ISONUCLEAR SEQUENCES IN ATOMIC SPECTROSCOPY

SECUENCIAS ISONUCLEARES EN ESPECTROSCOPIA ATOMICA

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ABSTRACT

The notion of isonuclear sequences is employed in this work for studying the p shell on Na, Mg, Al, Si. Observed Regularities of the ionization potentials and Slater's integrals are reported.

RESUMEN

En este trabajo la noción de secuencias isonucleares es empleada para estudiar la capa p en Na, Mg, Al y Si. Ciertas regularidades observadas en los potenciales de ionización e integrales de Slater son reportadas.

1. INTRODUCTION

In the single configuration approach, the energy of terms arising from pure couplings is expressed in function of the average energy of configuration E_{av} and of direct and exchange integrals, F^k and G^k. These integrals can be calculated by "ab initio" methods or they can be considered as adjustable parameters arising from the least-square fitting of empirically determined levels.

When considering the spin-orbit interaction, we must perform the diagonalization of the energy matrix for each J value, and their elements must be previously calculated or estimated. The eigenvalues gives the energy levels. The notion of isonuclear sequences is employed in this work for estimating the radial integrals. Precise experimental data for studying the p shell of Na, Mg, Al and Si, has been taken from the NBS revision of spectra of low Z elements (1).

2. ISONUCLEAR SEQUENCES

In the semiempirical analysis of atomic spectra, the general relations between similar spectra are of particular importance. Thus, the isoelectronic sequences (elements of different Z but equal numbers of external electrons) play an important role, and have been exhaustively studied by Edlen (2,3). Similarly, it is natural to think about homologous (or vertical isoionics) sequences, i.e. elements that are in the same column of the Periodic Table with the same ionization degree.

In both cases, the structure of levels is similar, so an inmediate correlation among spectra results, and it permits to study the departures from the pure schemes, and the importance of the configuration interaction.

When working in Xe III and Xe IV, we have met with the absence of isoelectronic or homologous sequences with which compare our analysis, and estimate Slater's parameters E_{av}, F^k, G^k and ξ_p.

This problem has taken us to study of isonuclear sequences (ions with equal Z but different net charge), taking into account that the structure of levels is now different for each ion.

In spite of this apparent difficulty, we have verified that the average electron energy in each configuration follows a similar tendency to that of the ionization potentials. For example, in Fig. 1 graphs in function of the net charge of the ionization potentials and the average energy of 3s, 3p and 3d electrons for the Na II (s^2 p^5 I) to Na VII (s^2 I) spectra are drawn. The ionization potentials were measured from the fundamental level of an ion, to the fundamental level of the following ion. They vary in a smooth way until the shell is semi-filled (p^3), then taking place an interruption of the slope tendency, but maintaing its smoothness. Something similar occurs for the isoionic horizontal sequences (See: Edlen (2), pag. 201).

However, it is possible to define the ionization potential in a different way, i.e., as the difference between the gravity center of the fundamental configuration of an ion and the gravity center of the fundamental configuration of the following ion.

In this case, the resulting curve is always smooth, and it perfectly fits a quadratic parabola in all the studied cases (Na, Mg, Al, Si) (Fig. 2).

In the following tables and graphs, the variable $X \equiv (6-q)$ is used, being q the number of electrons in the p shell (p^q). For the sodium case, denoting P as the ionization potential between gravity centers, divided by the ionization potential for $X = 0$, the adjusting curve, by construction of the polinomial, is:

$$P(X) = 1 + 0.5175\,X + 0.0325\,X^2$$

Likewise, in the magnesium, aluminium and silicium cases, the polinomials are:

$$P(X) = 1 + 0.3695\,X + 0.0185\,X^2,$$

$$P(X) = 1 + 0.2880\,X + 0.0120\,X^2 \quad \text{and}$$

$$P(X) = 1 + 0.2425\,X + 0.0075\,X^2$$

respectively. The experimental and theoretical values are in Tables I to IV.

To explain this behaviour, we must consider that the average energy of the s^2 p^q configuration is (2):

$$W_{av}(s^2\,p^q) =$$

$$= W(cs) + F^0(ss) + \frac{q(q-1)}{2}(F^0(pp) - 2F^2(pp)/25) +$$

$$+ 2q(F^0(sp) - G^1(sp)/6)$$

where W(cs) is the energy of the closed shells, i.e. of the internal shells to (s^2 p^q) that we consider, and F^k and G^k are the Slater's electrostatic integrals.
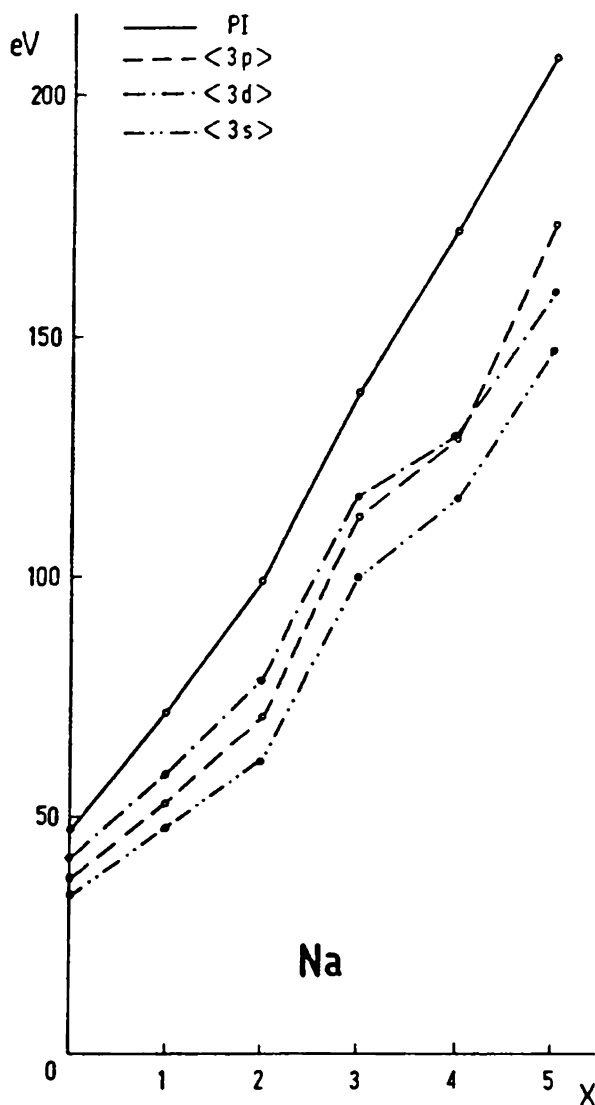

Fig. 1.— Ionization potentials and average energy of electrons for the Na isonuclear sequence. (Na II to Na VII).
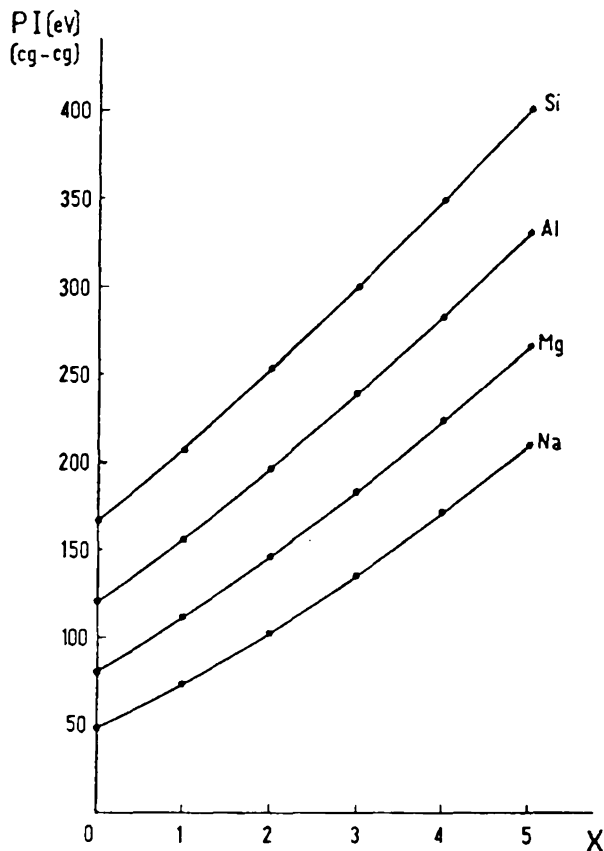
Fig. 2.— Ionization potentials measured between center of gravity
for Na, Mg, Al and Si isonuclear sequences.

TABLE I

*Experimental and theoretical values of
Ionization potentials between centers
of gravity (Na)*

	exp.(eV)	theo.(eV)
IP (p^5 nl)	47.34	47.34
IP (p^4 nl)	73.43	73.43
IP (p^3 nl)	102.77	102.77
IP (p^2 nl)	134.88	134.88
IP (p nl)	170.18	170.18
IP (s^2 nl)	208.33	208.33

TABLE III

*Experimental and theoretical values of
Ionization potentials between centers
of gravity (Al)*

	exp.(eV)	theo.(eV)
IP (p^5 nl)	120.14	120.14
IP (p^4 nl)	156.21	156.28
IP (p^3 nl)	195.34	195.11
IP (p^2 nl)	237.00	236.92
IP (p nl)	282.05	281.61
IP (s^2 nl)	329.71	329.18

TABLE IV

Experimental and theoretical values of Ionization potentials between centers of gravity (Si)

	exp.(eV)	theo.(eV)
IP (p^5 nl)	166.98	166.98
IP (p^4 nl)	207.95	208.73
IP (p^3 nl)	251.82	252.97
IP (p^2 nl)	298.72	299.73
IP (p nl)	348.30	348.99
IP (s^2 nl)	400.80	400.75

The energy of the following ion ($s^2 p^{q-1}$) was obtained in a similar way, replacing q by $(q-1)$ and $(q-1)$ by $(q-2)$. Then, the difference is:

$$W_{av} (s^2 p^{q-1}) - W_{av} (s^2 p^q) =$$

$$= (q-1) (2F^2(pp)/25 - F^0(pp)) + (G^1(sp)/3 - 2F^0(sp)) =$$

$$= (q-1)B + A.$$

If the Slater's parameters would remain equal for each ion, the previous equations would give us a straight line for the ionization potentials (gravity centers to gravity centers) in function of $X \equiv (6-q)$ or, in function of the net charge, ζ.

However, F^2 (pp) varies in a linear form with the net charge, and G^1 (sp) in a slightly quadratic form (figures 3 and 4), so permitting to explain the quadratic behavior of the ionization potentials between centers of gravity.
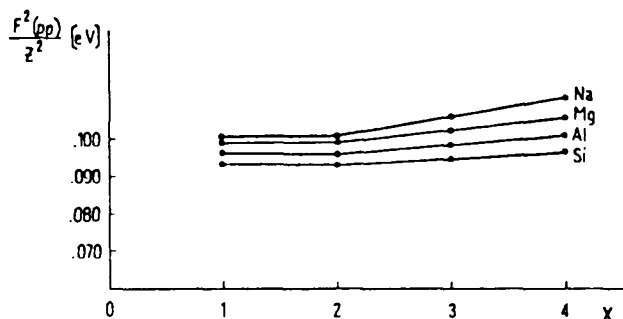

Fig. 3.— The quotient $F^2(pp)/Z^2$ for Na, Mg, Al and Si isonuclear sequences.
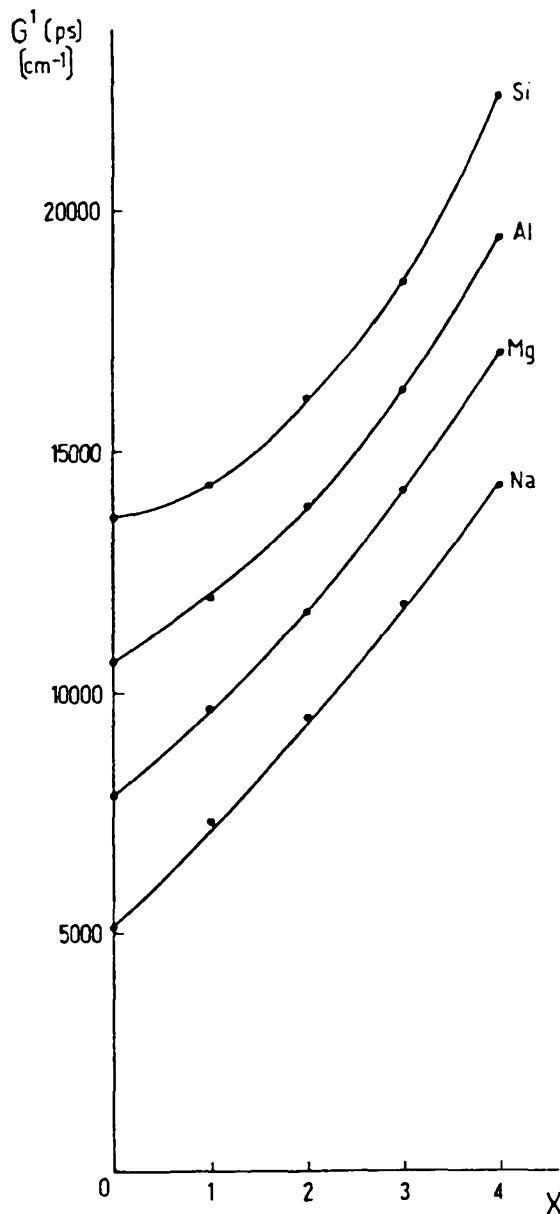

Fig. 4.— G^1 (ps) for Na, Mg, Al and Si isonuclear sequences.

When comparing the isonuclear ionization potentials, it is useful to consider $IP/Z^2\zeta$ for the different elements studied. This relation is important for its almost perfect linearity, as it allows to estimate the IP of an ion if known for $X = 0,1$. Table V shows the values for the $IP(cg\text{-}cg)/Z^2\zeta$ for the elements studied. Apart from linearity, we can see that the considered quotient gives comparable values for the different cases (fig. 5).

TABLE V

Ionization potentials between gravity centers divided by $Z^2\zeta$ for the different studied elements (in eV).

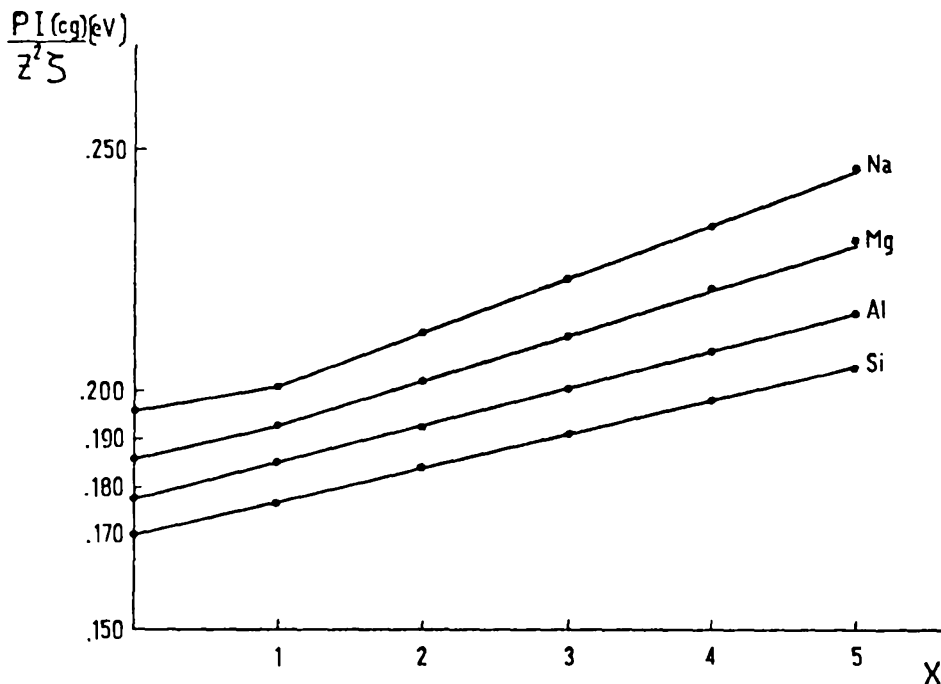|	Na	Mg	Al	Si
p^5 nl	0.196	0.186	0.178	0.170
p^4 nl	0.202	0.193	0.185	0.177
p^3 nl	0.212	0.202	0.192	0.184
p^2 nl	0.223	0.211	0.200	0.191
p nl	0.234	0.221	0.208	0.198
s^2 nl	0.246	0.231	0.216	0.204

Fig. 5.— Ionization potentials between centers of gravity divided $Z^2\zeta$ for Na, Mg, Al and Si iso-nuclear sequences.
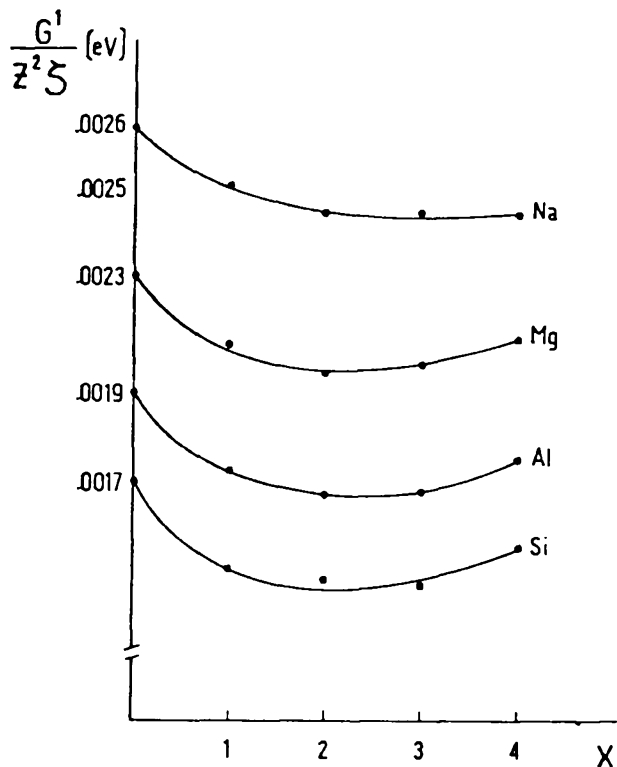
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Fig. 6.— G^1 (ps) divided $Z^2 \zeta$ for Na, Mg, Al and Si isonuclear sequences.

In a similar way we draw F^2(pp)/Z^2 changing the scale in a different way for each element, so resulting similar values. In fact, the F^2(pp) vary between 99000 cm^{-1} (Na IV) up to 152000 cm^{-1} (Si IX).

In the case of G^1(sp), whose values go from 5000 cm^{-1} to 22500 cm^{-1}, varying in slightly quadratic form for each element, the quotient G^1(sp)/$Z^2 \zeta$ gives easily comparable values, not adjusting to a straight line, but also to a parabola (Fig. 6).

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