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Electron Pairing and the Structure of the Periodic System: An Even/Odd Separation

Leonello Paoloni

Gruppo Chimica Teorica, Università, Via Archirafi, 20, 90123 Palermo, Italy

The separate plotting of the first ionization potential of the elements *versus* odd Z and even Z supports the separation of the atoms into two sets with similar periodic distribution, where each atom of the odd set is correlated to one of the even set through the number n of its electron pairs.

Key words: Periodic system – Atom ionization potentials – Electron pairs.

The purpose of this short paper is to put forward a kind of experimental evidence on the role of electron pairing in atoms which seems to have gone unnoticed so far. The first ionization potenzial (IP) of the elements [1] is a well known periodic function of the atomic number Z. However when the plotting is made by arranging separately odd and even Z atoms, a remarkable similarity of the two patterns appears (see Fig. 1). It is almost as if there were two periodic systems one with $Z' = 2n+1$ and another with $Z'' = 2(n+1)$, ($n = 0, 1, 2, \ldots$). This separation of the *odd* and the *even* series seems to have gone unnoticed before and should be considered a new experimental observation.

The number n correlates any odd atom (Z') to its successive even (Z'') in the sequence, and may have a deeper significance for the structure of the periodic system. The atoms having the same n, with the exception of not more than six couples, obey the rule

$$\mathrm{IP}\,(Z'') \geqslant \mathrm{IP}\,(Z'). \tag{1}$$

This holds with a difference $\Delta(\mathrm{IP}) \leqslant 0.1$ eV, which is close to the uncertainty of the data, when $n = 11, 21, 29, 30, 33, 36, 44$. The inequality is reversed when $n = 3, 7, 13, 16, 28, 38$. Among these one has $\Delta(\mathrm{IP}) = -0.92$ eV for the nitrogen–oxygen couple ($n = 3$) the others being between -0.23 and -0.06 eV.

A comparison of contiguous maximum and minimum values in each series is made in Table 1: the difference max (IP) − min (IP) is larger with the even atoms, and decreases and becomes nearly equal in both series when $Z \geqslant 79$.

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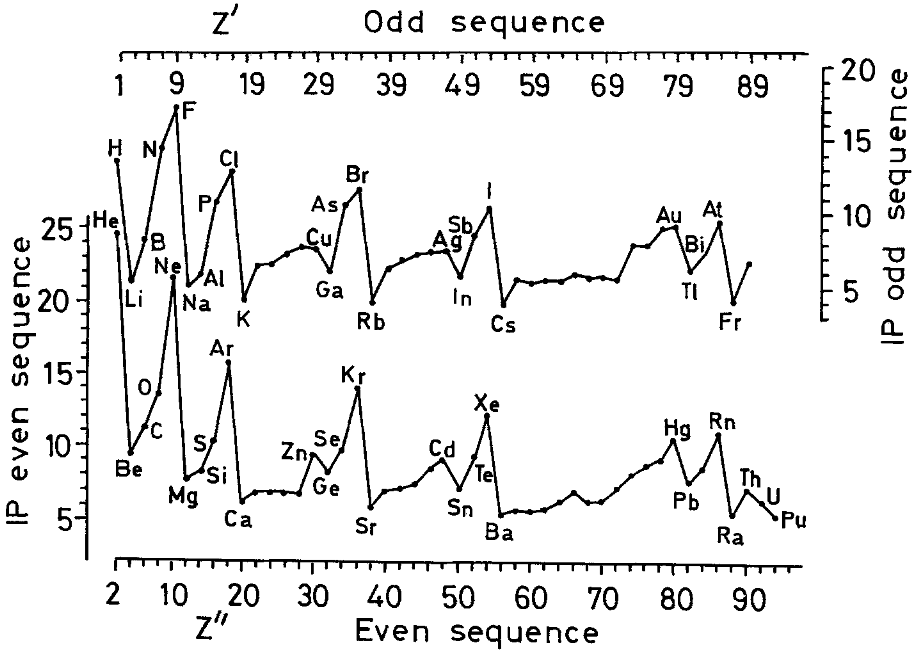

Fig. 1. First ionization potentials (Volt) of the elements plotted *versus* the atomic number in two separate sequences: $Z' = 2n+1$ for odd Z atoms and $Z'' = 2(n+1)$ for even Z atoms, $(n = 0, 1, 2, \ldots)$

Therefore the increment of binding energy for adding one electron pair at the end of each period ($\Delta Z = 2$) is larger for the even series at low Z values, and tends to become the same in both series for large Z.

The inequality (1) can be deduced from models which allow to express the atomic energy as a function of Z and of the number N of electrons. Adopting the statistical model given by Gazquez and Parr [2], from Eq. (10) of their paper one obtains $E(Z, N) - E(Z, N-1) = \mathrm{IP}(Z) \simeq \text{const } Z^{4/3}$, and hence

$$\mathrm{IP}(Z'') - \mathrm{IP}(Z') \propto \{[2(n+1)]^{4/3} - (2n+1)^{4/3}\} > 0. \quad (2)$$

Table 1. Ionization potential of atoms which are extremal of the two periodic sequences (see Fig. 1) and differences max (IP) − min (IP) = max Δ(IP) in each sequence (values in eV)

odd Z atoms (Z')			even Z atoms (Z'')		
max (IP)	min (IP)	max Δ(IP)	max (IP)	min (IP)	max Δ(IP)
H 13.60	Li 5.39	8.21	He 24.59	Be 9.32	15.27
F 17.42	Na 5.14	12.28	Ne 21.56	Mg 7.65	13.91
Cl 12.97	K 4.34	8.63	Ar 15.76	Ca 6.11	9.65
Br 11.81	Rb 4.18	7.63	Kr 14.00	Sr 5.69	8.31
I 10.45	Cs 3.89	6.56	Xe 12.13	Ba 5.21	6.92
At 9.5	Fr 4.0	5.5	Rn 10.75	Ra 5.28	5.47

The difference IP (Z'') − IP (Z') however fluctuates as n increases, showing not the regular trend that Eq. (2) suggests. Nevertheless the fluctuations seem to decrease, and the differences become somewhat stable for larger values of n (close to 1.2 eV for n between 39 and 43) [3].

A similar comparison cannot be established for the electron affinities (EA) since the experimental values for the rare gas and alkaline earth elements are not available [4].

As a final comment it seems possible to suggest that an electron pair within a neutral atom shows to a first approximation a "single particle" behaviour, n being the number of the pairs.

The experimental evidence of electron pairing had its first accurate review in the famous book by G. N. Lewis [5]. At about the end of his discussion he made the following remarks: "It is to be supposed that this tendency to form pairs is not a property of free electrons, but rather that it is a property of electrons within the atom".

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