Full-potential all-electron positron lifetime calculations: Assessment of local enhancement factors

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We report the implementation of positron wave function and lifetime calculations in the all-electron full-potential linearized augmented plane wave method. Calculations of lifetimes for more than 30 materials with two different forms of the enhancement factor were done and compared to prior calculations and experiment. We find that reasonable agreement with experiment can be obtained within the local density approximation when all-electron full-potential calculations are done.

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I. INTRODUCTION

Positron lifetimes are useful for detecting and characterizing vacancies and other defects in solids. The repulsive Coulomb potential of the nuclei pushes the positron into vacancies making positrons particularly sensitive to defects. In fact, positron lifetime measurements provide nondestructive and sensitive probes even for small concentrations of vacancies.[1,2] However, characterizing the defects in a sample requires knowledge of the specific lifetimes for various possible defect structures as well as the undefected bulk.

A case in point is provided by ZnO. In that material, bulk positron lifetimes of 170–189 ps had been reported.[3,4] However, more recent measurements that were better able to separate bulk and defect contributions showed that the bulk lifetimes are much shorter. In particular, Brauer *et al.*[5] obtained 151 ps, while Dutta *et al.*[6] obtained ~145 ps. Thus, it may be that accurate calculations can not only help identify the defects seen in lifetime measurements but can also be useful in separating bulk and defect contributions.

Methodology for positron wave function and lifetime calculations is well developed. Arponen and Pajanne (AP),[7] applying the boson formalism in a homogeneous gas, calculated the positron electron annihilation rates and correlation potential by using the generalized Tamm-Dancoff approximation. Chakraborty[8] derived the equations for the positron and electron based on the density functional theory (DFT),[9] the so-called two component DFT, and obtained the positron electron correlation potential and enhancement for the annihilation rate factor from AP. Lantto[10] derived equations for the annihilation rates and correlation potentials from the Fermi hypernetted-chain equations by using the approximate Euler-Lagrange equations. He computed several positron electron concentration ratios and, for the correlation potential, indicated that his data correspond to AP only in the lowest concentration ratio system, i.e., the positron density approaches zero ($\rho^+ \rightarrow 0$). Boroński and Nieminen[11] (BN) parametrized the electron positron correlation potentials and enhancement factors by using Lantto's results, respectively. They calculated the positron states and lifetimes of several elemental metals by using the linear muffin tin orbital method within the atomic sphere approximation (LMTO-ASA).

Sterne and Kaiser[12] explicitly gave an expression for the positron potential only within DFT parametrizing their own correlation potential from AP and an enhancement factor from Lantto. They then calculated the lifetimes of elemental metals for bulk and vacancy systems. Puska and co-workers[13,14] suggested that another enhancement factor for semiconductors and insulators could be needed.

All the correlation potentials and enhancement factors described above were local density approximation (LDA) forms. Barbiellini, Pusca, Torsti, and Nieminen (BPTN)[15] introduced a generalized gradient approximation (GGA) to the enhancement factor. First, they parametrized the enhancement factor of AP within LDA. Then, they developed a GGA enhancement factor modifying the LDA enhancement factor from AP. Panda *et al.*[16] calculated the positron states with a norm conserving pseudopotential method using plane waves (PPPWs). Makkonen *et al.*[17] used the projector augmented wave method for positron states. They concluded that a GGA was needed to obtain reasonable agreement with experimental results. Campillo Robles *et al.*[18] calculated positron lifetimes of the elements of the Periodic Table using BN containing the high-frequency dielectric constant by Puska *et al.* and GGA enhancement factors with the atomic superposition (ATSUP) approximation and LMTO-ASA method. For rare earth metals, each method provided quite the same lifetimes. The GGA mostly showed longer than the BN in another elemental metals. Campillo Robles *et al.* found this trend even for semiconductors. They showed that lifetimes of Xe and Ar were in good agreement with experimental data with the GGA.

One of the difficulties has been sorting out the effects of the electron positron correlation from those of the approximations in the computational (band-structure) methods. Here, we report calculations for a wide range of simple materials with the all-electron general potential linearized augmented plane wave (LAPW) method including local orbitals.[19,20] This method uses a very flexible basis set, makes no shape approximations to the charge density or potential, uses no pseudopotentials or frozen core approximations, and uses the relativistic effect inside sphere regions. This allows us to perform highly accurate LDA calculations and assess the electron positron correlation and enhancement factors. In this work, we do not tune the positron lifetime calculation techniques to experimental data. We use *ab initio* calculations with the correlation potential and enhancement factors obtained from many-body calculations by AP and Lantto. We find generally good agreement with established

experimental data at the local density level, when accurate band-structure methods are used. This differs from recent work that implied that beyond LDA methods were needed to obtain this level of agreement.

In this paper, we show implementation of the lifetime calculation in Sec. II. We report and discuss the positron lifetimes for several materials in Sec. IV. We present conclusions in Sec. V.

II. THEORY

We describe the implementation of the positron lifetime calculation in this section. Experimentally, the positron lifetimes are determined based on the Gaussian fitting[21,22] to measured positron lifetime spectra. On the other hand, theoretically, the lifetime τ means the inverse of the probability of the positron electron annihilation λ. This is the independent particle approximation, to which a correction is applied via an enhancement factor. To calculate τ, therefore, we need to obtain the ground state electron charge and positron charge densities. In this paper, we consider a system with a single positron for bulk systems without defects. As mentioned in Sec. I, we may regard this system to be the $\rho^+ \rightarrow 0$ limit. Thus, we adopt the electron positron correlation potential and enhancement factor obtained in this limit.

First of all, we obtain the electron charge density results from the conventional *ab initio* calculation. For the positron, we solve the equation expressed as

$$[-\nabla^2 + V^+(\mathbf{r})]\psi^+(\mathbf{r}) = \varepsilon^+\psi^+(\mathbf{r}), \tag{1}$$

where ψ^+ are positron wave functions and ε^+ are positron eigenvalues, which are the potentials sensed by the positron V^+. The V^+ is given by

$$V^+(\mathbf{r}) = -V_{Coul}(\mathbf{r}) + V_{corr}[\rho^-(\mathbf{r})], \tag{2}$$

where V_{Coul} is the Coulomb potential, V_{corr} is the correlation potential between electron and positron, and ρ^- is the electron charge density. The potential V_{Coul} is identical to the Coulomb potential for the electrons. The correlation potential V_{corr} is constructed only from ρ^- which we have already calculated. The wave function $\psi^+(\mathbf{r})$ that correspond to the lowest energy of ε^+ yields the positron charge density ρ^+ as follows:

$$\rho^+(\mathbf{r}) = |\psi^+(\mathbf{r})|^2. \tag{3}$$

Now, we obtain both the electron and positron charge densities. We, however, need to consider an influence of the positron on the electron charge density since the presence of the positron does affect the electronic states as in the correlation term in the potential. Accordingly, an enhancement factor is introduced into the annihilation rate. We, thus, may express the lifetime τ as

$$\tau = 1/\lambda = \left(\pi r_e^2 c \int d\mathbf{r}\rho^+(\mathbf{r})\rho^-(\mathbf{r})\Gamma[\rho^-(\mathbf{r})]\right)^{-1}, \tag{4}$$

where r_e is the classical electron radius, c is the speed of light, ρ^+ is the positron charge density, ρ^- is the electron charge density, and Γ is the enhancement factor. In Fig. 1, we illustrate the procedure for the lifetime calculation with a flowchart.

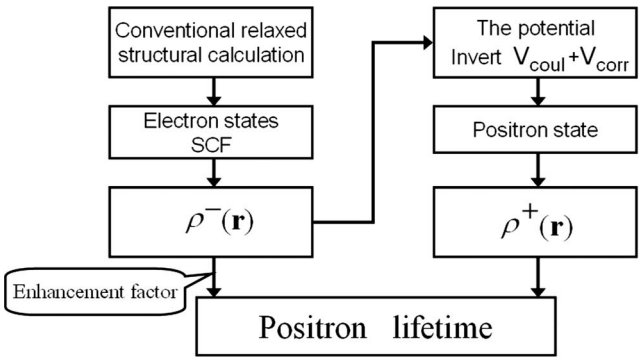

FIG. 1. Flowchart of the positron lifetime calculation. ρ^- is the electron charge density and ρ^+ is the positron charge density.

In this paper, we adopt the correlation potential and enhancement factors parametrized by BN[11] from Lantto[10] and as parametrized by BPTN[15] from AP[7] as a function of the Wigner-Seitz radius r_s as well as the exchange-correlation potential for the electron. The correlation potential is given by equations in various ranges of r_s as in the correlation potential for electrons parametrized by Perdew and Zunger.[23] These equations for the correlation potential are as follows:

$$V_{corr}(r_s \leq 0.302) = 1.14 - 1.56/\sqrt{r_s} + (0.051 \ln r_s - 0.081)\ln r_s,$$

$$V_{corr}(0.302 \leq r_s < 0.56) = -0.923\,05 - \frac{0.054\,59}{r_s^2},$$

$$V_{corr}(0.56 \leq r_s < 8.0) = -\frac{13.151\,11}{(r_s+2.5)^2} + \frac{2.8655}{r_s+2.5} - 0.6298,$$

$$V_{corr}(8.0 \leq r_s) = -179\,856.2768\left(\frac{3}{4\pi r_s^3}\right)^2 + 186.4207\frac{3}{4\pi r_s^3} - 0.524, \tag{5}$$

then the BN enhancement factor is expressed as

$$\Gamma(r_s) = 1 + 1.23r_s + 0.8295r_s^{1.5} - 1.26r_s^2 + 0.3286r_s^{2.5} + r_s^3/6, \tag{6}$$

and BPTN as

$$\Gamma(r_s) = 1 + 1.23r_s - 0.0742r_s^2 + r_s^3/6. \tag{7}$$

As mentioned, Sterne and Kaiser[12] (SK) also parametrized the correlation potential from AP,

$$V_{corr}(r_s) = 0.7207 - 1.56(\arctan r_s)^{-1/2} + 0.1324\exp\left[-\frac{(r_s-4.092)^2}{51.96}\right], \tag{8}$$

and enhancement factor from Lantto,

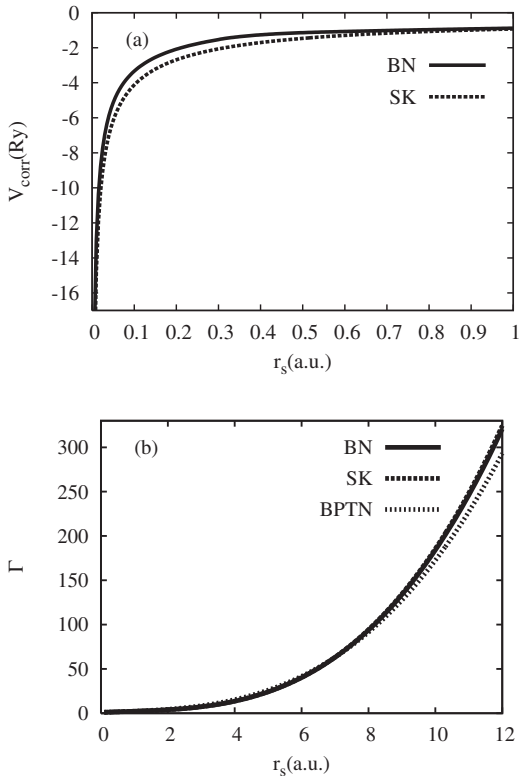

FIG. 2. (a) Comparison of the positron electron correlation potential between BN and SK as a function of r_s. The BK potential agrees with the SK as r_s is greater than 1. The enhancement factors Γ are shown in (b) with BPTN. Compared to BPTN, the BN and SK enhancement factors are identical.

$$\Gamma(r_s) = 1 + 0.1512r_s + 2.414r_s^{1.5} - 2.01r_s^2 + 0.4466r_s^{2.5} + r_s^3/6. \quad (9)$$

The SK potential in Eq. (8) is quite simplified compared to BN in Eq. (5). The SK enhancement factor in Eq. (9), however, is similar to BN in Eq. (6). In Fig. 2, we show the BN and SK correlation potential and enhancement factor as a function of r_s, and, for comparison, plot the BPTN enhancement factor in Eq. (7). The BN potential fits the SK potential as r_s increases over 0.9. However, a small difference between the SK and BN exists at smaller r_s. Mostly, positrons are confined to the interstitial region where r_s is not small (note the Coulomb repulsion of the nuclei). For the enhancement factors, the BN coincides with SK as shown. Therefore, we regard the BN and SK as identical. In practice, testing a few materials, we did not find any differences between BN and SK lifetimes.

III. COMPUTATIONAL DETAILS

We calculate both electron and positron charge densities by using the LAPW basis sets with the same parameters. The lattice constants are from experimental data. We used the converged basis sets and the Brillouin zone samplings for electrons in each material. The size of the basis sets was increased until total energy error converged to better than 1 mRy. The convergence of the lifetime was tested and the parameters were increased to obtain the errors of less than 1 ps.

For the positron, using the same size of the basis set, we calculate the wave functions in Eq. (1) at the Γ point. It is unnecessary to execute the self-consistent calculation for the positron because the potential in Eq. (2) is independent of the positron charge density.

TABLE I. Positron lifetimes for the bulk elemental metals in picoseconds. We show the lifetimes derived from the enhancement factor AP and BN and compare the results with Puska's work by using LMTO-ASA.

Material	LAPW[a] BPTN	LAPW[b] BN	LMTO-ASA[b] BN	Expt.
Li	258	298	305	291[c]
Be	122	136	137	142[c]
Na	285	322	337	338[c]
Mg	202	232	237	225[c]
Al	147	166	166	163[c]
K	339	374	387	397[c]
Ca	250	288	297	
Sc	173	197	199	230[d]
Ti	131	145	146	147[c]
V	105	115	116	130[c]
Cr	93	101	101	120[c]
Fe	93	100	101	106[c]
Co	89	96	97	118[d]
Ni	92	99	96	110[c]
Cu	99	107	106	110[c]
Zn	126	139	134	148[c]
Rb	344	378	396	406[c]
Sr	268	309	319	
Y	188	216	219	249[d]
Zr	141	158	159	165[c]
Nb	110	121	122	118[c]
Mo	96	104	111	103[c]
Tc	91	98	95	
Ru	86	92	90	
Rh	88	94	93	
Pd	95	102	103	
Ag	113	124	120	133[d]
Cd	143	160	153	175[c]

[a]This work.
[b]Reference 24.
[c]Reference 25.
[d]Reference 26.

IV. RESULTS AND DISCUSSIONS

We calculated positron lifetimes for several materials by using the BPTN and BN enhancement factors, respectively. First, we show the positron lifetimes for elemental metals in Table I. We refer to the Puska-Nieminen work[24] by using the

TABLE II. Positron lifetimes for the bulk semiconductors in picoseconds. Panda *et al.* have reported by using PPPW and LMTO-ASA. For the experimental result of ZnO, we refer to Dutta *et al.* The other experimental data are described in Panda's paper.

Material	LAPW[a] BPTN	LAPW[a] BN	PPPW[b] BPTN	LMTO-ASA[b] BPTN	Expt.
ZnO	132	144			~145[c]
Si	186	211	190	193	216[b]
GaAs	190	214	197	190	231[b]
Ge	190	215	198	191	228[b]
InP	199	225	213	201	244[b]
CdTe	227	256	245	228	285[b]

[a]This work.
[b]Reference 16.
[c]Reference 6.

LMTO-ASA method for comparison. Our and the results of Puska and Nieminen reasonably agree with experimental data when the BN enhancement factor is used. The usual trends are found. Each alkali metal has the longest lifetime among atoms in the corresponding row of the Periodic Table for these elemental metals. Generally, in the alkali metals, the electrons are localized around the nuclei with low density in the large interstitial. For the transition metals, the interstitial volume is smaller and the charge density is higher. Our results indicate that the BPTN underestimates the lifetimes. Lantto has reported on this already with respect to the positron electron annihilation rate λ for several metals. Lantto and AP both derived the equations from different formalisms and calculated λ using different methods. Lantto's results were lower than AP by 10%–15%. These λ of Lantto were closer to experimental data than those of AP. Lantto, however, did not claim that each λ from AP is inaccurate.

We show the lifetimes for semiconductors in Table II. In Puska's paper, they have used the BN enhancement factor for semiconductors by using the high-frequency dielectric constants ϵ_∞ suggested by Puska *et al.*,[13]

$$\Gamma(r_s) = 1 + 1.23r_s + 0.8295r_s^{1.5} - 1.26r_s^2 + 0.3286r_s^{2.5} + (1 - 1/\epsilon_\infty)r_s^3/6. \quad (10)$$

In the work of Panda *et al.*, the $1/\epsilon_\infty$ term is set to zero, and we adopt this here also. We, thus, compare the lifetimes with the paper of Panda *et al.*[16] where the dielectric term is not used similar to our calculations. They have calculated the lifetimes by using PPPW and LMTO-ASA. Experimental data have also been reported in their paper. We see the same trends in the lifetimes as in the LMTO-ASA. Even for the semiconductors, our results reveal that the AP enhancement factor results in ~10% or better underestimates of the lifetimes as for the elemental metals. This is a significantly lower level of error than with the BPTN function. The larger lifetime underestimates with the BPTN LDA function were, in fact, important in motivating the use of GGA functions. We, thus, may find that the lifetimes without ϵ_∞ are in good agreement with the positron lifetimes from BN compared to AP.

For ZnO, we refer to Dutta *et al.*[6] They measured the three types of the lifetime, i.e., the free annihilation, annihilation at intrinsic defects, and orthopositronium annihilation, in samples of single crystal ZnO annealed up to various temperatures, and then obtained the lifetimes from 141 to 155 ps in each sample. Brauer *et al.*[5] obtained 151 ps from slow positron spectroscopy by using monoenergetic positrons which can detect depth-dependent defects. Compared to these results, the long lifetimes were reported in earlier experimental literature. Brauer *et al.* suggested that the error between recent and earlier works resulted from grown-in defects which ZnO contained in earlier works. They also calculated the positron lifetimes using the ATSUP method with BN in Eq. (10) which contains $\epsilon_\infty = 4$ and GGA by Barbiellini *et al.* for the lifetimes. They showed 159 and 176 ps, respectively. Even for ATSUP, BN showed closer number to the recent experimental data. In addition, one can notice that their lifetime of 159 ps, longer than their experimental data and our result, arises from the correction term ϵ_∞.

The relative errors between our results and experimental data are found to be within around 10%, which is at a level where the results can be useful. Thus, our results without either an experimentally based dielectric correction or the use of the GGA are in reasonable accord with experiment. The GGA includes a parameter determined semiempirically as Panda *et al.* mentioned in their paper.

Finally, we show positron lifetimes of lanthanide trihalides, which are useful scintillators, in Table III, taking the BPTN and BN in Eq. (6) enhancement factors into account. These compounds have long lifetimes compared to semiconductors, as expected from their soft ionic bonding.

TABLE III. Positron lifetimes for the bulk lanthanide trihalides in picoseconds.

Material	BPTN	BN
$LaCl_3$	259	285
$LaBr_3$	269	297
$LuCl_3$	251	278
$LuBr_3$	249	279

V. CONCLUSIONS

We implemented the positron state and lifetime calculations in the LAPW method. In this work, we do not adjust anything except that we use the correlation potential and enhancement factors obtained from many-body calculations. Our result shows general agreement with the earlier works for the elemental metals and the experimental data for the semiconductors when using BN. In addition, we show a tendency to underestimate the lifetime with the BPTN enhancement factor by 10%–15% as compared to the BN factor. This is consistent with the many-body calculations reported by Lantto. We conclude that the positron lifetime is well described with the BN enhancement factor within the LDA, since the disagreement at the LDA level is smaller than previously thought.

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