JOINT INSTITUTE FOR NUCLEAR RESEARCH
Dzhelepov Laboratory of Nuclear Problems

FINAL REPORT ON THE INTEREST PROGRAMME
Monte Carlo vs. Two Component DFT

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Abstract

In this work, we explore how a positron behaves inside the 6H-SiC crystal and how it annihilates with electrons to produce measurable signals. First, we build the atomic structure of 6H-SiC and use Quantum ESPRESSO to calculate how electrons are arranged in this material. These electron orbitals are then fed into the CASINO Quantum Monte Carlo (QMC) code, which improves the accuracy by simulating the full many-body behavior using random sampling. This allows us to obtain highly reliable information about electron–positron interactions, including momentum densities and positron lifetimes—quantities central to positron annihilation spectroscopy (PAS). Compared to standard density-functional approaches, our method captures correlation effects more accurately and avoids the typical errors seen in large-volume or defect-sensitive materials. The approach demonstrated here can serve as a foundation for modeling positron behavior in a wide range of materials and future PAS-based investigations.

1 Introduction

Positron annihilation spectroscopy (PAS) is one of the most sensitive techniques for studying microstructural features in solids, including vacancies, dislocations, impurity complexes, porous structures, and electron density distributions. The technique relies on detecting changes in positron lifetime, Doppler broadening, and angular correlation signals—all of which depend critically on the electron–positron momentum density at the point of annihilation.

Significant discrepancies remain when comparing current theoretical models with experimental results. Traditionally, the theoretical interpretation of PAS experiments has relied heavily on density functional theory (DFT) using local density approximation (LDA) and generalised gradient approximation (GGA) correlation functionals. While these functionals have achieved reasonable success in some materials, their limitations become severe in systems exhibiting: large open volumes (vacancies, voids), strong inhomogeneity in electron density, surfaces and interfaces, multideterminantal electronic structures and strongly correlated electrons.

Relaxation Energy

$$\Delta\Omega = E_{\text{HEG+positron}} - E_{\text{HEG}} \tag{1}$$

Contact Pair-correlation Function

$$g(0) = \frac{\rho_{e^-e^+}(0)}{\rho_e \rho_p} \tag{2}$$

Annihilation Rate

$$\Gamma = \pi r_0^2 c \sum_i \left\langle \Psi \left| \hat{O}_s \delta(\mathbf{r}_i - \mathbf{r}_+) \right| \Psi \right\rangle \tag{3}$$

Alternative form:

$$\Gamma = 100.9 \frac{g(0) N_e^{\uparrow}}{V} \tag{4}$$

PositronLifetime

$$\tau = \frac{1}{\Gamma} \tag{5}$$

Enhancement Factor (GGA/LDA)

$$\gamma - 1 = (\gamma_{\text{LDA}} - 1)\exp(-\alpha\epsilon) \tag{6}$$

where reduced density gradient parameter

$$\epsilon = \frac{|\nabla\rho|^2}{(q_{\text{TF}}\rho)^2} \tag{7}$$

1.1 Traditional Method: DFT

Density Functional Theory (DFT) is a quantum-mechanical method used to compute the electronic structure of atoms, molecules, and solids. Instead of solving the many-electron Schrödinger equation directly—which is impossible for large systems—DFT reformulates the problem in terms of the electron density $\rho(r)$ rather than the full many-body wavefunction $\Psi(r, r, \dots)$.
Many-electron Schrödinger Equation

$$\hat{H}\Psi = E\Psi \tag{8}$$

with

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i v(\mathbf{r}_i) \tag{9}$$

In simple terms, DFT simplifies the problem by saying: "Instead of following every person, let's just track how crowded each area is." Instead of calculating the motion of each electron, DFT examines the electron density in space. This makes the calculation easier, while still allowing us to: predict material properties, understand bonding and study electronic behaviour. For very sensitive processes—such as positron annihilation, which requires accuracy better than 1 picosecond—this simplification becomes too crude. DFT's approximations sometimes work well and sometimes fail badly. That's why QMC is required.
Kohn–Sham DFT Equations

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\phi_i = \epsilon_i\phi_i \tag{10}$$

$$v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \tag{11}$$

Total Energy Functional

$$E[n] = T_s[n] + E_H[n] + E_{\text{xc}}[n] + \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \tag{12}$$

1.2 Why DFT is failing in this context?

Researchers have encountered numerous problems due to a "spatial-wave mismatch" between DFT software packages and real physical models. While experimental statistical accuracy for defect-free samples is around 1 ps, DFT calculations fall short of this. Different correlation functionals can yield lifetime predictions that differ by up to 30 ps for the same system. Local or semilocal correlation functionals are "doomed to fail" when applied to solid-state systems that contain large open volumes or surfaces.

This project is critical because it aims to bridge the gap between theory and experiment by shifting from DFT to Quantum Monte Carlo (QMC). The immediate importance of this work lies in the theoretical justification of electron momentum density via Monte Carlo calculation. Successfully completing this task will create the necessary foundation for the next major step: calculating the parameters of positron annihilation within structural defects. It enables the study of "structural features" and defects that arise from various interventions (such as radiation damage or mechanical stress). The use of many-body theory allows for the investigation of systems with a "multi-determinantal nature," which is unavoidable in many lattice defects but impossible to model with standard DFT methods.

1.3 Why use QMC?

Quantum Monte Carlo (QMC) refers to a family of stochastic (random sampling) methods used to solve the quantum many-body problem with extremely high accuracy. It is one of the most reliable numerical techniques for systems where electron–electron or electron–positron correlations are strong. QMC is used to compute: • Relaxation energy • Pair-correlation functions • Annihilating-pair momentum density for a positron in an electron gas. These quantities require extremely accurate treatment of correlation, which DFT cannot provide.

Trial Wavefunction (Slater–Jastrow)

$$\Psi(\mathbf{R}) = e^{J(\mathbf{R})} D_{\uparrow} D_{\downarrow} \tag{13}$$

Slater–Jastrow–Backflow (SJB) Wavefunction

$$\Psi_{\mathrm{SJB}}(\mathbf{R}) = e^{J(\mathbf{R})} D[\mathbf{r}_i + \xi_i(\mathbf{R})] \tag{14}$$

• VMC: Uses a trial wavefunction (Slater–Jastrow or Slater–Jastrow–Backflow) and optimises its parameters by minimising the energy or variance. Electron–positron or electron–electron cusp:

$$\left.\frac{1}{\Psi}\frac{\partial \Psi}{\partial r}\right|_{r\to 0} = \Gamma_{ij} \tag{15}$$

• DMC: Projects out the exact ground state by simulating diffusion in imaginary time, with a fixed-node approximation to handle fermions. Imaginary-time Schrödinger Equation

(DMC)

$$-\frac{\partial \Phi}{\partial t} = (\hat{H} - E_T)\Phi \tag{16}$$

(Drummond et al., 2011) used VMC and DMC as implemented in the CASINO code. QMC can give parameter-free, high-accuracy results for positron lifetimes and annihilation signatures. QMC can treat long-range correlation and multi-determinantal systems (defects). Quantum mechanics requires solving equations that involve all particles simultaneously. For many electrons and positrons, this is mathematically impossible. So, in short, QMC: i. Guesses a wavefunction, ii. Makes random moves (Monte Carlo sampling), iii. Keeps improving the guess, iv. Converges to the correct quantum energy and correlations.

This method is important to use because Positron annihilation depends on: • How close electrons get to the positron, and • How momentum is distributed during annihilation. These are extremely sensitive to correlation, which DFT struggles to capture accurately. QMC, however, directly samples the many-body correlations, so it gives: • More accurate lifetimes • More reliable momentum densities • Better modelling of defects or open volumes

2 Objectives

The primary objective of this work is to theoretically justify and calculate the electron momentum density by modelling positron annihilation using the Quantum Monte Carlo (QMC) method. The underlying motivations involve: • Overcoming DFT Limitations • Modelling Correlations: A key goal is to model the correlation effects of positron-electron wave functions, specifically including long-range correlations, using a Quantum Monte Carlo (QMC) approach.

2.1 Sub-Objectives

i. Reproduce and validate positron lifetime calculations in defect-free solids using QMC. ii. Construct accurate momentum densities of annihilating electron–positron pairs. iii. Prepare the framework to extend QMC calculations toward: vacancy defects, trapped positron states and structural inhomogeneities.

3 Methodology

3.1 Computational Framework

The project will utilise Variational Monte Carlo (VMC) and Diffusion Monte Carlo (DMC). These methods will be implemented using the CASINO code. To address the fermion-sign problem in DMC, the fixed-node approximation will be imposed, constraining the nodal surface of the wave function to match that of the optimised VMC wave function. Linear Expansion for Wavefunction Optimization

$$\Psi_{\mathrm{lin}} = \Psi_0 + \sum_i \Delta p_i \Psi_i \tag{17}$$

Generalized Eigenvalue Optimization

$$H\Delta\mathbf{p} = ES\Delta\mathbf{p} \tag{18}$$

3.2 Wave Function Construction

We will construct many-body trial wave functions for a system with one positron using two primary forms: • Slater-Jastrow (SJ): A product of single-particle Slater determinants (which fix the nodal surface) and a Jastrow factor (which describes interparticle correlations). • Slater-Jastrow-Backflow (SJB): This extends the SJ form by introducing parametrised shifts (backflow) to the particle coordinates, effectively going beyond the single-particle nodal surface.

3.3 Initialisation and Input Data (DFT)

Before running QMC, we will generate initial data using Density Functional Theory (DFT). Single-particle Kohn-Sham orbitals (ϕ) will be computed using DFT. We will use Quantum Espresso and their own custom positron package for these calculations. The PBE (Generalised Gradient Approximation) functional will be used for electron orbitals, and the Boroński-Nieminen (Local Density Approximation) functional will be used for positron orbitals. The orbitals will be represented in a localised B-spline (blip) basis.

3.4 Optimisation Strategy

Once the wave functions are constructed, parameters will be optimised: • Jastrow Factor: Optimisation will generally be done using a variance minimisation method. • Backflow Parameters: These will be optimised alongside the Jastrow factor using an energy minimisation algorithm. Optimising backflow helps increase variational freedom and reduces the fixed-node error in DMC.

3.5 Validation Steps

The approach includes a specific validation sequence: i. Lifetime Calculation: Calculate positron lifetimes in the perfect bulk of materials to test capabilities and compare with existing results (specifically those by K. A. Simula et al.) ii. Momentum Density: Proceed to construct the momentum density of the annihilating pairs15. iii. Defect Analysis: Eventually extend the method to calculate positron annihilation parameters in structural defects like vacancies. APMD Normalization:

$$\int_0^\infty 4\pi p^2 \rho(\mathbf{p}) dp = \frac{4}{3}\pi k_F^3 \tag{19}$$

3.6 Mathematical and Theoretical Framework

The primary goal of the project is to calculate the momentum density of annihilating electron-positron pairs in the material silicon carbide (SiC). This physical property is represented by a specific summation formula involving integrals, orbitals, and weighting factors. i. Gamma Coefficients (γ_j): The core computational challenge lies in determining these weighting factors. Obtaining them effectively completes the task. ii. Lambda Values (λ_j): The Gamma coefficients are derived from Lambda values. The team must calculate Lambda for two scenarios: iii. IPM (Independent Particle Approximation): A simplified case where the correlation term is 1. iv. Interacting Case: A complex case where a correlation term describes the interaction between positrons and electrons. This calculation will be based on a paper by Makkonen, though with slight modifications. v. Wave Function (Ψ_{SJ}): The team must model the system using a Slater-Jastrow wave function. This function includes: vi. Slater Determinants: Mathematical expressions describing multi-fermionic systems (handling spin-up and spin-down electrons). vii. Positron Orbital: An orbital function specifically for the positron. viii. Jastrow Factors ($e^{J(\mathbf{R})}$): Interaction parameters that need to be optimised.

4 Approach

To model electron–positron interactions in 6H-SiC, we first select the appropriate polytype and construct its primitive hexagonal lattice with the correct six-layer stacking, symmetry, and atomic positions. This primitive cell is expanded into a 2×2×1 supercell to provide sufficient periodicity for accurate k-point sampling and electronic structure calculations. Using Quantum ESPRESSO's PWscf module, we prepare the DFT input by defining the lattice parameters, pseudopotentials for Si and C, atomic coordinates, k-point mesh, and plane-wave cutoffs, employing PBE or LDA functionals compatible with the subsequent QMC workflow. A self-consistent DFT calculation is then performed to obtain Kohn–Sham orbitals, energies, charge density, and wavefunction files. These orbitals are converted into the CASINO format, after which Quantum Monte Carlo methods (VMC/DMC) are applied to accurately compute positron annihilation characteristics—including momentum densities, lifetimes, and electron–positron correlation effects.

Uses DFT Kohn–Sham orbitals as input for Slater determinants:

$$\phi_i(\mathbf{r}) \longrightarrow D(\phi_1, \phi_2, \ldots) \tag{20}$$

Then QMC reconstructs wavefunctions:

$$\Psi_{\mathrm{SJB}} = e^J \det[\phi_i(\mathbf{x}_j + \xi_j)] \tag{21}$$

5 Tools and Key Concepts

5.1 Quantum ESPRESSO

Quantum ESPRESSO is described as "an integrated suite of computer codes for electronic-structure calculations and materials modelling, based on density-functional theory, plane waves, and pseudopotentials." It uses DFT, plane-wave basis sets, and pseudopotentials, generates Kohn–Sham orbitals, total energies, forces, and performs structural optimisation. It handles: Phonons, electron–phonon interactions, Molecular dynamics (Car–Parrinello & Born–Oppenheimer), Electric fields, NEB transition states, Wannier functions. Written mainly in Fortran, optimised for HPC systems. Parallelisation is implemented using MPI (Message Passing Interface). "Parallelisation is achieved using the message-passing paradigm and calls to standard MPI libraries."

Quantum ESPRESSO is used to compute the single-particle Kohn–Sham orbitals (r) that serve as input for QMC trial wavefunctions (Slater–Jastrow forms). The KS orbitals are to be computed using the Quantum ESPRESSO software. In simple words: QE tells you how atoms behave, how they bond, how they vibrate, and how electrons move—using quantum mechanics. It is the standard toolbox for running DFT calculations on crystals, molecules, surfaces, or defects.

5.2 Crystal Structure

The 6H-SiC hexagonal crystal was chosen, and a 2×2×1 simulation cell was built. Electron orbitals were computed using Quantum ESPRESSO, and then these orbitals will be fed into QMC to study positron–electron behaviour. 6H-SiC is a hexagonal polytype of silicon carbide. The "6H" means: the unit stacking sequence repeats every 6 Si–C bilayers along the c-axis, this produces a hexagonal lattice symmetry, and it belongs to the P6mc space group.

This is used because Different SiC polytypes (3C, 4H, 6H) differ in their Band gap, Electronic properties, and crystal symmetry. 6H-SiC is widely used for semi-insulating applications and high-power devices. Each bilayer consists of Si–C pairs arranged in tetrahedral coordination. The stacking follows the ABCACB sequence (6-layer period).

5.3 Pseudopotential

A pseudopotential is a mathematical approximation used in electronic-structure calculations (such as DFT) to simplify the treatment of electrons in atoms, specifically, core electrons. ('Pseudopotential', 2025). Pseudopotentials are needed, as in an atom, Core electrons are tightly bound and do not participate significantly in chemical bonding, and valence electrons determine nearly all chemical and physical properties. Meanwhile, solving the Schrödinger equation for all electrons is extremely computationally expensive because core electrons oscillate rapidly near the nucleus, which requires a very large basis set (i.e., many plane waves). So, a pseudopotential reproduces: Valence electron energies, Scattering properties, and Wavefunctions outside the core region. Expansion of Wavefunctions in Plane-waves

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \tag{22}$$

While eliminating core electron states and rapid oscillations in the wavefunction near the nucleus. Quantum ESPRESSO uses pseudopotentials to compute: Kohn–Sham orbitals, Total energies, Forces and stress. Pseudopotentials enable us to neglect core electrons and replace their effects with a simpler potential, allowing for fast and accurate simulations of materials without compromising essential physics.

5.4 MPI

MPI is described as “a standardised and portable message-passing system designed to function on a wide variety of parallel computers.” MPI is a communication protocol allowing multiple processors to exchange data. Enables distributed-memory parallel computing. Essential for large-scale materials simulations because each CPU stores part of the wavefunctions, performs part of the FFT or linear algebra and sends/receives data during SCF loops. In simpler terms: MPI enables multiple computers to collaborate on solving a single large problem. Quantum ESPRESSO uses MPI so that: One CPU computes part of the wavefunction, another CPU computes a different k-point, another handles Fourier transforms and all CPUs share results and converge a self-consistent solution.

6 Conclusion

Quantum Monte Carlo (QMC) methods in positron annihilation spectroscopy (PAS) represent a rapidly developing approach designed to overcome the limitations of traditional Two-Component Density Functional Theory (TCDFT). Because QMC is parameter-free and treats electron–positron correlations explicitly, it offers a more accurate alternative in situations where standard local or semilocal functionals fail. Nevertheless, TCDFT remains essential, as it provides the initial electronic orbitals required to build accurate trial wavefunctions for QMC simulations.

In this work, we outline the complete workflow—from constructing the 6H-SiC crystal and generating Kohn–Sham orbitals in Quantum ESPRESSO to performing high-accuracy QMC calculations in CASINO. Our approach aims to more reliably capture annihilation characteristics, particularly in systems where semi-core or weakly bound electrons are present.

Future efforts must focus on validating the method through concrete calculations and comparisons with experimental data. Further challenges include extending QMC to treat deep-core annihilation, reducing computational cost, and applying these methods to complex systems such as surfaces, defects, and large open-volume structures where traditional DFT approaches are known to struggle.

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