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ADIABATIC RELAXATION ENERGY (ARE) FOR KL STATES OF ATOMS

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ABSTRACT

A method has been presented for calculating semiempirically the adiabatic relaxation energy (ARE) for excited states of atoms which are ionised in K- and L-shells simultaneously. The validity of the method has been tested by calculating the complete $K\alpha_3\alpha_4$ satellite spectrum of nickel, which is found to be in excellent agreement with the observed spectrum. Finally, the values of ARE for KL states of atoms with $Z = 12$ to 44 have been presented.

RESUMEN

Se presenta un método para calcular semi- empíricamente la energía de relajación adiabatica(ARE) para estados exitados de átomos, los cuales son ionizados simultáneamente en los niveles K y L. La validéz del método ha sido probado calculando el espectro satélite de níquel completo $K\alpha_3\alpha_4$ el cual se encontró en excelente concordancia con el espectro observado. Finalmente, se presentan los valores de ARE para los estados KL de átomos con $Z = 12$ al 44.

INTRODUCTION

The energy values of two hole excited states of atoms in inner shells are very useful and essential for explaining the presence of various satellites in X-ray spectra. Furthermore, such two hole states form final states for the emission of various diagram lines in Auger electron spectra. These also are the initial states for the emission of satellites in Auger electron spectra. Many papers on the calculations of KL, LL, LM, MM and MN states of atoms have been reported[1-7]. The KL state, in particular, has been dealt with by many authors, namely Candlin[1], Assad[2], Horak[3], Åberg[4], Demekhin and Sachenko[5] and Giantureo et. al.[6]. All these papers have used different principles for calculating the KL energy levels. The one, namely that by Demekhin and Sachenko[5] is based on the use of Slater integrals, F_K and G_K, for calculating the interaction between two holes. However, they have used the modified values of Slater integrals so as to include the effects of the presence of two inner shell holes on the ground state atomic wavefunctions. Contrary to this, Shirley[7] has suggested that it is possible to use neutral atom Slater integral values and a correction term, namely 'Adiabatic Relaxation Energy' (ARE) should be applied to Slater formulas[5,7]. This term represents the change in binding energy of an electron when outer orbits relax to smaller sizes due to effective increase in nuclear charge arising due to removal of an inner electron. Larkins[8] has used this technique and found very good results for various LL, LM, MM etc. states of all the atoms with $Z = 10$ to 100. However, he has not considered the KL states due to the fact that his study was confined only to diagram lines of Auger spectra. In the present paper, the values of ARE for these states of atoms from $_{11}$Na to $_{44}$Ru are reported. The method used for the calculation has been described in Sec. 2, while testing the validity of the method forms the subject matter of Sec. 3. Finally, in Sec. 4, the values of ARE for various atoms are presented and discussed.

2. METHOD OF CALCULATION

The present method of calculation is based on the assignment of the intense satellite $K\alpha_4$ to the transition $KL_2\,{}^1P_1 \rightarrow L_2L_3\,{}^1D_2$. This assignment has been suggested and confirmed by various X-ray Spectroscopists[1,2,4-6,9]. The assignment gets support from the fact that the satellite α_4 is the most intense line observed in the $\alpha_3\alpha_4$ spectrum and the transition under consideration has the maximum probability of occurrence[10] out of all the KL → LL transitions. The initial and final state energies for closed shell atoms, $_{20}$Ca and $_{30}$Zn, have been calculated by using the formulas[5,7].

$$E(KL_2\,{}^1P_1) = E(K) + E(L_2) + F^0(1s,\,2p) - \frac{3}{4}\,\zeta_{2p}$$

$$+ \left[\left\{\frac{1}{3}\,G^1(1s,\,2p) - \frac{1}{4}\,\zeta_{2p}\right\}^2 + \frac{1}{2}\,\zeta_{2p}^2\right]^{1/2} \qquad \ldots \quad (1)$$

and

$$E(L_2L_3\,{}^1D_2) = 2E(L_2) + F^0(2p,2p) - \frac{2}{25}F^2(2p,2p) - \frac{9}{4}\zeta_{2p}$$

$$+ \left[\left(\frac{3}{25}F^2(2p,2p) + \frac{1}{4}\zeta_{2p}\right)^2 + \frac{1}{2}\zeta_{2p}^2\right] \qquad \ldots \quad (2)$$

where

$$\zeta_{2p} = \frac{2}{3}\left[E(L_2) - E(L_3)\right] \qquad \ldots \quad (3)$$

In these equations, E(K) etc. are the one hole excited state energies, F^k and G^k are Slater integrals for the two hole pairs mentioned in the braces attached to them, and ζ_{2p} is the spin orbit interaction parameter for $^2P_{2p}$ state. The values of E(k), etc. have been taken from the Tables of Bearden and Burr[11] and the values of Slater integrals from the Tables of Mann[12]. These calculated initial and final state energies and the transition energies are shown in the columns 2,3,and 4 respectively of Table 1.

As suggested by Shirley[7], the two hole state energies (of columns 2 and 3) are to be reduced by adiabatic relaxation energies, say k_1 and k_2, for initial and final states respectively. Larkins[13] has suggested one more correction, namely solid state correction to account for the fact that formulas(1) and (2) apply for individual atoms and the experiment is performed with a solid bulk. However,this correction has been shown to be same for all two hole states of the atom and hence do not affect the transition energy. Therefore the calculated transition energy should be higher than the measured $K\alpha_4$ energy by Δk, the difference between k_1 and k_2. The $K\alpha_4$ energies, taken from Cauchois Tables [14] are shown in col 5 and the Δk values in col 6. In col 7, the values of k_2, namely ARE for L_2L_3 states, taken from Tables of Larkins[7] are shown and in last column, the values of $k(KL_2)$, estimated by adding values in columns 6 and 7 are shown.

3. TEST OF THE METHOD

Larkins[15] has shown that the ARE for a particular two hole state remains unchanged so far as the principal quantum numbers, n, of each of the two holes does not change. Thus, for all KL states of an atom, the values of ARE can be taken as same as that found for the $KL_2\,{}^1P_1$ state. Further,the values of ARE for a particular two hole state is found to increase linearly, to a first approximation, with increasing Z. Taking these two assumptions as valid for KL states, the k(KL) value for Z = 28 has been calculated by interpolation of the respctive values for Z = 20 and 30 (Table 1). The value comes out to be 52.2. eV.

In the second step of the test, the values of all KL and LL states of nickel have been calculated using formulas similar to equations (1) and (2)[5,7]. All KL state energies have been reduced by the ARE value 52.2 eV, while all LL values have been similarly corrected using 42.0 eV[8] as the ARE value for this state. The various allowed KL → LL transition energies have been calculated and compared with experimentally measured values of $K\alpha_3\alpha_4$ satellite spectrum of nickel[16-18]. All these calculated and observed values are shown in Table 2. An excellent agreement between values in last two columns confirms the validity of the method employed for estimation of ARE values for KL state.

4. VALUES OF (ARE) FOR KL STATES OF ATOMS

The above discussion has proved that the adiabatic relaxation energy can be semi-empirically estimated by comparing the theoretically calculated $KL_2\,{}^1P_1 \rightarrow L_2L_3\,{}^1D_2$ transition energy with $K\alpha_4$ satellite energy observed in the X-ray emission spectrum of the atom. A look at Table 2 further reveals that the mutual separations of various KL → LL transition energies are clearly reflected in similar separation of measured satellite energies of $\alpha_3\alpha_4$ spectrum. This shows that the Slater formulas can be used for calculating the doubly ionised KL states of atoms, even in transition metal atoms in which there are many holes in inner d subshell while outer s subshell is full. Further,this equality of calculated and observed separation energies confirms Larkins' suggestion that for all KL states, the adiabatic relaxation energy can be assumed to be invariant. Looking to these inferences, the values of ARE for KL states of all those atoms have been calculated, in spectra of which the satellite $K\alpha_4$ has been reported[14]. These values are shown in Table 3. A comparison of these values with similar values[8] for LL, LM, MM, MN and NN states of these atoms shows that as the position of either hole shifts inwards, the value of ARE, increases. This is expected due to the fact that atomic wavefunctions are more susceptible to inner vacancies compared to outer ones. This indicates that ARE for KK states should be highest among all doubly ionised states. These energies shall be presented somewhere else.

Another property of ARE, namely a linear increase with increasing Z is also shown by the k(KL) values presented in last column of Table 3. However, there are some departures from this linearity in case of elements with Z = 15,22 and 37 to 46, excepting 39. This is probably due to wrong identification of the satellite α_4 in their spectra. This can be confirmed only after a reinvestigation of these spectra.

Table 1 : Comparison of $KL_2\,^1P_1 \to L_2L_3\,^1D_2$ transition energies with $K\alpha_4$ satellite and evaluation of Adiabatic Relaxation Energies for $KL_2\,^1P_1$ state.

Z	Uncorrected energies of states (eV)		Uncorrected transition energy (eV)	Measured $K\alpha_4$ satellite energy (eV)	Value of Δk(a) (eV)	Value of $k(L_2L_3)$(b) (eV)	Value of $k(KL_2)$(c) (eV)
	$KL_2\,^1P_1$	$L_2L_3\,^1D_2$					
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
20	4496.3	773.3	3723.0	3715.3	7.7	25.3	33.0
30	10872.1	2187.0	8685.1	8673.7	11.4	45.6	57.0

(a) $\Delta k = k(KL_2) - k(L_2L_3)$ is found by subtracting measured $K\alpha_4$ energy (col. 5) from calculated transition energy (col. 4).

(b) Values taken from Tables of Larkins (Ref. 8).

(c) Sum of values in columns 6 and 7.

Table 2 : Comparison of KL → LL transition energies and measured $K\alpha_3\alpha_4$ satellite spectrum of nickel.

S. No.	Transition	Energies of states (eV)				Transition energy (eV)	Measured satellite energy (eV) (a)
		Initial		Final			
		Uncorrected	Corrected	Uncorrected	Corrected		
1.	$KL_3\,^3P_1 \to L_3L_3\,^3P_2$	9343.0	9290.8	1816.9	1774.9	7515.9	α_3'(P) 7514.6
2.	$KL_2\,^1P_1 \to L_2L_3\,^1D_2$	9363.2	9311.0	1841.7	1799.7	7511.3	α_4(P) 7511.8
3.	$KL_2\,^3P_0 \to L_3L_3\,^3P_1$	9352.8	9300.6	1831.4	1789.4	7511.2	
4.	$KL_3\,^3P_2 \to L_3L_3\,^3P_2$	9335.6	9283.4	1816.9	1774.9	7508.5	α_3(P) 7507.2
5.	$KL_1\,^3S_1 \to L_1L_3\,^3P_2$	9467.6	9415.4	1949.2	1907.2	7508.2	
6.	$KL_3\,^3P_1 \to L_3L_3\,^3P_0$	9343.0	9290.8	1827.2	1785.2	7505.6	α_3''(P) 7503.8
7.	$KL_3\,^3P_1 \to L_3L_3\,^3P_1$	9343.0	9290.8	1831.4	1789.4	7501.4	α'(P) 7500.6
8.	$KL_1\,^3S_1 \to L_1L_3\,^3P_1$	9467.6	9415.4	1958.8	1916.8	7498.6	α''(E) 7496.9
9.	$KL_3\,^3P_2 \to L_3L_3\,^3P_1$	9335.6	9283.4	1831.4	1789.4	7494.0	α"'(E) 7292.3
10.	$KL_1\,^3S_1 \to L_1L_2\,^3P_0$	9467.6	9415.4	1966.4	1924.4	7491.0	α''(H) 7491.3
11.	$KL_2\,^1P_1 \to L_2L_2\,^1S_0$	9363.2	9311.0	1863.3	1821.3	7489.7	-
12.	$KL_1\,^1S_0 \to L_1L_2\,^1P_1$	9493.4	9441.2	1997.6	1955.6	7485.6	-

(a) The letters in the braces denote the reference from which the measured values are taken, P = Parratt, H = Hayasi and E = Edamoto.

Table 3 : Adiabatic Relaxation Energy for KL states (in eV)

Z	ARE	Z	ARE	Z	ARE	Z	ARE
10	9.0	19	30.8	28	51.7	38	70
11	12.2	20	33.0	29	54.3	39	69
12	13.5	21	36.3	30	57.0	40	66
13	16.0	22	34.9	31	57.3	41	65
14	17.5	23	40.4	32	59.0	42	67
15	16.7	24	43.2	33	61.3	45	67
16	23.5	25	47.6	34	62.5	46	70
17	27.0	26	48.1	35	64.4	-	-
18	28.8	27	50.2	37	71.0	-	-

REFERENCES

1) D.J. CANDLIN : Proc. Phys. Soc. Lond. A68, 322, 1955.

2) W.N. ASSAD and E.H.S. BURHOP : Proc. Phys. Soc. Lond. 71, 369, 1958.

3) Z. HORAK : Proc. Phys. Soc. Lond. 77,980, 1961.

4) T. ABERG : Phys. Rev. 156, 35, 1967.

5) V.F. DEMEKHIN and V.P. SACHENKO : Bull. Acad. Sci. USSR, Phys. Ser. 31, 913, 1968.

6) F.A. GIANTUREO, E. SEMPRINI and F. STEFANI : Physica 80C 613, 1975.

7) D.A. SHIRLEY : Phys. Rev. A7(5), 1520, 1973.

8) F.P. LARKINS : At. data nucl. data Tables 20(4), 311, 1977.

9) J.P. BRIAND : "*Photoionisation and other probes of many electron interactions*"ed.F.J.Willeumier (Plenum) 1976.

10) E.U. CONDON and G.H. SHORTLEY:"*Theory of Atomic Spectra*", (Cambridge) 1953.

11) J.A. BEARDEN and A.F. BURR : Rev. Mod.Phys. 39, 78, 1967.

12) J.B. MANN : "*Atomic Structure Calculations I* ". Los Alamos. Sci. Lab. Rep. No. LA3690, 1967.

13) F.P. LARKINS : J. Phys. C. (Solid St. Phys.), 10, 2453, 1977.

14) Y. CAUCHOIS and H. HULUBEI : X-ray Wavelength Tables (Herman), 1947.

15) F.P. LARKINS : J. Phys. B. (GB) 9, 47, 1976.

16) L.G. PARRATT : Phys. Rev. 50, 1, 1936.

17) T. HAYASI : Sci. Rep. Tohoku Imp. Univ. Ser. A. 25, 785, 1936.

18) I. EDAMOTO : Sci. Rep. Res. Inst. Tohoku Univ. A2(4), 561, 1950.

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