_0(2s,2s) \quad . \tag{4}$$

These authors gave similar, but longer expressions for the other KLL energies. In most cases the required Slater integrals were not available, so empirical expressions of the form

$$F_0(2s,2s) \cong A(Z - Z_s)(1 + \alpha Z^n) \quad, \tag{5}$$

were used, with the parameters A, Z_s, α, and n determined by comparison with existing Auger energies. In this way semi-empirical KLL Auger energies were estimated and tabulated for the elements by several authors.[3-5]

More recently, Asaad has shown[6] that the relativity factor $1 + \alpha Z^n$ should have n = 2; whereas the value n = 3 was used in the semi-empirical tables. By itself this would not be too serious, because α could be readjusted to give a reasonably good fit of the data. However, in light of the availability now of accurate Slater integrals from the Hartree-Fock equations by J. B. Mann,[7] it is no longer desirable to regard A and Z_s as adjustable parameters. But if the calculated values of $F_0(2s,2s)$ are used, the calculated KL_IL_I energies disagree seriously with experiment, showing that Eq. (4) is not really viable.

The reason for this is rather simple. Equation (4) does not properly take into account the effect of relaxation in the passive outer orbitals. Dynamic relaxation effects (i.e., the binding-energy contribution arising from acceleration of the outgoing electron by adiabatic collapse of occupied outer orbitals toward the hole during the emission process) are automatically accounted for by the use of empirical binding energies in Eq. (4). However, there is also a static effect. The dynamic relaxation of the outer orbitals during ejection of the first electron from the L_I subshell creates a more repulsive environment for the second L_I electron, raising its orbital energy by an amount R. Thus the binding energy of Step (3a) is lowered by R, and Eq. (4) is replaced by

$$E(KL_IL_I) = E_B(K) - 2E_B(L_I) + R - F_0(2s,2s) \quad . \tag{16}$$

The energy R may be estimated by using an "equivalent cores" approach[8] that has proved successful recently in calculating the effects of relaxation on atomic binding energies. The essence of this approach is that a one-electron outer orbital of an atom of element Z which has a hole in an inner orbital may be rather accurately represented by the corresponding outer orbital of a neutral atom of element $Z + 1$. It follows[8] that

$$\left. \begin{array}{l} F_0(2s,n\ell;\ Z(\overline{2s})) \cong F_0(2s,n\ell;\ Z + 1) \\[3mm] G_\ell(2s,n\ell;\ Z(\overline{2s})) \cong G_\ell(2s,n\ell;\ Z + 1) \end{array} \right\} \quad . \tag{7}$$

where $n > 2$ and $Z(\overline{2s})$ denotes an atom of element Z with a hole in the 2s (or L_I) shell. This approach neglects inner-shell ($n = 1$) relaxation, which is negligible.[9] Intrashell effects are also small. They cannot be estimated by this method, but the results of Hedin and Johansson[9] can be used to estimate the intrashell relaxation energy in light elements. Straightforward calculation gives

$$R \cong \sum_{\substack{\ell \\ n>2}} \{N(n\ell)\ \Delta F_0(2s,n\ell) - \Delta G_\ell(2s,n\ell)\} \quad , \tag{8}$$

where $N(n\ell)$ is the occupation number of the $n\ell$ subshell and

$$\Delta F_0(2s,n\ell) \equiv F_0(2s,n\ell;\ Z + 1) - F_0(2s,n\ell;\ Z)$$

$$\Delta G_\ell(2s,n\ell) \equiv G_\ell(2s,n\ell;\ Z + 1) - G_\ell(2s,n\ell;\ Z) \quad . \tag{9}$$

In the actual evaluation of R it is not advisable to simply calculate R for each element, especially in the transition series, because a change in $N(n\ell)$ from Z to $Z + 1$ precludes the use of Eq. (7). Good estimates of R for all the elements above $Z = 10$ were obtained by calculating R for closed shells and subshells, using Eq. (8), and interpolating. For neon the intrashell energy given for Na^+ by Hedin and Johansson was used. No intrashell estimates were made for argon and above, because the R value for argon estimated using Eq. (8) accounted for all the relaxation energy.

Predicted KL_IL_I Auger energies of the elements are set out in Table I, together with experimental values, where available. The predicted values were calculated using empirical binding energies from Ref. 4. Outer-shell relaxation R was calculated using Mann's table,[7] and $F_0(2s,2s)$ was also taken from Mann's tables. Because these $F_0(2s,2s)$ values were calculated with a nonrelativistic theory, a relativity correction of the form given by Asaad was applied. Specifically, $F_0(2s,2s)$ was taken to have the form

$$F_0(2s,2s) = (1 + \alpha Z^2)\ F_0(2s,2s)_{\text{Nonrelativistic}} \quad , \tag{10}$$

and the single parameter α was adjusted. The value $\alpha = 4.2 \times 10^{-5}$ was adopted.

The agreement between predicted and experimental values of $E(KL_IL_I)$ is generally excellent, as perusal of Table I will show. It is even slightly better than that of the published semi-empirical values. Thus the necessity for considering the static relaxation energy R has been demonstrated, and a recipe has been given for calculating R with reasonable accuracy.

Further work is in progress. Preliminary results indicate that the R term, together with the intermediate-coupling model of Asaad and Burhop, will accurately predict the energies of all nine lines of the KLL multiplet throughout the Periodic Table. Applications to other Auger transitions are also encouraging. For example, this theory predicts the average energies of the xenon $M_4N_{4,5}N_{4,5}$ and $M_5N_{4,5}N_{4,5}$ patterns to fall at 534.7 eV and 522.1 eV, respectively, including a term R = 9.65 eV. The ^3P lines have been experimentally determined to fall at 534.0 and 521.4 eV.[10] From standard multiplet theory,[11] we calculate the average energies to come at 0.99 eV above the ^3P lines, at 535.0 eV and 522.4 eV, in excellent agreement with the predicted values.

Other applications are under study. A more detailed account of the static relaxation energy will be published elsewhere. The assistance of Mr. D. N. Shirley in calculating the Auger energies is gratefully acknowledged.

FOOTNOTES AND REFERENCES

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Table I. Predicted and Experimental $E(KL_I L_I)$ Energies of the Elements (in eV).

Z	R	$E(KL_I L_I)$ This Work	$E(KL_I L_I)$ Experiment[a]	Z	R	$E(KL_I L_I)$ This Work	$E(KL_I L_I)$ Experiment[a]
10	6	751	748.0(4)	56	92	25320	25251(6)
11	8	922	922.8(4)	57	93	26239	
12	10	1101	1101.3(4)	58	95	27190	
13	12	1296		59	96	28161	
14	14	1511		60	98	29153	
15	16	1739		61	99	30160	
16	18	1980		62	101	31188	31175(20)[b]
17	20	2247		63	103	32238	32224(20)[b]
18	22	2524		64	104	33305	
19	25	2814	2809	65	105	34393	34430(50)
20	28	3121		66	107	35502	35496(6)[b]
21	31	3451		67	109	36632	
22	33	3793		68	110	37781	
23	36	4163	4159(6)	69	112	38953	38958(25)
24	39	4552		70	113	40146	40149(4)
25	42	4953	4962(2)[b]	71	115	41359	41351(10)[b]
26	45	5373	5376[b]	72	117	42588	
27	48	5806		73	118	43832	
28	51	6265		74	120	45097	45080(40)
29	54	6734	6735(6)[b]	75	121	46387	46400(25)
30	57	7216	7220(4)	76	122	47694	
31	58	7713		77	123	49026	
32	60	8218	8212(6)	78	124	50382	50370(100)[b]
33	61	8749	8742(10)	79	126	51761	51780(20)[b]
34	62	9283		80	127	53160	53141(25)[b]
35	63	9839	9860(10)	81	129	54567	54510(100)
36	65	10411		82	130	56007	
37	67	10994		83	132	57468	57467(30)[b]
38	68	11593	11584.4(16)	84	133	58939	58920(50)
39	70	12211		85	135	60450	
40	72	12849	12851.8(15)	86	136	62006	
41	73	13501		87	137	63552	
42	75	14176	14176.1(13)	88	138	65134	
43	76	14862		89	139	66754	
44	78	15570		90	140	68379	
45	80	16294		91	141	70056	
46	81	17034		92	142	71748	71738(20)[b]
47	83	17793	17740(60)	93	143	73486	73555(150)[b]
48	85	18563		94	144	75257	75180(15)
49	85	19347	19352(1)	95	145	77116	
50	86	20149		96	146	78928	
51	87	20968		97	147	80660	
52	88	21806	21787(10)	98	148	83352	
53	88	22659	22652(10)	99	149	85294	
54	89	23516		100	150	87286	
55	90	24415	24395(14)[b]				

[a]From Ref. 5. Errors in last place appear parenthetically.

[b]In cases for which two or more experimental values are available. Either an average was taken or a single value chosen.