Proc. 2nd Japan-China Joint Workshop on Positron Science
JJAP Conf. Proc. **2** (2014) 011001

Assessment of Several Calculation Methods for Positron Lifetime

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(Received March 15, 2014)

We test seven different local density approximation (LDA) or generalized gradient approximation (GGA) forms of the enhancement factor and correlation potential for positron-lifetime calculations by using a useful database of experimental values based on the all-electrons approach: full-potential linearized augmented plane wave (FLAPW). To make a numerical assessment of these calculation methods, we use the mean-deviation and the reduced chi-squared as model selection criterions. We find that the two recent LDA forms of the enhancement factor make distinct improvements upon the calculations for positron-lifetime compared with the older LDA form proposed by Arponen and Pajanne. However, all the LDA forms are still disfavored by the experimental data compared with the GGA forms. In addition, the two recent GGA forms do not yield any improvement when compared to experimental data over the original from given by Barbiellini *et al.*, which is found to give the best agreement.

1. Introduction

During recent years positron annihilation spectroscopy (PAS) has become a valuable method to study the microscopic structure of solids [1] and gives detailed information on the electron density and momentum distribution in the regions scanned by positrons. For a thorough understanding and interpretation of experimental results an accompanying theory is needed. Based on the density functional theory (DFT), there are two main approaches: the conventional scheme and the full two-component scheme [2,3]. The conventional scheme is more convenient and produces consistent results for physical observables compared with the full two-component scheme [3–5], and has been employed in most applications for positron states so far. In this short paper we focus on theoretical calculations of the positron lifetime based on the conventional scheme.

To help analyse experimental data on positron lifetime, we should find a practical method accurate enough to reliably predict the theorical lifetime. Based on the FLAPW method for electronic-structures calculations, Takenaka and Singh [6] calculated positron lifetimes for many materials with two different forms of the enhancement factor and found that reasonable agreement with experiment can be obtained within the local density approximation. Moreover, within the same method for electronic-structures calculations, Kuriplach and Barbiellini [7] implemented more calculations by using the gradient corrections based on perturbed hypernetted-chain and on quantum Monte Carlo results and showed that the recent forms of the enhancement factor generally improve the calculated positron lifetimes when they are compared with experiment. (For more recent studies about the calculations for positron lifetime, see e.g. [8,9].)

However, to our knowledge, a numerical assessment of calculation methods for positron lifetime

has not been made, and the estimatied errors in the experimental data have not been considered in the papers mentioned above. In this work, by utilizing the mean-deviation and the reduced chi-squared as model selection criterions, we test seven LDA or GGA forms of the enhancement factor for positron lifetime calculations and give a numerical assessment of these models.

This paper is organized as follows: In Sec. 2, we give a brief and overall description of the models considered here as well as the analysis methods we used. In Sec. 3, we introduce the experimental data on positron lifetime used in our work. In Sec. 4, we test our calculations in the cases of Si and Al, then the calculated results are presented and discussed. In Sec. 5, we make a summary of this work.

2. Theory and methodology

2.1 Theory

In this part, we introduce in detail the theory for calculating the positron lifetime and the forms of the enhancement factor we investigate in this work.

The conventional scheme is based on normal one-component density functional theory. First, the electronic-structure is calculated to obtain the ground-state electronic density $n_{e^-}(\vec{r})$ and Coulomb potential $V_{\mathrm{Coul}}(\vec{r})$ sensed by positron. Then, the positron density $n_{e^+}(\vec{r})$ is determined by solving the Kohn-Sham equation:

$$\left[-\frac{1}{2}\nabla_{\vec{r}} + V_{\mathrm{Coul}}(\vec{r}) + V_{\mathrm{corr}}(\vec{r})\right]\psi^+ = \varepsilon^+\psi^+,\ n_{e^+}(\vec{r}) = |\psi^+(\vec{r})|^2, \tag{1}$$

where $V_{\mathrm{corr}}(\vec{r})$ is the correlation potential between electron and positron. Finally, the positron lifetime τ is equal to the inverse of the annihilation rate λ, which is proportional to the product of positron density and electron density accompanied by the so-called enhancement factor arising from the correlation energy between a positron and electrons [1, 10]. The equations are written as follows:

$$\tau = \frac{1}{\lambda},\ \ \lambda = \pi r_0^2 c \int d\vec{r} n_{e^-}(\vec{r}) n_{e^+}(\vec{r}) \gamma(n_{e^-}), \tag{2}$$

where r_0 is the classical electron radius, c is the speed of light, and $\gamma(n_{e^-})$ is the enhancement factor of the electron density at the position $\vec{r}$. This method is accurate for a perfect lattice, as in this case the positron is delocalized and does not affect the bulk electronic structure [3, 4].

In this work, the ground-state electronic density and Coulomb potential mentioned above will be calculated by using the all-electrons approach: full-potential linearized augmented plane wave (FLAPW) [11], which is widely considered to be the most precise method for electronic-structure calculations. The seven forms of enhancement factor can be divided into two categories: the local density approximation (LDA) and the generalized gradient approximation (GGA). Within the LDA, the corresponding correlation potential $V_{\mathrm{corr}}^{\mathrm{LDA}}$ is given by the following equations (in Ry) [3, 12]:

$$\begin{cases} V_{\mathrm{corr}}^{\mathrm{LDA}} = 1.14 - 1.56/\sqrt{r_s} + (0.051 \ln r_s - 0.081) \ln r_s, & r_s \le 0.302\ ; \\ V_{\mathrm{corr}}^{\mathrm{LDA}} = -0.92305 - 0.05459/r_s^2, & 0.302 \le r_s \le 0.56\ ; \\ V_{\mathrm{corr}}^{\mathrm{LDA}} = -13.15111/(r_s + 2.5)^2 + 2.8655/(r_s + 2.5) - 0.6298, & 0.56 \le r_s \le 8.0\ ; \\ V_{\mathrm{corr}}^{\mathrm{LDA}} = -179856.2768\left(\frac{3}{4\pi r_s^3}\right)^2 + 186.4207\left(\frac{3}{4\pi r_s^3}\right) - 0.524, & r_s \ge 8.0\ ; \end{cases} \tag{3}$$

where r_s is defined as $r_s = \left(\dfrac{3}{4\pi n_{e^-}}\right)^{1/3}$. Within the GGA, the corresponding correlation potential takes the form

$$V_{\mathrm{corr}}^{\mathrm{GGA}} = V_{\mathrm{corr}}^{\mathrm{LDA}} \exp(-\alpha\epsilon), \tag{4}$$

here α is an adjustable parameter, and ϵ is defined as $\epsilon = \dfrac{|\nabla \ln(n_{e^-})|^2}{q_{TF}^2}$ (q_{TF}^{-1} is the local Thomas-Fermi screening length). All forms of the enhancement factor will be introduced one by one as follows.

(1) The common LDA form proposed in Ref. [3] (called BNLDA hereafter) which is written as follows,

$$\gamma_{BNLDA} = 1 + 1.23r_s + 0.8295r_s^{\frac{3}{2}} - 1.26r_s^2 + 0.3286r_s^{\frac{5}{2}} + \frac{1}{6}\left(1 - \frac{1}{\epsilon_\infty}\right), \tag{5}$$

where ϵ_∞ is the high-frequency dielectric constant of each material.

(2) The LDA form introduced by Barbiellini *et al.* [13] based on the results by Arponen and Pajanne [12] (called APLDA hereafter) which takes the form

$$\gamma_{APLDA} = 1 + 1.23r_s - 0.0742r_s^2 + \frac{1}{6}r_s^3. \tag{6}$$

(3) The original GGA form given by Barbiellini *et al.* [13] (called APGGA hereafter) which reads as follows,

$$\gamma_{APGGA} = 1 + (\gamma_{APLDA} - 1)\exp(-\alpha\epsilon),\ \alpha = 0.22. \tag{7}$$

(4) The LDA form suggested by Stachowiak and Lach [14] within perturbed hypernetted-chain approximation (called PHCLDA hereafter) which is expressed as

$$\gamma_{PHCLDA} = 1 + 1.23r_s - 0.137r_s^2 + \frac{1}{6}r_s^3. \tag{8}$$

(5) The GGA form suggested by *Boroński* [8] (called PHCGGA hereafter) which is expressed as

$$\gamma_{PHCGGA} = 1 + (\gamma_{PHCLDA} - 1)\exp(-\alpha\epsilon),\ \alpha = 0.10. \tag{9}$$

(6) The LDA form suggested by Kuriplach and Barbiellini [7] to fit recent quantum Monte Carlo data given by Drummond *et al.* [15] (called QMCLDA hereafter) which is expressed as

$$\gamma_{QMCLDA} = 1 + 1.23r_s - 0.22r_s^2 + \frac{1}{6}r_s^3. \tag{10}$$

(7) The recent GGA form, corresponding to the QMCLDA form, which is written as follows [7],

$$\gamma_{QMCGGA} = 1 + (\gamma_{QMCLDA} - 1)\exp(-\alpha\epsilon),\ \alpha = 0.05. \tag{11}$$

2.2 Computational Details

During the self-consistent calculations for electronic-structures, the PBE-GGA approach [16] is used for electron-electron exchange-correlations and numerical parameters (energy-cutoff, k-points, etc.) are checked carefully to achieve the full convergence. To obtain the positron-states, the three-dimensional Kohn-Sham equation Eq. (1) is solved by the finite-difference method while the unit cell of each material is divided into more than $100 \times 100 \times 100$ mesh spaces. All variable parameters have been adjusted to ensure that the computational precision of lifetime values are less than 0.1 ps.

2.3 Model Comparison

To enforce a comparison between different models, a statistical variable must be chosen. The simplest one is the mean-deviation (MD) which is defined as the average of the absolute value of difference between the experimental and the theoretical results:

$$\mathrm{MD} = \sum_{i=1}^{N} |X_i^{\mathrm{Exp.}} - X_i^{\mathrm{Th.}}|/N \,, \tag{12}$$

here N denotes the number of experimental values. We also quote the reduced chi-squared as another model selection criterion:

$$\chi^2_{\mathrm{R}} = \sum_{i=1}^{N} \frac{\left(X_i^{\mathrm{Exp.}} - X_i^{\mathrm{Th.}}\right)^2}{N \cdot \sigma_i^2}, \tag{13}$$

where σ_i is the standard deviation of each experimental value.

From the above definitions, we can see that the experimental data favor models producing lower values of the two criterions. It should be mentioned that the quantity χ^2_{R} may not be better than the above quantity MD due to the large differences of lifetime results obtained by different groups.

3. Experimental data

The experimental data used in our work are listed in Table I and come from the database of Ref. [17]. Due to the fact that the difference in measured lifetime obtained by different groups at a level of ~10 ps is not rare, we carefully choose those data having both small error estimations and being consistent with most other results.

Table I. The experimental data of positron lifetime $\tau_{\mathrm{Exp.}}$ which come from Ref. [17] and the high-frequency dielectric constant ϵ_∞ used in this work.

Element	$\tau_{\mathrm{Exp.}}$ [ps]	$\sigma_{\mathrm{Exp.}}$ [ps]	ϵ_∞
Li	291	6	∞
Be	137	3	∞
C	97.5	1.5	5.62
Na	338	7	∞
Mg	225	2	∞
Al	164.1	3.7	∞
Si	218	1	11.9
K	397	10	∞
Ti	147	5	∞
Fe	111	1	∞
Ni	110	4	∞
Cu	122	5	∞
Zn	153	1	∞
Ga	198	2	∞
Ge	230	3	16.0
Zr	165	5	∞

In this work, we just tested the calculation methods by using bulk-lifetime data of single-crystals since the conventional scheme is strictly accurate only for bulk-lifetime calculations. It should be

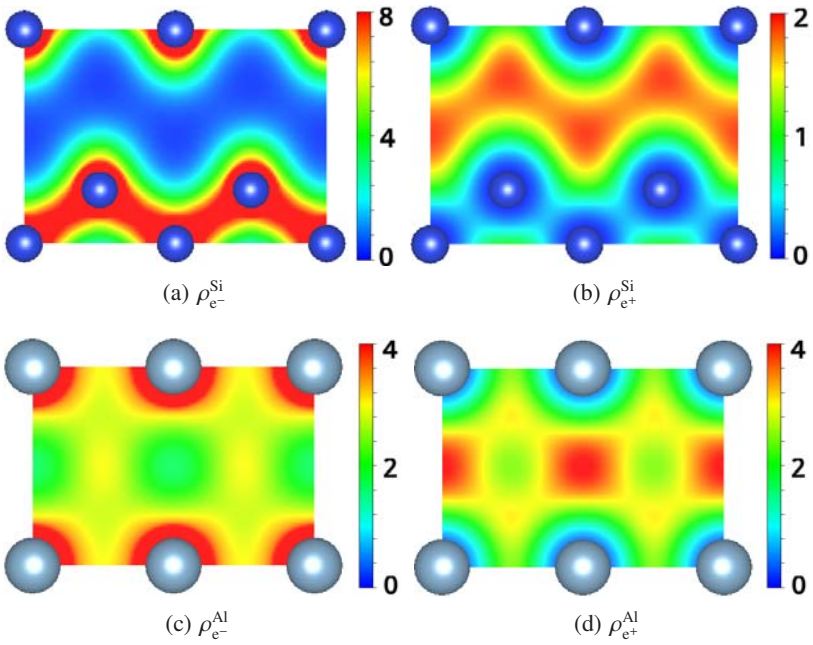
noted that calculations for positron lifetimes in defects based on the full two-component scheme need to be performed for a more comprehensive assessment.

4. Tests and results

In the following, we firstly test our calculations in the cases of Si and Al to check on the validity and appropriateness of our program. Then we give a visualized comparison between different forms of the enhancement factor based on the results of all materials we consider. Finally, the calculated results of all materials, alkali metals and group-IV semiconductors are presented and discussed respectively.

4.1 Application of calculation methods to Si and Al

The calculated electron and positron density on plane $(1\bar{1}0)$ for Si and Al based on the BNLDA approach are presented in Fig. 1. It is reasonable to obtain from Fig. 1 that the panel 1(a) shows clear bonding states of Si while for panel 1(c) shows a no bonding state. From the panels 1(b) and 1(d), it can be seen that the positron rarely appears in the core regions of atoms. To explore the effects of core-electrons on the final positron lifetimes for Si and Al, we also calculated the positron lifetimes corresponding to annihilation with the valence-electrons $3s^2 3p^2$ for Si and $2p^6 3s^2 3p^1$ for Al. All the calculated results of positron lifetimes for Si and Al are list in Table II, which are consistent with previous works [6, 7]. From Table II, we can see that annihilation with the core and semicore electrons $1s^2 2s^2 2p^6$ of Si or the core electrons $1s^2 2s^2$ of Al has little influence on the results of positron lifetimes for Si or Al. This is because the positron lifetime is an integrated quantity, and for other measurements such as Doppler broadening the annihilation of positron with core electrons gives much more significant information [18].



(a) $\rho_{e^-}^{Si}$ (b) $\rho_{e^+}^{Si}$

(c) $\rho_{e^-}^{Al}$ (d) $\rho_{e^+}^{Al}$

Fig. 1. Calculated electron and positron density on plane $(1\bar{1}0)$ for Si (upper panels) and Al (lower panels) based on the BNLDA approach.

Table II. Calculated results of positron lifetimes for Si and Al based on different forms of the enhancement factor. The Si_A and Al_A indicate that the following results correspond to the annihilation with all-electrons, while the Si_V and Al_V indicate the following results correspond to the annihilation with the valence-electrons $3s^2 3p^2$ for Si and $2p^6 3s^2 3p^1$ for Al. To make a comparison, we also list the expereimental results.

τ [ps]	APLDA	APGGA	BNLDA	PHCLDA	PHCGGA	QMCLDA	QMCGGA	Exp.
Si_A	181.62	216.90	213.48	192.71	209.55	204.66	213.42	218
Si_V	187.18	220.83	221.31	198.85	214.73	211.07	219.42	—
Al_A	145.67	154.10	164.53	154.14	159.51	161.19	164.23	164.1
Al_V	148.10	154.95	167.73	156.83	161.12	163.88	166.30	—

4.2 Results and discussion

Figure 2 shows visualized comparisons between experimental values and calculated results based on different forms of the enhancement factor for each material respectively. We see that, the calculated results based on the GGA forms of the enhancement factor are in much better agreement with experimental values compared with those based on the LDA forms of the enhancement factor. Furthermore, the APLDA and PHCLDA forms of the enhancement factor always overestimate the annihilation rate, which is consistent with previous works.

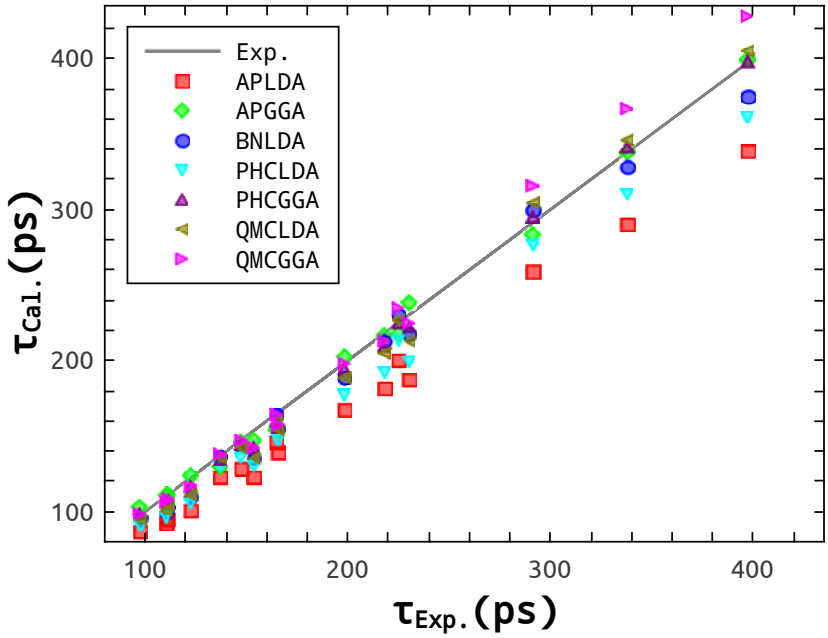


Fig. 2. Visualized comparisons between experimental values $\tau_{Exp.}$ and calculated results $\tau_{Cal.}$ based on different forms of the enhancement factor for all materials.

To make a numerical comparison, we list the values of MD and χ^2_R in Table III for different forms of the enhancement factor and for different categories of materials. As shown in the Table III, the PHCGGA and the APGGA approaches are best for all-materials calculations within the MD and χ^2_R criterions respectively, the PHCGGA approach is best for alkali-metals calculations, the QMCGGA and APGGA approaches are best for semiconductor calculations within the MD and χ^2_R criterions

Table III. Values of the mean deviation MD and the reduced chi-squared χ^2_R for different forms of the enhancement factor and different categories of materials. The numbers in bold type indicate the best values of MD/χ^2_R.

MD/χ^2_R	All-Materials	Alkali-Metals	Semiconductor	Transition-Metals
APLDA	27.7/210.09	45.4/35.4	29.9/525.8	22.8/210.5
APGGA	4.7/**6.1**	3.5/0.6	4.8/**7.0**	**3.6**/**6.5**
BNLDA	8.5/29.3	13.4/2.9	6.3/13.2	10.1/59.1
PHCLDA	17.8/106.3	25.7/11.3	21.2/256.9	16.5/120.9
PHCGGA	**4.3**/13.5	**2.8**/**0.2**	5.4/25.8	5.3/19.4
QMCLDA	8.6/37.5	9.4/2.1	11.1/71.7	9.8/53.7
QMCGGA	8.4/13	28.2/14.6	**3.7**/8.2	4.1/16.7

respectively, and APGGA approach is best for transition-metals calculations. In addition, distinct improvements upon the calculations for positron lifetime are made by recent LDA forms, especially the QMCLDA form. Considering that the common BNLDA form requires the high-frequency dielectric constant for calculating the positron lifetime, the QMCLDA is the best LDA form. However, the recent GGA forms do not yield remarkable reductions of the MD and χ^2_R while the original GGA form (APGGA) always shows a good agreement with the experimental data.

5. Summary

In this work, we test seven forms of the enhancement factor by using a useful database of experimental values based on the all-electrons approach: FLAPW. To make a numerical assessment, we used the mean-deviation and the reduced chi-squared as model selection criterions. We found that, while the PHCLDA and the QMCLDA forms of the enhancement factor make distinct improvements upon the calculations for positron lifetime compared with the older LDA form proposed by Arponen and Pajanne, the LDA forms are still disfavored by the experimental data compared with the GGA forms. Among the LDA forms, considering that the common BNLDA form requires the high-frequency dielectric for calculating the positron lifetime, the QMCLDA form is the best one supported by the experimental data used in this work. In addition, the recent GGA forms (PHCGGA and QMCGGA) do not yield remarkable reductions of the mean-deviation and the reduced chi-squared, and the orignal-GGA form given by Barbiellini et al. is still the most favored. It should be noted that, since a poor criterion result might arise from the imprecision of the selected data, further accurate experiments are needed.

Acknowledgment

This work has been supported by National Natural Science Foundation of China (Grant Nos. 11175171 and 11105139).

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