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# Positron lifetime calculation for the elements of the periodic table

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## Abstract

Theoretical positron lifetime values have been calculated systematically 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, as well as different parametrizations for the positron enhancement factor and correlation energy. The results obtained have been studied and compared with experimental data, confirming the theoretical trends. As 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 effects of enhancement factors used in calculations have been commented upon. Finally, we have analysed the effects that f and d electrons have on positron lifetimes.

## 1. Introduction

The classification of the elements has been one of the major achievements in the history of science. This classification was originally derived from empirical experimental results, because the concept of atomic number was unknown to Mendeleev [1]. Since then, the resulting periodic order has been most strikingly reflected in a quantitative manner by most of the physical properties of the elements. A proof of this fact is that about 700 forms of the periodic table have been proposed (classified into 146 different types or subtypes) [2, 3].

Positron-annihilation spectroscopy (PAS) is a powerful and versatile tool for the study of the microscopic structure of materials [4–7]. Using PAS, detailed experimental information about electronic and atomic structure from the region of the material sampled by the positrons is obtained. PAS measurements for material characterization generally use three techniques: positron lifetime spectroscopy, Doppler broadening analysis and angular correlation measurements. Positron lifetime measurements give information about electron

density at the annihilation place. On the other hand, Doppler broadening and angular correlation measurements give information about electron momentum distribution. So, the electronic configuration of the material studied is reflected in the positron annihilation parameters. For example, in Doppler broadening experiments, the high-momentum part is used to distinguish different non-adjacent elements in the periodic table [8, 9].

As the annihilation properties of the positron are related to the electronic structure, they also show a periodic behaviour. In 1963, Rodda and Stewart [10] studied the behaviour of the experimental positron lifetime of rare-earth metals and compared it with the radius of the sphere whose volume is equal to the volume per conduction electron,  $r'_s$  (correcting the value by excluding the volume of the ion). However, MacKenzie *et al* set a stronger relation in 1975 [11]. They collected experimental bulk lifetimes of many elements and reported their 'systematic dependence on atomic number'. Also that year, Brandt *et al* [12] calculated the lifetime of some elements. They explained that the periodic behaviour of positron lifetime 'is linked *prima facie* to the virtual excitation of coupled valence-electron-plasma and single-particle modes in the collective response of the metal electrons to screen the positron charge'. Later, in 1976, Welch and Lynn studied the variations of the experimental mean lifetime versus the atomic number, and stated that it 'is strikingly similar to that of the atomic volume' [13]. In 1991 Puska found that the trends observed in bulk lifetimes along the 3d, 4d and 5d rows of the periodic table are very similar to the behaviour of the Wigner–Seitz radii [14]. However, this periodicity is not only reflected in the positron lifetime. Doppler broadening experiments [9, 15] and positron affinity of elemental metals [16] also show periodic behaviour.

In this work, a systematic density functional theory (DFT) calculation of positron lifetimes has been performed for bulk and monovacancies of most of the elements of the periodic table. The main factors influencing bulk and vacancy positron lifetimes for elemental solids have been well understood for more than 30 years. So our main aim is to show the periodic trends appearing in bulk and monovacancy positron lifetimes. The effort made to calculate and compile systematically the annihilation parameters is important to go deeply into the study of the calculation methods, improving the theoretical background required for a good interpretation of the experimental data. The organization of this paper is as follows: the computational method is explained in section 2; section 3 contains the results of the calculations, the correlation between lifetimes, and the periodic properties of the elements, information about the enhancement factors used in the calculations and the analysis of the effects of f and d electrons; and finally, the conclusions of the work are presented in section 4.

## 2. Computational method

The calculation of positron properties in solids can be traced back to the late 1960s and early 1970s (see for instance [17–20]) and since then numerical simulations have become a well developed technique (see the reviews [4, 6] and the recently published paper [21]). Positron states must be calculated self-consistently within the two-component DFT for positron and electron densities. However, the conventional way to treat positron states in solids simplifies the two-component DFT. Within the conventional scheme, an unperturbed electronic ground state for the system is constructed. Then, the positron distribution is calculated by assuming the electron density remains rigid, and by accounting for the electron–positron correlation in terms of a correlation (screening) potential dependent on the electron density. In the case of delocalized positron states, the positron density is vanishingly small at every point of the lattice, and it does not influence the electronic structure. As a result, for bulk positron states the conventional scheme runs very well. In the case of a positron localized at a lattice defect, the situation is more complicated because the positron attracts electrons, and the average electron

density increases near the defect (positron). However, in most applications for positron states at defects, the conventional scheme works very well too. Indeed, the two-component DFT calculations performed by Nieminen *et al* [22] and Boronski and Nieminen [23] support the use of the conventional scheme, since the annihilation rates are very close to those obtained with the conventional scheme. This similarity of results between the conventional scheme and the two-component DFT calculation is due to the fact that the larger short-range enhancement compensates the smaller electron density at the positron.

Therefore, in the present work we have used the conventional method of calculation. Firstly, we have solved the electron density of the perfect or defected solid, then we have calculated the positron wavefunction, and finally, we have determined the positron annihilation rate. We have used a supercell method to compute the electronic densities following (a) the atomic superposition approximation (AT-SUP) developed by Puska and Nieminen [24] and (b) the tight binding version of the linear muffin-tin orbital method within the atomic-spheres approximation (LMTO-ASA) [25, 26].

(a) *AT-SUP method*

The AT-SUP approximation of Puska and Nieminen is a simple method that makes use of non-self-consistent unrelaxed electronic densities. It gives satisfactory values of positron lifetimes in metals and semiconductors [24, 27–29]. The good agreement between the experimental and theoretical lifetimes is mainly due to the fact that the positron annihilation rate is obtained as an integral over the product of positron and electron densities. The positron density relaxes following the electron charge transfer, keeping the value of the positron–electron overlap integral constant. For this reason, positron lifetime calculations are not too sensitive to self-consistency.

In the AT-SUP approximation the electron density  $n_-(\mathbf{r})$  of the solid is constructed by superimposing individual atomic charge densities:

$$n_-(\mathbf{r}) = \sum_i n_-^{\text{at}}(|\mathbf{r} - \mathbf{R}_i|) \quad (1)$$

where  $n_-^{\text{at}}$  is the free-atom electron density and  $\mathbf{R}_i$  runs over the occupied atomic sites. For the crystalline Coulomb potential  $V_c(\mathbf{r})$  the same procedure has been used:

$$V_c(\mathbf{r}) = \sum_i V_{\text{at}}(|\mathbf{r} - \mathbf{R}_i|) \quad (2)$$

where  $V_{\text{at}}$  is the atomic Coulomb potential due to the electron density and the nucleus. Densities and potentials of the atomic ground-state electronic configuration are obtained self-consistently within the DFT. The potential felt by the positron in the solid,  $V_+(\mathbf{r})$ , is obtained by adding to the Coulomb potential,  $V_c(\mathbf{r})$ , the positron–electron correlation energy,  $V_{\text{corr}}(n_-(\mathbf{r}))$ :

$$V_+(\mathbf{r}) = V_c(\mathbf{r}) + V_{\text{corr}}(n_-(\mathbf{r})) \quad (3)$$

where  $n_-(r)$  is the electron density. The space is discretized in a three-dimensional mesh that forms an orthorhombic Bravais lattice, where the potential is projected. The discretized Schrödinger equation is solved iteratively at the mesh points by using a numerical relaxation method [30] to obtain the positron wavefunction and its energy eigenvalue. Depending on the structure of the element, the density of the cubic mesh varies between one and three points per atomic unit in each direction. We have checked in some elements that this difference in the density of the mesh does not affect the lifetimes.

(b) *LMTO-ASA method*

LMTO-ASA is a method that makes use of self-consistent electronic densities. It gives satisfactory values for positron lifetimes in metals and semiconductors [14, 28, 29]. In LMTO-ASA calculations the electron density and Coulomb potential are determined self-consistently

within spheres centred around nuclei and interstitial sites (when the atomic packing is not dense) of the structure. The spheres fill the whole lattice space and the atomic ones have equal radii. The potential and the charge densities are assumed to be spherically symmetric inside each sphere. The potential felt by a positron is constructed according to equation (3), and the positron state is solved by using the same methods as used for electron states in the LMTO-ASA. From now on, all the references made to this method will be labelled as LMTO.

The f electrons are a strongly correlated system. However, we have treated the 4f electrons of the lanthanides and the 5f electrons of the actinides as band electrons, and the 4f electrons of the actinides as core-like states.

Once we have calculated the electron and positron densities, the positron annihilation rate, the inverse of the positron lifetime, is obtained from the overlap of positron and electron densities as:

$$\lambda = \pi r_o^2 c \int dr n_+(\mathbf{r}) n_-(\mathbf{r}) \gamma(\mathbf{r}) \quad (4)$$

where  $r_o$  is the classical electron radius,  $c$  is the speed of light in a vacuum,  $n_+(\mathbf{r})$  is the positron density and  $\gamma(\mathbf{r})$  is the so-called enhancement factor.  $V_{\text{corr}}(\mathbf{r})$  and  $\gamma(\mathbf{r})$  have been taken into account by using two different schemes:

1. *Within the local density approximation.* For the correlation energy the interpolation formula by Boroński and Nieminen [23] based on the results by Arponen and Pajanne [31] is used; and for the enhancement factor the widely used form [23] based on Lantto's [32] hypernetted chain approximation calculations:

$$\gamma_{\text{BN}}(r_s) = 1 + 1.23r_s + 0.8295r_s^{3/2} - 1.26r_s^2 + 0.3286r_s^{5/2} + \frac{1}{6} \left(1 - \frac{1}{\varepsilon_\infty}\right) r_s^3, \quad (5)$$

where  $\varepsilon_\infty$  is the high-frequency dielectric constant of the material and  $r_s$  is the radius of a sphere whose volume is equal to the volume per conduction electron. This last parameter is related to the electron density,  $n_-(\mathbf{r})$ , by:

$$r_s = \left(\frac{3}{4\pi n_-}\right)^{1/3}. \quad (6)$$

Results obtained with this scheme are labelled BN.

2. *Within the generalized gradient approximation (GGA).* The correlation energy and the enhancement factor due to Barbiellini *et al* [28, 33] are used, both based on the results by Arponen and Pajanne [31]. In this scheme the enhancement factor is given by:

$$\gamma_{\text{GGA}} = 1 + (\gamma_{\text{LDA}} - 1)e^{-\alpha\varepsilon}, \quad (7)$$

where  $\gamma_{\text{LDA}}$  is:

$$\gamma_{\text{LDA}}(r_s) = 1 + 1.23r_s - 0.0742r_s^2 + \frac{1}{6}r_s^3, \quad (8)$$

$\alpha$  is an adjustable parameter and  $\varepsilon$  is obtained from this expression:

$$\varepsilon = \frac{|\nabla n_-|^2}{(n_- - q_{\text{TF}})^2} = \frac{|\nabla \ln n_-|^2}{q_{\text{TF}}^2}, \quad (9)$$

with  $(q_{\text{TF}})^{-1}$  the local Thomas–Fermi screening length.  $\varepsilon$  is a parameter proportional to the lowest-order gradient correction to the correlation hole density in the local density approximation. The results obtained with these two schemes will be labelled LDA and GGA.

The  $\alpha$  parameter is determined so that the calculated and experimental lifetimes agree as well as possible for a large number of different types of solid. Barbiellini *et al* [28, 33]

found that  $\alpha = 0.22$  value gives lifetimes in good agreement with experiments for different types of electronic environment, including simple metals (Na and K of the 1st group), transition metals (Fe, 8th group; Ni, 10th group; Cu, 11th group; Al, 13th group), group-IV semiconductors (Si and Ge) and III-V and II-V compound semiconductors (GaAs, InP and CdTe).  $\alpha = 0$  gives the local density approximation limit of this enhancement factor, that is to say  $\gamma_{\text{LDA}}$ . As was pointed out before [28, 34], the lifetimes calculated by using  $\gamma_{\text{LDA}}$  are always much shorter than those calculated with  $\gamma_{\text{BN}}$  and  $\gamma_{\text{GGA}}$ , and the experimental ones.

The positron lifetime calculations have been performed for most of the elements of the periodic table. The unit cell of the crystalline structure has been used as the supercell for bulk calculations. In vacancy calculations one atom is removed from the supercell to produce a vacancy. If the supercell is large enough, the vacancy does not interact with its periodic image and the system describes an isolated vacancy quite well. However, in practice, the size of the supercell cannot be made arbitrarily large. The size of the supercells in the AT-SUP method has been increased until convergence. The maximum number of atoms per supercell used to reach convergence was: 511 atoms (orthorhombic structure), 511 atoms (diamond structure), 499 atoms (tetragonal structure), 463 atoms (cubic structure), 255 atoms (FCC structure), 249 atoms (hexagonal structure), 383 atoms (rhombohedral structure) and 127 atoms (BCC structure). Self-consistent calculations within the LMTO method for monovacancies are much more computationally demanding than the ones performed with the AT-SUP method, particularly for large supercells. Moreover, for large supercells, calculations performed employing the  $\Gamma$  point for the positron density or the lowest lying band in the Brillouin zone give identical values for the monovacancy positron lifetime [29]. Therefore, for calculations within the LMTO method for monovacancies we have integrated over the lowest positron band in the Brillouin zone, because it gives faster convergence in the supercell approach [29]. The maximum number of atoms used within the LMTO was: 127 atoms (hexagonal structure), 124 atoms (BCC structure), 107 atoms (rhombohedral structure), 63 atoms (FCC structure), 53 atoms (tetragonal structure), 53 atoms (diamond structure), 31 atoms (orthorhombic structure) and 28 atoms (cubic structure).

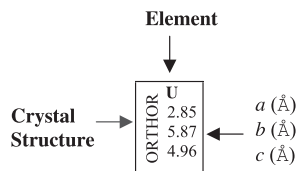
For the monovacancy supercells no relaxation in the atomic positions has been performed; this means that the ions neighbouring the vacancy are not allowed to relax from their ideal lattice positions. It is known that an accurate calculation of the monovacancy lifetime needs atomic relaxation. In insulators and semiconductors the atomic relaxation may be important, and can change with the charge state of the defect and with the localization of the positron [35, 36], but it is not large in metals [37–39]. However, the study of the effects of these relaxations goes beyond the aims of this work.

Some elements get a different crystal structure for different conditions of pressure and temperature. When an element has more than one possible structure, we have chosen the most common one in normal conditions. The rare gases are not solid in normal conditions, so we have studied the solid state at very low temperature. The crystal structure and the lattice parameters used in the calculations are shown in table 1, and have been taken from experimental data [40–42].

In BN calculations, the semi-empirical correction based on high-frequency dielectric constant of equation (5) [43] is used for the elements of table 2, which shows experimental values of dielectric constants [41, 42, 44]. No values have been found for the dielectric constants of several insulators (As, Cl, Br and I) in the literature. So these insulators and rare gases have been treated as metals, using  $\epsilon_{\infty} = \infty$ . In the rare gases a special treatment is needed; however, it goes beyond the aim of this work. In LDA and GGA frameworks, this correction is not necessary.

**Table 1.** Structural data for the elements. The crystal structures of the elements are: cubic (CUB), body-centred cubic (BCC), face-centred cubic (FCC), cubic diamond (DIAM), rhombohedral (RHOMB), tetragonal (TETRA), orthorhombic (ORTHOR), hexagonal close-packed (HEX) and double hexagonal close-packed (HEX/abac). (\*) Manganese has a cubic complex structure (see Donohue [40]).

H — — —		He — — —																									
Li 3.49 BCC	Be 2.29 HEX 3.59													B — — —	C 3.57 DIAM	N — — —	O — — —	F — — —	Ne 4.43 FCC								
Na 4.23 BCC	Mg 3.21 HEX 5.21													Al 4.05 FCC	Si 5.43 DIAM	P 3.32 ORTHOR 10.52 4.39	S — — —	Cl 6.24 ORTHOR 4.48 8.26	Ar 5.31 FCC								
K 5.23 BCC	Ca 5.58 FCC	Sc 3.31 HEX 5.28	Ti 2.95 HEX 4.68	V 3.03 BCC	Cr 2.88 BCC	Mn 8.91 CUB (*)	α-Fe 2.87 BCC	α-Co 2.51 HEX 4.07	Ni 3.52 FCC	Cu 3.61 FCC	Zn 2.66 HEX 4.94	Ga 4.52 ORTHOR 7.66 4.53	Ge 5.66 DIAM	As 3.76 RHOMB 10.55	Se 4.36 HEX 4.95	Br 6.67 ORTHOR 4.48 8.72	Kr 5.64 FCC										
Rb 5.59 BCC	Sr 6.08 FCC	Y 3.65 HEX 5.73	Zr 3.23 HEX 5.15	Nb 3.30 BCC	Mo 3.15 BCC	Tc 2.74 HEX 4.40	Ru 2.70 HEX 4.28	Rh 3.80 FCC	Pd 3.89 FCC	Ag 4.09 FCC	Cd 2.98 HEX 5.62	In 3.25 TETRA 4.95	β-Sn 5.83 TETRA 3.18	Sb 4.31 RHOMB 11.27	Te 4.45 HEX 5.92	I 7.27 ORTHOR 4.80 9.80	Xe 6.13 FCC										
Cs 6.05 BCC	Ba 5.02 BCC	La 3.75 HEX 6.07	Hf 3.20 HEX 5.06	Ta 3.31 BCC	W 3.16 BCC	Re 2.76 HEX 4.46	Os 2.74 HEX 4.33	Ir 3.84 FCC	Pt 3.92 FCC	Au 4.08 FCC	β-Hg 4.00 TETRA 2.83	Tl 3.46 HEX 5.53	Pb 4.95 FCC	Bi 4.55 RHOMB 11.86	Po 3.35 CUB	At — — —	Rn — — —										
Fr — — —	Ra 5.15 BCC	Ac 5.31 FCC																									
γ-Ce 5.16 FCC	Pr 3.67 HEX/abac 11.83	Nd 3.66 HEX 5.91	Pm 3.65 HEX/abac 11.65	Sm 3.63 RHOMB 26.22	Eu 4.61 BCC	Gd 3.64 HEX 5.78	Tb 3.60 HEX 5.69	Dy 3.59 HEX 5.65	Ho 3.58 HEX 5.62	Er 3.56 HEX 5.59	Tm 3.54 HEX 5.56	Yb 5.49 FCC	Lu 3.51 HEX 5.56	Th 5.08 FCC	Pa 3.93 TETRA 3.24	U 2.85 ORTHOR 5.87 4.96	Np 4.72 ORTHOR 4.89 6.66	Pu 4.64 FCC	Am 3.47 HEX/abac 11.24	Cm 3.50 HEX/abac 11.33	Bk 5.00 FCC	Cf — — —	Es — — —	Fm — — —	Md — — —	No — — —	Lr — — —



**Table 2.** High-frequency dielectric constant of some elements used in calculations.

Element	$\epsilon_{\infty}$
C	5.62
Si	11.9
P	6.1
Ge	16.0
Se	13.98
Sn	23.8
Te	29.5

### 3. Results and discussion

#### 3.1. Bulk and monovacancy lifetimes

The positron lifetime values calculated for the bulk state are given in tables 3 and 4. The values in table 3 correspond to calculations made within the AT-SUP method with BN and GGA approximations. The results obtained within the LMTO method with BN and GGA approximations are given in table 4.

On the other hand, the results of monovacancy lifetime calculations (BN and GGA) are shown in tables 5 and 6 for AT-SUP and LMTO methods, respectively. Table 6 does not present monovacancy lifetimes of actinides due to convergence problems with the LMTO code. The bulk and monovacancy lifetime results are in agreement with previously reported values [28, 33].

Table 7 shows the AT-SUP results of bulk and monovacancy lifetimes obtained within the LDA framework. As mentioned before, these values are shorter than BN and GGA ones, but show the same trend.

Finally, experimental positron lifetime values in bulk and monovacancy states (see [45] and the references therein) are given in table 8 for comparison with theoretical ones. Even though the first positron lifetime measurements were made more than 50 years ago [46–49], nowadays the experimental data do not reach to all elements of the periodic table. Moreover, there are many more data for bulk than for monovacancy lifetimes. For some elements there are no experimental data, but for others there are many experimental data and the scattering among them is large. Therefore, the selection of the measurements is a difficult affair, and we have fixed some conditions to select data with a minimum of quality and coherence. The chosen conditions might not be the best ones; however, a selection has to be made. First of all, we have considered data from 1975 up to now. We have chosen this requirement because the POSITRONFIT program was developed around 1972 [50], and improved in 1974 [51], becoming a common, or even standard, tool for use by positron scientists to analyse experimental spectra. Furthermore, we have chosen a maximum of 320 ps for the full width at half maximum of the resolution function. Finally, we have taken as the limit value for the error of the measurement  $\pm 5$  ps in bulk lifetimes, and  $\pm 10$  ps in monovacancy lifetimes. In cases where the literature gives different lifetime values following the previous requirements, the average value has been calculated. It is expected that the systematic errors from various experiments would be cancelled. In order to fill the extremes of the periodic table, we have taken into account two experimental works on alkalines (Li, Na, K, Rb, Cs) [52] and ideal gases (Ar, Xe) [53] that do not fit the previous requirements. However, these works have been used in previous reviews.



**Table 3.** Calculated positron bulk lifetimes using the AT-SUP method with BN and GGA parametrizations.

Element																		He			
H																		He			
—																		—			
—																		—			
Li	Be															B	C	N	O	F	Ne
301	137															—	93	—	—	—	237
285	129															—	93	—	—	—	566
Na	Mg															Al	Si	P	S	Cl	Ar
322	233															168	218	230	—	248	271
342	226															160	207	226	—	352	483
K	Ca	Sc	Ti	V	Cr	Mn	$\alpha$ -Fe	$\alpha$ -Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
367	288	197	147	116	104	106	102	97	96	108	139	190	222	184	286	245	281				
402	281	199	153	124	118	115	112	108	108	130	158	202	228	195	355	322	459				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	$\beta$ -Sn	Sb	Te	I	Xe				
376	309	217	160	126	109	98	94	97	107	125	159	183	193	213	289	262	297				
420	305	215	162	134	118	105	106	110	130	150	184	201	201	227	345	325	444				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	$\beta$ -Hg	Tl	Pb	Bi	Po	At	Rn				
387	305	209	150	119	102	94	89	90	99	112	154	185	190	230	231	—	—				
437	303	209	156	125	108	101	96	98	116	131	184	214	214	257	262	—	—				
Fr	Ra	Ac																			
—	307	199																			
—	308	197																			
$\gamma$ -Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu								
204	207	207	206	206	273	204	204	204	204	202	201	256	196								
210	213	214	214	214	278	207	214	214	215	214	213	265	202								
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr								
173	139	117	119	145	171	172	176	—	—	—	—	—	—								
171	142	121	125	155	182	180	181	—	—	—	—	—	—								

**Bulk Lifetimes**

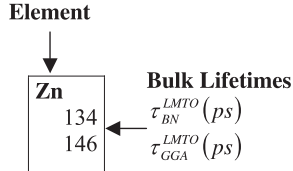
$\tau_{BN}^{AT-SUP} (ps)$

$\tau_{GGA}^{AT-SUP} (ps)$

Zn  
139  
158

**Table 4.** Calculated positron bulk lifetimes using the LMTO method with BN and GGA parametrizations.

Element																		H	He		
																		—	—		
<b>Li</b>	<b>Be</b>															<b>B</b>	<b>C</b>	<b>N</b>	<b>O</b>	<b>F</b>	<b>Ne</b>
301	137															—	99	—	—	—	206
281	128															—	97	—	—	—	534
<b>Na</b>	<b>Mg</b>															<b>Al</b>	<b>Si</b>	<b>P</b>	<b>S</b>	<b>Cl</b>	<b>Ar</b>
324	232															165	222	237	—	250	268
334	216															153	211	223	—	275	435
<b>K</b>	<b>Ca</b>	<b>Sc</b>	<b>Ti</b>	<b>V</b>	<b>Cr</b>	<b>Mn</b>	$\alpha$ - <b>Fe</b>	$\alpha$ - <b>Co</b>	<b>Ni</b>	<b>Cu</b>	<b>Zn</b>	<b>Ga</b>	<b>Ge</b>	<b>As</b>	<b>Se</b>	<b>Br</b>	<b>Kr</b>				
368	290	196	144	114	99	102	101	96	96	105	134	165	223	181	281	248	289				
391	279	193	146	119	105	109	110	107	108	118	146	167	228	188	313	270	448				
<b>Rb</b>	<b>Sr</b>	<b>Y</b>	<b>Zr</b>	<b>Nb</b>	<b>Mo</b>	<b>Tc</b>	<b>Ru</b>	<b>Rh</b>	<b>Pd</b>	<b>Ag</b>	<b>Cd</b>	<b>In</b>	$\beta$ - <b>Sn</b>	<b>Sb</b>	<b>Te</b>	<b>I</b>	<b>Xe</b>				
377	311	215	156	120	103	94	89	92	102	122	154	181	182	208	286	260	299				
408	300	208	154	122	106	99	95	100	113	137	167	190	179	211	307	268	416				
<b>Cs</b>	<b>Ba</b>	<b>La</b>	<b>Hf</b>	<b>Ta</b>	<b>W</b>	<b>Re</b>	<b>Os</b>	<b>Ir</b>	<b>Pt</b>	<b>Au</b>	$\beta$ - <b>Hg</b>	<b>Tl</b>	<b>Pb</b>	<b>Bi</b>	<b>Po</b>	<b>At</b>	<b>Rn</b>				
387	307	208	146	115	98	90	85	86	93	108	146	183	188	224	214	—	—				
426	304	207	146	117	100	93	89	92	101	119	161	203	197	233	216	—	—				
<b>Fr</b>	<b>Ra</b>	<b>Ac</b>																			
—	308	195																			
—	309	192																			
$\gamma$ - <b>Ce</b>	<b>Pr</b>	<b>Nd</b>	<b>Pm</b>	<b>Sm</b>	<b>Eu</b>	<b>Gd</b>	<b>Tb</b>	<b>Dy</b>	<b>Ho</b>	<b>Er</b>	<b>Tm</b>	<b>Yb</b>	<b>Lu</b>								
197	200	202	201	200	271	205	201	200	200	199	198	254	193								
196	200	202	202	203	266	209	205	205	206	205	203	253	192								
<b>Th</b>	<b>Pa</b>	<b>U</b>	<b>Np</b>	<b>Pu</b>	<b>Am</b>	<b>Cm</b>	<b>Bk</b>	<b>Cf</b>	<b>Es</b>	<b>Fm</b>	<b>Md</b>	<b>No</b>	<b>Lr</b>								
170	125	107	116	137	164	171	181	—	—	—	—	—	—								
167	125	108	117	141	171	180	193	—	—	—	—	—	—								



**Table 5.** Calculated positron monovacancy lifetimes using the AT-SUP method with BN and GGA parametrizations.

Element																		H	He		
																		—	—		
																		—	—		
																		<b>Monovacancy Lifetimes</b> $\tau_{BN}^{AT-SUP} (ps)$ $\tau_{GGA}^{AT-SUP} (ps)$			
<b>Li</b>	<b>Be</b>															<b>B</b>	<b>C</b>	<b>N</b>	<b>O</b>	<b>F</b>	<b>Ne</b>
338	180															—	110	—	—	—	239
315	165															—	109	—	—	—	562
<b>Na</b>	<b>Mg</b>															<b>Al</b>	<b>Si</b>	<b>P</b>	<b>S</b>	<b>Cl</b>	<b>Ar</b>
362	299															244	252	251	—	249	274
384	292															231	241	245	—	353	483
<b>K</b>	<b>Ca</b>	<b>Sc</b>	<b>Ti</b>	<b>V</b>	<b>Cr</b>	<b>Mn</b>	$\alpha$ - <b>Fe</b>	$\alpha$ - <b>Co</b>	<b>Ni</b>	<b>Cu</b>	<b>Zn</b>	<b>Ga</b>	<b>Ge</b>	<b>As</b>	<b>Se</b>	<b>Br</b>	<b>Kr</b>				
411	366	291	236	198	180	198	177	168	166	169	196	239	254	236	297	251	287				
452	367	281	228	194	188	199	183	177	177	200	224	255	263	255	359	324	458				
<b>Rb</b>	<b>Sr</b>	<b>Y</b>	<b>Zr</b>	<b>Nb</b>	<b>Mo</b>	<b>Tc</b>	<b>Ru</b>	<b>Rh</b>	<b>Pd</b>	<b>Ag</b>	<b>Cd</b>	<b>In</b>	$\beta$ - <b>Sn</b>	<b>Sb</b>	<b>Te</b>	<b>I</b>	<b>Xe</b>				
419	387	319	262	222	200	185	177	178	173	200	231	273	277	275	329	290	320				
475	398	311	254	224	206	186	191	198	220	245	276	303	294	303	353	329	444				
<b>Cs</b>	<b>Ba</b>	<b>La</b>	<b>Hf</b>	<b>Ta</b>	<b>W</b>	<b>Re</b>	<b>Os</b>	<b>Ir</b>	<b>Pt</b>	<b>Au</b>	$\beta$ - <b>Hg</b>	<b>Tl</b>	<b>Pb</b>	<b>Bi</b>	<b>Po</b>	<b>At</b>	<b>Rn</b>				
429	392	322	254	217	194	183	175	175	177	191	218	268	277	288	293	—	—				
496	399	310	252	217	197	188	184	189	191	233	270	325	329	335	345	—	—				
<b>Fr</b>	<b>Ra</b>	<b>Ac</b>																			
—	394	317																			
—	415	306																			
$\gamma$ - <b>Ce</b>	<b>Pr</b>	<b>Nd</b>	<b>Pm</b>	<b>Sm</b>	<b>Eu</b>	<b>Gd</b>	<b>Tb</b>	<b>Dy</b>	<b>Ho</b>	<b>Er</b>	<b>Tm</b>	<b>Yb</b>	<b>Lu</b>								
316	318	318	316	314	366	312	311	310	309	307	305	346	300								
302	306	306	307	307	378	309	307	307	307	307	306	364	301								
<b>Th</b>	<b>Pa</b>	<b>U</b>	<b>Np</b>	<b>Pu</b>	<b>Am</b>	<b>Cm</b>	<b>Bk</b>	<b>Cf</b>	<b>Es</b>	<b>Fm</b>	<b>Md</b>	<b>No</b>	<b>Lr</b>								
292	250	218	203	259	285	287	290	—	—	—	—	—	—								
284	238	208	199	255	287	289	299	—	—	—	—	—	—								

**Table 6.** Calculated positron monovacancy lifetimes using the LMTO method with BN and GGA parametrizations.

Element																		He			
H																		He			
—																		—			
—																		—			
Li	Be															B	C	N	O	F	Ne
330	183															—	118	—	—	—	244
308	161															—	114	—	—	—	556
Na	Mg															Al	Si	P	S	Cl	Ar
363	308															250	262	275	—	280	290
377	292															237	245	260	—	321	456
K	Ca	Sc	Ti	V	Cr	Mn	$\alpha$ -Fe	$\alpha$ -Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
409	374	298	242	203	184	194	181	172	169	178	217	238	265	253	326	300	323				
446	364	282	234	200	184	196	188	182	182	194	229	240	266	267	392	337	482				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	$\beta$ -Sn	Sb	Te	I	Xe				
415	388	324	269	226	205	191	183	185	192	212	251	278	280	290	350	329	353				
466	393	311	258	220	204	191	187	194	209	236	273	298	283	307	400	370	473				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	$\beta$ -Hg	Tl	Pb	Bi	Po	At	Rn				
423	395	328	261	224	203	191	184	185	192	206	234	278	293	299	312	—	—				
499	395	321	253	219	203	191	188	193	206	228	264	320	324	318	346	—	—				
Fr	Ra	Ac																			
—	393	324																			
—	426	324																			
$\gamma$ -Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu								
315	317	317	315	314	362	316	312	311	311	309	307	350	305								
312	312	312	311	311	373	314	308	308	307	305	304	355	297								

Element



Zn
217
229

Monovacancy Lifetimes

$$\tau_{BN}^{LMTO} (ps)$$

$$\tau_{GGA}^{LMTO} (ps)$$

**Table 7.** Calculated positron lifetimes using the AT-SUP method with LDA parametrization for bulk and monovacancy states.

Element																		H	He												
																		—	—												
																		—	—												
<b>Li</b>	<b>Be</b>															<b>B</b>	<b>C</b>	<b>N</b>	<b>O</b>	<b>F</b>	<b>Ne</b>										
261	123															—	84	—	—	—	222										
294	158															—	98	—	—	—	223										
<b>Na</b>	<b>Mg</b>															<b>Al</b>	<b>Si</b>	<b>P</b>	<b>S</b>	<b>Cl</b>	<b>Ar</b>										
286	203															148	184	188	—	221	246										
326	260															212	210	205	—	223	250										
<b>K</b>	<b>Ca</b>	<b>Sc</b>	<b>Ti</b>	<b>V</b>	<b>Cr</b>	<b>Mn</b>	$\alpha$ -Fe	$\alpha$ -Co	<b>Ni</b>	<b>Cu</b>	<b>Zn</b>	<b>Ga</b>	<b>Ge</b>	<b>As</b>	<b>Se</b>	<b>Br</b>	<b>Kr</b>														
332	249	173	132	106	96	98	94	90	90	100	125	168	190	163	244	218	253														
387	326	253	206	174	160	175	157	150	149	153	177	210	216	208	257	223	260														
<b>Rb</b>	<b>Sr</b>	<b>Y</b>	<b>Zr</b>	<b>Nb</b>	<b>Mo</b>	<b>Tc</b>	<b>Ru</b>	<b>Rh</b>	<b>Pd</b>	<b>Ag</b>	<b>Cd</b>	<b>In</b>	$\beta$ -Sn	<b>Sb</b>	<b>Te</b>	<b>I</b>	<b>Xe</b>														
343	269	189	142	114	100	91	88	90	99	115	143	162	171	187	250	231	267														
401	350	278	228	195	176	163	158	159	157	180	205	241	243	242	289	260	294														
<b>Cs</b>	<b>Ba</b>	<b>La</b>	<b>Hf</b>	<b>Ta</b>	<b>W</b>	<b>Re</b>	<b>Os</b>	<b>Ir</b>	<b>Pt</b>	<b>Au</b>	$\beta$ -Hg	<b>Tl</b>	<b>Pb</b>	<b>Bi</b>	<b>Po</b>	<b>At</b>	<b>Rn</b>														
356	265	183	135	109	94	88	83	84	92	103	139	165	169	202	204	—	—														
420	355	281	221	191	172	162	156	157	160	172	196	239	247	256	261	—	—														
<b>Fr</b>	<b>Ra</b>	<b>Ac</b>																													
—	267	174																													
—	360	276																													
																		<b>Ce</b>	<b>Pr</b>	<b>Nd</b>	<b>Pm</b>	<b>Sm</b>	<b>Eu</b>	<b>Gd</b>	<b>Tb</b>	<b>Dy</b>	<b>Ho</b>	<b>Er</b>	<b>Tm</b>	<b>Yb</b>	<b>Lu</b>
																		179	182	182	181	181	238	179	180	179	179	178	177	223	172
																		275	277	277	275	274	327	273	272	271	270	268	267	308	262
																		<b>Th</b>	<b>Pa</b>	<b>U</b>	<b>Np</b>	<b>Pu</b>	<b>Am</b>	<b>Cm</b>	<b>Bk</b>	<b>Cf</b>	<b>Es</b>	<b>Fm</b>	<b>Md</b>	<b>No</b>	<b>Lr</b>
																		153	125	107	109	131	152	153	156	—	—	—	—	—	—
																		254	217	190	178	225	249	251	254	—	—	—	—	—	—

Element



<b>Ga</b>
168
210

 $\tau_{bulk}^{LDA} (ps)$  $\tau_{vac}^{LDA} (ps)$

**Table 8.** Experimental positron lifetimes for bulk and monovacancy states.

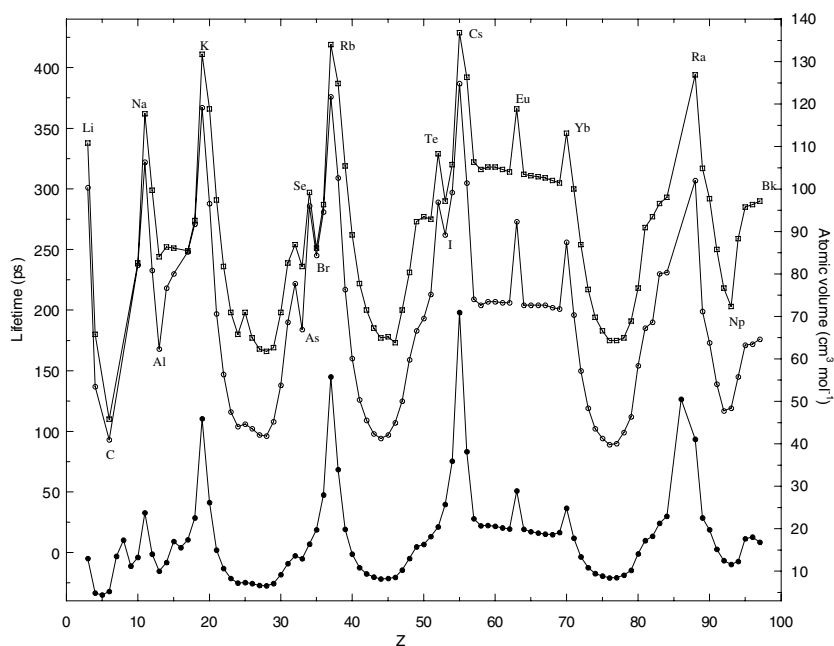
<b>H</b>																	<b>He</b>		
—																	—		
—																	—		
<b>Li</b>	<b>Be</b>													<b>B</b>	<b>C</b>	<b>N</b>	<b>O</b>	<b>F</b>	<b>Ne</b>
291	137													—	107	—	—	—	—
—	—													—	—	—	—	—	
<b>Na</b>	<b>Mg</b>													<b>Al</b>	<b>Si</b>	<b>P</b>	<b>S</b>	<b>Cl</b>	<b>Ar</b>
338	225													165	219		—		430
—	254													244	272		—		—
<b>K</b>	<b>Ca</b>	<b>Sc</b>	<b>Ti</b>	<b>V</b>	<b>Cr</b>	<b>Mn</b>	<b><math>\alpha</math>-Fe</b>	<b><math>\alpha</math>-Co</b>	<b>Ni</b>	<b>Cu</b>	<b>Zn</b>	<b>Ga</b>	<b>Ge</b>	<b>As</b>	<b>Se</b>	<b>Br</b>	<b>Kr</b>		
397		230	150	124	120		111	119	109	120	153	198	228		335				
—		—	222	191	150		175	—	180	180	220	—	279		—				
<b>Rb</b>	<b>Sr</b>	<b>Y</b>	<b>Zr</b>	<b>Nb</b>	<b>Mo</b>	<b>Tc</b>	<b>Ru</b>	<b>Rh</b>	<b>Pd</b>	<b>Ag</b>	<b>Cd</b>	<b>In</b>	<b><math>\beta</math>-Sn</b>	<b>Sb</b>	<b>Te</b>	<b>I</b>	<b>Xe</b>		
406		249	164	120	106				98	130	184	196	200	214			400		
—		—	252	210	170				—	208	252	270	242	275			—		
<b>Cs</b>	<b>Ba</b>	<b>La</b>	<b>Hf</b>	<b>Ta</b>	<b>W</b>	<b>Re</b>	<b>Os</b>	<b>Ir</b>	<b>Pt</b>	<b>Au</b>	<b><math>\beta</math>-Hg</b>	<b>Tl</b>	<b>Pb</b>	<b>Bi</b>	<b>Po</b>	<b>At</b>	<b>Rn</b>		
418		241		120	105				99	116		226	204	240		—	—		
—		—		203	195				168	205		258	294	325		—	—		
<b>Fr</b>	<b>Ra</b>	<b>Ac</b>																	
—																			
—																			
			<b><math>\gamma</math>-Ce</b>	<b>Pr</b>	<b>Nd</b>	<b>Pm</b>	<b>Sm</b>	<b>Eu</b>	<b>Gd</b>	<b>Tb</b>	<b>Dy</b>	<b>Ho</b>	<b>Er</b>	<b>Tm</b>	<b>Yb</b>	<b>Lu</b>			
							199		230										
							—		—										

Element



<b>Zn</b>
153
220

$\tau_{bulk}^{exp}(ps)$   
 $\tau_{vac}^{exp}(ps)$



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

### 3.2. Positron lifetime among periodic properties

In order to present the expected periodic behaviour of the positron lifetime, figure 1 shows calculated bulk (circles) and monovacancy (squares) positron lifetimes versus atomic number. Plotted lifetimes have been calculated within the AT-SUP method using the BN approximation for the enhancement factor and correlation energy. The experimental values of table 8 have not been plotted, but follow the same theoretical trends.

The atomic volume of the elements [54] has been plotted against atomic number in figure 1, too. The atomic volume (defined as the product of the atomic weight and the specific volume of an element at normal conditions) is a good magnitude for measuring the size of one single atom in its own structure and is defined for all the elements in the same way. This is one of the main reasons why the atomic volume has been chosen, even though different magnitudes such as metallic radius, ionic radius, covalent radius etc. have been defined for the quantification of the atomic size. However, from these last magnitudes it is not possible to obtain an accurate value for the volume. Besides, most radii types are defined only for some elements and not for all. The atomic volume, as other properties of the elements, has a strong relation with the arrangement of the electrons in atomic shells [55–59]. For this reason, the atomic volume is a periodic function of the atomic number, as was first formulated by Lothar Meyer in 1870 (with reference to atomic weight, not to atomic number) [60].

The similarity between the atomic volume curve and the two positron lifetime curves on figure 1 is great. Different factors affect positron lifetimes, like many-body enhancements, the region occupied by the positron (which in the bulk is less than the atomic volume), and the electrons available for annihilation in that region. However, the three graphics show the same periodic behaviour, also reproducing many small details. Although the lifetime has

been compared with other periodic properties like the  $r_s$  parameter, Wigner–Seitz radii etc the relation with the atomic volume seems to be more fundamental. This work confirms previous statements [13], but also proves that the monovacancy lifetimes exhibit the same periodic behaviour. Despite the localization of the wavefunction, the positron lifetime in bulk (delocalized state) and at a monovacancy (localized state) is still related to the volume of a single atom, and this is independent of the method of calculation used in this work. When an atom is removed from a perfect crystal structure, the remaining volume is mainly related to that atom. But on the removal of more than one atom the remaining volume is more structure dependent [34].

The lifetimes of some elements (As, Br, Kr, I and Xe) do not follow the trends of atomic volume (see figure 1). This special behaviour will be analysed in section 3.3.

The periodic behaviour of the positron lifetime found for the AT-SUP method within the BN approximation is also found using the GGA and LDA frameworks, as well as in the calculations performed with the LMTO code using the BN and GGA approximations.

### 3.3. Enhancement factors

The enhancement factor is of crucial importance in positron lifetime calculations ([61–63] and references therein). For this reason, it is necessary to study the behaviour of enhancement factors used in these calculations.

As has been pointed before, in figure 1 the lifetimes of some elements (As, Br, Kr, I and Xe) do not follow the periodic trends as could be predicted from the atomic volume. In the case of insulators, a model based on atomic polarizabilities, estimated from the Clausius–Mossotti relation, has been used too [43], where the dielectric constant of the solid is also needed. For the rare gases a special framework is needed. However, in these calculations, some insulators (As, Cl, Br and I) and all the rare gases (Ne, Ar, Kr and Xe) have been considered as metals ( $\epsilon_\infty = \infty$ ). So the real lifetimes of the BN approximation for these eight elements are really longer and closer to GGA values than the calculated ones (see tables 3–6).

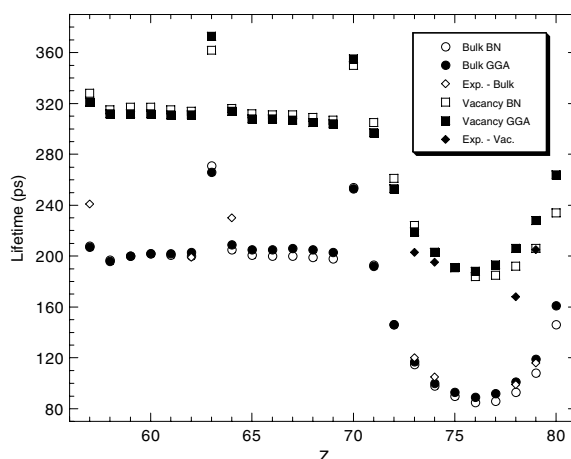
Boroński–Nieminen enhancement,  $\gamma_{\text{BN}}$  (equation (5)), is based on the many-body calculations performed by Lantto [32]. Stachowiak and Boroński reported that the calculations of Lantto start from a physically oversimplified trial function [64]. Fraser, in her PhD thesis, failed to reproduce Lantto’s results using a quantum Monte Carlo approach [65]. However, Boroński reported that the lifetimes calculated based on Fraser’s results are quite inaccurate, becoming even unreasonable for  $r_s > 4$  [66].

The Boroński–Nieminen parametrization, used in this work, agrees very well with the positron enhancements calculated by Arponen and Pajanne [67], Gondzik and Stachowiak [68] and Rubaszek and Stachowiak [69] for  $r_s \leq 8$  (see Fraser’s thesis [65], page 143). Indeed, Stachowiak and Boroński [64] pointed out that  $\gamma_{\text{BN}}$  is the best formula to fit the experimental lifetimes in metals. In bulk metals,  $r_s$  usually runs from 2 to 6 (in Cs it gets the maximum value, 5.6). However, the enhancement factor of the Boroński–Nieminen approach has two important problems at low densities (see figure 1 in [28]):

- (a) The scaled proton limit rule [70] is violated for  $r_s \geq 9$ . This is the upper bound for all the enhancement factors.
- (b) For  $r_s$  greater than 6 the lifetimes obtained with  $\gamma_{\text{BN}}$  do not increase monotonically with  $r_s$ . For this reason, the lifetimes cannot reach the 500 ps limit.

These two problems appear when the electronic density is low (semiconductors, insulators, rare gases, vacancies, voids, etc). In the case of semiconductors and insulators, the problem has been tackled using semi-empirical corrections introduced by Puska *et al* [43]. Using this





**Figure 2.** Bulk (circles) and monovacancy (squares) positron lifetimes of elements from La to Hg (6th row of the periodic table) versus atomic number. Lifetimes have been calculated within the LMTO using BN (open symbols) and GGA (filled symbols) approximations.

correction, calculated lifetimes in the BN approximation fit well the experimental ones, even when the densities are low.

In the case of  $\gamma_{\text{LDA}}$  (equation (8)), the enhancement factor has the same form as that used by Stachowiak and Lach [71].  $\gamma_{\text{LDA}}$  has been obtained fitting the Arponen–Pajanne data points only up to  $r_s = 5$  [28]. In the Arponen–Pajanne data, the Friedel sum rule is violated for  $r_s = 6$  and 8, and the scaled proton limit value is crossed at  $r_s = 8$  [31]. As  $\gamma_{\text{GGA}}$  (equation (7)) is obtained from  $\gamma_{\text{LDA}}$ , neither the LDA nor the GGA enhancements are very reliable for low electron densities, like BN enhancement. Calculations made in systems of low electron density using the GGA approximation with the universal value  $\alpha = 0.22$  do not give reasonable lifetimes [63, 72]. For example, in order to get lifetime values near the experimental ones for  $\text{C}_{60}$ , it is necessary to fit the  $\alpha$  parameter to a ‘suitable’ value [72].

As a result of all of these problems in the enhancements, we have to be very careful with all of the calculated lifetimes near to or greater than 400 ps. So more theoretical work is needed for low density systems.

### 3.4. *f* and *d* electrons

Figure 2 represents the behaviour of positron lifetimes for bulk (circles) and monovacancy (squares) in elements from  $_{57}\text{La}$  to  $_{80}\text{Hg}$  of the 6th row of the periodic table. As *f* and *d* shells get filled between  $_{57}\text{La}$  and  $_{80}\text{Hg}$ , the positron lifetimes of these elements can be used for studying the effects of *f* and *d* electrons on positron annihilation properties. The represented lifetimes are those obtained within the LMTO method using BN (empty symbols) and GGA (full symbols) approximations (see tables 4 and 6). Experimental lifetimes from table 8 have been plotted as a reference. As is known, the GGA calculation method uses the gradient of electronic density. So, for an accurate calculation, it is necessary to use a self-consistent electronic density, enabling charge-transfer in the system. Therefore, in order to make a better comparison between BN and GGA calculation methods, we have represented LMTO results.

First of all, we must remark that figure 2 shows the same general behaviour for bulk and for monovacancy lifetimes. As electrons fill the *d* shell between  $_{71}\text{Lu}$  and  $_{80}\text{Hg}$ , the bulk and monovacancy lifetimes show the same parabolic behaviour. As *d* electrons start filling the shell,

the lifetime reduces considerably, and, after reaching a minimum near the half-filled shell ( $d^6$ ), it increases again. This trend is explained simply with the behaviour of the atomic volume (see figure 1). This general dependence of positron lifetime with the outermost d electrons in bulk and monovacancies is independent of the row of the periodic table. The 4th row, from  ${}_{21}\text{Sc}$  to  ${}_{30}\text{Zn}$  elements, and the 5th row, from  ${}_{39}\text{Y}$  to  ${}_{48}\text{Cd}$  elements, show the same behaviour.

On the other hand, in lanthanides (from  ${}_{57}\text{La}$  to  ${}_{70}\text{Yb}$ ) the positron lifetime remains nearly constant as the 4f shell fills up ( $\tau_{\text{bulk}} \approx 200$  ps and  $\tau_{\text{vacancy}} \approx 315$  ps). The increasing number of f inner electrons is responsible for the magnetic properties of lanthanides, and the outermost s–d electrons determine the bonding and other electronic properties [73–75]. So, the f inner electrons cannot cause appreciable changes in positron lifetimes, since the positron wavefunction is mainly located in the interstitial space. However, the lifetimes of  ${}_{63}\text{Eu}$  and  ${}_{70}\text{Yb}$  are larger than the other lanthanides, because they have a half-filled ( ${}_{63}\text{Eu}$ ) or completely filled 4f shell ( ${}_{70}\text{Yb}$ ). For this reason, Eu and Yb get a more closed electronic structure and show a particular behaviour in several properties (atomic volume, electronegativity, melting point, ionization potentials etc). It has to be remarked that in the case of actinides (from  ${}_{90}\text{Th}$  to  ${}_{97}\text{Bk}$ ), the positron lifetime does not remain constant (see table 4). Indeed, it follows a parabolic behaviour (see figure 1) similar to the one found in d shells. This behaviour is in agreement with previous statements [76–78], which indicate that, in contrast to 4f electrons, 5f electrons are relatively delocalized and can contribute to the bonding. This special electronic structure makes positron lifetime (and other physical properties) behaviour more complex.

However, there are some especial features superimposed on to these general trends. In bulk, for the first lanthanide elements (from  ${}_{57}\text{La}$  to  ${}_{62}\text{Sm}$ ) GGA lifetimes are similar to BN ones. But, between  ${}_{64}\text{Gd}$  and  ${}_{69}\text{Tm}$ , GGA lifetime is a little bit larger than the BN one, about 4 ps (see table 4). There are only three experimental bulk lifetimes from the literature. These experimental lifetimes are from different research groups and not from very recent measurements. So, it would be interesting to get new experimental data for the lanthanides.

In monovacancies, the lifetimes of lanthanides have a particular behaviour (see figure 2). For most of the elements of the periodic table, GGA lifetimes are usually larger than BN ones (see table 6). Opposite to this general trend, the GGA lifetimes of lanthanides are shorter than BN ones, by about 3–5 ps (see table 6). As is known, the positron is very localized in a monovacancy and the probability of annihilation with inner electrons is much lower than in bulk. Taking into account that f electrons are inner electrons, they do not have an appreciable effect on these lifetimes. So, the values of these lifetimes are due to the external electronic configuration, similar to the outer electronic configuration of  ${}_{57}\text{La}$ . As in the bulk case,  ${}_{63}\text{Eu}$  and  ${}_{70}\text{Yb}$  are outside this trend, showing a special feature. It could be expected that they would follow the same trend as the other lanthanides. However, they show the opposite—GGA lifetimes are longer than BN ones.

A lot of work has been done to try and understand the behaviour of d electrons [34, 79]. In the bulk case (see figure 2), for La, Ce and Lu the BN lifetimes are longer than the GGA ones. However, as electrons start to fill the d shell, the difference gets smaller. And from  $d^3$  ( ${}_{73}\text{Ta}$ ) to  $d^{10}$  ( ${}_{80}\text{Hg}$ ) the GGA lifetime is longer than the BN one, increasing the difference as d orbitals are being occupied. The GGA correction to the local density approximation is roughly proportional to the number of outermost d-electrons in the atom [34]. The four experimental lifetimes found in the literature fit very well GGA values in this region. Local density approximation calculations made with different parametrizations, BN (table 3) and LDA (table 7), show that the positron lifetimes for bulk transition metals are systematically too short in comparison with the experimental values, and GGA fits the experimental values better.

In monovacancies the trend is similar to that of the bulk. The BN lifetime is longer than the GGA one for the first elements, from Lu( $d^1$ ) to Ta( $d^3$ ). At W( $d^4$ ) and Re( $d^5$ ) BN and GGA

lifetimes are the same. And finally, from Os(d<sup>6</sup>) to Hg(d<sup>10</sup>) GGA lifetimes are longer than BN ones. So, the trend is the same, but in monovacancies more d electrons are needed for GGA lifetimes to get longer than BN ones. In monovacancies, the calculated lifetimes and the experimental ones show a larger difference than in the bulk case.

In lifetimes calculated within the AT-SUP method, BN and GGA values follow the very same general trends. However, the differences between GGA and BN lifetimes are much greater, due to the lack of self-consistency of the electronic densities used in calculations.

#### 4. Conclusions

The systematic calculations performed in this work set a theoretical support for understanding and interpreting different positron lifetime experiments. It has to be remarked that there are many elements among these lifetimes calculated for the first time.

As a result of these positron lifetime calculations, a well-known trend for the bulk lifetimes has been systematically proved again, and the same trend has been established for the calculated monovacancy lifetimes too. However, a direct quantitative extrapolation on the absolute values cannot be done for the whole periodic table due to the fact that positron lifetimes reach saturation at 500 ps. This fact deforms the trends compared to the atomic volume. So, it is concluded that the positron lifetime of the bulk and vacancies is a periodic property of the elements.

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