

Calculation of positron characteristics for elements of the periodic table

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Abstract. Positron characteristics have been calculated in bulk and monovacancies for most of the elements of the periodic table. Self-consistent and non-self-consistent schemes have been used for the calculation of the electronic structure in the solid, and different parametrizations for the positron enhancement factor and correlation energy. As it is known, positron lifetimes in bulk show a periodic behaviour with atomic number. These calculations also confirm that monovacancy lifetimes follow the same behaviour. The results obtained have been compared with selected experimental lifetime data, which confirms the calculated theoretical trends. Positron binding energies to a monovacancy have been calculated also for most of the elements of the periodic table. The binding energy shows a periodic behaviour with atomic number too.

1. Introduction

At the end of XIX century Mendeleev stated the periodic arrangement of the elements [1]. Since then, a lot of research has been made on elements and their properties. As a result of this, periodic behaviours have been tested in most of physical and chemical properties of the elements [2, 3]. Electronic properties of the elements show periodic trends too, and for this reason, positron annihilation characteristics are related to these periodic trends. MacKenzie et al discovered that experimental positron bulk lifetime shows a periodic behaviour with atomic number [4]. However, this periodicity is not only reflected in positron bulk lifetime; Doppler broadening experiments [5, 6] and positron affinity of elemental metals [7] also show periodic behaviour.

In this work, a systematic Density Functional Theory (DFT) calculation of positron characteristics has been performed for bulk and monovacancies of most of the elements of the periodic table. The effort made to calculate systematically the annihilation parameters is important to deepen into the knowledge of the calculation methods [8, 9], improving the theoretical background required for a good interpretation of the experimental data.

2. Calculation Method

Positron characteristics have been calculated for most of the elements of the periodic table. Our computational methods are described in more detail in reference 10, here we will only explain the

main features. We have used two schemes for treating the electronic densities in calculations. First, we have used a non-self-consistent scheme, the atomic superposition approximation of Puska and Nieminen (AT-SUP) [11]. Moreover, we have used a self-consistent scheme, the linear muffin-tin orbital method within the atomic-spheres approximation (LMTO-ASA) [12, 13]. The exchange and correlation effects of the positron-electrons system have been simulated using two different approximations, one, within the local density approximation (BN), and the other, within the general gradient approximation (GGA) [14]. For the monovacancy supercells no relaxation has been performed in the atomic positions.

As a result of the computation of the positron state, the positron energy eigenvalue for that state can be obtained. In bulk state, delocalized positron, it is correct to use the zero-positron-density ($n_+ \rightarrow 0$) limit of the two-component density-functional theory (TCDFD). In monovacancy state, the positron is localized in the defect, and the positron density is not zero. However, the previous approximation, “conventional scheme”, works well because the positron and its screening cloud of electrons can be considered as a neutral quasiparticle, which does not affect the average electron density [15]. For this reason, the positron binding energy to the monovacancy can be defined as the difference between positron energy eigenvalues in bulk (ε_{bulk}^+) and monovacancy (ε_{vac}^+):

$$E = \varepsilon_{bulk}^+ - \varepsilon_{vac}^+.$$

The trapping of a positron in a monovacancy reduces the energy eigenvalue of the positron, releasing binding energy to the host.

3. Results and discussion

For most of the elements of the periodic table the bulk and monovacancy positron lifetime have been calculated using AT-SUP and LMTO-ASA within BN and GGA approximations. Calculated lifetimes can be consulted in reference 10. It is known from the work of MacKenzie et al [4], that experimental positron bulk lifetime shows a periodic trend with atomic number. The calculations presented in this work support MacKenzie et al results. However, we have proved that the periodic behaviour of bulk lifetime also appears in monovacancy lifetime. These periodic trends are independent of the calculation scheme, and follow the same behaviour as atomic volume (see figure 1). Monovacancy lifetimes for actinides do not appear in Fig. 1 because of convergence problems with the LMTO-ASA code. On the other hand, we have collected experimental positron lifetimes from reference 16. We have fixed some conditions to select the experimental values from this data-base with a minimum of quality and coherence [10]. As a result, the collected experimental values confirm our calculated theoretical trends.

We have calculated the binding energy of positron to a monovacancy for each element using AT-SUP and LMTO-ASA within BN and GGA approximations. Table 1 shows the LMTO-ASA results of positron binding energies within BN and GGA approximations. AT-SUP results are given in table 2.

There are not many values of binding energies in the literature. In order to determine experimentally the positron binding energy for a particular defect type it is necessary to observe detrapping from the defect [17]. In this way, Dannefaer and Kerr measured the binding energy of monovacancies in GaAs and InSb [18]. To our knowledge Hautojärvi et al [19] gave the first theoretical binding energy for Mg (0.3-0.4 eV). This value range is much lower than the ones presented in tables 1 and 2. Puska et al calculated binding energies in semiconductors [20]. The values corresponding to C, Si and Ge, performed by atomic superposition calculations, are larger than the ones presented in table 2 (BN) and the difference increases with atomic number. Moreover, latter Puska presented binding energies in Si and GaAs calculated by atomic superposition and LMTO-ASA-Green’s function model in charged defects [21]. The non-self-consistent value of Si is identical to that of table 2, but the self-consistent value is larger than the one in table 1, which gives the value for an ideal vacancy. The most recent work in binding energies is the one of Makkonen and Puska [22]. They present binding energies for relaxed monovacancies in several metals and semiconductors, where they describe the electron-ion interaction on the projector augmented-wave method,

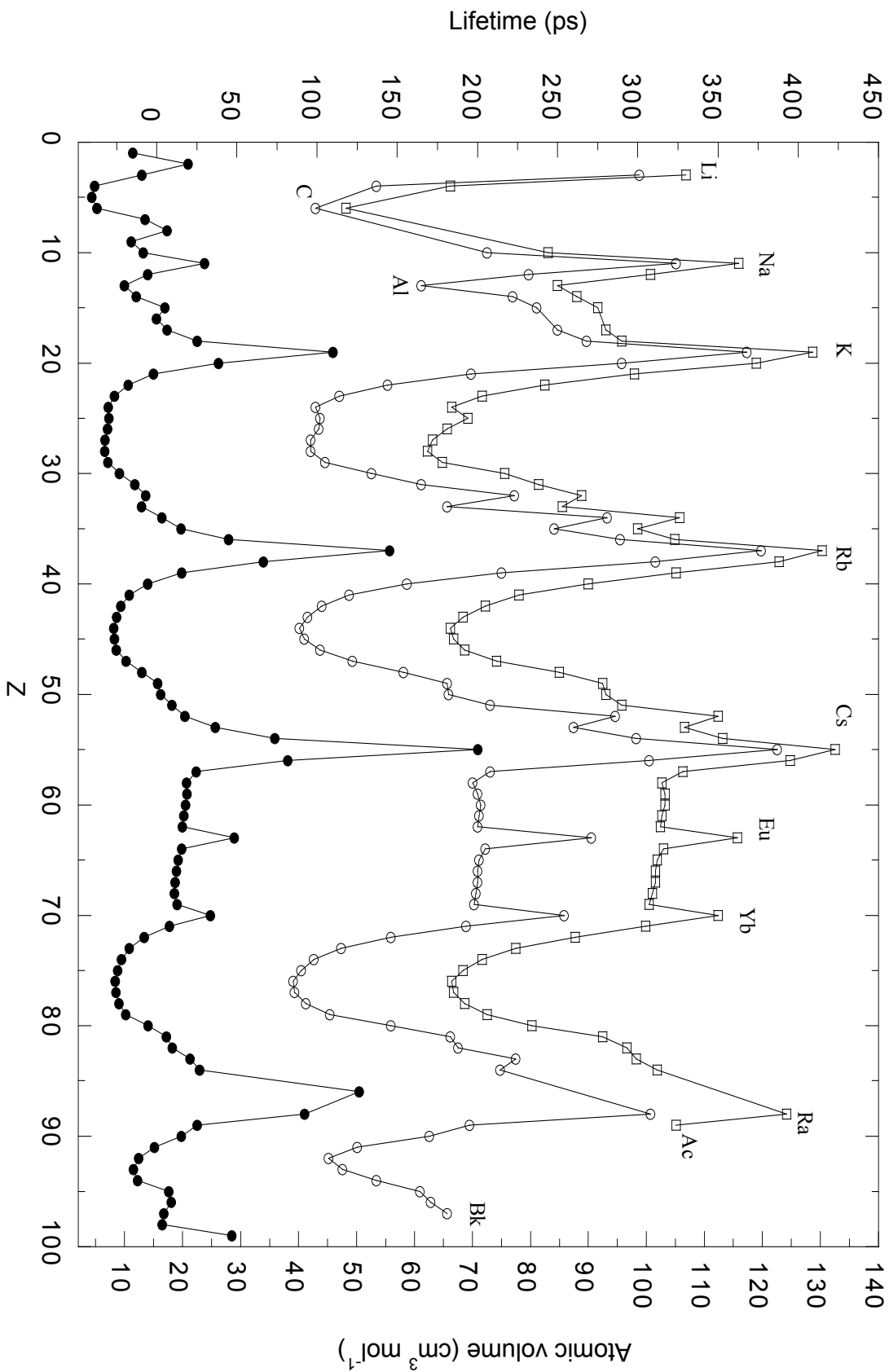
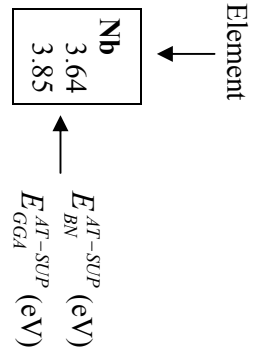


Figure 1. Atomic volume (filled circles) and positron lifetimes plotted against atomic number. Positron lifetimes are calculated in bulk (open circles) and monovacancy (squares) states within the LMTO-ASA method using the BN approximation.

Table 2. Positron binding energies calculated with the AT-SUP method within BN and GGA.

H																			He															
—																			—															
Li	Be																	B	C	N	O	F	Ne											
0.46	1.81																	—	0.56	—	—	—	—	0.01										
0.55	1.84																	—	0.53	—	—	—	—	0.01										
Na	Mg																	Al	Si	P	S	Cl	Ar											
0.22	0.72																	2.13	0.36	0.13	—	0.01	0.02											
0.32	0.71																	2.10	0.32	0.09	—	0.00	0.00											
K	Ca	Sc	Ti	V	Cr	Mn	α-Fe	α-Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																	
0.33	1.01	2.17	3.20	4.06	3.28	4.20	3.26	3.11	2.75	1.25	0.82	0.64	0.26	0.53	0.04	0.02	0.03																	
0.46	1.03	2.30	3.40	4.32	3.61	4.43	3.49	3.33	2.96	1.47	0.87	0.64	0.23	0.43	0.01	0.00	0.00																	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	β-Sn	Sb	Te	I	Xe																	
0.35	0.98	2.18	3.38	3.64	3.91	4.94	3.62	2.95	1.10	1.15	0.75	1.13	1.03	0.57	0.13	0.08	0.07																	
0.47	0.98	2.27	3.51	3.85	4.12	5.12	3.82	3.14	1.16	1.28	0.76	1.19	1.00	0.47	0.01	0.01	0.00																	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	β-Hg	Tl	Pb	Bi	Po	At	Rn																	
0.44	1.40	3.02	3.11	4.13	4.73	4.77	4.60	4.02	1.92	1.50	0.57	0.74	0.79	0.42	0.39	—	—																	
0.55	1.46	3.16	3.23	4.26	4.85	4.86	4.67	4.05	1.93	1.47	0.46	0.76	0.74	0.33	0.25	—	—																	
Fr	Ra	Ac																Th	Pa	U	Np	Pu	Am	Cm	Bk	Dy	Ho	Er	Tm	Yb	Lu			
—	1.23	3.34																3.81	5.40	5.60	6.41	4.13	2.93	2.87	2.47	—	—	—	—	—	—	—	2.04	
—	1.26	3.45																3.87	5.58	5.76	6.67	4.39	3.15	3.01	2.51	—	—	—	—	—	—	—	—	2.15



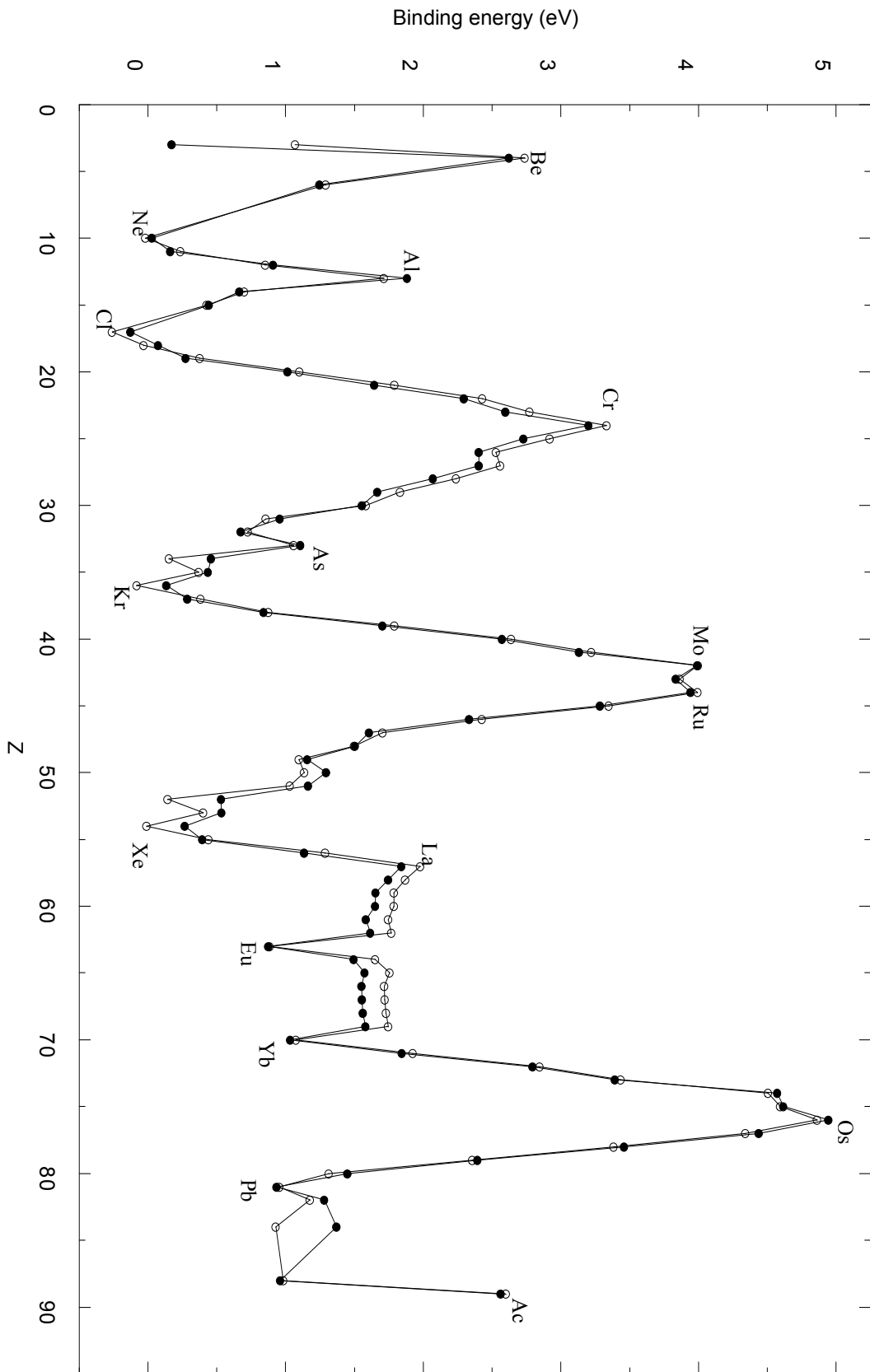


Figure 2. Positron binding energies as a function of the atomic number. Binding energies calculated with the LMT0 method within BN (filled circles) and GGGA (open circles).

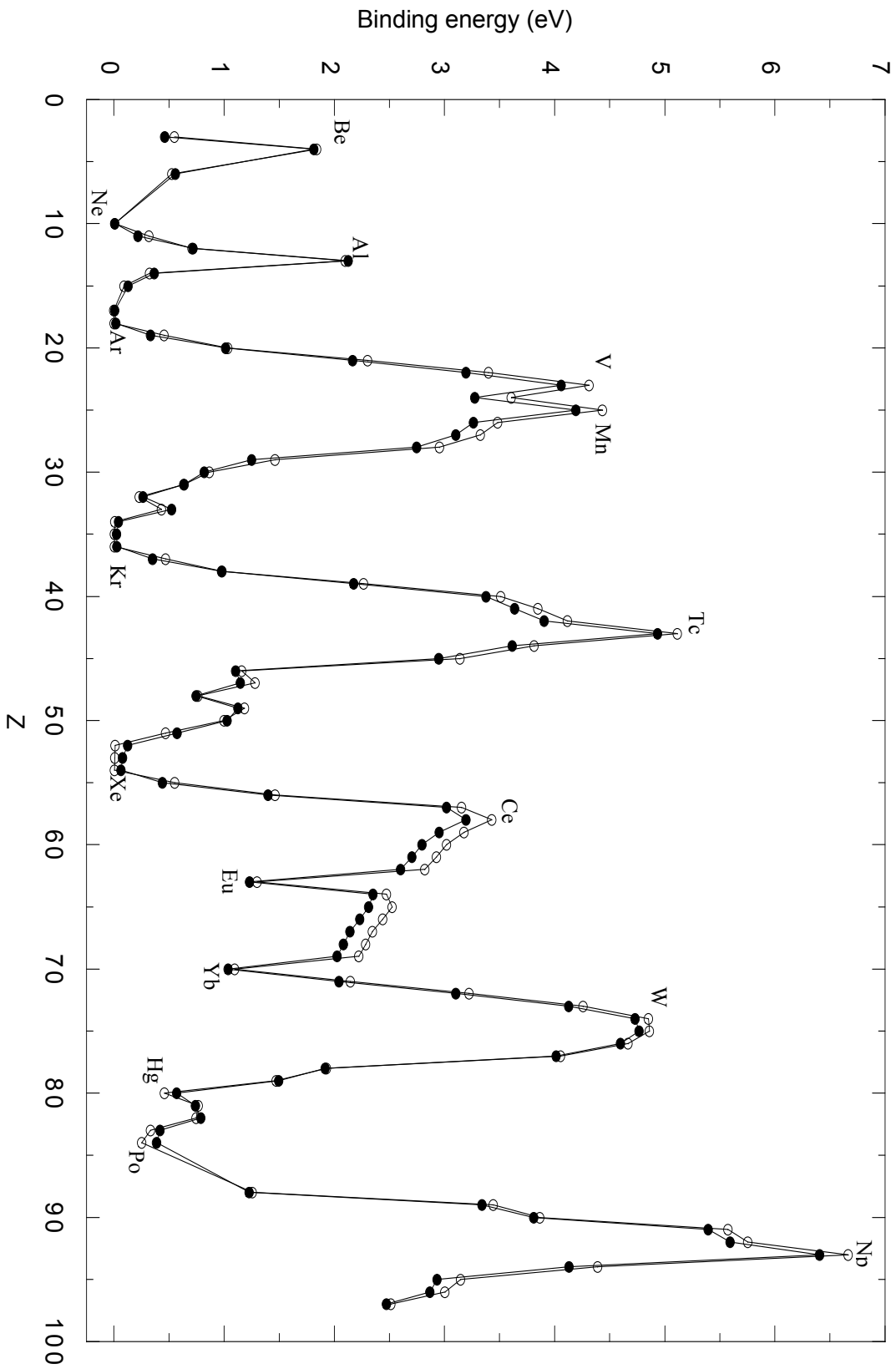


Figure 3. Positron binding energies as a function of the atomic number. Binding energies calculated with the AT-SUP method within BN (filled circles) and GGA (open circles).

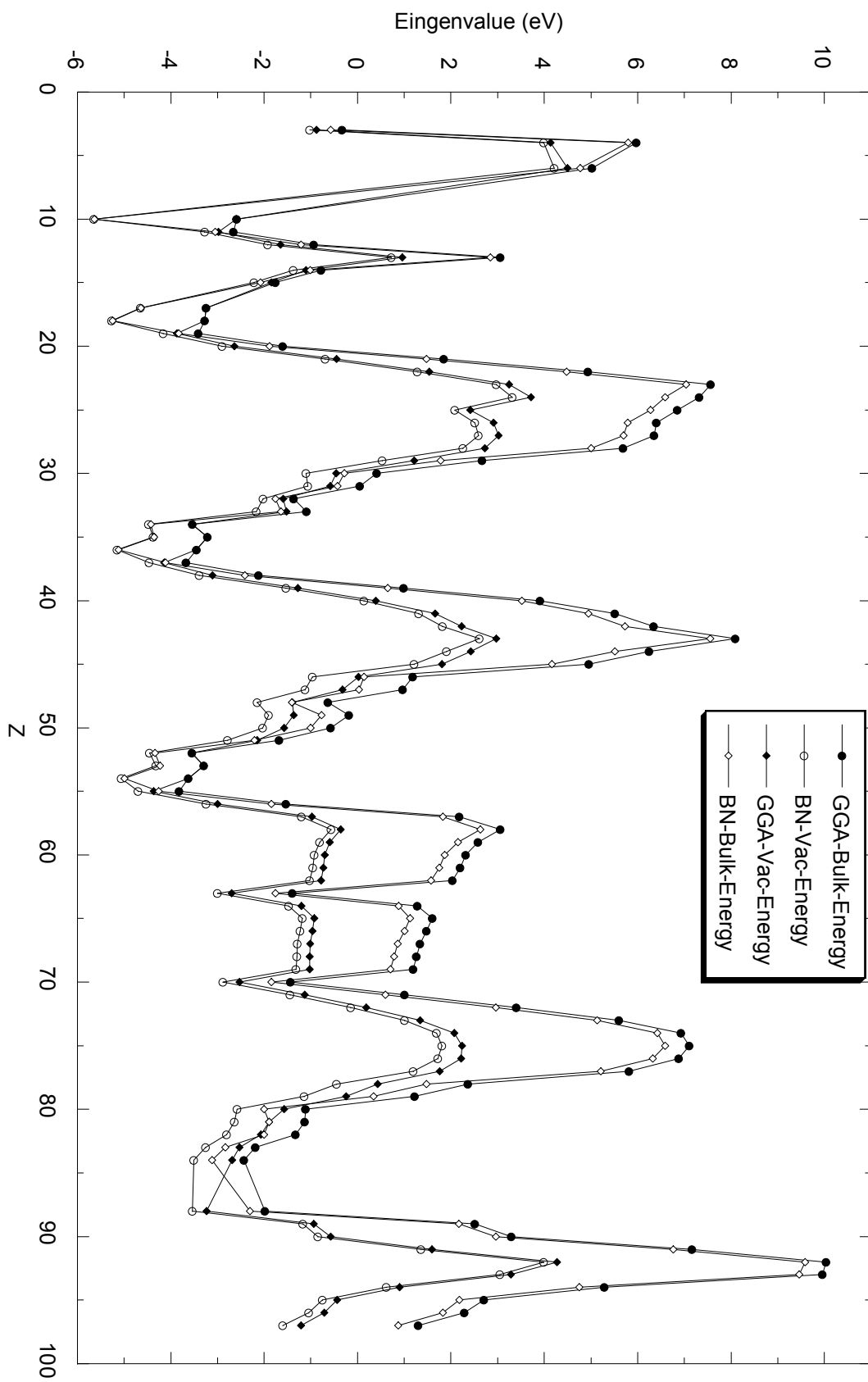


Figure 4. Positron energy eigenvalues of bulk (circles) and monovacancy (rhombuses) states plotted against atomic number. Positron energy eigenvalues are calculated with the AT-SUP method within BN (filled symbols) and GGA (open symbols).

implemented in the plane-wave code VASP. The values for Si and Fe are quite similar to the ones presented in table 1 (BN), but table 1 presents smaller values for Al and Cu and larger for Mg. This last work has been performed under the TCDFT, and this scheme has been showed to lead to rather localized positron states and too low core electron annihilation rates in comparison with experiments [15].

LMTO-ASA results of positron binding energies have been plotted in figure 2 as a function of atomic number. Figure 2 shows a very clear periodic trend. Comparing binding energy with atomic volume (lowest line in figure 1), it can be seen that binding energy shows an inverse behaviour compared to that of atomic volume. Binding energy has minima near the noble gases, where the atomic volume gets its maxima, and maxima near the centers of “d” series, where atomic volume reaches its minima. In the case of lanthanides, binding energy is practically constant. Moreover, BN and GGA values are similar for most of the calculated elements. Anyway, GGA values are lower than BN ones in the previously cited minima of binding energy. The opposite happens in the case of 3d and 4d series and in lanthanides. However, for Eu there is no difference and in Yb the difference is very small.

Figure 3 shows binding energies calculated within AT-SUP plotted against the atomic number. All the periodic trends are similar to those of LMTO-ASA results. However, the difference in binding energies, $E_{GGA} - E_{BN}$, ranges between (-0.1 ± 0.3) eV in AT-SUP calculations, which is smaller than the one obtained with LMTO-ASA (-0.4 ± 0.2) eV. So, self-consistent calculations give larger values for BN binding energies. Moreover, in AT-SUP calculations there is a monotonous decrease of binding energies of lanthanides with atomic number increase, independently of the approximation (see figure 3). To understand this behaviour we have plotted in figure 4 energy eigenvalues of positron in bulk and monovacancy versus atomic number for AT-SUP. Figure 4 shows that monovacancy energy eigenvalue remains almost constant with atomic number, but in the case of bulk it decreases monotonically. It indicates that such variation is due to the inner f electrons, which increase with atomic number. Therefore, for lanthanides AT-SUP calculations give a relatively large annihilation with inner f electrons in bulk states. This behaviour is not observed in the case of binding energies calculations by LMTO calculations (see figure 2). Indeed, energy eigenvalues of lanthanides remain almost constant in bulk and monovacancy states (not shown). This last result indicates that non-self-consistent calculations give an enhanced contribution of f electrons in respect to self-consistent ones.

4. Conclusions

We have performed self- and non-self-consistent calculations of positron annihilation parameters in most of the elements of the periodic table, using BN and GGA approximations. The binding energies, as it has been shown for positron lifetimes, present a periodic behaviour too. However, the behaviour of binding energies is opposite to the one of positron lifetimes.

Acknowledgements

This work has been undertaken under CICYT and Basque government projects MAT2006-12743 and IT44310, respectively. The SGI/IZO-SGIker UPV/EHU is gratefully acknowledged for allocation of computational resources.

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