Positron States in Solids and at Surfaces Studied by Two-component Density Functional Theory

(二成分密度汸関数法による
固体中および固体表面の陽電子状態の研究)

submitted to the Department of Physics,
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Abstract

In this thesis, we investigated positron states in solids and at metal surfaces by using two-component density functional theory (TC-DFT) within the projector augmented wave method framework. Present studies not only elucidate the key physical quantities for positron states in solids and at the surfaces, but also emphasizes the excellent performance of TC-DFT for prediction of the positron state on real materials.

First, we improved TC-DFT method to calculate the positron states at metal surfaces. Trapping of positrons by the image potential and the effect of the positron band-shift energy in the surface region are described by corrugated mirror model and ramp potential, respectively. Our method does not include any empirical parameters. The results for various physical quantities of the positron state at Al(100) clean surface are in good agreement with previous experimental results. The positron states at Li-adsorbed Al(100) surface highly depends on the coverage-atoms. Especially, the value of positronium negative ion (Ps\(^-\)) becomes negative at low Li coverage surface. This result indicates that possible emission of Ps\(^-\) from adsorbed surface. In addition to Ps\(^-\) emission, the present result for activation energy of positronium (Ps) also shows the negative value, which indicates that low energy Ps can easily emit toward vacuum from Li adsorbed Al(100) surface.

Second, we carried out performance evaluation of various positron-electron (p-e) correlation functionals for calculating positron states at surfaces using TC-DFT. As a result of the performance evaluation, we found that the p-e functionals based on generalized gradient approximation (GGA) show good performance comparing to that based on local density approximation (LDA). Since the GGA functional contains the effect of density gradient, the GGA functional well describes inhomogeneous electron density distribution rather than LDA functional. Thus, the GGA functional is suitable to describe positron states at the surface, properly.

Third, positron state in GaN with ferromagnetic Ga vacancy was investigated by using fully self-consistent TC-DFT, which includes the effect of positron for electronic states and lattice structures. Positron lifetime for Ga vacancy increases from pristine GaN because of decrease in the p-e overlap. The spin-dependent positron lifetime for ferromagnetic vacancy defect shows clear dependence on change
in the magnetization around the defects induced by change in the charge state of Ga vacancy. Thus, the positron state is sensitive to either the existence of vacancy defects or the spin-state at vacancy type defects. Hence, we conclude that spin-polarized positron annihilation spectroscopy plays an important role to prove and reveal the magnetic state of d$^0$ ferromagnetism.

Last, we studied positron state at Li- and O- adsorbed Fe(001) ferromagnetic surface by TC-DFT to understand interaction between the positron and magnetic surface. Positron lifetimes and binding energy clearly depends on change in the surface atomic geometries and electronic structures caused by adatoms. These results can be understood by change in the positron density distributions and potentials. The results for spin-dependent positron lifetime fraction are in good agreement with spin-polarization fraction at the topmost surface because the localized positrons at the surface are sensitive to the surface magnetic states. In conclusion, our theoretical prediction provides that spin-polarized positron beam can extract the outermost surface magnetic state.
Acknowledgement

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List of abbreviations

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<th>Meaning</th>
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<tr>
<td>p-e</td>
<td>positron-electron</td>
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<td>Ps</td>
<td>positronium</td>
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<td>o-Ps</td>
<td>ortho-positronium</td>
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<td>Ps⁻</td>
<td>positronium negative ion</td>
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<td>PAS</td>
<td>positron annihilation spectroscopy</td>
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<td>PALS</td>
<td>positron annihilation lifetime spectroscopy</td>
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<td>DBS</td>
<td>Doppler broadening spectroscopy</td>
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<td>ACAR</td>
<td>angular correlation of positron-electron annihilation radiation</td>
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<td>RI</td>
<td>radioisotope</td>
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<td>PAES</td>
<td>positron-annihilation induced Auger electron spectroscopy</td>
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<td>PAID</td>
<td>positron-annihilation induced ion desorption</td>
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<td>RPELS</td>
<td>re-emitted positron energy loss spectroscopy</td>
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<td>TRHEPD</td>
<td>total reflection high-energy positron diffraction</td>
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<tr>
<td>PsTOF</td>
<td>positronium time-of-flight (or -spectroscopy)</td>
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<tr>
<td>SP</td>
<td>spin-polarized</td>
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<tr>
<td>↑ (↓)</td>
<td>majority (minority) spin</td>
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<tr>
<td>DFT</td>
<td>density-functional theory</td>
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<td>PAW</td>
<td>projector-augmented wave</td>
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<td>TC-DFT</td>
<td>two-component density functional theory</td>
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<tr>
<td>SE</td>
<td>Schrödinger equation</td>
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<td>KS</td>
<td>Kohn-Sham</td>
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<td>Abbreviation</td>
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<tr>
<td>LDA</td>
<td>local-density approximation</td>
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<td>GGA</td>
<td>generalized-gradient approximation</td>
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<td>PBE</td>
<td>Perdew, Burke and Ernzerhof</td>
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<td>WDA</td>
<td>weighted-density approximation</td>
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<tr>
<td>PP</td>
<td>pseudopotential</td>
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<tr>
<td>NC</td>
<td>norm-conserving</td>
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<td>AE</td>
<td>all-electron</td>
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<td>PS</td>
<td>pseudo-</td>
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<td>US</td>
<td>ultra-soft</td>
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<tr>
<td>CV</td>
<td>conventional</td>
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<td>TC</td>
<td>two-component</td>
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<tr>
<td>ML</td>
<td>mono layer</td>
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<td>AP</td>
<td>Arponen and Pajanne</td>
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<td>QMC</td>
<td>quantum Monte-Carlo</td>
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<tr>
<td>PF</td>
<td>parameter-free</td>
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<tr>
<td>CMM</td>
<td>corrugated-mirror model</td>
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<tr>
<td>SA</td>
<td>superimposed atom</td>
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<tr>
<td>BN</td>
<td>Boroński and Nieminen</td>
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<td>SK</td>
<td>Sterne and Kaiser</td>
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<tr>
<td>DOS</td>
<td>density of state</td>
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Chapter 1

Introduction

The existence of an antiparticle of the electron, i.e., the positron, was theoretically predicted by P. M. Dirac [1] in 1930. After two years, the positron was experimentally observed by C. D. Anderson [2] in cosmic-rays. The positron has the same mass, spin (1/2) and charge as an electron, but its sign of charge is opposite to that of the electron. When a positron meets an electron, positron-electron (p-e) pair annihilation occurs, and the formed p-e pair creates $\gamma$-rays. p-e pair annihilation was investigated throughout the 1940s and 1950s, and experimental methods have been developed. By the late 1960s, it was understood that positrons were sensitive to the lattice defects in metals. In addition to p-e annihilation, it is known that a positron can create a positronium (Ps) atom [3], which is a bound state of a single positron and an electron, and a positronium negative ion (Ps$^-$), which is a bound state of a single positron and two electrons. In recent years, positron annihilation spectroscopy (PAS), utilizing p-e pair annihilation, has been shown to be a sensitive tool to detect the electronic and atomic structures at polar regions in condensed matter, such as point-defects, voids, interfaces and surfaces, among others.

As an introduction, we first mention the basics of positron annihilation and the application of PAS to solids in Sec. 1.1. Next, we discuss the slow positron beam experiment together with the positron re-emission process in Sec. 1.2. Section 1.3 explains spin-dependent positron annihilation and spin-polarized positron beam experiments. Finally, we give the organization of this thesis in Sec. 1.4.
1.1 Positron annihilation spectroscopy

PAS is a promising tool for studying defects, interfaces and voids in materials. First, we introduce p-e pair annihilation without Ps creation, which is so-called “free-positron annihilation”, in materials. Then, an experiment of PAS is briefly mentioned.

1.1.1 Positron-electron pair annihilation

Annihilation process

In this subsection, we introduce the free-positron annihilation process and its cross-section. When a positron meets an electron, p-e pair annihilation occurs, and the formed p-e pair creates $\gamma$-rays. In the p-e annihilation process, the number of $\gamma$-rays depends on the spin state of the annihilation pair. For simplicity, we consider a system of a single positron and a single electron. In such a system, the total wave function $\Psi^{p-e}$ is written as,

$$\Psi^{p-e} = \psi(r_+, r_-)\chi(+, -). \quad (1.1.1)$$

Here, $\psi(r_+, r_-)$ and $\chi(+, -)$ are the orbital and spin parts, respectively, of the total wave function $\Psi^{p-e}$. $r$ indicates the position of a particle. The indices + and − represent the positron and electron, respectively. The quantum number of the total spin $S$ for a p-e annihilation pair is one or zero because the spins for both the electron and positron are 1/2. Thus, the eigenstate of a p-e annihilation pair can be written, for the spin part, as $|S, m\rangle$ using $m$, which is the $z$-component of $S$. For the $S = 1$ state, $|S = 1, m\rangle$ is a spin triplet state, and $m$ can take three states ($m = -1, 0, 1$), and, for the $S = 0$ state, $|S = 0, m\rangle$ is a spin singlet state, and $m$ can take only the $m = 0$ state. The spin state $S$ and the number of generated photons $n$ has the following relationship, owing to the condition on the charge conjugation invariance [4],

$$(-1)^S = (-1)^n. \quad (1.1.2)$$

Because of this, $n$ depends on the spin state of the annihilation pair. For example, if $S$ is zero (and thus a spin-singlet state), $n$ can be 2, 4, 6 · · · . In general, we consider two- and three-photon ($2\gamma$ and $3\gamma$) annihilation processes to study solid-state physics, because of the much lower probability of the higher-order annihilation processes than the $3\gamma$ process.

In addition to the classification of $2\gamma$ and $3\gamma$ annihilation, it is important that the $2\gamma$ annihilation rate for the singlet state is approximately 1135 times higher
than the $3\gamma$ annihilation rate for the triplet state [5]. The positron spin states take spin-up or -down states ($|\uparrow\rangle$ or $|\downarrow\rangle$). The electron spin states also take spin-up or -down states ($|\uparrow\rangle$ or $|\downarrow\rangle$). Thus, the combinations of spin states for a p-e annihilation pair are $|\uparrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$, and $|\downarrow\downarrow\rangle$. The relationship between these spin-states for a p-e annihilation pair and the eigenstate $|S, m\rangle$, which is relative to the number of annihilation $\gamma$-rays, is expressed as:

$$|11\rangle = |\uparrow\uparrow\rangle,$$

$$|10\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle),$$

$$|1 - 1\rangle = |\downarrow\downarrow\rangle,$$

$$|00\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle).$$

These relationships are also written as:

$$|\uparrow\uparrow\rangle = |11\rangle,$$

$$|\uparrow\downarrow\rangle = \frac{1}{\sqrt{2}}(|10\rangle + |00\rangle),$$

$$|\downarrow\uparrow\rangle = \frac{1}{\sqrt{2}}(|10\rangle - |00\rangle),$$

$$|\downarrow\downarrow\rangle = |1 - 1\rangle.$$  

Since $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$ are spin triplet states, these annihilation processes provide $3\gamma$. On the other hand, $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$ are constructed with superposition of $|10\rangle$ and $|10\rangle$, which is in the ratio of 1:1. Therefore, the chance for $2\gamma$ annihilation in $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$ is equal to that for $3\gamma$ annihilation in those states. However, the p-e annihilation probability is quite different from “annihilation chance” because the annihilation probability depends on the positron annihilation rate, and again, the $2\gamma$ annihilation rate for the singlet state is 1135 times higher than $3\gamma$ annihilation rate for the triplet state.

**Cross-section for positron-electron annihilation**

In 1934, P. M. Dirac provided the spin-averaged $2\gamma$-annihilation cross-section for the $2\gamma$-annihilation process [3]. According to the Dirac formula, the p-e pair annihilation cross-section in the non-relativistic limit, i.e., $v \ll c$, is written as

$$\sigma_{2\gamma} = \frac{\pi r_0^2 c}{v},$$  

where $r_0 = e^2/(4\pi\epsilon_0 mc^2)$ and $v$ are the classical electron radius and the positron velocity relative to that of the electron, respectively. Here, $e$, $m$, $c$ and $\epsilon_0$ indicate
the electron charge, electron mass, velocity of light and permittivity of the vacuum, respectively. If we assume that the electron density at the positron site is \( n_- \), the 2\( \gamma \)-annihilation rate (\( \lambda_{2\gamma} \)) is obtained as,

\[
\lambda_{2\gamma} = \sigma_{2\gamma} n_- v = \pi r_0^2 c n_- .
\] (1.1.12)

Thus, the positron annihilation rate depends on only \( n_- \). The positron annihilation lifetime obtained by the inverse of \( \lambda \) also depends on \( n_- \). Thanks to the \( n_- \)-dependence of \( \lambda \), we can simply understand experimental results. It is noted that the electron density in eq. (1.1.12) differs from that without a positron. Because of p-e Coulomb interaction, a positron in the solid is screened by electrons. Therefore, the true positron annihilation rate is larger than that without screened electrons. The ratio of the screened to unscreened \( \lambda \) is the so-called enhancement factor, which will be discussed in Sec. 2.2.3.

In addition to 2\( \gamma \)-annihilation, the spin-averaged three-photon p-e annihilation cross-section \( \sigma_{3\gamma} \) was obtained by Ore and Powell [5]:

\[
\sigma_{3\gamma} = \frac{4(\pi^2 - 9) \alpha r_0^2 c}{3 v},
\] (1.1.13)

where, \( \alpha = e^2/(4\pi\varepsilon_0 hc) \) is the fine structure constant. Since the 3\( \gamma \)-annihilation probability is approximately 378 times smaller than the 2\( \gamma \)-annihilation probability \(^1\), 2\( \gamma \)-annihilation predominantly occurs in solids. For this reason, 2\( \gamma \)-annihilation is mainly considered in solid-state physics using positron annihilation, which will be discussed the next subsection.

### 1.1.2 Positron annihilation spectroscopy

When the positron is bombarded into the solid, the positron is immediately thermalized by plasmon-, phonon- and ionization-excitation processes, among others. The thermalized positron moves in the solid via thermal diffusion and annihilates with the electrons. Then, annihilation \( \gamma \)-rays are generated, and the \( \gamma \)-rays carry information of the solid-state electrons. Thus, we can extract the electronic properties of a solid via positron annihilation.

PAS is an experimental technique using p-e pair annihilation. PAS is a non-destructive spectroscopy method that allows studying a variety of phenomena and material properties on an atomic scale. Figure 1.1 shows a schematic image of PAS. PAS experiments usually utilize 2\( \gamma \)-annihilation. In a PAS experiment, there are

\(^1\)The ratio of 2\( \gamma \)- to 3\( \gamma \)-annihilation rates is 1135: 1, and the ratio of 2\( \gamma \)- to 3\( \gamma \)-annihilation events is 1:3, owing to the spin state of p-e annihilation pair. Because of this, the ratio of 2\( \gamma \)- to 3\( \gamma \)-annihilation probabilities is obtained as approximately 378: 1.
three widely used techniques [3,6–8]: (i) positron annihilation lifetime spectroscopy (PALS), (ii) Doppler broadening spectroscopy (DBS), and (iii) Angular correlation of p-e annihilation radiation (ACAR). Here, we focus on a PALS experiment, while DBS and ACAR experiments will be discussed in Appendix A.

A PALS experiment measures $2\gamma$-annihilation $\gamma$-rays as a function of measurement time. First, a positron is generated by $\beta^+$ decay from a radioisotope (RI) (typically, $^{22}$Na is used for a PAS experiment), and $\beta^+$ decay also generates a $\gamma$-ray (its energy is 1.27 MeV for $^{22}$Na). The $\gamma$-ray radiated from the RI is used as the initial time, and the $\gamma$-ray generated by p-e annihilation is used as the stop signal. The differences in times between start and stop signals provide an annihilation lifetime spectrum. The slope of lifetime spectrum provides the averaged positron lifetime.

In addition to p-e annihilation, the positron annihilation site is also important for understanding the experimental positron lifetime. Generally, if defects exist in a solid, thermal positrons are easily trapped by the defects, owing to the lower repulsive Coulomb interaction between the nuclei and positrons than in a pristine region. Trapped positrons annihilate with electrons around the defect, and the positron lifetime becomes longer than that in pristine bulk because the positron annihilation rate is proportional to electron density as mentioned in Sec. 1.1.1. Thus, we can extract information on the electron density around lattice defects in a solid via the change in positron lifetime. For this reason, PAS is a promising tool for identifying the existence of defects in solids.
1.2 Slow positron beam

A slow positron beam technique [9] has been developed to study the surface electronic and atomic structures [10]; PALS [11], one- and two-dimensional ACAR [12–14], positron-annihilation induced Auger electron spectroscopy (PAES) [15,16], positron annihilation-induced ion desorption (PAID) [17,18], re-emitted positron energy loss spectroscopy (RPELS) [19] and total reflection high-energy positron diffraction (TRHEPD) [20,21]. Furthermore, experimental methods using Ps have also been developed for the study of surface analysis, such as Ps time-of-flight spectroscopy (PsTOF) [22,23]. In this section, the positron re-emission processes are discussed together with the key factors for determining the positron re-emission process, *i.e.*, the work functions for the positron, Ps and Ps⁻.

1.2.1 Positron re-emission process

The positron re-emission process plays an important role for the detection of electronic structure at a material surface using a slow positron beam technique. Figure 1.2 shows a schematic image of positron re-emission processes. When positrons

![Figure 1.2: Schematic image of positron re-emission processes.](image)

are slowly incident onto a material surface, the positrons are immediately thermal-
ized by plasmon-, phonon- and ionization-excitation processes, and then a fraction of
these thermal positrons returns from the bulk to the surface via thermal diffusion.
The returned positrons mainly experience the following five processes: a positron
(i) is emitted toward the vacuum owing to the negative work function, (ii) creates
a Ps and is emitted toward the vacuum, (iii) creates a Ps and is emitted toward
the vacuum, (iv) is trapped by the surface induced image-potential and annihilates
with a surface electron, or (v) is trapped by the surface induced image-potential and
creates a physisorbed state of a Ps atom. In the processes (i), (ii) and (iii), the work
functions for the positron, Ps and Ps are important factors for the determination of
whether thermal positrons can be emitted toward the vacuum. This determination
will be discussed in the following sections. The slow positron beam experiment de-
tects surface electronic and atomic structures using the positron re-emission process.
Therefore, the energetics of surface positrons, i.e., work functions of the positron,
Ps and Ps, positron binding energy and activation energy of Ps essentially play
key roles in the positron re-emission processes.

1.2.2 Positron work function

In this subsection, we first consider the metal surface using a jellium model [24],
which gives a good representation of the electronic properties of simple metal sur-
faces, to understand the essential relationship between the positron surface poten-
tial and work function. Figure 1.3 shows a schematic representation of the electron
density distribution and potential at the metal surface. At the metal surface, the
electron density slightly spills out into the vacuum region, which results in a surface
dipole layer that acts like a potential barrier for the electrons. The electron work
function (Φ−) is defined by the difference between the height of the surface dipole
barrier (D (> 0)) and the electron chemical potential (μ−) in the metal:

\[ Φ− = D − μ−. \]  (1.2.1)

For a positron, the surface dipole barrier repulsively acts on the positron because of
its positive charge. Therefore, positron work function (Φ+) is defined by,

\[ Φ+ = −D − μ+. \]  (1.2.2)

Here, μ+ is the chemical potential of the positron in metals, which is determined by
the p-e correlation energy and positron-lattice electrostatic interaction energy [25].
As a result of the repulsive surface dipole barrier, some metal surfaces have negative
positron work functions. For example, W, Pt, Al, Ni and Cu surfaces have negative
work functions [10,26]. The negative value of Φ+ indicates that a positron at the
surface can be ejected into the vacuum spontaneously, and the absolute value of Φ+
Figure 1.3: Schematic image of (a) electron density distribution at a metal surface. The blue and red curves represent the electron density distribution and uniform background, respectively. (b) Various energies relevant to a study on the electron work function. The red curve represents the effective potential of the electron. The $z$-axis indicates the normal to the surface plane, and $z = 0$ corresponds to the background edge [24].

is the maximum kinetic energy of the emitted positron in the re-emission process. Recent positron beams utilize W mesh as the moderator, owing to the high negative value of positron work function (approximately $-3$ eV) [7,26].

1.2.3 Work functions for Ps and Ps$^-$

Positronium emission from a surface

In the positron re-emission process, Ps creation is one of the important phenomena because the Ps atom cannot be formed in the metal, owing to the strong electron screening effect [27]. Since the electron density decreases at the surface and the electron screening effect also decrease, the Ps atom can be created at the topmost metal surface. Thus, Ps creation in the re-emission process has the information of the electronic structure only at the topmost surface [23,28]. The absolute value of the negative work function of Ps ($\Phi_{Ps}$) indicates the maximum kinetic energy of the emitted Ps. $\Phi_{Ps}$ is defined by,

$$\Phi_{Ps} = \Phi_- + \Phi_+ - E^b_{Ps},$$

(1.2.3)
where, $E_{Ps}^b$ is the binding energy of the $1s$ state of Ps, which is 6.8 eV. From eqs. (1.2.1) and (1.2.2), $\Phi_{Ps}$ is also expressed as,

$$\Phi_{Ps} = -(\mu_- + \mu_+) - E_{Ps}^b.$$ (1.2.4)

Therefore, the maximum value of the Ps kinetic energy does not depend on the surface dipole barrier. Furthermore, $\Phi_{Ps}$ is estimated by the experimental Ps energy distribution spectrum, and the value of $\Phi_{Ps}$ corresponds to the tail of the Ps energy distribution spectrum in the higher-energy region [29,30].

**Positronium negative ion emission from a surface**

The first observation of Ps$^-$ was done by A. P. Mills Jr. [31]. He found Ps$^-$ emission from a graphite thin film. Y. Nagashima *et al.* have also found spontaneous Ps$^-$ emission from a polycrystalline W surface [32]. After this observation, Y. Nagashima *et al.* have found that the increases in Ps$^-$ yield from alkali-metal-adsorbed W surfaces [33,34]. Increase in Ps$^-$ yield and durable emission sources of Ps$^-$ open the door to a new experimental probe, which is the energy-tunable Ps beam. Unfortunately, a Ps cannot be directly accelerated by an electric field because Ps is a neutrally charged atom. On the other hand, a Ps$^-$ can be accelerated by an electric field, owing to its negative charge. After the acceleration of a Ps$^-$, the Ps beam is produced using photodetachment of Ps$^-$ [35]. Thus, we can obtain the energy-tunable Ps beam by controlling the electric-field acceleration of Ps$^-$. If the Ps$^-$ can be steadily formed in such a way to produce a large number of Ps$^-$, the Ps beam can be produced with stronger intensity, which can be used to significantly advance the study of surface physics. The work function of Ps$^-$ is defined as [32]

$$\Phi_{Ps^-} = 2\Phi_+ + \Phi_+ - E_{Ps^-}^b,$$ (1.2.5)

where $E_{Ps^-}^b$ is the formation energy of Ps$^-$, which is approximately 7.13 eV, as obtained by theoretical calculation. If $\Phi_{Ps^-}$ is negative, a re-emitted positron can be ejected into the vacuum as a Ps$^-$ from the host surface. In addition to the context of solid-state physics, the high yield of Ps$^-$ plays an important role in the experimental study of quantum electrodynamics because Ps$^-$ is known as the lightest and most fundamental three-body bound state. For example, recently, Michishio *et al.* have observed a shape resonance of the Ps$^-$ using spontaneously emitted Ps$^-$ from a Na-coated W surface [36].
1.3 Spin-polarized positron annihilation

In Sec. 1.1, we described spin-unpolarized positron annihilation processes and rates. In this section, we introduce the spin-dependent positron annihilation and its application to bulk and surface analysis. After thermalization of incident positrons in ferromagnets, thermalized positrons annihilate with spin-polarized electrons. The positron lifetime has two components corresponding to majority and minority spin (\(\uparrow\) and \(\downarrow\)) electrons, owing to the spin-selection rule [37]. Figure 1.4 shows a schematic image of spin-dependent positron annihilation for ferromagnetic materials. Here, we focus on the \(2\gamma\)-annihilation process. Since the incident positron that is generated by \(\beta^+\) decay of a RI has spin-polarization in the direction of movement, positron annihilation selectively occurs. If the spin-configuration of an annihilation pair of spin-polarized electrons and a positron is parallel (anti-parallel), such as in the left (right) panel in Fig. 1.4, a positron annihilates with \(\uparrow\) (\(\downarrow\)) electrons. For this reason, we can extract information on spin-polarization of magnetic materials via the spin-polarized (SP-) PAS by controlling the direction of the magnetic field.

![Figure 1.4: Schematic image of spin-dependent positron annihilation in a ferromagnet. The blue and red arrows represent the direction of spin-polarization of positron and electrons, respectively. In this figure, we consider only the \(2\gamma\)-annihilation.](image)

Recently, a SP-positron beam and positron source have been developed and used for studying magnetism [38–40]. Kawasuso et al. have carried out an experiment of SP-PAS for typical ferromagnets [41–43]. They have verified that SP-positron lifetime and intensity of SP-DBS correlated with the magnetization of ferromagnetic materials. In addition, the spin-resolved Fermi surface of the localized ferromagnetic Heusler compound [44] and the on-site coulomb interaction energy (so-called Hubbard \(U\)) for bulk Ni [45] were also investigated using SP-PAS experiments.

For investigating the surface magnetism, SP-positron beam is also a useful tool utilizing the positron surface re-emission process. The SP-slow positron beam for
studying surface magnetism was carried out by Gidley et al. in 1982 [46] for the first time. Their experiment extracted the electron spin-polarization at a Ni surface via o-Ps creation at the outermost metal surface. However, SP-slow positron beam experiments for studying surface magnetism have not been carried out for approximately 30 years. Recently, Kawasuso et al. have measured the accumulation of current-induced spin-polarization at various metal surfaces [47,48] and the phenomena of charge-spin conversion and spin diffusion at one mono-layer Bi-coated Ag surface [49] using the reliable SP-positron beams. For these reasons, a SP-positron beam experiment is expected to be a useful probe for studying spin-polarization at the topmost surface.

1.4 Organization of this thesis

This thesis is organized as follows. General theoretical frameworks that can be found in the literature are briefly described in Chap. 2. Sections 2.1 and 2.2 give brief descriptions of the density functional theory and two-component density functional theory, respectively. Chapters 3, 4, 5 and 6 provide the results of our studies. First, in Chap. 3, we discuss the results of positron states at Li-adsorbed Al(100) surfaces. Second, we show the results of positron states at Li-adsorbed Al(100) surfaces using various positron-electron correlation functionals in Chap. 4. Then, Chap. 5 shows the results of spin-dependent positron lifetimes for localized positron at a Ga vacancy in GaN. Next, in Chap. 6, we give the results of positron states at Li- and O-adsorbed Fe(001) ferromagnetic surfaces. Finally, the summary of this thesis is given in Chap. 7.
Chapter 2
Method

In this chapter, we describe the theoretical methods used throughout this thesis. First, Secs. 2.1.1-2.1.5 and 2.1.6 provide theoretical overviews of density functional theory (DFT) and projector augmented wave (PAW) method, respectively. Next, theoretical framework of two-component DFT is summarized in Sec. 2.2. Section 2.2.1 shows the formalisms of positron-electron DFT. Then, the computational method of positron lifetime and details of positron surface potential are given in Sec. 2.2.3. Last, we briefly describe our computational code ABINIT in Sec. 2.3. Unless otherwise specified, Hartree atomic units, \( m = \hbar = e = 1 \), are used throughout this thesis.

2.1 Density functional theory

To get things started, it is worth noting that the DFT is a great successful method to solve the Schrödinger equation (SE) of the three dimensional many-body system. The formulation of the DFT was developed by Hohenberg and Kohn [50] and Kohn and Sham [51] in 1960’s. In materials science, we need the many-body wave function for electrons, which is the solution of the SE, to describe the ground state properties of the system. However, in the DFT, the many-body wave function is not required, and the electron density, which only depends on the three dimensional spatial coordinates, is essentially important to describe the electronic ground state in the materials. Thanks to the DFT, we can describe the system energy and other ground-state properties as a functional of one-body electron density. Since DFT can reduce the computational costs for this reason, nowadays the DFT is applied to wide variety of research fields: atomic physics, molecular physics, solid state physics, chemistry, bioscience, engineering, etc.

In this section, first, we introduce basic theorem of DFT, which is so-called
Hohenberg-Kohn theorem. Then, we describe the derivation of Kohn-Sham (KS) equation, which is exact single particle self-consistent equation similar to the Hartree-Fock equation. Last, we introduce local-density approximation for exchange-correlation term in KS equation.

2.1.1 Hohenberg-Kohn theorem

As preparation for giving proof of Hohenberg-Kohn theorem, first, we consider a system of interacting \( N \)-electrons, and the Hamiltonian for a such system can be written as

\[
\hat{H} = \hat{T} + U + V. \tag{2.1.1}
\]

The first term is the kinetic energy of the electrons

\[
\hat{T} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{i}^{2}. \tag{2.1.2}
\]

The second term of Hamiltonian represents the electron-electron Coulomb interaction energy

\[
U = \sum_{i<j} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|}, \tag{2.1.3}
\]

and the last term is given by the following form

\[
V = \sum_{i=1}^{N} v(\mathbf{r}_{i}), \tag{2.1.4}
\]

which can include the electron-nuclear interaction or external electric field potential. Furthermore, we define the density operator as

\[
\hat{n}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_{i}). \tag{2.1.5}
\]

In this expression, electron density is given by the expectation value of the density operator, \( n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle \).

From these preparations, we show the two theorems, which were given by Hohenberg and Kohn.

**Hohenberg-Kohn theorem 1:** If the ground state is not degenerated, external field \( v(\mathbf{r}) \) and wave function \( \Psi \) is uniquely determined by ground state density
This is Hohenberg-Kohn’s first theorem, which is so-called “one-to-one correspondence”. This gentle lemma represents that all ground state properties can be expressed by the universal density functional. For examples, total energy functional for ground state electron density \( E[n] \) can be written as

\[
E[n] = F[n] + \int d\mathbf{r} v(\mathbf{r}) n(\mathbf{r}),
\]

\[
F[n] = \langle \Psi | (\hat{T} + U) | \Psi \rangle.
\]

The Hohenberg-Kohn’s second theorem is related to the variational principle for ground-state total energy functional \( E[n] \).

**Hohenberg-Kohn theorem 2:** Minimum value of total energy functional \( E[n(\mathbf{r})] \) is given by correct \( n(\mathbf{r}) \). Hohenberg-Kohn’s second theorem gives the following variational principle,

\[
E_{GS} \leq E[\hat{n}(\mathbf{r})],
\]

where \( E_{GS} \) and \( \hat{n}(\mathbf{r}) \) represent ground state system energy and arbitrary electron density satisfying \( \hat{n}(\mathbf{r}) \geq 0 \) and \( \int d\mathbf{r} \hat{n}(\mathbf{r}) = N \) (\( N \) is the number of electrons), respectively. This theorem allows us to search the ground state using following variational principle,

\[
\frac{\delta}{\delta n(\mathbf{r})} \left[ E[n(\mathbf{r})] - \mu \left( \int n(\mathbf{r}) d\mathbf{r} \right) \right] = 0,
\]

where, \( \mu \) is Lagrange multiplier, which ensures the correct total number of electrons.

In this subsection, we discussed the Hohenberg-Kohn theorem. This theorem is a rigid lemma for describing ground state \( N \)-electron system. Hence, the solution of DFT is equal to that of SE. For this reason, the electronic state calculation based on DFT is called “\( ab \) initio” method.

### 2.1.2 The Kohn-Sham equations

In the Hohenberg-Kohn variational principle, the many-body wave function is not necessary, and the electron density, which only depends on the three dimensional spatial coordinates, is an important physical quantity to describe the electronic ground state in the materials. After a report on Hohenberg-Kohn theorem, Kohn and Sham proposed a clever method to evaluate the total energy functional \( E[n] \) using single particle orbital of non-interactive system \( \psi_i(\mathbf{r}) \). Traditionally, the single particle orbital and the non-interactive system are called the Kohn-Sham (KS)
orbital and KS system, respectively. The KS orbital is obtained as the solution of following self-consistent equations,

\[
-\frac{1}{2} \nabla^2 + V_{\text{eff}}(r) \psi_i(r) = \varepsilon_i \psi_i(r),
\]

\[
n(r) = \sum_i f_i |\psi_i(r)|^2,
\]

\[
V_{\text{eff}}(r) = V_{\text{ext}}(r) + \int \frac{n(r')}{|r-r'|} dr' + v_{\text{xc}}(r).
\]

Here, \(V_{\text{eff}}(r), \varepsilon_i\) and \(f_i\) indicate a local single electron potential, KS eigenvalue and occupation number, respectively. \(V_{\text{ext}}(r)\) is the term of external field. In the calculation of solids, this term represents the electrostatic electron-nuclei interaction. Hereafter, we use \(V_{\text{ion}}(r)\) for the expression of external term. The local electron-electron exchange-correlation potential \(v_{\text{xc}}(r)\) is defined as

\[
v_{\text{xc}}(r) = \frac{\delta E_{\text{xc}}[n(r)]}{\delta n(r)},
\]

\[
E_{\text{xc}}[n(r)] = F[n(r)] - \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|} drdr' - T_s[n(r)].
\]

Here, \(T_s[n(r)]\) is a kinetic energy functional of KS system. In eq. (2.1.14), exchange-correlation functional \(E_{\text{xc}}[n(r)]\), which includes all many-body effects of interacting system, is defined. Thanks to KS representation, the problem of solving many-body SE is replaced by solving the single-electron eqs. (2.1.11)–(2.1.12), self-consistently.

The KS orbitals are a good basis for qualitative interpretation of molecular orbitals. Furthermore, the KS eigenvalues \(\varepsilon_i\) have a certain physical interpretation. Janak [52] shows the following relation,

\[
\varepsilon_i = \frac{\partial E}{\partial f_i}.
\]

This relationship is called Janak’s theorem. Since the energy level of highest occupied state in the metal indicates Fermi energy \(E_F\), the highest occupied KS eigenvalue of metal system gives the Fermi energy \(E_F\) of the system.

2.1.3 Local density approximation

If the exact form of \(E_{\text{xc}}[n]\) is once obtained, all of the electronic ground state properties of materials are completely determined because DFT is a formally exact theory. However, such a functional form has not been found thus far. There are some approximate forms of \(E_{\text{xc}}[n]\). The local-density approximation (LDA) is one of the
most widely used approximations to the $E_{xc}[n]$. In the LDA, exchange-correlation functional is written as,

$$E_{xc}[n(r)] \approx \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}[n(\mathbf{r})],$$

(2.1.16)

where $\varepsilon_{xc}[n(\mathbf{r})]$ is chosen by a very accurately determined exchange-correlation energy per particle of a uniform electron gas of density $n$. The LDA is a good approximation for a system that has a slowly varying density. Thus, the LDA would be suitable to describe simple metallic systems because electrons in the systems behave as nearly free electrons. Although the LDA is the simple approximation for the $E_{xc}[n]$, the LDA functional has given surprisingly good results for many systems. However, the LDA functionals fail to describe the electronic structures of the systems such as transition metals.

### 2.1.4 Generalized gradient approximation

To go beyond the LDA, a generalized gradient approximation (GGA) has been developed to carry out more reliable electronic structure calculations. In the GGA, the exchange-correlation functional is written as,

$$E_{xc}[n] \approx \int d\mathbf{r} f_{xc}(n(\mathbf{r}), |\nabla n(\mathbf{r})|).$$

(2.1.17)

The exchange-correlation potential in the GGA can be written as

$$v_{xc}(\mathbf{r}) = \frac{\partial f_{xc}}{\partial n} - \nabla \cdot \frac{\partial f_{xc}}{\partial \nabla n(\mathbf{r})}.$$  

(2.1.18)

The GGA functionals are called “semi-local functionals” because the functionals contain the terms that are the functional of $\nabla n(\mathbf{r})$. Thus, GGA functionals can be more suitable to describe the highly varying electron-density systems than LDA functionals. One of the most popular GGA functionals is that proposed by Perdew, Burke and Ernzerhof (PBE) [53].

Both LDA and GGA work successfully in describing many physical properties. However, these functionals have a serious error in determining excited properties. The typical one is underestimate of a fundamental bandgap of semiconductors and insulators [54]. To overcome these bandgap problems and improve computational accuracy, many functionals have been developed such as meta-GGA [55, 56], HSE hybrid-functional [57–59], weighted-density approximation (WDA) functional [60–64], etc.

Throughout this thesis, we use the PBE functional because the functional well reproduces non-uniform electronic properties of the bulks with vacancies and solid surfaces.
2.1.5 Plane-wave basis set

For solid state physics, plane-wave basis sets are very useful and suitable for the electronic wave functions in bulk and at solid surfaces. The plane-wave basis sets are most useful in systems where the potential is periodic,

\[ V(r + R) = V(r), \]  

(2.1.19)

where \( R = n_1a_1 + n_2a_2 + n_3a_3 \), \( n_1, n_2 \) and \( n_3 \) are integers. \( a_1, a_2 \) and \( a_3 \) are the base vectors of the lattice. According to the Bloch theorem, the KS wave function of the electrons \( \psi_{i,k}(r) \) (\( i \) is a band index, and \( k \) is a crystal momentum) can be written as a product of a periodic part

\[ u_{i,k}(r + R) = u_{i,k}(r), \]

and a wave-like part \( e^{ik \cdot r} \)

\[ \psi_{i,k}(r) = u_{i,k}(r)e^{ik \cdot r}, \]  

(2.1.20)

for each crystal momentum \( k \). Because of its periodicity, \( u_{i,k}(r) \) can be expanded in terms of plane-waves

\[ u_{i,k}(r) = \sum_G C_{i,G+k} e^{iG \cdot r}. \]  

(2.1.21)

These functions are orthogonal

\[ \int_{\Omega} d\boldsymbol{r} \psi_{i,k}^*(r) \psi_{j,k}(r) = \Omega \delta_{i,j}, \]  

(2.1.22)

where \( \Omega \) is crystal volume of the periodically repeated cell. From the above, the KS wave function \( \psi_{i,k}(r) \) within plane-wave basis set is represented as

\[ \psi_{i,k}(r) = \sum_G C_{i,G+k} e^{i(G+k) \cdot r}. \]  

(2.1.23)

The combination of a plane-wave expansion and a pseudopotential approach allows us to reduce the computational costs and describe valence electron states with periodic boundary condition, precisely. For this reason, many first-principles computational codes employ plane-wave basis sets within pseudopotential framework for describing solid state electronic structures.
2.1.6 Projector-augmented wave method

The properties of electronic structure in solids are mainly determined by valence electrons. For this reason, the pseudopotential (PP) approximation has been usually used in the DFT calculations. In the PP approximation, core electrons are frozen and treated as a potential function for valence electrons. Thanks to the PP approach, one can reduce the computational costs and efficiently describe the valence states in the DFT calculation.

Historical remarks of pseudopotential approach

Norm-conserving (NC) PPs from ab initio calculation were introduced by Hammann, Schlüter and Chiang [65] for the first time. In their scheme, the all-electron (AE) wave function is replaced by a nodeless soft wave function (so-called pseudo (PS) wave function) inside the core radius. NC-PPs have the important condition that the PS wave function must have the same norm as the AE wave function within the core radius. Unfortunately, as a result of satisfying the NC condition, NC-PP calculation requires huge plane-wave basis sets to reproduces the properties of elements with strongly localized orbitals such as first-row, 3\textit{d} and rare-earth elements.

In 1990, Vanderbilt proposed ultrasoft (US) PP framework to overcome huge computational costs of NC-PP [66]. In his method, the NC constraint is relaxed, and localized atom-centered augmentation charges are introduced to make up for the resulting charge deficit. These augmentation charges are defined by the charge density difference between the AE and the PS wave function. The US-PP approach is now widely applied to DFT calculation of 3\textit{d}-transition metals for reducing computational costs and improving computational accuracy.

The concept of US-PP has been developed by Blöchl in 1994 [67]. Blöchl’s method is called projector-augmented wave (PAW) method, which is an intermediate method between the PP and AE approaches. Here, we briefly describe the basics and main ideas of PAW formalism for electron wave functions and valence-electron energies. Further details are found in Refs. [67], [68], and [69].

Formalism of projector-augmented wave method

Here, we briefly describe the formalisms of wave functions and total energy functional within the PAW framework. The basic idea of PAW formalism is a linear and invertible transformation (the PAW transformation) that connects the true KS wave functions $|\Psi_{ik}\rangle$ with the pseudo-wave functions $|\tilde{\Psi}_{ik}\rangle$:

$$|\Psi_{ik}\rangle = |\tilde{\Psi}_{ik}\rangle + \sum_{\alpha} (|\phi_{\alpha}\rangle - |\tilde{\phi}_{\alpha}\rangle) \langle \tilde{\rho}_{\alpha} | \tilde{\Psi}_{ik}\rangle,$$

(2.1.24)
where the index $\alpha$ indicates identification of a set of partial waves (with angular momentum quantum numbers $(l_\alpha, m_\alpha)$) located at different atomic positions $\mathbf{R}_\alpha$. The partial waves $|\phi_\alpha\rangle$ forms a atomic orbitals, and the $|\tilde{\phi}_\alpha\rangle$ are pseudized-partial waves obtained from $|\phi_\alpha\rangle$ without the condition of norm-conservation. $|\tilde{p}_\alpha\rangle$ are dual functions of $|\tilde{\phi}_\alpha\rangle$, called projectors. It is noted that the PS wave functions $|\tilde{\Psi}_{ik}\rangle$ can directly compare to the PS wave functions within US-PP framework. Thus, the computational cost of PAW method is comparable to that of the US-PP calculation [68]. From eq. (2.1.24), total electron density $n(\mathbf{r})$ can be written as

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + n^1(\mathbf{r}) - \tilde{n}^1(\mathbf{r}) + n_c(\mathbf{r}),$$  

(2.1.25)

where $n_c(\mathbf{r})$ is frozen core electron density. $\tilde{n}$, $n^1$ and $\tilde{n}^1$ are PS plane-wave, AE and PS atomic on-site contributions to the total valence electron density, respectively. The definitions of PS plane-wave, AE and PS on-site terms are

$$\tilde{n}(\mathbf{r}) = \sum_{ik} f_{ik} \langle \tilde{\Psi}_{ik} | \tilde{\Psi}_{ik} \rangle,$$

$$n^1(\mathbf{r}) = \sum_{\alpha \beta} \rho_{\alpha \beta} \langle \phi_\alpha | \phi_\beta \rangle,$$

$$\tilde{n}^1(\mathbf{r}) = \sum_{\alpha \beta} \rho_{\alpha \beta} \langle \tilde{\phi}_\alpha | \tilde{\phi}_\beta \rangle.$$

Here, $f_{ik}$ are occupation numbers of KS eigenstates and $\rho_{\alpha \beta}$ are occupancies of each $(\alpha, \beta)$ sites, respectively. The definition of $\rho_{\alpha \beta}$ is

$$\rho_{\alpha \beta} = \sum_{ik} f_{ik} \langle \tilde{\Psi}_{ik} | \tilde{p}_\alpha \rangle \langle \tilde{p}_\beta | \tilde{\Psi}_{ik} \rangle.$$  

For these derivations, PS wave function and PS density are transformed to AE valence wave function and AE density. Thus, we can carry out the electronic structure calculations within AE accuracy by using the PAW method.

Blöchl has also derived KS total energy density functional within the PAW framework. From eq. (2.1.25), we obtain a direct expression for the total energy functional as

$$E = \tilde{E} + E^1 - \tilde{E}^1,$$  

(2.1.26)
with
\[
\tilde{E} = \sum_{ik} f_{ik} \langle \tilde{\Psi}_{ik} \rangle - \frac{\nabla^2}{2} |\tilde{\Psi}_{ik}| + E_{xc}[\tilde{n} + \tilde{n} + \tilde{n}_c] \\
+ E_H[\tilde{n} + \tilde{n}] + \int d\mathbf{r} v_H[\tilde{n}_{Zc}](\tilde{n} + \tilde{n}) + U(\mathbf{R}, Z_{\text{ion}}),
\]
\[
E^1 = \sum_{\alpha \beta} \rho_{\alpha \beta} \langle \phi_{\alpha} \rangle - \frac{\nabla^2}{2} |\phi_{\beta}| + E_{xc}[n^1 + n_c] \\
+ E_H[n^1] + \int_{V_R} dr v_H[\tilde{n}_{Zc}](n^1),
\]
\[
\tilde{E}^1 = \sum_{\alpha \beta} \rho_{\alpha \beta} \langle \tilde{\phi}_{\alpha} \rangle - \frac{\nabla^2}{2} |\tilde{\phi}_{\beta}| + E_{xc}[\tilde{n}^1 + \tilde{n} + \tilde{n}_c] \\
+ E_H[\tilde{n}^1 + \tilde{n}] + \int d\mathbf{r} v_H[\tilde{n}_{Zc}](\tilde{n}^1 + \tilde{n}),
\]
where \(\tilde{E}\) corresponds to the plane-wave contribution to the total energy. \(E^1\) and \(\tilde{E}^1\) are AE and PS atom on-site contributions, respectively. \(U(\mathbf{R}, Z_{\text{ion}})\) represents ionic energy term using Ewald summation. \(\tilde{n}\) is the compensation charge density, which is added to the PS plane-wave and PS atomic on-site densities (\(\tilde{n}\) and \(\tilde{n}_c\)) to correctly reproduce the multipole moment of the AE density. \(\tilde{n}_c\) indicates pseudized core electron density. \(n_{Zc} (\tilde{n}_{Zc})\) is the sum of nucleus charge and \(n_c (\tilde{n}_c)\). The PAW total valence electron energy is also described within the accuracy of AE calculation level.

## 2.2 Two-component density functional theory

In this section, we mention the DFT for positron-electron system, which is called as two-component density functional theory (TC-DFT) \([6,70]\).

### 2.2.1 Two-component density functional theory

The main ideas of TC-DFT are based on the ordinary one-particle DFT, which was discussed in Sec. 2.1. In the TC-DFT, the total energy of the system is given by the functionals of electron and positron densities,

\[
E(n_-, n_+) = F[n_-] + F[n_+] \\
+ \int d\mathbf{r} V_{\text{ion}}(\mathbf{r}) \{n_- (\mathbf{r}) - n_+ (\mathbf{r})\} \\
- \int d\mathbf{r} \int d\mathbf{r}' \frac{n_- (\mathbf{r}) n_+ (\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\
+ E_{\text{corr}}^{n_- n_+}[n_+, n_-],
\]  
(2.2.1)
where $n_-$ and $n_+$ are the electron and positron densities, respectively, and $E_{\text{corr}}^{p-e}[n_+, n_-]$ is the p-e correlation energy functional. Here, $F[n]$ is the universal one-component energy functional, which is defined as

$$F[n] = T_s[n] + \frac{1}{2} \int dr \int dr' \frac{n(r)n(r')}{|r - r'|} + E_{\text{xc}}[n], \quad (2.2.2)$$

where $T_s[n]$ is the kinetic energy for KS system and $E_{\text{xc}}[n]$ is the electron (positron) exchange-correlation energy. The variational KS procedure applied to $E[n_-, n_+]$ then leads to a set of KS equations for electrons and positrons:

$$\left[ -\nabla^2 + \frac{\delta E_{\text{xc}}[n_-]}{\delta n_-} - \phi(r) + \frac{\delta E_{\text{corr}}^{p-e}[n_-, n_+]}{\delta n_-} \right] \psi^-_i(r) = \epsilon^-_i \psi^-_i(r), \quad (2.2.3)$$

$$\left[ -\nabla^2 + \frac{\delta E_{\text{xc}}[n_+]}{\delta n_+} + \phi(r) + \frac{\delta E_{\text{corr}}^{p-e}[n_-, n_+]}{\delta n_+} \right] \psi^+_j(r) = \epsilon^+_j \psi^+_j(r), \quad (2.2.4)$$

where

$$\phi(r) = \int dr' \frac{-n_-(r') + n_+(r')}{|r - r'|} + V_{\text{ion}}(r). \quad (2.2.5)$$

Here, $\psi^-_i$ ($\psi^+_j$) and $\epsilon^-_i$ ($\epsilon^+_j$) are KS orbitals and eigen-energies for electrons (positrons), $\phi(r)$ is the electrostatic potential, respectively. $V_{\text{ion}}(r)$ indicates the interaction between the particles and nuclei. Throughout this thesis, the interaction between the valence and core electrons are described within PAW pseudopotential framework.

We assume a single positron in the calculation box, so that the self-interaction terms in the positron KS equation are removed. Thus, the KS equation for the positron becomes

$$\left[ -\nabla^2 + \phi'(r) + \frac{\delta E_{\text{corr}}^{p-e}[n_-, n_+]}{\delta n_+} \right] \psi^+_j(r) = \epsilon^+_j \psi^+_j(r), \quad (2.2.6)$$

with

$$\phi'(r) = \int dr' \frac{-n_-(r')}{|r - r'|} + V_{\text{ion}}(r). \quad (2.2.7)$$

Practically, there are two computational schemes within TC-DFT framework; conventional TC-DFT scheme (CV scheme) [71] and fully self-consistent TC-DFT scheme (TC scheme) [72].

**CV scheme:** The CV scheme is known as the most convenient calculation scheme for positron ground state. First, the electron equation, eq. (2.2.3), is solved by the ordinary DFT scheme without a positron, and then the self-consistent electronic structure of the relaxed atomic geometry is obtained. Next, the positron equation,
eq. (2.2.6), is solved with the electron ground-state density to obtain the positron ground-state.

**TC scheme:** In the TC scheme, the electronic and positronic KS equations are solved simultaneously, by taking into account the self-consistent p-e charges. After the convergence in the p-e states, forces acting on atoms are calculated including contributions from the electrons and the positron. The p-e ground state of stable atomic structures can be determined by relaxing the atomic positions according to the forces and repeating the self-consistent calculations for p-e states until the global convergence is obtained.

### 2.2.2 Positron-electron correlation potential

Here, we explain the details of positron-electron correlation potential with the generalized gradient approximation. First, we mention the GGA functional formalism. The early GGA functionals include one adjustable parameter $\alpha$ to determine the positron lifetime precisely. Then, the best choice of $\alpha$ to reproduce the positron properties in many materials is described. Last, the most recent GGA functional without the adjustable parameter is described.

**Generalized gradient approximation for positron-electron correlation functional**

In the electronic structure calculations, the LDA shows a clear tendency in overestimating the magnitude of the correlation energy. The overestimation of the correlation energy has been traced back to the shape of the correlation hole close to the electron. In the GGA for electrons the correlation energy is improved by reducing the charge redistributed by the correlation hole near the fixed electron for a definition of this redistributed charge. Similarly, the gradient correction for the p-e correlation reduces the electron density near the positron and thereby decreases the enhancement factor and increases the positron lifetime. This will also reduce the magnitude of the p-e correlation energy.

The formalism of GGA for p-e correlation potential was introduced by Barbiellini et al., in 1995 [73]. In the GGA, the effects of the nonuniform electron density are described in terms of the ratio between the local length scale of the density variations $|\nabla \ln n_\gamma|$ and the local Thomas-Fermi screening length $1/q_{TF}$. The lowest order gradient correction to the LDA correlation hole density is proportional to the parameter ($\epsilon$) as:

$$\epsilon = |\nabla \ln n_-|^2 / q_{TF}^2. \quad (2.2.8)$$
This parameter is taken to describe also the reduction of the electron screening cloud near the positron. In the limit of homogeneous electron gas, $\epsilon$ is equal to zero, while $\epsilon$ can be an extremely large value in the case of rapid density variations. In order to interpolate between the limits $\epsilon = 0$ and $\epsilon \to \infty$, the screening electron density ($\Delta n_-$) is introduced as:

$$\Delta n_\text{GGA} = \Delta n_\text{LDA} e^{-\alpha \epsilon},$$

(2.2.9)

where the superscripts GGA and LDA indicate screened electron density with GGA and LDA, respectively. The enhancement factor corresponding to the above relation is

$$\Gamma^\text{GGA} = 1 + (\Gamma^\text{LDA} - 1) e^{-\alpha \epsilon}.$$  

(2.2.10)

Here, $\alpha$ is an adjustable parameter to be determined so that the calculated positron lifetimes and affinities reproduce the experimental values for a large number of different types of solids. The best choice of $\alpha$ will be mentioned later.

The gradient correction to p-e correlation energy is obtained by using the relationship between annihilation rate and correlation energy [74]:

$$E^\text{corr} \sim (\lambda - \lambda_{\text{IPM}})^{1/3},$$

(2.2.11)

where $\lambda$ and $\lambda_{\text{IPM}}$ are p-e pair annihilation rate with and without the enhancement (the enhancement will be discussed in Sec. 2.2.3). Using eq. (2.2.11), we can scale the LDA correlation energy to the GGA correlation energy:

$$E^\text{GGA}_\text{corr} = E^\text{LDA}_\text{corr} \left( \frac{\lambda^\text{GGA} - \lambda_{\text{IPM}}}{\lambda^\text{LDA} - \lambda_{\text{IPM}}} \right)^{1/3} = E^\text{LDA}_\text{corr} e^{-\alpha \epsilon/3}.$$  

(2.2.12)

Thus, the p-e correlation functional in GGA is given as

$$V^\text{GGA}_\text{corr} (\mathbf{r}) = V^\text{LDA}_\text{corr} (\mathbf{r}) e^{-\alpha \epsilon/3}.$$  

(2.2.13)

**The description of $\alpha$**

The early GGA functionals for p-e correlation energy include one adjustable parameter $\alpha$. The choice of $\alpha$ depends on the original p-e correlation energy data. There are two p-e correlation energy data: one is provided by Arponen and Pajanne (AP) [75], the other is recently provided by Drummond et al. For the LDA functionals based on Arponen and Pajanne (AP) data, 0.22 is the best choice of the $\alpha$ [73], while 0.05 is the best choice for a LDA functional based on Drummond et al. data [76].
In early GGA p-e correlation functional, constant adjustable parameter \( \alpha \) was used. Recently, Barbiellini and Kuriplach pointed out the drawback of constant \( \alpha \): the p-e correlation potential has unphysical oscillations near the nuclei due to the shell structure of core electrons. In order to remove the drawback of GGA p-e correlation functionals with the constant \( \alpha \), Barbiellini and Kuriplach provides local density dependent form of \( \alpha \) [77]. This new GGA functional is called as the parameter-free GGA (PF-GGA) functional. In the PF-GGA, the local density dependence of \( \alpha \) is found as

\[
\alpha(r) = -\frac{3}{16} \frac{\beta}{V_{LDA}^{\text{corr}}(r)},
\]

(2.2.14)

where the constant \( \beta = 0.066725 \) Ha is also found in the coefficient of density gradient [78] in the limit of high density for the electron-electron correlation energy [53]. It is noted that QMC-LDA correlation potential is used for determining the \( \alpha(r) \) in the PF-GGA.

### 2.2.3 Positron lifetime

#### Lifetime formulation

Here, we mention the formulation and computational method of positron lifetimes. The electron and positron densities obtained by the TC-DFT calculation are used for the calculation of positron lifetime for \( 2\gamma \)-annihilation [6]

\[
\frac{1}{\tau} = \lambda = \pi c r_0^2 \int dr n_{-}(r)n_{+}(r)\Gamma[n_-].
\]

(2.2.15)

Here, \( \Gamma[n_-] \) is the enhancement factor, which corresponds to the screening of positron by electrons. The enhancement factor is represented by p-e pair correlation functional, which was obtained by the first-principles calculation of a single positron in the homogeneous electron gas [75,79]. Thus the practical form of enhancement factor is determined by the approximate form of p-e correlation energy functional and potential [6]. The spin-polarized positron lifetimes for majority and minority spin electrons (\( \tau^\uparrow \) and \( \tau^\downarrow \)) are also calculated by [80,81]

\[
\frac{1}{\tau^{\uparrow(\downarrow)}} = \lambda^{\uparrow(\downarrow)} = 2\pi c r_0^2 \int dr n_{-}^{\uparrow(\downarrow)}(r)n_{+}(r)\Gamma[n_-].
\]

(2.2.16)

Owing to the spin-selection rule and assumption of a single positron in the unit cell, we can determine \( \tau^{\uparrow(\downarrow)} \) for \( 2\gamma \) annihilation by only the spin states of the electron densities.
Enhancement factor

Since the enhancement factor $\Gamma$ is very important in determining the positron lifetime as shown in eqs. (2.2.15) and (2.2.16), the physical meaning of enhancement factor is mentioned here. First, we introduce the momentum distribution of p-e annihilation pair density ($\rho(p)$), which is observed in the DBS and ACAR experiments, as

$$\rho(p) = \sum_{i_{\text{occ}}} \left| \int dr \Psi_{i}^{\text{ep}}(r, r) e^{-ip \cdot r} \right|^2,$$  \hspace{1cm} (2.2.17)

where $p = (p_x, p_y, p_z)$ is p-e pair momentum, and $\Psi_{i}^{\text{ep}}(r_-, r_+)$ are p-e pair wave functions of the positron at $r_+$ and electron in the state $i$ at $r_-$. The summation in eq. (2.2.17) runs over all occupied electronic states $i_{\text{occ}}$. Inverse of total spin-unpolarized positron lifetime $\tau$ or annihilation rate $\lambda$ is expressed as

$$\frac{1}{\tau} = \frac{\pi r_0^2 c}{2(\pi)^{3}} \int dp \rho(p) \hspace{1cm} = \pi r_0^2 c \int dr \sum_{i_{\text{occ}}} |\Psi_{i}^{\text{ep}}(r, r)|^2,$$ \hspace{1cm} (2.2.18)

The p-e pair wave function is expressed using electron wave functions $\Psi_{i}^{-}(r_-; r_+)$, which includes the positron effect and positron wave function $\Psi_{+}(r_+)$ as

$$\Psi_{i}^{\text{ep}}(r_-, r_+) = \Psi_{+}(r_+) \Psi_{i}^{-}(r_-; r_+).$$ \hspace{1cm} (2.2.19)

Second, we introduce unperturbed electron wave function ($\Psi_{i}^{0}(r_-)$). The electron screening density ($\Delta n_{-}(r_-; r_+)$) induced by the positron is written using unperturbed electron wave function;

$$\Delta n_{-}(r_-; r_+) = \sum_{i_{\text{occ}}} \left| \Psi_{i}^{-}(r_-; r_+) \right|^2 - \sum_{i_{\text{occ}}} \left| \Psi_{i}^{0}(r_-) \right|^2 = \sum_{i_{\text{occ}}} \left| \Psi_{i}^{-}(r_-; r_+) \right|^2 - n_{-}^{0}(r_-).$$ \hspace{1cm} (2.2.20)

Here $n_{-}^{0}(r_-)$ is unperturbed electron density. The screening electron density distribution $\Delta n_{-}(r_-; r_+)$ should satisfy the charge-neutrality condition at any $r_+$

$$\int \Delta n_{-}(r_-; r_+) dr_- = 1.$$ \hspace{1cm} (2.2.21)
In terms of the conditional wave functions eq. (2.2.19) and screening charge density eq. (2.2.20), eqs. (2.2.17) and (2.2.18) can be respectively re-written as

\[
\rho(p) = \sum_{i_{occ}} \left| \int d^3r \Psi_{i_{occ}}^p(r, \mathbf{r}) e^{-ip \cdot r} \right|^2
\]

\[
= \sum_{i_{occ}} \left| \int d^3r \Psi_+(r) \Psi_i^-(r; \mathbf{r}) e^{-ip \cdot r} \right|^2
\]

\[
= \sum_{i_{occ}} \left| \int d^3r \Psi_+(r) \Psi_i^0(r; \mathbf{r}) \sqrt{\gamma(r, i)} e^{-ip \cdot r} \right|^2, \quad (2.2.22)
\]

and

\[
\frac{1}{\tau} = \lambda = \frac{\pi r_0^2 c}{(2\pi)^3} \int d\mathbf{p} \rho(p)
\]

\[
= \pi r_0^2 c \int d\mathbf{r} \sum_{i_{occ}} |\Psi_{i_{occ}}^p(r, \mathbf{r})|^2
\]

\[
= \pi r_0^2 c \int d\mathbf{r} \sum_{i_{occ}} |\Psi_+(r) \Psi_i^-(r; \mathbf{r})|^2
\]

\[
= \pi r_0^2 c \int d\mathbf{r} |\Psi_+(r)|^2 \sum_{i_{occ}} |\Psi_i^-(r; \mathbf{r})|^2
\]

\[
= \pi r_0^2 c \int d\mathbf{r} n_+(r) \sum_{i_{occ}} |\Psi_i^-(r; \mathbf{r})|^2
\]

\[
= \pi r_0^2 c \int d\mathbf{r} n_+(r) n_i^0(r) \left(1 + \frac{\Delta n_-(r; \mathbf{r})}{n_0^0(\mathbf{r})} \right), \quad (2.2.23)
\]

where the two-particle enhancement functions \((\gamma(r, i))\) are defined as

\[
\gamma(r, i) = \frac{|\Psi_i^-(r; \mathbf{r})|^2}{|\Psi_i^0(\mathbf{r})|^2}. \quad (2.2.24)
\]

Each of the functions \(\gamma(r, i)\), as well as the function

\[
\Gamma(r) = 1 + \frac{\Delta n_-(r; \mathbf{r})}{n_0^0(\mathbf{r})}, \quad (2.2.25)
\]

has the following clear physical meaning. \(\gamma(r, i)\) describes the enhancement of the density of the each electronic state \(i\) at the positron site from its initial density \(|\Psi_i^0(r; \mathbf{r})|^2\), under the condition that the positron is at the position \(\mathbf{r}\). While the \(\Gamma(r)\) corresponds to the charge redistribution of total electron density at the positron site. The functions \(\gamma(r, i)\) and \(\Gamma(r)\) are so-called enhancement factors, which were introduced in Sec. 1.1.1.
Figure 2.1: (a) Schematic of the potentials for a positron at a clean metal surface. The solid black curve represents the effective potential for the positron, and the red and blue dotted curves represent the electrostatic and p-e correlation potential, respectively. The positron work function is denoted as $\Phi_+$, which has a negative value. The band-sift energy measured from the bottom of the effective potential is denoted by $E_0$. Coordinates $z_1$ and $z_0$ denote the positions of the topmost surface layer and the effective image plane, respectively. The figure has been adapted with permission from Ref. [82] and is copyrighted by the American Physical Society. (b) Schematic of the ramp potential and image potential at the surface. Blue and red curves are ramp potential and asymptotic behavior of image potential, respectively. The depth of the ramp potential is $E_0$. The definitions of coordinates $z_1$ and $z_0$ are the same as in (a). $z_2$ represents the position at jellium background edge. Blue circles indicate the positions of atomic layers. The distance between the atomic layers is $d$. 

\[ z_1 \quad z_0 \quad \frac{d}{2} \quad z_0 \]

\[ E \quad \frac{d}{2} \quad E_0 \quad \text{Ramp potential} \]

\[ \sim -\frac{1}{4(z-z_0)} \]

\[ \text{Image potential} \]
2.2.4 Positron surface potential

Thermalized positrons near a surface are considered to be trapped by the surface image potential. To study the state of a surface-trapped positron, a slab model is used to represent the metal surface, as in typical DFT calculations. However, simulation of the surface trapping state of positron in the slab model has two problems. One is the p-e correlation potential in the vacuum region and the other is the positron KS potential in the slab region [83, 84].

Corrugated mirror model

The p-e correlation potential can be well given in the bulk using the ordinary TC-DFT. However, the p-e correlation potential in the slab model within the ordinal TC-DFT can not generate the asymptotic behavior of the image potential [70], and thus the surface trapping state of positron can not be correctly calculated. To overcome this problem, the so-called corrugated mirror model (CMM) [85] was implemented to correct the positron surface potential in the vacuum region. The image potential in the CMM is expressed by:

\[ V_{\text{corr}}(z \to \infty) = -\frac{1}{4(z-z_0)}, \quad z_0 < z. \]  
(2.2.26)

Here, the z-axis is perpendicular to the surface and \( z_0 \) is the position of the effective image plane, which corresponds to the center of mass of surface charge distributions (in Fig. 2.1 (a) and (b)). The value of \( z_0 \) is determined using the method reported by Lang and Kohn [86]. It is noted that eq. (2.2.26) has an unphysical divergence near the \( z = z_0 \) region. To remove this divergence, a cut-off energy of 6.8 eV is used, which corresponds to the binding energy of Ps, for the magnitude of the image potential [85]. The image potential is smoothly connected to the p-e correlation potential in the bulk region of the slab.

Ramp potential

The other problem in the description of the positron effective potential in the slab calculation is related to the positron band-shift energy (\( E_0 \)), which is the positron zero-point energy in the crystal arising from the positron-ion interaction [25]. To take account of this effect, band-shift energy is added to the positron effective potential as the form of the ramp potential [87–91]:

\[ V_{\text{ramp}}(z) = \begin{cases} 
  E_0, & z < z_1, \\
  E_0(z - z_2)/(z_1 - z_2), & z_1 < z < z_2, \\
  0, & z_2 < z. 
\end{cases} \]  
(2.2.27)
where \( z_1 \) is the atomic position in the topmost surface layer and \( z_2 \) is the position distant from \( z_1 \) to the vacuum by a half of the interlayer distance of the atomic layer (in Fig. 2.1 (a) and (b)). \( z_2 \) is regarded as the physical edge position of the metal surface in the jellium model [86]. \( E_0 \) is given by [92]:

\[
E_0 = \Phi_+ - |D + E_{\text{corr}}|,
\]

where \( \Phi_+ \) is the positron work function, \( D \) is the surface dipole barrier, \( E_{\text{corr}} \) is the p-e correlation energy, and \( |D + E_{\text{corr}}| \) is the energy of the bottom of the positron effective potential with respect to the vacuum level. A schematic illustration of these potentials is shown in Fig. 2.1. The TC-DFT calculation for a positron in the crystal is conducted first and the positron affinity \( A_+ \) is obtained from the electron (positron) chemical potential, \( \mu_- (\mu_+) \) as [93,94]:

\[
A_+ = \mu_- + \mu_+.
\]

The electron work function \( \Phi_- \), which is obtained in the DFT calculation using the slab model, is then used to determine the positron work function as:

\[
\Phi_+ = -D - \mu_+ = -(\Phi_+ + \mu_-) - \mu_+ = -A_+ - \Phi_-.
\]

\( E_0 \) (in Eq. (2.2.28)) is thus determined by the first-principles calculations. For comparison, the compensation potential is obtained by resorting to the experimental positron work function in the previous studies of superimposed-atom methods [87–91] (superimposed atom method will be given in Appendix. B).

To calculate the \( \tau \) for the surface, the enhancement factor \( \Gamma(n_-) \) in eqs. (2.2.15) and (2.2.16) is set to zero in the image potential region (\( z > z_0 \) in Fig. 2.1), where the electron screening effect is negligible [95].

### 2.3 Computational code

Here, we briefly describe the computational code used in this thesis. Our calculations of electron and positron states have been done using first-principles computational code ABINIT [96–98]. ABINIT is a free-source program package to simulate the total energy, charge density and electronic structure of systems made of electrons and nuclei (molecules and periodic solids) using DFT within the pseudopotential and plane-wave basis set framework. The excited-state properties are determined by many-body \( GW \) approximation, many-body Bethe-Salpeter calculation and time-dependent DFT calculation (for molecule). The further details of ABINIT code
are given in the ABINIT homepage [99]. The brief and useful tutorials for many calculations are also given in the website. The implementations of DFT and TC-DFT in the ABINIT are based on plane-wave basis sets within the PAW method framework. The PAW potentials were generated by ATOMPAW code [69,100]. We implemented CMM, ramp potential, formalism of spin-dependent positron lifetime and various p-e correlation functionals in the ABINIT code.
Chapter 3

Positron states at Li-adsorbed Al(100) surface

The positron surface state and the energetics for positron reemission are investigated using TC-DFT in the PAW framework. Trapping of positrons by the surface image potential and the effect of the positron band-shift energy in the surface region are appropriately described by the CMM and the ramp potential, respectively, without empirical parameters. The results obtained for various physical quantities of positron states on a clean Al(100) surface, i.e., the affinity, work function, lifetime, binding energy, and activation energy, are in good agreement with the experimental results. The positron states on Li-adsorbed Al(100) surfaces are highly dependent on the Li coverage. In particular, the work function of Ps\(^-\) becomes negative at low Li coverage, which indicates the possible emission of Ps\(^-\) from the adsorbed surface. The present study not only elucidates the key energetics that are responsible for positron re-emission from the surface, but also emphasizes the excellent performance of TC-DFT for prediction of the positron state on real surfaces. The results in this chapter were published in Ref [82].

3.1 Introduction

Theoretical studies on the positron states at the solid surfaces are not yet complete, particularly with the first-principles calculation methods. Puska and Nieminen [101] have developed a flexible superimposed-atom (SA) method for the study of positrons under various conditions. The electron density is constructed simply by superimposing free atoms in the appropriate geometry. This technique has been shown to produce reliable results for many practical applications [87–91]. On the other hand, studies on the positron states in the bulk crystal using the self-consistent electron
densities of optimized atomic geometries have been conducted using TC-DFT [6,70], which is known to well reproduce the experimentally measured positron lifetimes, both in perfect crystals and crystals with vacancy defects. However, for the surface, the TC-DFT scheme has only been applied to the study of positrons at jellium substrates that have neither realistic atomic configurations nor variation of electron density near atoms [83,84,102].

In our study, we aim to understand the basics of positron states at metal surfaces using TC-DFT calculations of surfaces with realistic atomic configurations. The self-consistent electron density of the fully relaxed atomic geometry is used for calculation of the positron states. The CMM is used together with the ramp potential without any empirical parameters by taking account of the surface image potential and the band-shift energy. This scheme is applied to Al(100) surfaces with various Li-coverage.

3.2 Computational details

TC-DFT calculations were conducted for the positron surface state at the Li-adsorbed Al(100) surfaces. The surface is represented by a slab model having seven atomic layers and a vacuum region with a thickness of 40 Å. The atomic geometry in the slab is optimized and all calculations of the electron and positron states are carried out using the ABINIT code within the PAW method.

3.2.1 The electron states

The PAW potentials were generated using all-electron calculation code ATOMPAW. For Al and Li atoms, the valence electron configurations were 2s²2p⁶3s²3p¹ and 1s²2s¹, respectively. The number of k-point sampling was 10 × 10 × 10 for bulk and 10 × 10 × 1 for slab calculations. The cut-off energy for plane-wave expansion was 20 Ha for Al bulk and clean surface, and 25 Ha for the Li-adsorbed Al surfaces. The PBE functional [53] was used for description of exchange-correlation functional. Cell optimization was performed for the Al bulk and the theoretical lattice constant was obtained as 4.04 Å, which was used for construction of the Al slab. The atomic geometry in the slab was relaxed until all forces acting on the atoms were smaller than 5.0 × 10⁻⁴ Ha/bohr. The adsorption sites of Li atoms on the Al(100) surface were chosen as hollow sites. For the relaxation of the slab geometry, we used the Broyden-Fletcher-Goldfarb-Shanno minimization method [103–106].
3.2.2 The positron states

The positron ground state is calculated by the CV scheme. The cut-off energy for plane-wave expansion was the same as that for calculations of the electron ground state. \( k \)-point sampling was only \( \Gamma \) point (\( k = 0 \)). The LDA functional parameterized by Boroński and Nieminen (BN-LDA) \cite{70} was used for the p-e correlation functional. The CMM and ramp potential were implemented in the ABINIT code for the positron calculation.

3.3 Results and discussions

3.3.1 Positron states in Al bulk

First, we briefly show the results of the positron lifetime and affinity in the pristine Al bulk. Table 3.1 shows the results of \( \tau \) and \( A_+ \) for Al bulk as well as experimental data. Present results are in good agreement with previous experimental data \cite{22, 107}.

<table>
<thead>
<tr>
<th>( \tau ) (ps)</th>
<th>( A_+ ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>163</td>
</tr>
<tr>
<td>Experimental</td>
<td>166</td>
</tr>
</tbody>
</table>

\( A_+ \) is an important factor to calculate the key-energetic values in determining the positron re-emission process. For instance, work function of Ps can be determined by

\[
\Phi_{Ps} = -A_+ - E^Ps_b.
\]

This equation is derived from eqs. (1.2.4) and (2.2.29) and \( E^Ps_b = 6.8 \) eV is binding energy of Ps. Here, the \( \Phi_{Ps} \) is -2.45 eV, which is in good agreement with PsTOF measurement value of \( \Phi_{Ps} \) (-2.6 eV) \cite{22}. The negative value of Ps work function indicates that the positron tends to be ejected into the vacuum as Ps atom. Other key-energetic values will be discussed in Sec. 3.3.3.

3.3.2 Positron states at Li-adsorbed Al(100) surfaces

Next, we present the results of positron states at Li-adsorbed Al(100) surfaces using CMM and ramp potential method. Table 3.2 shows the results of \( \tau \) at Al(100) surfaces with various Li coverages. The result of \( \tau \) for clean surface well reproduces
Table 3.2: Positron lifetimes ($\tau$) at Al(100) surfaces with various Li coverage as well as experimental lifetime for clean surface observed by Lynn et al. [108](in ps). Here, the mono-layer is abbreviated as ML.

<table>
<thead>
<tr>
<th>Coverage</th>
<th>Calculated</th>
<th>0.25 ML</th>
<th>0.50 ML</th>
<th>0.75 ML</th>
<th>1.00 ML</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean</td>
<td>562</td>
<td>432</td>
<td>311</td>
<td>263</td>
<td>172</td>
</tr>
<tr>
<td>Experimental</td>
<td>580±10</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

regarding the dependence of $\tau$ on the coverage in Table 3.2, we found a monotonic decrease in $\tau$ with increasing Li coverage. In particular, $\tau$ at 1.00 mono-layer (ML) becomes close to that in the Al bulk, which is shown in Table 3.1. To understand this aspect, the positron KS potential ($V_{\text{eff}}^+$) are plotted together with the positron density distribution along the $z$-direction in Fig. 3.1.

Figure 3.1: Laterally averaged (a) positron effective potential ($V_{\text{eff}}^+$) and (b) positron density distribution ($n_+$) along the $z$ direction (perpendicular to the Al(100) surface). $V_{\text{eff}}^+$ = 0 is the vacuum level and $z = 0$ is the atomic position of the topmost surface layer. The black, red, blue, green, and orange curves represent $V_{\text{eff}}^+(z)$ and $n_+(z)$ for the clean Al(100) surface and that with 0.25 ML, 0.50 ML, 0.75 ML, and 1.00 ML coverage, respectively. The figure has been adapted with permission from Ref. [82] and is copyrighted by the American Physical Society.

has a positive charge, so that there are repulsive (attractive) interactions between positrons and ions (electrons), which explains the $V_{\text{eff}}^+$ in the interior region of the Al slab in Fig. 3.1 (a). On the other hand, there are significant changes in the $V_{\text{eff}}^+$ with different Li coverage, which indicates that Li adatoms have a significant influence on the positron properties. In Fig. 3.1 (b), there is an apparent shift of the $n_+(z)$ peak.
Figure 3.2: Side and top views of positron density distributions in Al(100) surfaces with various Li coverage; (a) clean, (b) 0.25 ML, and (c) 0.50 ML. The positron density is shown as a blue transparent isosurface with an isovalue of 0.0015 a.u. The Al and Li atoms are represented by light brown and green colored balls, respectively. The figure has been adapted with permission from Ref. [82] and is copyrighted by the American Physical Society.

position toward the $-z$ direction (the interior region of the slab) with increasing Li coverage. For the clean surface, the positron is localized in the image potential region. However, when the Li adatoms are adsorbed, $n_+(z)$ is pushed from the Li-adatoms to the Al substrate and broadened. This feature is also clearly evident in Fig. 3.2 for the Li coverage up to 0.5 ML, where the positron is distributed so as to avoid the Li-adatoms. The high electron density in the Al substrate means that a positron can easily annihilate with an electron, which is $\tau$ decreases with increasing Li coverage. It is noted that at 1.00 ML coverage, $n_+(z)$ spreads in the interior region of the slab, as shown in Fig. 3.1 (b). Therefore, the $\tau$ at 1.00 ML becomes close to that in the Al bulk. For these reasons, we can conclude that the positron states at the surface is highly sensitive to the surface electronic states, which are modified by Li adsorption.

### 3.3.3 Energetics of positron re-emission processes

Here, we discuss the coverage dependence of key-energetic values for positron re-emission processes at Li-adsorbed Al(100) surfaces. Figure 3.3 shows the results of work function of electron ($\Phi_-$), positron ($\Phi_+$), Ps$^-$ ($\Phi_{Ps^-}$), binding energy ($E_b$) and activation energy for Ps ($E_a$) at Al(100) surfaces with various Li coverages.

First, we discuss coverage dependence of $\Phi_-$ (black circles), which is calculated by difference between energy level of vacuum ($V_{vac}$) and Fermi energy of the system $E_F$ as

$$\Phi_- = V_{vac} - E_F.$$  

(3.3.2)
Figure 3.3: Coverage dependence of work function of electron ($\Phi_-$), positron ($\Phi_+$), Ps$^-$ ($\Phi_{Ps^-}$), binding energy ($E_b$) and activation energy for Ps ($E_a$) (in eV). Black, red, orange, blue and green circles represent the results of $\Phi_-$, $\Phi_+$, $\Phi_{Ps^-}$, $E_b$ and $E_a$, respectively. Black, red, orange, blue and green cross symbols indicate the experimental values of $\Phi_-$, $\Phi_+$, $\Phi_{Ps^-}$, $E_b$ and $E_a$, respectively. Dotted curves are drawn to help guide the eyes. The data of this figure is listed in Ref. [82]. They are copyrighted by the American Physical Society.

For the clean surface, calculated $\Phi_-$ that is 4.39 eV well reproduces experimental $\Phi_-$ that is 4.41 eV [109]. Over all features of $\Phi_-$ at adsorbed surfaces, the $\Phi_-$ decreases comparing to the clean surface, which is caused by charge transfer from Li adatoms to the Al substrate. As a result of the charge transfer, surface dipole barrier decreases, and $\Phi_-$ becomes smaller than clean surface. The minimum value of $\Phi_-$ is realized at 0.25 ML covered surface. For higher coverage than the 0.25 ML, $\Phi_-$ increases with increasing coverage. This feature comes from the fact that bonding between the lone 2s electrons of Li atoms can occur and this suppresses electron transfer from Li atoms to the Al substrate.

Second, positron work function is mentioned (red circles). The work function of
positron ($\Phi_+$) is calculated by

$$\Phi_+ = -A_+ - \Phi_-.$$  

(3.3.3)

Generally, the value of positron affinity is negative [6], thus negative value of $\Phi_+$ can be determined by eq. (3.3.3). The result of $\Phi_+$ at clean surface, -0.05 eV is slightly higher than experimental value of -0.19 eV [9]. This overestimation comes from the p-e LDA functional, which will be discussed in Chap. 4. The coverage dependence of $\Phi_+$ shows a tendency opposite to that of $\Phi_-$. This behavior is easily understood by eq. (3.3.3). Owing to a positive charge of the positron, the positron oppositely experiences change in surface dipole barrier comparing with the electrons. The dependence of $\Phi_+$ on the Li coverage can also be understood in this way and is consistent with the experimental results for other metal surfaces with different species of adsorbed atoms [33,110]. It is noted that $\Phi_+$ becomes positive at finite Li coverage, which means that positrons are easily trapped inside an Al(100) surface with Li adatoms.

Third we discuss the results of work function for Ps$^-$ (orange circles), which is calculated by

$$\Phi_{\text{Ps}^-} = 2\Phi_- + \Phi_+ - E_{\text{Ps}^-} = -A_+ + \Phi_- - E_{\text{Ps}^-},$$  

(3.3.4)

where $E_{\text{Ps}^-} = 7.13$ eV is the binding energy for Ps$^-$ [33]. For the clean surface, $\Phi_{\text{Ps}^-}$ is calculated to be positive and higher than experimental value [111]. When the surface is covered with Li atoms, $\Phi_{\text{Ps}^-}$ shows strong dependence on Li coverage; $\Phi_{\text{Ps}^-}$ significantly decreases at 0.25 ML coverage, and increases again at higher coverage until 1.00 ML. A notable feature of $\Phi_{\text{Ps}^-}$ is the large negative values at low Li coverage, 0.25-0.50 ML. This is essentially important for efficient emission of Ps$^-$ from the surface. Therefore, Ps$^-$ can be spontaneously ejected into the vacuum from a Li-adsorbed Al(100) surface.

Fourth, we discuss the results of positron binding energy ($E_b$) (blue circles), which is calculated as the difference between the vacuum level and the energy level of the positron trapped by the surface. The result of $E_b$ for clean surface is in good agreement with the experimental data [112]. $E_b$ increases after 0.25 ML Li adsorption and decreases with increasing Li coverage. The dependence of $E_b$ on the Li coverage is similar to that for the positron work function (red circles), which is due to the change in the surface dipole layer. This can be interpreted from Fig. 3.1 (a); the positron effective potential has a well near the effective image plane ($z_0 = 1.63$ Å for the clean surface), where the well depth is the largest at 0.25 ML coverage and then decreases with increasing Li coverage, having a tendency similar to that for $E_b$. Accordingly, the dependence of $E_b$ on the Li coverage is attributed to the
rearrangement of the surface-electron charge distribution caused by electron transfer from the Li adatoms to the Al substrate.

Finally, the activation energy $E_a$ for a thermalized Ps atom, which is created by the positron trapped by the surface image potential, is discussed (green circles). $E_a$ is calculated from [9]

$$E_a = E_b + \Phi_+ - E_{Ps}^b.$$  

For the clean Al(100) surface, the calculated $E_a$ is positive and in good agreement with the experimental value [113]. This agreement is not trivial. In a previous study, Cuthbert has studied $E_a$ for Al clean surface and shown the negative value of $E_a$ in the hydrodynamic model considering the interaction of a positron with the electron gas (so-called positron channel), whereas the $E_a$ becomes positive with interaction between Ps and metal surface (so-called Ps channel) [114]. The work of Cuthbert has been confirmed by Platzman and Tzoar [115]. Furthermore, the Ps channel has been recently considered within robust formalism based on the DFT calculation and applied to the studies of Ps states at the $\alpha$-quartz [116] and the topological insulator surfaces [117]. In our TC-DFT simulation, electrons and a positron are treated on an equal footing, and it relies on the p-e correlation functional to give correct p-e interaction. The fact that our result of the Al clean surface agrees with those of previous Ps channel calculations indicates the effectiveness of the present TC-DFT implementation.

After the Li adsorption, $E_a$ becomes negative and decreases with increasing Li coverages up to 0.75 ML. This dependence of $E_a$ on the coverage is not a general property for adsorbed surfaces but rather specific to Li-adsorbed Al(100) surface. In fact, dependence of $E_a$ on the coverage was found to be different with respect to the adsorbed surfaces in previous studies [118,119]. The feature is due to the fact that $E_a$ is determined by two factors, $E_b$ and $\Phi_+$, which have different dependence on the coverage. The negative value of $E_a$ indicates that if the positron that is trapped by image potential combines with a single electron and create a Ps atom, Ps atom can be ejected into the vacuum. Following these results and discussions, we predict that Ps emission from the Al(100) surface is considerably enhanced with increasing Li adsorption.

### 3.4 Conclusion

We extended the TC-DFT method to the calculation of the positron states at the metal surfaces, and the method was applied to Li-adsorbed Al(100) surfaces with real atomic geometries. The calculations for positron states at the clean Al(100)
surface well reproduces experimentally observed lifetime, binding energy and activation energy. The positron lifetime decreases with increasing Li coverage because the positron densities are pushed towards the bulk region by the adatoms. The dependence of binding energy on the Li coverage shows the similar behavior to that for positron work function. Thus, we can naturally consider that the change in the binding energy correlates with change in the surface dipole barrier. In addition, the key-energetic values for determining positron re-emission process are calculated by positron affinity and positron binding energy. For the surfaces covered with Li adatoms, the calculated results indicate a strong dependence of the work functions for electrons, positrons and Ps$^-$ on the coverage, which can be understood from analysis of the surface dipole barrier. The activation energy of Ps is significantly reduced at certain Li coverage. This result suggests an abrupt increase in slow Ps emission from such Li-adsorbed Al(100) surfaces. In particular, the Ps$^-$ work function is significantly reduced at low Li-coverage, and becomes negative, similar to that for Ps. Therefore, injected positrons can be re-emitted as Ps$^-$ together with Ps.
Chapter 4

Positron states at Li-adsorbed Al(100) surface: the effect of positron-electron correlation functional

We carried out performance evaluation of various p-e correlation functionals for calculating positron state at surface using TC-DFT. The results thus obtained by using the semi-local p-e correlation functionals with the GGA well reproduce the experimental results, showing that reliable p-e correlation functionals are needed to properly describe the various properties of a positron at a surface. The results in this chapter were published in Ref. [82] and to be published in Ref. [120].

4.1 Introduction

The ideal combination of a positron annihilation spectroscopy experiment and a first-principles study with DFT calculations provides reliable information for the advanced characterization of materials. Concerning the theory, a new p-e correlation functional within the LDA framework for a positron in an electron gas, which was determined by accurate quantum Monte Carlo (QMC) calculations, was introduced by Drummond et al. [79]. Later, Barbiellini and Kurilach improved the GGA with an adjustable parameter to properly describe the e-p correlation effects [76]. Recently, a PF-GGA functional was also reported by them [77]. Thus far, these functionals have been applied to the calculations of positron states in bulk materials only. In the present chapter, we applied the various LDA and GGA functionals to the calculations of positron states at Al(100) surfaces covered with the Li adatoms.
from clean to 0.50 ML.

4.2 Method and computational details

For a comparative study of the dependence of physical quantities for the positron on the e-p correlation energy functionals, we employ various types of LDA and GGA functionals; the LDA functional based on AP data, which is parameterized by Sterne and Kaiser [121] (SK-LDA), the QMC-LDA functional, the GGA functional based on BN-LDA and SK-LDA with $\alpha = 0.22$ (these are abbreviated by BN-GGA and SK-LDA, respectively), the GGA functional based on QMC-LDA with $\alpha = 0.05$ (QMC-GGA) and the PF-GGA functional based on the QMC-LDA. We implemented QMC-LDA, QMC-GGA and PF-GGA schemes in the ABINIT code.

4.3 Results and discussions

Positron in the Al bulk

We first calculate the positron state in the Al bulk. Table 4.1 shows the results of positron lifetime ($\tau$) and affinity ($A_+$) in the Al bulk with the various p-e correlation functionals. $A_+$ is defined as the sum of electron and positron chemical potentials in the solid. Both the LDA and GGA well reproduce the experimental values. The lower values of $A_+$ and $\tau$ in the LDA than in the GGA were obtained in the previous theoretical studies [73, 76]. In addition, the results of $A_+$, which is obtained with QMC-LDA, QMC-GGA and PF-GGA are lower than those obtained by using BN and SK schemes, which are based on the AP data. This tendency is also found in the previous study on the p-e correlation functionals for the positron states in bulks [77].

Table 4.1: Positron lifetimes and affinities calculated with the SK-LDA, QMC-LDA BN-GGA, SK-GGA and PF-GGA, and the experimental data discussed in Refs. [22, 77, 107].

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SK</td>
<td>QMC</td>
</tr>
<tr>
<td>$\tau$ (ps)</td>
<td>163</td>
<td>160</td>
</tr>
<tr>
<td>$A_+$ (eV)</td>
<td>-4.33</td>
<td>-4.01</td>
</tr>
</tbody>
</table>
Work functions of electron and positron

Next, we give the results of work functions for a Li-adsorbed Al(100) surface. Calculated electron work functions for clean, 0.25 ML and 0.50 ML Li covered Al(100) surfaces are 4.39 eV, 2.18 eV and 2.47 eV, respectively. The work function of an electron, $\Phi^-$, first decreases and then increases with increasing Li coverage because the electron transfer from Li adatom to Al substrate reduces the surface dipole barrier in the low coverage, leading to the decrease in $\Phi^-$, but electrons start to accumulate in the Li-Li bonding instead of transferring to Al with further increase in the Li coverage. The positron work functions ($\Phi^+$) are given in Table 4.2. $\Phi^+$ is obtained by $\Phi^+ = -A^+ - \Phi^-$. Both the LDA and GGA well reproduce the experimental value for Al(100) clean surface. $\Phi^+$, behaves oppositely to $\Phi^-$, due to the opposite charge of electron. This property, which was also shown in the Chap. 3, holds for the models with different functionals as shown in Table 4.2. There is a tendency that the LDA gives a higher $\Phi^+$ than GGA, which is opposite to that for $A^+$ in Table 4.1 (note that $-A^+$ contributes to $\Phi^+$).

Table 4.2: Positron work function (in eV) calculated with the SK-LDA, QMC-LDA BN-GGA, SK-GGA and PF-GGA, and the experimental data discussed in Ref. [9].

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SK</td>
<td>QMC</td>
</tr>
<tr>
<td>clean</td>
<td>-0.061</td>
<td>-0.38</td>
</tr>
<tr>
<td>Li adsorbed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25 ML</td>
<td>2.14</td>
<td>1.83</td>
</tr>
<tr>
<td>0.50 ML</td>
<td>1.85</td>
<td>1.54</td>
</tr>
</tbody>
</table>

Positron states at Li-adsorbed Al(100) surfaces

Here, we present the results for the positron surface trapping state at Li-adsorbed Al(100) surfaces. Table 4.3 shows the results of the positron lifetimes $\tau$ at Al(100) surfaces with 0.25 ML- and 0.50ML-Li coverages. For overall trend, the GGA calculation gives larger $\tau$ than the LDA. For a clean surface, the calculated lifetimes are in good agreement with experimental values. In particular, the results of $\tau$ obtained by SK-GGA and PF-GGA are in excellent agreement with the experimental $\tau$, while $\tau$ calculated by SK-LDA shows a large deviation. In general, the electron density at the surface is obtained with GGA more adequately than that with LDA, because the electron density distribution becomes highly inhomogeneous at the surface. Thus,
Table 4.3: The lifetime of positron at Al(100) surfaces with various Li coverages obtained with the SK-LDA, QMC-LDA BN-GGA, SK-GGA and PF-GGA, and the experimental data discussed in Ref. [9] (in ps).

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>GGA</th>
<th>exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SK</td>
<td>QMC</td>
<td>BN</td>
</tr>
<tr>
<td>clean</td>
<td>507</td>
<td>561</td>
<td>613</td>
</tr>
<tr>
<td>Li adsorbed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25 ML</td>
<td>396</td>
<td>395</td>
<td>455</td>
</tr>
<tr>
<td>0.50 ML</td>
<td>295</td>
<td>275</td>
<td>288</td>
</tr>
</tbody>
</table>

The p-e correlation functionals with GGA become more important for the calculation of positron states at the surfaces than that in the bulk. The differences in the \( \tau \) between LDA and GGA becomes smaller after the Li adsorption. This tendency can be interpreted by positron density distribution at the surface, which is shown in Fig. 4.1. Since the positron density is pushed into the bulk (toward the left) after Li adsorption, the positron largely overlaps electrons in the Al bulk. Therefore, the \( \tau \) decreases and is close to lifetime in the bulk, and the difference in \( \tau \) between the p-e correlation functionals becomes close to that in the bulk.

Figure 4.1: Laterally averaged positron density distributions \( n_+(z) \) on Al(100) surfaces with various Li coverages. \( z = 0 \) is the atomic position of the topmost Al layer. The black, red, and blue curves indicate \( n_+(z) \) for a clean surface, 0.25 ML, and 0.50 ML, respectively. Black down arrow indicates the position of Li adatom at 0.25 ML [120]. ©(2016) Trans Tech Publications [to be published].

For the results of positron binding-energies \( E_b \), the calculated \( E_b \) for clean surface well reproduces the experimental value, which is shown in table 4.4. In particular, the results of QMC-LDA and GGAs show good agreement with experimental \( E_b \) [9].
Table 4.4: The positron binding-energy at Al(100) surfaces with various Li coverages calculated with the SK-LDA, QMC-LDA BN-GGA, SK-GGA and PF-GGA, and the experimental data discussed in Ref. [9] (in eV).

<table>
<thead>
<tr>
<th></th>
<th>LDA SK</th>
<th>QMC</th>
<th>GGA BN SK QMC PF exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>clean</td>
<td>3.10</td>
<td>2.93</td>
<td>2.89 2.89 2.89 2.89 2.80</td>
</tr>
<tr>
<td>Li adsorbed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25 ML</td>
<td>4.51 4.36</td>
<td>4.29 4.31 4.29 4.30 –</td>
<td></td>
</tr>
<tr>
<td>0.50 ML</td>
<td>4.07 3.94</td>
<td>3.92 3.90 3.83 3.84 –</td>
<td></td>
</tr>
</tbody>
</table>

This result indicates the improvement of the new LDA and GGA p-e correlation functionals in the present study. As the coverage dependence of $E_b$ is similar to that of $\Phi_+^+$, $E_b$ is considered to be proportional to the surface-dipole barrier.

Last, the activation energy of Ps ($E_a$) is described. $E_a$ is calculated as $E_a = E_b + \Phi_+^+ - 6.8$eV. $E_a$ for clean, 0.25 ML, and 0.50 ML Al(100) surfaces, which are calculated by $E_b$ with the PF-GGA functional, are 0.48, -0.32, and -0.48 eV, respectively. $E_a$ of the clean surface, 0.48 eV, agrees well with the experimental value, 0.46 eV [9]. The negative values of $E_a$ with Li adsorption are of interest to note because they indicate that a positron can be ejected into the vacuum as a Ps. From the experimental point of view, this phenomenon can be observed as increase in the low energy component of PsTOF spectrum of Al(100) surface after the Li adsorption.

4.4 Conclusion

We investigated the positron state at Li-adsorbed Al(100) surface by using the TC-DFT with various LDA and GGA functionals. The work function, lifetime, binding energy, and activation energy of the positron for a clean Al(100) surface by the GGA are all in excellent agreement with the experimental results. The coverage dependences of these quantities, which have not yet been observed in experiments, are interpreted by the change in surface dipole layer with increasing coverage. The negative activation energies of Ps at the surfaces with increasing Li coverage indicate that a positron is likely emitted toward the vacuum as a Ps atom.
Chapter 5

Spin-dependent positron lifetime for dilute ferromagnetism of GaN induced by Ga vacancies

The spin-dependent annihilation lifetime of a positron trapped by the Ga vacancies in GaN was investigated using TC-DFT simulations. The spin-dependent positron lifetime clearly depends on the charged states of the Ga vacancies and the induced magnetization. This dependence is attributed to the overlap between the positron and electron densities around the vacancy-type defect. Thus, the present study proves the useful role of spin-polarized positron annihilation spectroscopy for probing and revealing the mechanism of $d^0$ ferromagnetism. The results of this chapter were published in Ref. [122].

5.1 Introduction

Recently, spin-polarized positron annihilation spectroscopy (SP-PAS) experiments have attracted considerable interest because of their application to the study of magnetic phenomena [41,42]. Li et al. applied the SP-PAS experiments to ferromagnetic metals such as Fe, Co, and Ni [43], and observed that the spin-dependent positron lifetime differs depending on whether the positron annihilates with the majority or minority spin ($\uparrow$ or $\downarrow$) electrons owing to the spin-selection rule of positron-electron (p-e) annihilation [37]. Since positrons are easily trapped by vacancy defects, SP-PAS is expected to be a useful and direct tool for studying the defect-induced magnetism such as $d^0$ ferromagnetism.

$d^0$ ferromagnetism is a new class of magnetism in which the materials contain no magnetic ions that have partially filled $d$ or $f$ orbitals [123]. This has been
the subject of increasing interest because of the unexpected finding that $p$ bands can spontaneously polarize and give a ferromagnetic state through the introduction of defects and/or non-magnetic impurities. Recently, Xu et al. observed $d^0$ ferromagnetism in a GaN film after N ion irradiation at room temperature [124]. GaN, which is well known as one of the most important III-V group semiconductors, has also been extensively investigated in the field of spintronics because of its potential applications such as blue or green optoelectronic devices [125] and concentrator solar cells [126]. To understand the origin of the magnetization, Xu et al. also performed Raman spectroscopy and an experiment of PAS, and concluded that the saturation magnetization in GaN is attributed to Ga cation vacancies.

In contrast, there have been very few theoretical reports of spin-dependent positron lifetime ($\tau^{\uparrow(\downarrow)}$) in magnetic materials [80,81]. In particular, there has been no report investigating $\tau^{\uparrow(\downarrow)}$ in $d^0$ ferromagnetic materials by using self-consistent first-principles calculation. In this chapter, we investigate the $\tau^{\uparrow(\downarrow)}$ in a GaN wurtzite structure (WS-GaN) with a Ga cation vacancy (V$_{Ga}$) by TC-DFT simulation [70] in order to reveal the microscopic mechanism of $d^0$ ferromagnetism induced by defects and to clarify the relationship between $d^0$ ferromagnetism and $\tau^{\uparrow(\downarrow)}$.

5.2 Computational details

Here, we used two methods, namely CV scheme and TC scheme. The CV scheme is known as one of the most convenient schemes, in which the positron ground-state is calculated via the electronic ground-states obtained by DFT. In the TC scheme, the electronic and positronic KS equations are solved simultaneously, by taking account of the effect of a positron on the electronic states. In this study, a single positron in the unit cell was assumed, i.e., the positron–positron interaction term was omitted [70]. In recent theoretical studies, Ishibashi [72] and Wiktor et al. [127,128] pointed out that the positron trapped by a defect is localized and alters the atomic and electronic structure around the defect. As a result of the localization of the positron, its annihilation lifetime changes owing to the electronic states around the defect and the new atomic geometry. Therefore, self-consistent TC-DFT calculation is required to precisely determine the defect-localized positron state and the positron lifetime (see Refs. [72] and [129] for further details).

We calculated spin-unpolarized and spin-polarized positron lifetime ($\tau$ and $\tau^{\uparrow(\downarrow)}$) to understand the dependence of the positron lifetimes on defect states, clearly. $\tau$ and $\tau^{\uparrow(\downarrow)}$ are calculated using eqs. (2.2.15) and (2.2.16), respectively. We assumed that the spin states of electrons do not affect the positron density distribution and that p-e correlation potential does not include the spin-polarization effect. Thus, the spin-polarized effect was included only in the electronic structure calculation.
and $\tau^{\uparrow(\downarrow)}$ formula [81]. All electronic and positronic calculations were performed by ABINIT code using the plane-wave and PAW method. We implemented the formula of $\tau^{\uparrow(\downarrow)}$ in the ABINIT.

We chose the WS-GaN with neutral, singly and doubly negatively charged $V_{\text{Ga}}$ ($V_{\text{Ga}}^0$, $V_{\text{Ga}}^1$ and $V_{\text{Ga}}^2$) as the defect induced magnetic materials. The electronic configurations of PAW pseudo-potentials are $3p^63d^{10}4s^24p^1$ for Ga, and $2s^22p^3$ for N. The spin-polarized electronic ground-state structure was calculated by using the PBE exchange-correlation functional [53]. For the p-e correlation potential and enhancement factor, we employed the LDA functional developed by Drummond et al., which was determined by using the accurate QMC method [79]. The $k$-point sampling for a supercell with and without a vacancy defect is $3 \times 3 \times 3$. The cut-off energy for the plane-wave was 18 Ha for both electrons and a positron. The atomic geometry in the supercell was relaxed until all the forces acting on each atom were smaller than $5.0 \times 10^{-4}$ Ha/bohr. Cell optimization was performed for the pristine WS-GaN, and the lattice constants were obtained as $a = b = 3.224$ Å, $c = 5.242$ Å. These lattice constants were used for constructing the supercell. To carry out the defect calculation, $3 \times 3 \times 2$ supercell containing 71 atoms ($\text{Ga}_{35}\text{N}_{36}$) was used.

### 5.3 Results and discussions

First, we show the present calculation results of electronic and magnetic properties for WS-GaN with the various negatively charged Ga vacancies, because we need the accurate electronic structure in order to obtain the precise $\tau^{\uparrow(\downarrow)}$. Our results are similar to previous theoretical results [130, 131]. Figure 5.1(a) shows the results of total density of states (DOS) and projected DOS (PDOS) of the $2p$ orbital of N around a Ga vacancy. Figure 5.1(b) shows a Ga vacancy-induced spin polarization distribution (red isosurfaces), i.e., the difference in the electron densities between the $\uparrow$ and $\downarrow$ spins that distribute around a Ga vacancy. The positions of N atoms around the Ga vacancy show outward relaxation by 0.33 Å because of the anion–anion repulsive interaction between N atoms without the Ga atom. The introduction of a neutral Ga vacancy induces the difference in the PDOS of the N atom between the $\uparrow$ and $\downarrow$ spins, as shown by the two solid curves in Fig. 5.1 (a). The induced spin polarization is found to distribute around a vacancy and generates 3.0 $\mu_B$ per unit cell. Furthermore, the present calculation gives the magnetic moments of the cell 2.0 $\mu_B$ and 1.0 $\mu_B$ for the $V_{\text{Ga}}^0$, $V_{\text{Ga}}^1$ and $V_{\text{Ga}}^2$, respectively. This is because the extra electrons fill the partially occupied $2p$ orbitals of the $\downarrow$ spin up to 0.6 eV above the Fermi level (two prominent peaks above the Fermi level in the lower part of Fig. 5.1 (a)) leading to reduction in the magnetic moment.

Next, we briefly mention the result of p-e charge re-distribution. Figure 5.2 shows
Figure 5.1: The electronic structure of WS-GaN with a Ga vacancy. (a) The total density of states (DOS) (broken curve) and projected DOS (PDOS) (solid curve) of the 2p states of a N atom for majority spin (blue) and minority spin (red) are respectively shown in the upper and lower parts. (b) The red transparent isosurfaces represent the difference in the electron densities between the majority and minority spins (the isovalue is 0.002 au). The broken circle indicates the Ga vacancy. The white and blue balls denote the Ga and N atoms, respectively [122]. Copyright (2016) The Japan Society of Applied Physics.

the electron and positron distributions along the [0001] direction that is through the position of a Ga vacancy calculated by the TC and CV schemes. The positron tends to localize at a vacancy defect, and charge re-distributions occur by the p-e attractive interactions, as shown in Fig. 5.2. This tendency was also seen in previous theoretical studies for Si [132] and GaAs [133].

For the effect of positron on the atomic structure, we found the slightly decreased N-N distance of 0.04 Å around the defect. This is because a positive charge of a positron reduces the anion–anion repulsive interaction. In contrast to our inward relaxation, Saito and Oshiyama carried out TC scheme calculations for Si crystals with various Si vacancies [134]. Their calculation results show that the nearest-neighbor Si atoms around a defect move inward (without a positron), but move outward owing to the presence of a positron.

Table 5.1 shows the results of $\tau$ calculated by the TC and CV schemes using eq. (2.2.15). The results of $\tau$ in WS-GaN with and without a $V_{Ga}^0$ are in good agreement with previous experimental data [135]. $\tau$ increases by the introduction
Figure 5.2: The total electron density $n_-$ and positron density $n_+$ distributions calculated by the TC scheme and CV scheme. The black and red solid curves represent the electron and positron density distributions calculated by the TC scheme, respectively. The black and red broken curves represent the electron and positron density distributions calculated by the CV scheme, respectively. The open broken circle denotes the position of a Ga vacancy. This figure is shown in Ref. [122]. Copyright (2016) The Japan Society of Applied Physics.

of a Ga vacancy, because the overlap of p-e densities decreases around the vacancy. However, the $\tau$ decreases with increasing charge negativity of the vacancy due to the increase in p-e overlap. For charged vacancy, in a previous theoretical study, Makkonen and Puska [136] obtained the same $\tau = 216$ ps at both $V_{Ga}^{2-}$ and $V_{Ga}^{3-}$ in WS-GaN by using a modified CV scheme [137]. In the present study with the TC scheme, we obtained different $\tau$ at the $V_{Ga}$ with different charges; $\tau = 217$ ps at $V_{Ga}^{2-}$ and 212 ps at $V_{Ga}^{3-}$. Thus, the present result of $\tau$ in negatively charged $V_{Ga}$ indicates the important role of p-e charge re-distribution in determining the $\tau$ around the negatively charged vacancies.

Here, we mention the scheme dependence of $\tau$ obtained by TC and CV. The $\tau$ obtained by the TC scheme is found to be smaller than that by the CV scheme (in parentheses) for each charge state of vacancies in Table 5.1. This is attributed to the self-consistent charge re-distribution effects, which was shown in Fig. 5.2. The $\tau$ at $V_{Ga}^{0}$ obtained by the CV scheme is slightly closer to experimental data than that obtained by the TC scheme, which is considered as the feedback effect [133]. However, the values of $\tau$ may change quantitatively by replacing present p-e correlation functional and enhancement factor with the parameter-free GGA.
Table 5.1: The spin-unpolarized positron lifetimes $\tau$ in pristine WS-GaN and WS-GaN with the neutral, singly and doubly negatively charged Ga vacancies are calculated by the TC and CV schemes. $\tau$ of the pristine WS-GaN is calculated by the CV scheme. The values in parentheses show the results obtained by the CV scheme. The $\tau^{\text{expt}}$ shows the previous experimental data [135]. All values are in ps.

<table>
<thead>
<tr>
<th>$\tau$</th>
<th>$\tau_{\text{Ga}}^{\text{V0}}$</th>
<th>$\tau_{\text{Ga}}^{\text{V1}}$</th>
<th>$\tau_{\text{Ga}}^{\text{V2}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau^{\text{expt}}$</td>
<td>158</td>
<td>227(232)</td>
<td>223(228)</td>
</tr>
</tbody>
</table>

Table 5.2: The results of $\tau^{\uparrow}$ and $\tau^{\downarrow}$ differences $\tau^{\text{diff}} = \tau^{\downarrow} - \tau^{\uparrow}$ for WS-GaN with various negatively charged $V_{\text{Ga}}$ (in ps). First column contains the calculated magnetization $m_s$ (in $\mu_B$). The values in brackets indicate the results by the CV scheme.

<table>
<thead>
<tr>
<th>$m_s$</th>
<th>$\tau^{\uparrow}$</th>
<th>$\tau^{\downarrow}$</th>
<th>$\tau^{\text{diff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{\text{Ga}}^{\text{V0}}$</td>
<td>3.0</td>
<td>215(213)</td>
<td>242(255)</td>
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<tr>
<td>$V_{\text{Ga}}^{\text{V1}}$</td>
<td>2.0</td>
<td>214(215)</td>
<td>234(242)</td>
</tr>
<tr>
<td>$V_{\text{Ga}}^{\text{V2}}$</td>
<td>1.0</td>
<td>213(218)</td>
<td>223(231)</td>
</tr>
</tbody>
</table>

Table 5.2 shows the results of $\tau^{\uparrow}$ calculated by eq. (2.2.16). For the overall trend of $\tau^{\uparrow}$, the $\tau^{\uparrow}$ is smaller than the $\tau^{\downarrow}$ because the p-e overlap for $\uparrow$ electrons is larger than that for $\downarrow$ electrons. The $\tau^{\uparrow}$ shows strong (weak) dependence on the charged vacancy states, because the electrons of negatively charged $V_{\text{Ga}}$ were injected in the $\downarrow$ band, as shown in Fig. 5.1 (a). As a result, both the lifetime differences $\tau^{\text{diff}} = \tau^{\downarrow} - \tau^{\uparrow}$ and magnetization $m_s$ decrease with increasing number of electrons of the Ga vacancy. Thus, the $\tau^{\uparrow}$ can directly probe the magnetic moment around the defect. This feature has also been observed in $\tau^{\uparrow}$ in typical bulk ferromagnets by Li et al. [43] and in the intensity of the spin-polarized Doppler broadening spectrum by Kawasuso et al. [41]. Thus, the relationship between the $\tau^{\text{diff}}$ and the $m_s$ is understood as the common property of $\tau^{\uparrow}$.

Last, we note the advantages of the TC scheme over the CV scheme for evaluation of $\tau^{\uparrow}$. The charge re-distribution due to the presence of the positron, which is taken
into account by the TC scheme, experiences a difference in the DOS between the \(\uparrow\) and \(\downarrow\) electronic states, as shown in Fig. 5.1 (a). Therefore, the \(\tau^{\uparrow(\downarrow)}\) is properly evaluated by the TC scheme.

### 5.4 Conclusion

In conclusion, we investigated the \(\tau^{\uparrow(\downarrow)}\) in WS-GaN with and without the Ga vacancies by using the first-principles TC-DFT. Defect-induced ferromagnetism in GaN mainly originates from \(2p\) orbitals of N atoms around the vacancy defect. The result of structure optimization, including the effect of the positron, shows the inward relaxation of N atoms around a Ga vacancy because the positron reduces the anion–anion repulsive interaction. When the positron is trapped by the Ga vacancy, \(\tau\) significantly increases from that of pristine GaN and decreases with an increase in the degree of negativity of the Ga vacancy owing to an increase in the p-e overlap around the vacancy. The \(\tau^{\uparrow(\downarrow)}\) shows clear dependence on the charge states of the Ga vacancy, and the lifetime difference is proportional to the magnetization around the Ga vacancy. Since the positron is sensitive to defects and the magnetization around the vacancy defects, it can be a useful tool for directly observing the magnetic moment around the vacancy defect. We emphasize that the combination of SP-PAS experiments and theoretical \(\tau^{\uparrow(\downarrow)}\) by using TC-DFT is an ideal tool for revealing the mechanism of defect-induced magnetism such as \(d^0\) ferromagnetism.
Chapter 6

Positron states at Li- and O-adsorbed Fe(001) ferromagnetic surfaces

The positron states for Li- and O-adsorbed Fe(001) ferromagnetic surfaces are studied by using TC-DFT. Positron surface lifetimes and positron binding energies are found to be sensitive to changes in the surface structure and the dipole barrier induced by adatoms, which can be understood by the positron density distribution and surface potential. Spin-dependent positron lifetime fractions are in excellent agreement with spin-polarization fractions at the topmost surface because the localized positrons at the surface are sensitive to the surface magnetic state. Therefore, the present results show that spin-polarized positron annihilation spectroscopy can extract the outermost surface magnetic state. The results in this chapter were published in Ref. [138].

6.1 Introduction

An experiment of PAS can probe the electron spin states in magnetic materials by using spin-polarized (SP) positron annihilation because positron annihilation selectively occurs owing to the spin-selection rule [37]. Experimentally, SP-PAS has been performed by Kawasuso and co-workers [41–43], and they have shown that the spin-dependent DBS and/or positron lifetime correlates with magnetization in ferromagnets. Consequently, SP-PAS has attracted much attention as a sensitive probe for studying the electron-spin polarizations of ferromagnets.

Recently, Kawasuso et al. [47] and Zhang et al. [48] have measured the accumulation of current-induced spin polarization at various metal surfaces and the
phomena of charge-spin conversion and spin diffusion at the surface of the Bi/Ag system [49] using an SP positron beam. Because of these recent observations, SP positron beam experiments are expected to be a useful tool for detecting spin polarization at the outermost surface.

Further development of SP positron beam experiments requires understanding the interaction between positrons and the magnetic surface. Theoretically, a first-principles study can be a reliable tool for interpreting the interaction between positrons and electrons in the bulk and at the surface. However, there have thus far been no theoretical reports on the positron states at magnetic surfaces. In this chapter, positron states at ferromagnetic surfaces are studied by using a TC-DFT that includes the effect of spin polarization in order to reveal the relationship between positron states and magnetization at ferromagnetic surfaces. We determine spin-unpolarized and spin-polarized positron lifetimes, positron binding energy, and change in the electron work functions for Li- and O-adsorbed Fe(001) surfaces.

6.2 Computational details

In this chapter, we calculate the positron states in the Fe bulk and at Fe(001) surfaces based on the CV scheme. Spin-unpolarized and -polarized positron lifetimes are calculated using eqs. (2.2.15) and (2.2.16) ($\tau$ and $\tau^{\uparrow}(\downarrow)$), respectively. We assume a single spin-unpolarized positron in the unit cell [81,122]. This assumption allows us to omit the positron-positron self-interaction term and determine $\tau^{\uparrow}(\downarrow)$ only by using the spin states of the electron densities. We already know that these calculations well describe the positron state in the bulk [81,122]. However, the TC-DFT scheme does not include two factors that are necessary for calculating the positron at surfaces: the asymptotic behavior of the image potential [70] and the positron band-shift energy, which is the positron zero-point energy arising from the positron-ion interaction [25]. To take these factors into account, we employed the CMM and ramp potential in the TC-DFT scheme [82]. In the CMM, the asymptotic behavior of the image potential is adapted to the correlation potential in the vacuum region. The depth of the ramp potential corresponds to the band-shift energy calculated by using a first-principles calculation. In the calculation of $\tau$ and $\tau^{\uparrow}(\downarrow)$ at surfaces, we assumed no electron screening on a positron in the region from the effective image plane to the edge of vacuum and thus we set the enhancement factor to zero in this region [95].

Here, we describe the computational details of the slab calculation. Fe(001) surfaces were represented by a periodic repeated slab of 11 layers, each separated by a 40 Å thick vacuum, with Li and O adsorbed on both surfaces of the slabs with 0.25 and 0.5 ML coverages. We chose the most stable hollow site for the adsorption and the $c(2 \times 2)$ structure for 0.5 ML adsorbed surfaces.
Electron states

Electronic structure calculations were performed within the plane-wave basis set and PAW scheme. Valence electron configurations of PAW pseudo-potentials were $3s^23p^64s^13d^7$ for Fe, $1s^22s^1$ for Li, and $2s^22p^4$ for O, respectively. $k$-point sampling for each supercell of slabs was $4 \times 4 \times 1$. The cutoff energies for the plane-wave expansion and charge were 15 and 20 Ha, respectively. The PBE functional [53] was used for the spin-polarized electron exchange-correlation functional. Structure optimization was done until all the forces acting on each atom were $< 5.0 \times 10^{-4}$ Ha/bohr. Cell optimization was done for the bcc Fe bulk, and the obtained lattice constant is 2.829 Å, which was used for constructing the slabs.

Positron states

Positron wave functions were also represented as plane-wave basis sets. Their cutoff energies for the plane-wave expansion and charge were the same as those of electrons. Only the Γ-point ($k = 0$) was chosen in the $k$-point sampling. For the electron-positron correlation functional, we used a parameter-free GGA functional [77] that is based on the LDA functional determined by an accurate QMC method [79].

All calculations for electrons and positrons were performed by using the first-principles calculation code ABINIT.

6.3 Results and discussions

In this section, first, we briefly describe the results for $\tau$, $\tau^{\uparrow(\downarrow)}$, and positron affinity in the Fe bulk. Next, we discuss the results for $\tau$ at Fe(001) surfaces and the relationship between positron density distributions and positron binding energy. Finally, we clarify the relationship between ferromagnetic surface states and $\tau^{\uparrow(\downarrow)}$.

6.3.1 Positron states in bulk Fe

Table 6.1 shows that the results for $\tau$, $\tau^{\uparrow(\downarrow)}$, lifetime difference ($\tau^{\text{diff}} = \tau^\downarrow - \tau^\uparrow$), and positron affinity ($A_\uparrow$). $A_\uparrow$ is a factor for the work functions of the positron and Ps, which are not discussed in this chapter. We determine the band-shift energy in Fe from a first-principles result for the positron work function. Our results are in good agreement with previous experimental data, as shown in Table 6.1.
Table 6.1: Positron lifetimes ($\tau$, $\tau^{↑(↓)}$, lifetime difference ($\tau^{\text{diff}} = \tau^{↑} - \tau^{↓}$)) and positron affinity ($A_+$) for Fe bulk as well as experimental data discussed in Refs. [43] and [77] (in ps for lifetimes and in eV for $A_+$).

<table>
<thead>
<tr>
<th></th>
<th>$\tau$</th>
<th>$\tau^{↑}$</th>
<th>$\tau^{↓}$</th>
<th>$\tau^{\text{diff}}$</th>
<th>$A_+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>102</td>
<td>97</td>
<td>107</td>
<td>10</td>
<td>-3.23</td>
</tr>
<tr>
<td>Experimental</td>
<td>105</td>
<td>109</td>
<td>120</td>
<td>11</td>
<td>-3.3</td>
</tr>
</tbody>
</table>

6.3.2 Positron states at surfaces

In this subsection, we discuss the results for $\tau$ and $\tau^{↑(↓)}$ for adsorbed Fe(001). First, we show the results for $\tau$ and positron binding energy for adsorbed surfaces. Then we discuss $\tau^{↑(↓)}$ and spin-polarization fractions for adsorbed Fe(001).

Spin-unpolarized positron lifetimes

We discuss the results for $\tau$ at adsorbed Fe(001) to understand the adsorbate-dependent positron states at surfaces. Figure 6.1 shows the coverage dependence for $\tau$ and $\tau^{↑(↓)}$ at Fe(001). $\tau^{↑(↓)}$ will be discussed later. $\tau$ for the clean surface is 531 ps in the calculation, which is comparable with that for Fe bulk with voids, 450–500 ps [139]. The positron trapping state in voids has been explained in the context of positron states at surfaces [140,141]. The larger $\tau$ at the surface is considered to stem from smaller electron-positron overlap at surfaces than that around voids, from the good agreement in calculated and experimental $\tau$ values, as shown for the bulk in Table 6.1. We found a remarkable difference in the coverage dependence of $\tau$ between O-Fe(001) (in Fig. 6.1(a)) and Li-Fe(001) (in Fig. 6.1(b)). The value of $\tau$ increases with increasing O coverage; in contrast, it decreases with increasing Li coverage. We can interpret the difference from the qualitatively different properties of the positron density distributions for O adsorption and Li adsorption on the surfaces, as shown in Fig. 6.2. The laterally averaged positron density distribution of a clean Fe surface is pushed toward the vacuum upon O adsorption, but it is pushed inward upon Li adsorption, as clearly seen in Fig. 6.2(a). These behaviors are consistent with the laterally averaged KS potentials that a positron at the surface experiences ($\tilde{V}_{\text{eff}}(z)$) in Fig. 6.2(b). $\tilde{V}_{\text{eff}}(z)$ shifts toward vacuum and inward upon O adsorption and Li adsorption, respectively. The adsorption-induced tendency in the shift of either the positron density distribution or the potential profile essentially comes from the adsorption site of O and Li atoms. The stable site of O atoms is close to the position between the topmost Fe atoms, so the positron near the image potential minimum is pushed toward vacuum. In contrast, Li adatoms
Figure 6.1: Coverage-dependent positron lifetimes (τ and τ↑↓ (τ↓↑)) (in ps) at the (a) O-Fe(001) and (b) Li-Fe(001) surfaces. Black, blue, and red dots indicate τ, τ↑, and τ↓, respectively. Dotted lines are drawn to help guide the eyes. ©[2016] The Physical Society of Japan (J. Phys. Soc. Jpn. [85], [11/ 114703].) [138].

sit above the topmost Fe atoms, pushing back the positron to the bulk. The details of the stable atomic geometries of O- and Li-adsorbed surfaces will be shown later in Fig. 6.6. Figure 6.3 shows the coverage dependence of positron binding energy (E_b) and the change in the electron work function Δφ for Fe(001) surfaces upon adsorption. Our Δφ values for O-adsorbed surfaces are in good agreement with previous results calculated by Hugosson et al. within the PAW method [142]. Δφ in our calculations slightly increases with O adsorption; in contrast, Δφ decreases with Li adsorption. In general, Δφ is understood as a change in the surface dipole barrier, which is caused by the difference in electronegativity between the substrate and the adatoms. For the Li-Fe(001) surface, the electron cloud moves from Li to Fe, because of the smaller electronegativity of Li compared with that of Fe. As a result of the reduction in surface dipole moment, Δφ decreases. In contrast, it slightly increases because of the larger electronegativity of O than Fe.
Figure 6.2: Laterally averaged positron density distributions $\tilde{n}_+(z)$ and effective potentials for a positron, $\tilde{V}^\text{eff}_+(z)$, at clean and 0.5 ML adsorbed Fe(001) surfaces. (a) $\tilde{n}_+(z)$. (b) $\tilde{V}^\text{eff}_+(z)$. $z = 0$ indicates the outermost atom position of the substrate. $\tilde{V}^\text{eff}_+(z) = 0$ indicates the vacuum level. Black, blue, and red curves are for clean and 0.5 ML Li- and O-adsorbed Fe(001) surfaces, respectively. ©[2016] The Physical Society of Japan (J. Phys. Soc. Jpn. [85], [11/ 114703].) [138].

$E_b$ is obtained from the difference between the positron energy level at the surface and vacuum level of the positron electrostatic potential. The calculated $E_b$ for a clean Fe(001) surface is 2.15 eV. In a previous study [143], Fazleev et al. reported a theoretical value of 2.43 eV for a clean Fe(001) surface using a superimposed atom method with BN-LDA functional [70]. The difference between our theoretical result and that of previous study is mainly caused by different methods and functional types. The coverage dependences of $E_b$ for Li- and O-adsorbed Fe(001) are almost opposite to that of $\Delta \phi$. Since the sign of the positron charge is opposite to that of an electron, the positron experiences an opposite change in the surface dipole barrier. Thus, the opposite dependence of $E_b$ to $\Delta \phi$ indicates that the positron state at the surface is affected by the change in the surface dipole moment. This
coverage dependence of $E_b$ was also found for other metal surfaces with various alkali adatoms in both experiment [119] and theoretical calculations [82]. $E_b$ for O-Fe(001) decreases with increasing coverage. This result indicates that positron trapping becomes weaker after O adsorption, because the trapped positron is pushed toward vacuum, as was discussed in Fig. 6.2.

**Spin-polarized positron lifetimes**

Here, we discuss the results for $\tau^{\uparrow(\downarrow)}$. $\tau^{\uparrow(\downarrow)}$ are observed experimentally by controlling the direction of electron magnetization under an external magnetic field [43]. Figures 6.1 (a) and (b) show the results for $\tau^{\uparrow}$ (blue dots) and $\tau^{\downarrow}$ (red dots) for O- and Li-adsorbed Fe(001) surfaces, respectively. As a common feature for $\tau^{\uparrow(\downarrow)}$, $\tau^{\uparrow}$ is smaller than $\tau^{\downarrow}$. This feature comes from that the $\uparrow$ electron-positron overlap being...
larger than the ↓ electron-positron overlap, as clearly seen in Fig. 6.4. The coverage dependences of $\tau^{\uparrow(\downarrow)}$ at adsorbed surfaces are similar to those of $\tau$ and are also interpreted as the change in the positron density distributions and surface potentials, which was discussed in Figs. 6.2 and 6.3.

For further analysis of $\tau^{\uparrow(\downarrow)}$, we introduce the $\tau^{\uparrow(\downarrow)}$ fraction ($R$) by

$$R \equiv \frac{\tau^{\uparrow} - \tau^{\downarrow}}{\tau^{\uparrow} + \tau^{\downarrow}} = \frac{\lambda^{\uparrow} - \lambda^{\downarrow}}{\lambda^{\uparrow} + \lambda^{\downarrow}},$$

(6.3.1)

where the second equality comes from eq. (2.2.16). For comparison with $R$, we also
introduce the spin-polarization fraction \( P \) as

\[
P = \frac{N^{\uparrow} - N^{\downarrow}}{N^{\text{tot}}},
\]

where \( N^{\uparrow} \) and \( N^{\text{tot}} \) are the number of \( \uparrow \) (\( \downarrow \)) spin electrons and total number of electrons, respectively. From eq. (2.2.16), we naturally expect a correlation between \( R \) and \( P \) corresponding to the area of p-e overlap distribution. Since \( P \) of eq. (6.3.2) is proportional to magnetization \((M = \mu_B(N^{\uparrow} - N^{\downarrow}))\), where \( \mu_B \) is the Bohr magneton, the surface electron spin polarization can be probed by the surface positron annihilation lifetime. To verify the relationship between \( R \) and \( P \), we plot the results of \( R \) and \( P \) as a function of coverage in Figs. 6.5 (a) and (b). In the calculation of \( P \), we considered the number of valence and core electrons for \( N^{\text{tot}} \) of the topmost surface Fe and adsorbed atoms. \( P \) slightly decreases with increasing coverage for the adsorbed surface. The present \( P \) results for O-Fe(001) are similar to those obtained by using previous electronic state calculations [142]. We also found a decrease in \( P \) at Li-Fe(001) with increasing Li coverage. In a previous study [144], Johnson et al. have pointed out the decrease in \( M \) of the topmost Fe atoms at the K-adsorbed Fe(001) surface by using both an experiment of spin-polarized photoemission and a reliable full-potential linear augmented wave method calculation. The present result indicating a decrease in \( P \) for Li-Fe(001) is consistent with the previous K-Fe(001) results.

The coverage dependence of \( R \) is found to be similar to that of \( P \), especially for the Li-Fe(001) surface, as clearly seen in Fig. 6.5. Since positron states at the surfaces are localized at the outermost surface and are distributed within interstitial regions, the positron well experiences the surface electronic states and selectively annihilates with spin-polarized electrons near the surfaces for Li-Fe(001). However, \( R \) deviates from \( P \) after O adsorption, compared to Li-Fe(001); in particular, the deviation of \( R \) from \( P \) becomes the largest at 0.5 ML O-Fe(001). This is explained by loosely bounded positrons at O-Fe(001), which was discussed in Fig. 6.2 (a). The shift of the positron density distribution toward vacuum after O adsorption reduces the p-e overlap. Therefore, positrons cannot easily annihilate with surface electrons, especially at the 0.5 ML O-Fe(001).

Finally, we show contour plots of spin polarizations \( (m_-(r)) \) and overlap distributions \( (S_{e-p}(r)) \) for clean and adsorbed surfaces in Fig. 6.6. We define \( m_-(r) \) and \( S_{e-p}(r) \) by

\[
m_-(r) = n^+_-(r) - n^+_+(r),
S_{e-p}(r) = m_-(r)n_+(r).
\]

\( m_-(r) \) is distributed mainly around Fe atoms, and that at the topmost layer slightly
Figure 6.5: Coverage dependence of spin-polarization fraction $P$ for the outermost layer of Fe(001) surfaces and adatoms at (a) O-Fe(001) and (b) Li-Fe(001). Closed and open circles indicate the results of $R$ (eq. (6.3.1)) and $P$ (eq. (6.3.2)), respectively. The doted curve is drawn to help guide the eyes. ©2016 The Physical Society of Japan (J. Phys. Soc. Jpn. [85], [11/114703]). [138].
Figure 6.6: Contour map of (left) electron-spin polarization \( m_-(\mathbf{r}) = n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r}) \) and (right) overlap of positron density \( S_{e-p}(\mathbf{r}) = m_-(\mathbf{r})n_+(\mathbf{r}) \) at clean and 0.5 ML adsorbed surfaces. Positions of contour planes are shown by black dotted lines in the bottom panels. Color bars for \( m_-(\mathbf{r}) [1/\text{bohr}^3] \) and \( S_{e-p}(\mathbf{r}) [1/\text{bohr}^6] \) are shown on the right sides of the top panels, respectively. Grey, cyan, and blue balls represent Fe, Li, and O atoms, respectively. ©[2016] The Physical Society of Japan (J. Phys. Soc. Jpn. [85], [11/ 114703].) [138].
extends toward vacuum in the left panels of Fig. 6.6. In contrast, $S_{e-p}(r)$ is localized at the topmost layer in the right panels of Fig. 6.6. This localization of $S_{e-p}(r)$ comes from the positron surface trapping state. Since the positron densities are localized at the surfaces, as shown in Figs. 6.2 and 6.4, surface positrons selectively annihilate with the topmost surface electrons. Because of this, $R$ shows a clear coverage dependence and is in good agreement with $P$ at the topmost surface. From the discussions above in this section, we conclude that an SP positron beam clearly extracts magnetizations at the topmost surface via spin-polarized positron annihilation at the material surface.
6.4 Conclusion

We investigated the positron states for a ferromagnetic Fe(001) surface with and without Li and O adsorption by using TC-DFT, and we determined $\tau$, $\tau^{\uparrow}$, binding energies, and the change in the electron work function. $\tau$ and $\tau^{\uparrow}$ are sensitive to changes in the electron and positron density distributions, which are induced by adatoms. Changes in the surface dipole barrier play an important role in the determination of positron surface states. The positrons are strongly bound to the surface after Li adsorption; in contrast, positron binding energies decrease upon O adsorption. This result can be understood by the shift in the positron distribution at the surface. The spin-polarization fraction at Li- and O-adsorbed Fe(001) surfaces, which are estimated by $\tau^{\uparrow}$, are in good agreement with that at the topmost surfaces obtained by using DFT. Thus, positron density distributions, which are localized around the topmost surface, capture the information of spin states at the topmost surface. Since $\tau^{\uparrow}$ is sensitive to the surface electronic states and spins, SP-PAS can be an important tool for detecting surface magnetization.
Chapter 7

Summary

We have investigated positron states in solids and at metal surfaces using TC-DFT simulations.

First, we extended the TC-DFT scheme to the calculation of the positron states at Li-adsorbed Al(100) surfaces. The results of various physical quantities for the clean surface are in good agreement with previous experimental results. Positron states at Li-adsorbed Al(100) surfaces highly depend on the coverage. Positron lifetime at the surface decreases with increase in the coverage. This tendency can be interpreted by the change in positron density distributions after Li adsorption. Positrons at the Li adsorbed surfaces are pushed toward the Al substrate by the adatoms and easily annihilate with electrons. From the energetics, positron re-emission processes are found to be sensitive to changes in the surface-dipole barrier induced by the coverage. In particular, the work function of Ps\(^-\) becomes negative at the low coverage surfaces. Thus, Ps\(^-\) at the Li-adsorbed Al(100) surface can be formed and spontaneously emitted toward the vacuum. In addition to Ps\(^-\) emission, we found that the activation energy of Ps becomes negative after Li adsorption. Thus, when the positron is trapped by Li-adsorbed surface and becomes Ps, the Ps tends to be ejected into the vacuum.

Second, we carried out the TC-DFT simulations of positron states at Li-adsorbed surfaces with various p-e correlation functionals. The results of positron lifetime, work function, binding energy, and activation energy for the Al(100) clean surface are in excellent agreement with the experimental data. The coverage dependences of these quantities, which have not yet been observed in experiments, are interpreted by the change in the surface-dipole barrier with increasing coverage. The negative activation energies of Ps at the surfaces with increasing Li coverage indicate that a positron is likely emitted toward the vacuum as a Ps atom.

Third, we investigated the electron and positron states localized at Ga vacancies
in GaN and precisely determined the spin-polarized positron lifetime using self-consistent TC-DFT simulations. The results are found to be highly sensitive to the vacancy-induced atomic relaxation, the charge states and magnetization around Ga vacancies. Thus, the present study has shown the important role of the spin-polarized positron lifetime to probe and reveal the mechanism of newly discovered $d^0$ ferromagnetism.

Fourth, we elucidated positron states at Li- and O-adsorbed Fe(001) ferromagnetic surfaces using TC-DFT calculations. The results show that the positron states at the Fe surfaces are highly sensitive to the electronic and atomic structures. The spin-polarization fractions were evaluated by the spin-polarized positron lifetimes. The results are in good agreement with the spin-polarization fractions at the topmost surfaces evaluated by DFT calculations. This result comes from the localization of positron density distribution at the topmost surfaces. For this reason, positron fully captures the electronic states at the topmost surfaces. Therefore, we can extract the magnetic structures at the topmost surfaces via the spin-polarized positron lifetimes.

Last, we have indicated the validity of first-principles calculation of positron states in solids and at metal surfaces for revealing the positron-electron interaction. The positron annihilation has reliable information of electronic structures in solids, at defects and at topmost surfaces. Since the recent developments of surface science are supported by many spectroscopic studies, the importance of positron annihilation as the spectroscopy rapidly increases to clarify the local electronic structures in materials. Therefore, positron annihilation spectroscopy plays a responsible role to understand the more details of electronic structures than any other. We believe that the studies of this thesis contribute toward the complete understanding of positron annihilation properties.
Appendix

A Doppler broadening and angular correlation of positron-electron annihilation radiation

Experiments of Doppler broadening spectrum (DBS) and angular correlation of positron-electron annihilation radiation (ACAR) spectrum are obtained by the positron annihilation spectroscopy experiment. In these experiments, momentum distribution of positron-electron annihilation pair is observed. Here, we briefly describe principles of DBS and ACAR, and the $2\gamma$-annihilation process is considered. After the $2\gamma$-annihilation, two $\gamma$-rays are emitted with energy of 511 keV ($= mc^2$) and momentum of $mc$. The energy and momentum of positron and electron pair must be conserved before and after the positron-electron pair annihilation. However, electron and positron momenta are much smaller than those of $\gamma$-rays. Thus, radiated two $\gamma$-rays have total energy $2mc^2$ and almost zero total momentum (but it has finite momentum). For satisfying those conditions, the $2\gamma$-annihilation creates the two $\gamma$-rays in almost opposite directions as shown in Fig. A.1. When a positron annihilates

![Figure A.1: Schematics of 2γ-annihilation. Blue and red arrows represent momentums of initial p-e pair and generated γ-rays, respectively. $p_L$, $p_1$ and $p_2$ are momentums for initial p-e pair, $\gamma_1$ and $\gamma_2$, respectively. $\gamma_1$ and $\gamma_2$ are radiated two-photons.](image)

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with an electron that has finite momentum $\mathbf{p}_L$, two photons, which have momentums $\mathbf{p}_1$ and $\mathbf{p}_2$, are generated after $2\gamma$-annihilation. The momentum conservation law before and after $2\gamma$-annihilation can be written as,

$$\mathbf{p}_L = \mathbf{p}_1 + \mathbf{p}_2. \quad (A.1)$$

For $x$ and $z$ directions (see Fig. A.1), the momentum conservation low can be respectively written as,

$$p_x = |\mathbf{p}_1| - |\mathbf{p}_2| \cos \theta, \quad (A.2)$$

$$p_z = |\mathbf{p}_2| \sin \theta, \quad (A.3)$$

$$|\mathbf{p}_L|^2 = p_x^2 + p_z^2 = |\mathbf{p}_1|^2 + |\mathbf{p}_2|^2 - 2|\mathbf{p}_1||\mathbf{p}_2| \cos \theta. \quad (A.4)$$

Next, we consider the energy conservation low, and it can be written as,

$$2mc^2 + \frac{|\mathbf{p}_L|^2}{2 : 2m} = c|\mathbf{p}_1| + c|\mathbf{p}_2|, \quad (A.5)$$

where, $m$ and $c$ are electron mass and the velocity of light, respectively. Since $mc^2$ is much higher than typical kinetic energy of electrons in solids, which is about $10^{-4}mc^2$, eq. (A.5) can be given

$$2mc^2 = c|\mathbf{p}_1| + c|\mathbf{p}_2|. \quad (A.6)$$

From eqs. (A.6) and (A.4), we can write the $|\mathbf{p}_1|$ and $|\mathbf{p}_2|$ using $|\mathbf{p}_L|$ and $\theta$ as,

$$|\mathbf{p}_1| = mc + \frac{\sqrt{2}}{2\zeta} \left[|\mathbf{p}_L|\zeta - 2m^2c^2 \sin^2 \theta \right]^{1/2}, \quad (A.7)$$

$$|\mathbf{p}_2| = mc - \frac{\sqrt{2}}{2\zeta} \left[|\mathbf{p}_L|\zeta - 2m^2c^2 \sin^2 \theta \right]^{1/2}, \quad (A.8)$$

$$\zeta = 1 + \cos \theta. \quad (A.9)$$

Here, we assume that $|\mathbf{p}_1|$ is larger than $|\mathbf{p}_2|$. Then, in the limit of $\theta \to 0$, the energies of radiated photons ($E_1$ and $E_2$) are obtained as

$$E_1 = c|\mathbf{p}_1| = mc^2 + \frac{c|\mathbf{p}_L|}{2}, \quad (A.10)$$

$$E_2 = c|\mathbf{p}_2| = mc^2 - \frac{c|\mathbf{p}_L|}{2}. \quad (A.11)$$

Thus, $2\gamma$-annihilation energy spectrum is slightly broadened from $mc^2$ by $c|\mathbf{p}_L|/2$. In the DBS experiments, this energy shift is observed, and the number of generated
photons is plotted as a function of momentum $|p_L|$. Hence, we can extract the momentum distribution of positron-electron annihilation pair before the annihilation via the Doppler shift.

In addition to the DBS, the angle $\theta$, which was shown in Fig. A.1, is observed in the ACAR experiment. Using eqs. (A.3) and (A.11), $p_z$ can be written in the limit of $\theta \to 0$,

$$p_z = |p_2| \sin \theta \sim mc\theta. \quad (A.12)$$

Since the angle $\theta$ becomes a function of $p_z$, we can observe the $p_z$ via the observation of the angle of two photons.

From the above, we can extract the momentum distribution of positron-electron annihilation pair just before the annihilation from both DBS and ACAR experiments. Since the positron in the solids is thermalized, the momentum of DBS and ACAR spectrum mainly depends on the electron momentums in the solids. Thus, the momentum distribution of annihilation pair indicates electron momentum density weighted by the positron density. Because of this, DBS and ACAR experiments are powerful tools for detecting the electronic structure in the solids and at the surfaces. In particular, since the experiment of ACAR has higher resolution than the DBS, we can extract the information on the Fermi surface of metals using ACAR experiment.
B Superimposed atom method

Here, we briefly describe the formulation of superimposed-atom method developed by Puska and Nieminen in 1983. This method is based on the very simple formulation, but gives the accurate results for positron lifetime in many solids. First of all, the superimposed-atom method assumes that the electron density of the solid is approximated by the superposition of electron densities of free-atoms \( n_{\text{at}}(r) \),

\[
n_-(r) = \sum_R n_{\text{at}}(|r - R|),
\]

where \( R \) summation runs over the positions of the host nuclei. The total potential for the positron, \( V_+(r) \), is constructed in a similar way,

\[
V_+(r) = -\sum_R V_{\text{Coul}}^\text{at}(|r - R|) + V_{\text{corr}}[n_-(r)],
\]

where \( V_{\text{Coul}}^\text{at} \) and \( V_{\text{corr}}[n_-(r)] \) are the Coulomb potential for free atoms and p-e correlation potential, respectively. \( V_+(r) \) is used in the three dimensional Schrödinger equation for a positron,

\[
\left[-\frac{\nabla^2}{2} + V_+(r)\right] \psi_+(r) = E_+ \psi_+(r).
\]

Here, \( E_+ \) and \( \psi_+ \) are eigenvalue and wave function for the positron, respectively. The electron density and the positron potential are calculated in the node points of a three dimensional mesh, and the Schrödinger equation is solved by numerical relaxation technique for the \( E_+ \) and \( \psi_+ \) at the node points.

The superimposed-atom method well reproduces positron lifetimes for many simple materials and allows us to use huge systems for positron calculation because of low computational costs of the method. However, there are well known drawbacks in the superimposed-atom method. The electron density and potential are fixed in the method. This assumption is not good enough for calculating the positron states in ionic solids and at surfaces because electron density distributions in such systems are highly deviated from these of the atoms. For DBS calculation, the method is also not good because of the fixed electron densities and wave functions.
Bibliography


