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Accurate theoretical prediction on positron lifetime of bulk materials

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ABSTRACT

Based on the first-principles calculations, we perform an initiatory statistical assessment on the reliability level of theoretical positron lifetime of bulk material. We found the original generalized gradient approximation (GGA) form of the enhancement factor and correlation potentials overestimates the effect of the gradient factor. Furthermore, an excellent agreement between model and data with the difference being the noise level of the data is found in this work. In addition, we suggest a new GGA form of the correlation scheme which gives the best performance. This work demonstrates that a brand-new reliability level is achieved for the theoretical prediction on positron lifetime of bulk material and the accuracy of the best theoretical scheme can be independent on the type of materials.

1. Introduction

During recent years positron annihilation spectroscopy (PAS) has become a valuable method to study the microscopic structure of solids [1,2] and gives detailed information on the electron density and momentum distribution [3–5] in the regions scanned by positrons. For a thorough understanding and interpretation of experimental results, an accurate theory is needed. Exact many-body theory calculations on annihilation rate and scattering dynamics can be implemented for the positron in small atom or molecule system [6–8], but is time-consuming for the positron in large many-electron system. Based on the density functional theory (DFT) [9], a full two-component self-consistent scheme [10,11] has been developed for calculating positron states in solids. Especially in bulk material where the positron is delocalized and does not affect the electron states, the full two-component scheme can be reduced without losing accuracy to the conventional scheme [10,11] in which the electronic-structure is determined by usual one-component formalism. However, there are various kinds of approximations on electron–positron correlation can be adjusted within this calculations. To improve the analyses of experimental data [12,13], we should find out which approximations are more credible to predict the positron lifetimes. Thus, in this short paper, we focus on probing the reliability level of these approximations for calculating the positron lifetimes in bulk materials.

Recently, Drummond et al. [14] made the most accurate calculations for a positron in a homogeneous electron gas by using Quantum Monte Carlo (QMC) method and gave a smaller enhancement factor compared with the popular expression [15]. Very recently, Kuriplach and Barbiellini [16,17] implemented multiple calculations of positron-annihilation characteristics in solid based on the local density approximation (LDA) or generalized gradient approximation (GGA) forms of the enhancement factor and correlation potential provided by the perturbed hypernetted chain (PHC) calculation [18,19] or reparameterized from Drummond et al.'s QMC results. Their results showed that the recent two GGA forms of the correlation schemes are needed to improve the calculated positron lifetimes. But it's hard to clearly judge and distinguish the reliability level of these two GGA models based on one by one comparisons with a small number of materials. For more recent studies on the calculations of positron lifetimes, see Refs. [19,20].

In this paper, we investigate nine LDA/GGA correlation schemes containing a new GGA form for positron lifetime calculations based on the full-potential linearized augmented plane-wave (FLAPW) plus local orbitals approach [21] for accurate electronic-structure calculations. The experimental data used in this work are composed of many observed values of materials more than twice as much as previous works [16,17,19,20]. To take into account the fact that the materials having more credible experimental values should play more important roles in these assessments, the measurement errors of these experimental values are assumed being Gaussian and then estimated by the standard deviations of collected observed values from different literatures and/or groups as in Ref. [22]. Furthermore, five subsets are structured depending

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on the number of observed values of each material to make a subtler probe. By utilizing this data, we do the initiatory numerical and statistic assessment on the reliability level of various LDA and/or GGA correlation schemes for positron lifetime calculations.

This paper is organized as follows: In Section 2, we give a brief description of the models considered here as well as the analysis methods we used. In Section 3, we introduce the experimental data on positron lifetime used in this work. In Section 4, we give the results and make some discussion based on the visualized and statistic analyses. In Section 5, we make some conclusions of this work. In addition, we present a appendix with a table listing all calculated theoretical lifetimes.

2. Theory and methodology

2.1. Theory

The positron lifetime which is the inverse of positron annihilation rate can be obtained by the following equations [15] in bulk materials,

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

where r_0 is the classical electron radius, c is the speed of light, and $\gamma(n_{e-})$ is the enhancement factor arising from the contact pair-correlation between positron and electrons. For a perfect lattice, the conventional scheme is still accurate as in this case the positron density is delocalized and vanishingly small at every point thus does not affect the bulk electronic-structure [11,15]. So in this paper the electronic density $n_{e-}(\vec{r})$ were calculated without considering the perturbation by positron based on the FLAPW approach [21] which is regarded as the most accurate method for electronic-structure calculations. The total potential sensed by positron is composed of the Coulomb potential and the correlation potential [15] between electrons and positron. Then, the positron density can be determined by solving the Kohn–Sham equation [16]. The forms of enhancement factor and correlation potential can be divided into two categories: the LDA and the GGA. Within the LDA, the corresponding correlation potential V_{corr}^{LDA} given by Ref. [15] is used. Within the GGA, the corresponding correlation potential takes the form [24,25] $V_{corr}^{\mathrm{GGA}} = V_{corr}^{\mathrm{LDA}} e^{-\alpha\epsilon/3}$, here α is an experiential parameter, and ϵ is defined as $\epsilon = |\nabla \ln(n_{e-})|^2/q_{\mathrm{TF}}^2$, ($q_{\mathrm{TF}}^{-1}$ is the local Thomas–Fermi screening length). We investigated eight existing forms of the enhancement factor and correlation potential marked by BNLDA [23], APLDA [24], APGGA [24,25], PHCLDA [18], PHCGGA [19], QMCLDA [14], fQMCLDA [16] and fQMCGGA [16], plus a new GGA form QMCGGA. All forms of the enhancement factor can be parameterized by the following equation,

$$\gamma = 1 + (1.23 r_s + a_2 r_s^2 + a_3 r_s^3 + a_{3/2} r_s^{3/2} + a_{5/2} r_s^{5/2} + a_{7/3} r_s^{7/3} + a_{8/3} r_s^{8/3}) e^{-\alpha\epsilon}, \quad (2)$$

here r_s is defined by $r_s = (3/4\pi n_{e-})^{1/3}$, and the values of the parameters a_2, a_3, $a_{3/2}$, $a_{5/2}$, $a_{7/3}$, $a_{8/3}$, and α are listed in Table 1 according to specific kind of the correlation scheme. The QMCGGA form proposed in this work is derived from the original QMCLDA parametrization introduced by Drummond et al. [14], instead of the APLDA parametrization used to fit the QMCLDA results within the fQMCLDA and the fQMCGGA. The adoption of the QMCLDA parametrization is due to the fact that the existence of positive $a_{8/3}$ term and the lager a_3 term lead to a much lager enhancement in the high r_s rigion compared with the fQMCLDA form. Nevertheless, the difference between QMCLDA and fQMCLDA at low r_s ($r_s < 6$) is minor and the fitted parameter α is only slightly changed from 0.05 to 0.063, which will result in similar lifetime values for most materials.

2.2. Computational details

In practice of this work, The WIEN2k code [26] was used for the FLAPW electronic-structure calculations. The PBE-GGA approach [27] was adopted for electron–electron exchange–correlations, the total number of k-points in the whole Brillouin zone (BZ) was set to 3375, the default values of muffin-tin radius were used, and the self-consistency was achieved up to both levels of 0.0001 Ry for total energy and 0.001 e for charge distance. To obtain the positron-state, the three-dimensional Kohn–Sham equation was solved by the finite-difference method while the unit cell of each material was divided into about 10 mesh spaces per *bohr* in each dimension. All important variable parameters were checked carefully to achieve that the computational precision of lifetime values are at most the order of 0.1 ps.

2.3. Model comparison

To make a comparison between different models, an appropriate criterion must be chosen. The popular one is the root mean squared deviation (RMSD) which is defined as the square root of the mean of the squared deviation between experimental and theoretical results. Beyond this, a comprehensive statistical analysis should be employed where the credibility of observed lifetimes can be estimated by the standard deviations. Therefore, based on the chi-squared analysis, we also adopted $\chi^2/dof = \sum_{i=1}^{N}[(X_i^{\mathrm{exp}} - X_i^{\mathbf{theo}})^2/\sigma_i^2 N]$ as another selection criterion for different models and datasets, where σ_i is the standard deviation of experimental value for each material, and the *dof* (degree of freedom) is set to N (the size of corresponding dataset) since the parameters of each model are fixed in this work. In addition, the *p*-value corresponding to each χ^2 is much more meaningful to explore the agreement level of theoretical models and experimental data. From the above definitions, one can see that the experimental data favor models producing lower (higher) values of the RMSD and/or χ^2/dof (*p*-values). Especially, the models with *p*-value < 0.01 are most likely rejected by current collected data.

Table 1
Nine parameterized LDA/GGA correlation schemes.

γ	a_2	a_3	$a_{3/2}$	$a_{5/2}$	$a_{7/3}$	$a_{8/3}$	α
BNLDA	−1.26	$1/6 - 1/6\epsilon_\infty$	0.8295	0.3286	0	0	0
APLDA	−0.0742	1/6	0	0	0	0	0
APGGA	−0.0742	1/6	0	0	0	0	0.22
PHCLDA	−0.137	1/6	0	0	0	0	0
PHCGGA	−0.137	1/6	0	0	0	0	0.10
QMCLDA	8.6957	0.1737	−3.382	0	−7.37	1.756	0
QMCGGA	8.6957	0.1737	−3.382	0	−7.37	1.756	0.063
fQMCLDA	−0.22	1/6	0	0	0	0	0
fQMCGGA	−0.22	1/6	0	0	0	0	0.05