
First-principles Computational Methods for Composite Bosons in Many Body Physics: Excitons and Cooper pairs

First-principles Computational Methods for Composite Bosons in Many Body Physics:
Excitons and Cooper pairs
PhD Thesis

Riccardo Reho

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First-principles Computational Methods for Composite Bosons in Many Body Physics: Excitons and Cooper pairs

Numerieke methoden vanuit eerste principes voor samengestelde
Bosonen in de veel-deeltjes fysica: Excitonen en Cooperparen

(met een samenvatting in het Nederlands)

Proefschrift

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To my family

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Introduction

Progress in society has been driven by the discovery of new functional materials, as seen in the silicon revolution. Physics, chemistry, and mathematics have been the core sciences for understanding the fundamental interactions that govern the world around us. In the past century, the emergence of computer science has radically changed how we study nature. The possibility of designing materials through computer simulations has revolutionized the way we approach material science, offering a cost-effective alternative while complementing traditional experimental methods. Computational approaches based on first-principles methods, such as Density Functional Theory (DFT), enable the prediction of materials' properties directly from fundamental physical laws. The development and computational implementation of DFT enhance our understanding of fundamental interactions in matter and drive the discovery of new material properties; both of these are considered to constitute key steps in technological progress. The roots of DFT trace back to the early 20th century, with the advent of quantum mechanics. The Schrödinger's equation¹ (1927) provides a framework for describing the energies and dynamics of electrons in atoms and molecules, but solving it for many-electron systems is computationally prohibitive and still impossible analytically. An early attempt to solve this challenge was made by Thomas and Fermi, who proposed that the total energy of a system could be expressed as a functional of the electron density (1927)^{2,3}. However, their approach relied on a semiclassical approximation, assuming a uniform electron gas, which led to an oversimplified treatment of kinetic energy and, therefore, entirely neglecting exchange and correlation effects. The breakthrough came with the seminal works of Hohenberg and Kohn (1964), who rigorously demonstrated that the ground-state properties of a many-electron system are uniquely determined by its ground-state electron density⁴. In principle, their theorem allows to bypass the need for the complex many-body wavefunction but does not provide a scheme to find the ground state density. Unlike the Thomas-Fermi model, their theorem established a formal foundation for DFT, showing that an exact energy functional which include exchange and correlation effects exists. Building on this, Kohn and Sham (1965) further introduced practical computational schemes to solve DFT equations using exchange-correlation functionals⁵. This paradigm shift made it feasible to compute the electronic structure of materials with remarkable accuracy. Over the decades, DFT has become indispensable for both

industrial applications and fundamental science. Its success is attributed to the collaborative efforts of scientists who developed advanced theoretical methods, improved approximations, and scaled computational capabilities towards the exascale revolutions⁶. Among others, modern applications of DFT extend to clarifying two pivotal research areas: the phenomenon of superconductivity and the optical properties of 2D materials.

Superconductivity, holds the promise of societal advancements, ranging from dissipationless energy transmission to quantum computing. The microscopic theory of superconductivity is grounded in the Bogoliubov-de Gennes (BdG) equations, a formulation based on the Bardeen-Cooper-Schrieffer (BCS) theory, which describes spatially varying superconducting order parameters. Solving the BdG equations enables the exploration of exotic phenomena like zero energy Majorana modes in topological superconductors, which could enable fault-tolerant quantum computing.

Understanding light-matter interactions in two-dimensional (2D) materials is essential for unlocking their potential in optoelectronic and photonic devices, such as solar cells, high-speed modulators, and quantum information systems. The reduced dimensionality of 2D materials enhances quantum confinement and reduces the effect of electronic screening, giving rise to strongly bound electron-hole pairs known as excitons. In 2D materials, excitons exhibit large binding energies, leading to unique electronic properties that make them ideal platforms for studying fundamental photon-electron interactions. However, accurately modeling these interactions requires going beyond standard electronic structure methods. While Density Functional Theory (DFT) is a powerful tool for ground-state calculations, it fails to capture excited-state properties, such as band gaps and optical spectra, which are crucial for understanding excitonic effects. Many-Body Perturbation Theory (MBPT) provides a more robust framework for describing these phenomena, enabling the accurate treatment of excitons, plasmons, and nonlinear optical responses in quantum materials.

As an interesting and personal remark, I chose the title of this thesis because both excitons and Cooper pairs are bosonic particles, sharing the same quantum statistical classification. It is fascinating how their distinct formation mechanisms and physical contexts set them apart, giving rise to a wealth of intriguing and diverse scientific phenomena. I hope that, by reading this thesis, the reader will gain a deeper understanding of these differences and become intrigued by the unique properties and behaviors they lead to.

Outline of this thesis

This thesis describes how we exploited and developed first-principles methods to predict and interpret the properties of quantum materials, focusing on the field of superconductivity, and theoretical spectroscopy. We integrated the Bogoliubov-de Gennes (BdG) equations into the DFT framework of SIESTA, enabling first-principles studies of superconductivity. Using this method, we investigated proximity-induced superconductivity in semiconductor-superconductor devices such as PbTe/Pb, and clarified the microscopic mechanism behind the enhancement of the superconducting critical temperature (T_C) in FeSe monolayers deposited on SrTiO₃ (STO)

substrate. In parallel, we have advanced the development of Many-Body Perturbation Theory (MBPT) for light-matter interactions in 2D materials, implementing photoluminescence calculations in the YAMBO code. This approach has deepened our understanding of the electronic and optical properties of 2D materials, including van der Waals (vdW) transition metal dichalcogenides (TMDs) heterostructures and few layers Bi_2Se_3 systems.

Our contributions provide powerful tools for exploring novel quantum phases and designing materials with unprecedented functionalities, paving the way for transformative technological innovations.

In **Chapter 2** we provide an overview of many-body physics. It introduces Density Functional Theory (DFT), focusing on its foundational principles, including the Born-Oppenheimer approximation, the two Hohenberg-Kohn theorems, and the Kohn-Sham approach (self-consistent field solution method). It discusses the limitations of DFT such as the band-gap underestimation and the applicability of DFT to excited systems. It reviews advanced methods such as the GW approximation and Bethe-Salpeter Equation, that can be used to overcome these shortcomings. Most importantly, this chapter contains an original introduction to superconductivity, explaining the Bogoliubov-de Gennes formalism, which is essential for understanding the microscopic theory of superconductivity. It also covers unconventional superconductivity, highlighting the difference with traditional BCS theory.

In **Chapter 3** we lay down the theoretical formalism of the SIESTA-BdG method. In this work, we combined the BdG equations with DFT in a unified framework, Superconducting Density Functional Theory (SCDFT). We integrated this approach in the open source SIESTA code, establishing the SIESTA-BdG method. We demonstrated its accuracy and efficiency by applying the method for both conventional and unconventional superconductors.

In **Chapter 4** we apply the SIESTA-BdG method to a PbTe/Pb heterostructure. We predict the emergence of proximity induced superconductivity at the interface between the two materials and focus on the potential applicability of this system for hosting Majorana Zero Modes (MZMs).

In **Chapter 5** we apply the SIESTA-BdG method to monolayer FeSe , both in its freestanding form and when placed on a SrTiO_3 substrate (STO). We demonstrate that the substrate profoundly alters both the normal-state and superconducting properties of FeSe . We identify proximity-induced superconductivity in the interfacial TiO_2 layer of STO and propose interface engineering as a potential pathway potential pathway for discovering novel high-temperature FeSe -based superconductors.

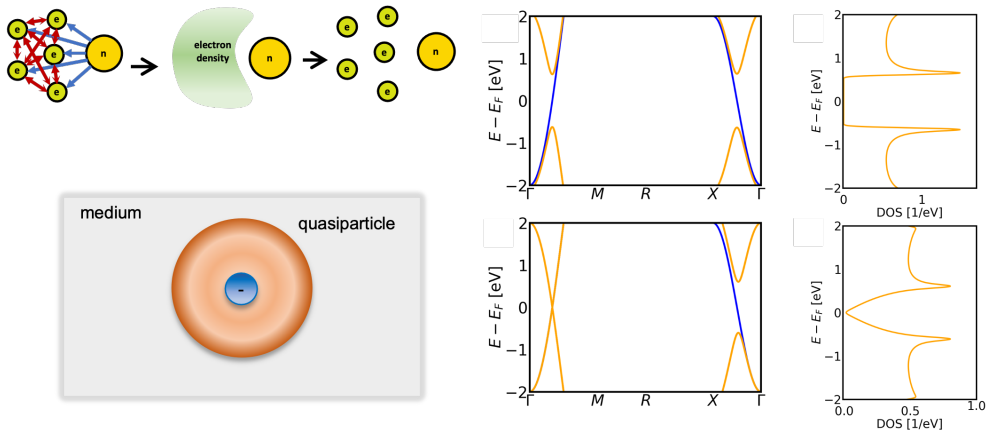
In **Chapter 6** we discuss multilayer 2D heterostructures of TMDs as a class of materials with significant potential for optoelectronic applications. Despite over 13 years of research⁷, many fundamental aspect of their properties remain to be fully understood, highlighting the ongoing challenges and opportunities in this field. We discuss how the properties of these materials can be engineered by tuning various degrees of freedom, including: chemical composition, stacking order, strain, and twisting. Using Many-Body Perturbation Theory (MBPT), we investigated how these factors influence the excitonic responses of MoS_2/WS_2 and $\text{MoSe}_2/\text{WSe}_2$ van der Waals heterostructures.

In **Chapter 7**, we present our results on Bi_2Se_3 , a textbook example of a strong topological insulator. This study is the result of a collaboration that combines experimental and theoretical approaches. Using Density Functional Theory and pump-probe spectroscopy, we investigate the impact of hybridized surface states on optical transitions and carrier dynamics in two-dimensional Bi_2Se_3 few-layer nanoplatelets. Our findings highlight the crucial role of surface states in shaping the optical and electronic properties of Bi_2Se_3 .

Bibliography

- 1** E. Schrödinger, Physical review **28**, 1049 (1926).
- 2** L. H. Thomas, in *Mathematical proceedings of the Cambridge philosophical society*, Vol. 23 (Cambridge University Press, 1927) pp. 542–548.
- 3** E. Fermi, Rend. Accad. Naz. Lincei **6**, 32 (1927).
- 4** P. Hohenberg and W. Kohn, Physical review **136**, B864 (1964).
- 5** W. Kohn and L. J. Sham, Physical review **140**, A1133 (1965).
- 6** V. Gavini, S. Baroni, V. Blum, D. R. Bowler, A. Bucchieri, J. R. Chelikowsky, S. Das, W. Dawson, P. Delugas, M. Dogan, *et al.*, Modelling and Simulation in Materials Science and Engineering **31**, 063301 (2023).
- 7** K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Physical Review Letters **105**, 136805 (2010).

Density Functional Theory and beyond ground-state approaches



Based on

This chapter is written for this thesis by the author. It contains an original introduction to superconductivity, written by the author and reviewed by Zeila Zanolli.

In this chapter we give an overview of the many-body problem and computational strategies to tackle its numerical solution. We introduce density functional theory (DFT) as one of the most powerful and widely employed methods for studying the ground-state properties of materials. We discuss the limitations of DFT focussing on aspects relevant for the work outlined in this thesis. We provide the theoretical background on how DFT can be extended to describe spectroscopy (Section 4) and superconductivity (Section 5). This discussion sets the stage for the research chapters.

1 The many-body problem: quantum mechanical formulation

The fundamental challenge in quantum many-body physics lies in solving the many-body Schrödinger equation¹ for a collection of **interacting** particles. For a system consisting of N electrons (labelled by i), and M nuclei (labelled by I) interacting with each other via Coulomb interactions, the full many-body Hamiltonian (H_{MB}) can be written as²:

$$\begin{aligned} \hat{H}_{\text{MB}} = & \underbrace{\sum_i^N \frac{\hat{\mathbf{p}}_i^2}{2m}}_{\hat{T}} + \underbrace{\frac{1}{2} \sum_{\substack{i,j \\ i \neq j}}^N \frac{e^2}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|}}_{\widehat{v_{ee}}} \\ & + \underbrace{\sum_I^M \frac{\hat{\mathbf{P}}_I^2}{2M_I}}_{\hat{T}_n} + \underbrace{\frac{1}{2} \sum_{\substack{I,J \\ I \neq J}}^M \frac{Z_I Z_J e^2}{|\hat{\mathbf{R}}_I - \hat{\mathbf{R}}_J|}}_{\widehat{v_{nn}}} + \underbrace{\sum_{i,I}^{N,M} \frac{-Z_I e^2}{|\hat{\mathbf{r}}_i - \hat{\mathbf{R}}_I|}}_{\widehat{v_{en}}}, \end{aligned} \quad (1)$$

where $\hat{T}/\hat{T}_n$ represent the kinetic energy of electrons/ions (in terms of their momentum $\hat{\mathbf{p}}_i/\hat{\mathbf{P}}_I$ and positions $\hat{\mathbf{r}}_i/\hat{\mathbf{R}}_I$) and $\widehat{v_{ee}}, \widehat{v_{nn}}, \widehat{v_{en}}$ the electron-electron, nuclear-nuclear and electron-nuclear Coulomb interactions. The nuclei carry charges $Z_I e$, and the masses of electrons and nuclei are denoted by m and M_I , the electron charge is given by $-e < 0$. For simplicity, we ignored spin-orbit coupling but it can be included (research chapters). By solving the many-body Hamiltonian eigenproblem, we acquire the spectrum and eigenstates of $\hat{H}_{\text{MB}}$.

Solving the many-body problem Eq. (1) is a formidable task already in classical mechanics. In fields like astrophysics, for example, the many-body problem cannot be solved analytically for systems with more than three particles ($N > 3$)³. Hence, it is necessary to rely on approximations and numerical/computational approaches to obtain results. This challenge is even more pronounced in quantum mechanics. In quantum systems, the behaviour of particles is not only influenced by classical forces but also by their intrinsic statistical properties. The Pauli exclusion principle⁴ states that no two fermions can occupy the same quantum states simultaneously. This fact, introduces a significant layer of complexity when accounting for particle correlation and exchange effects.

To make the many-body problem more tractable, researchers developed several approximation techniques. One of those is the *Born-Oppenheimer approximation* (Section 2), which

simplifies the many-body problem Eq. (1) by decoupling the motion of nuclei and electrons, assuming that the nuclei move much more slowly than the electrons (*adiabatic approximation*).

The two main numerical approaches to solve the many-body problem are: wavefunction - based methods, such as Hartree-Fock (HF)⁵⁻⁷, and functional-based methods, as DFT^{8,9}. Wavefunction methods require an initial guess for the wavefunction, and the total energy is computed using the Rayleigh-Ritz variational principle¹⁰. In the HF method, the many-body wavefunction is approximated by a single Slater determinant, which describes the system's wavefunction as a product of one-electron wavefunctions. While this approach is sufficiently accurate for molecular systems, it performs poorly for solids because it neglects electron correlation effects beyond the mean-field approximation. Moreover, wavefunction methods face scalability challenges, both in terms of memory and computational complexity. The electronic wavefunction depends on $3N$ electron coordinates, and storing it explicitly requires an impractically large amount of memory. For instance, even with a modest grid of $M = 10$ points per coordinate, representing the wavefunction for a carbon atom ($N = 6$) would require $10^{6.3} \times 16 \text{ bytes} = 16 \text{ exabytes}$, far exceeding any feasible storage capacity. Beyond memory limitations, in the HF approximation, the many-body wave function $\psi_{\mathbf{r}_1, \dots, \mathbf{r}_N}$ is expanded in terms of N single-particle orbitals. In a computational framework, each of this orbital is expanded in a set of N_G functions (such as plane waves, $\sim 100 - 1000$). The size of the matrices that have to be diagonalized will be of the order of $\binom{N_G}{N} = \frac{N_G!}{N!(N_G-N)!}$, which grows exponentially². As a consequence, exact diagonalizations is computationally intractable for systems beyond a few hundred of electrons, even on modern supercomputers.

In DFT, instead, physical observables, such as the total energy, are functional of the density which is a function of three coordinates, rather than $3N$ degrees of freedom (without accounting spin)¹. This approach, simplifies the description of interacting electrons and is reviewed in Section 3.

2 The Born-Oppenheimer approximation

Electrons, as elementary particles, follow the laws of quantum mechanics, while the more massive nuclei can be regarded as classical particles, simplifying the many-body Hamiltonian H_{MB} [Eq. (1)]. The interactions between different nuclei $\widehat{v}_{nn}$ and between electrons and nuclei $\widehat{v}_{en}$ are particularly challenging to compute. To address this, it is common practice to employ the *Born-Oppenheimer approximation*¹¹ (BO) where the electronic part of the wave function is solved keeping the nuclei's position fixed. This approximation is justified because nuclei are significantly heavier than electrons, about 15 times more massive, making their kinetic energy T_n relatively small with respect to the electronic one. Additionally, in typical semiconductors, electronic excitations are one order of magnitude higher in energy than phononic excitations. As a result, electrons relax much faster than nuclei, allowing us to treat electronic motion independently of nuclear dynamics.

¹As we will see in Section 3, this assumption breaks down in practical calculations when dealing with observables that explicitly depend on the wavefunction, such as excitation spectra.

The BO approximation:

- Decouples the electron and nuclei wavefunctions:

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{R}_1, \dots, \mathbf{R}_M) = \Phi_e(\mathbf{r}_1, \dots, \mathbf{r}_N) \Phi_n(\mathbf{R}_1, \dots, \mathbf{R}_M). \quad (2)$$

This factorization separates the electronic and nuclear degrees of freedom, simplifying the problem².

- Neglects contributions to $\hat{T}_n$ that involve transitions between different electronic states for the same nuclear configuration, as well as terms involving couplings between electronic and nuclear states¹³.

The BO approximation greatly simplifies the many-body problem. However, the complexity of the electrons' mutual interactions remains a major challenge. Accounting for this interaction is crucial to provide accurate predictions of binding energies, bond lengths and interatomic distances in materials. Moreover, the electron-electron Coulomb interaction ($\widehat{v}_{ee}$) is responsible for many of the most intriguing phenomena in solids.

2.1 Mean-Field approaches

One way to do address the complexity of $\widehat{v}_{ee}$ involves replacing the complex two-body Coulomb interaction with an effective, one-particle potential (*mean-field approximation*). In this approach, each electron experiences an average potential generated by all other electrons. The difference between the exact two-body interaction and its approximation is treated as a small perturbation, which can be handled using perturbation theory. The HF approximation has been, historically, one of the first mean-field theories employed to determine the wavefunction and the energy of a quantum many-body system. However, the HF approximation neglects many-body correlations effects, such as the screening of the Coulomb interaction. Hence, it severely overestimates binding energies and bond strengths in extended systems^{5,6,13}.

3 Density Functional Theory

DFT is a mean-field method, capable of capturing all higher-order correlation effects. It is an *exact* formulation of the many-body problem as a functional of the density and yields a Hamiltonian that can be efficiently diagonalized within practical computational limits.

Hohenberg and Kohn⁹ considered the Hamiltonian Eq. (1), rewriting it in second quantization formalism as:

$$\begin{aligned} \hat{H}_{\text{HK}} = & \int d\mathbf{r} \hat{\psi}^\dagger(\mathbf{r}) \left(-\frac{\nabla^2}{2m} \right) \hat{\psi}(\mathbf{r}) + \int d\mathbf{r} \hat{n}(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) \\ & + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \hat{\psi}(\mathbf{r}') \hat{\psi}(\mathbf{r}), \end{aligned} \quad (3)$$

²For a discussion about the dependence of Φ_n on Φ_e we refer to the thesis of Reichardt¹²

where $n(\mathbf{r})$ is the electron density, $\hat{\psi}(\mathbf{r})/\hat{\psi}^\dagger(\mathbf{r})$ annihilate/create an electron at position $\mathbf{r}$ and $V_{\text{ext}}(\mathbf{r})$ is an external potential that, within the BO approximation, includes the electrostatic potentials of the nuclei.

DFT relies on two key theorems⁹:

1. First Hohenberg-Kohn Theorem:

For a system of interacting electrons in an external potential $V_{\text{ext}}(\mathbf{r})$, the potential itself is uniquely determined, up to a constant, by the ground-state electronic density $n^0(\mathbf{r})$. In other words, different external potentials cannot lead to the same ground-state density. Since the ground-state density uniquely determines the Hamiltonian, all properties of the system are fully determined by the density.

2. Second Hohenberg-Kohn Theorem:

Assuming a non-degenerate ground-state, the total energy of the system is a functional of the electron density $n(\mathbf{r})$ and can be written as:

$$E[n] = E_{\text{HK}}[n] + \int d\mathbf{r} n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}). \quad (4)$$

Here, $E_{\text{HK}}[n]$ is a universal functional of the density, independent of the external potential and the number and species Z of the nuclei. It can be written as

$$E_{\text{HK}}[n] = T[n] + V_{\text{HK}}[n], \quad (5)$$

where $T[n]$ represents the kinetic energy functional and $V_{\text{HK}}[n]$ accounts for the electron-electron interaction energy. The ground-state density $n^0(\mathbf{r})$ minimizes the functional $E[n]$.

The Hohenberg-Kohn theorems do not specify a practical way to compute the spectrum and eigenstates of $\hat{H}_{\text{HK}}$ [Eq. (3)]. A procedure was proposed by Kohn and Sham (KS)^{8,14}. They postulated an ansatz to compute the many-body electronic density $n(\mathbf{r})$ from an auxiliary independent one-particle system with Hamiltonian $\hat{H}_{\text{KS}}$, wavefunctions ϕ_i and density $n(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2$. The electronic density $n(\mathbf{r})$ in the KS system is the same as the one in the interacting system. The KS approach is based on the idea that the expression for $E[n]$ in Eq. (4) can be separated into *known* and *un-known* terms. The known terms can be computed exactly, while the un-known terms are contained in what is called the exchange-correlation functional ($E_{\text{xc}}[n]$). $E_{\text{xc}}[n]$ is not known exactly and we use approximation to compute it (Section 3.2). To be specific, a new functional $E_{\text{KS}}[\{\phi_i\}]$ is introduced, demanding that $E_{\text{KS}}[\{\phi_i\}] = E_{\text{HK}}[n]$. E_{KS} is further partitioned into the kinetic energy of interacting electrons $T[n]$, the Hartree energy $E_{\text{H}}[n]$ and the exchange-correlation functional $E_{\text{xc}}[n]$. The kinetic energy of interaction electrons is further partitioned into the kinetic energy of the non-interacting system $T_{\text{S}}[\{\phi_i\}]$ (known) and the correlation contribution to the interacting kinetic energy $T_{\text{correlation}}[n]$ (un-known), namely $T[n] = T_{\text{S}}[\{\phi_i\}] + T_{\text{correlation}}[n]$. All the terms mentioned above are defined as follow:

$$T_S [\{\phi_i\}] \equiv \sum_i \int d\mathbf{r} \phi_i^*(\mathbf{r}) \left(-\frac{\nabla^2}{2m} \right) \phi_i(\mathbf{r}), \quad (6)$$

$$E_H[n] \equiv \frac{e^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (7)$$

$$E_{xc}[n] \equiv E_{HK}[n] - T_{HK}[n] - E_H[n]. \quad (8)$$

The external energy term in Eq. (4) is written in terms of the KS orbitals as:

$$E_{\text{ext}} [\{\phi_i\}] = \sum_i \int d\mathbf{r} \phi_i^*(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) \phi_i(\mathbf{r}). \quad (9)$$

Hence, the energy functional in Eq. 4 is rewritten in the KS approach as:

$$E_{\text{KS}}[\phi_i] = \underbrace{T_S [\{\phi_i\}] + E_H[n] + E_{\text{ext}}[n]}_{\text{known terms}} + \underbrace{T_{\text{correlation}}[n] + E_{xc}[n]}_{\text{un-known terms}}. \quad (10)$$

Lastly, the total energy is minimized via a variational method and the *Kohn-Sham equations* are derived as:

$$\left\{ -\frac{\nabla^2}{2m} + V_{\text{ext}}(\mathbf{r}) + V_H[n](\mathbf{r}) + V_{xc}[n](\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \quad i = 1, \dots, N, \quad (11)$$

where:

$$\begin{aligned} V_H[n](\mathbf{r}) &\equiv \frac{\delta E_H[n]}{\delta n(\mathbf{r})} = e^2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \\ V_{xc}[n](\mathbf{r}) &\equiv \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \end{aligned} \quad (12)$$

The Kohn-Sham equations are a set of N one-electron Schrödinger equation of non-interacting electrons. Thus, they transform the complex many-body problem of interacting electrons into an effective single-particle problem. They provide the exact ground-state density and have been successfully applied to describe electronic properties of materials.

To summarize, the system of N interacting electrons is described by a many-body wavefunction that depends on $3N$ spatial coordinates (plus a factor of 2 to account for spin s), making direct computation infeasible for large N . The Hohenberg-Kohn theorems establish that the ground-state energy of the system can be expressed as a functional of the electron density $n(\mathbf{r})$, which depends only on 3 spatial variables, significantly reducing the complexity of the problem. The Kohn-Sham formalism maps the interacting system onto an auxiliary system of non-interacting electrons that reproduces the same ground-state electron density $n(\mathbf{r})$ as the original many-body system, providing a practical framework for calculating electronic properties (Fig. 3.1). At this point, it is important to highlight a fundamental *caveat* of DFT. All ground-state observables are, in principle, functionals of the electron density. This would imply that the many-body wavefunction is unnecessary. However, the Kohn-Sham (KS) approach models an auxiliary system of non-interacting electrons, whose ground-state density matches that of the interacting system. The electrons are described by single-particle orbitals that

form a Slater determinant, representing the ground-state wavefunction of the non-interacting reference system. The KS wavefunction does not correspond to the true interacting system, and thus DFT is inherently limited in its ability to capture observables that depend explicitly on the many-body wavefunction, such as excitation spectra. The limitations of DFT and strategies to go beyond it are discussed in Sections 3.2 and 4. The Kohn-Sham equations are solved in different codes, such as Quantum Espresso (QE)^{15,16} or SIESTA¹⁷.

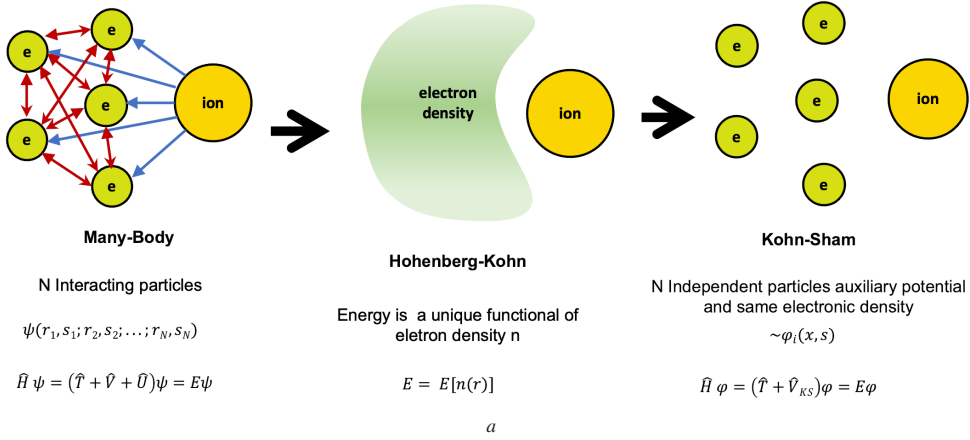


Figure 3.1 The N -electrons system depends on $3N$ spatial variables (plus spin), making direct computation infeasible. The Hohenberg-Kohn theorems reduce the problem to the electron density $n(\mathbf{r})$ (3 variables). The Kohn-Sham formalism maps the interacting system to a non-interacting one with the same $n(\mathbf{r})$.

^aSee the end of Section 3 for a discussion about the KS wavefunction.

3.1 The self-consistent field solution method

The KS equations [Eq. (11)] depend on the electron density ($n(\mathbf{r})$). However, this density is also obtained from their solutions. As a result, they form a set of nonlinear equations that must be solved self-consistently through an iterative process. The standard approach is to solve those equations -via the *self-consistent field* (SCF) approach, depicted in Fig. 3.2. First, one sets an initial guess for the electron density n ($n^{\uparrow/\downarrow}$ for spin densities) which is typically set to be the sum of atomic densities $n = \sum_I n_I(\mathbf{r} - \mathbf{R}_I)$. Then, one computes the SCF potential $V_{\text{scf}}(\mathbf{r})$ as:

$$V_{\text{scf}}(\mathbf{r}) \equiv V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}[n](\mathbf{r}) + V_{\text{xc}}[n](\mathbf{r}). \quad (13)$$

The KS equations are solved to obtain an updated electron density. This initiates a self-consistent cycle where the electron density is iteratively refined at each step. If the newly computed density differs from the previous one, the process is repeated, mixing the old and new densities, until convergence is reached and self-consistency is achieved. The final n is used to build the one-particle KS Hamiltonian, which serves as a first approximation to the real

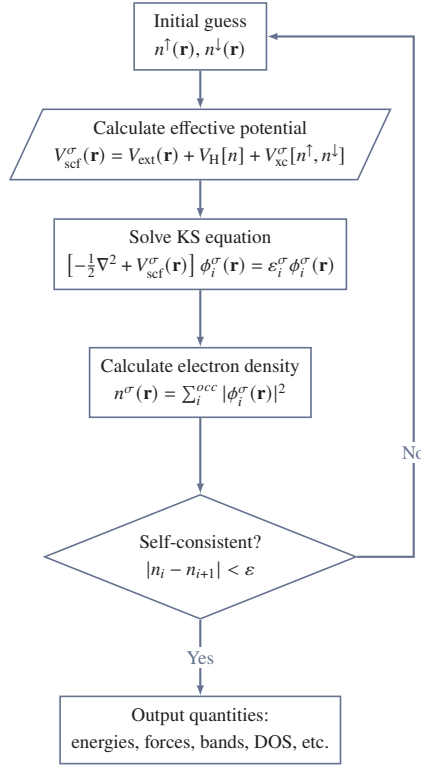


Figure 3.2 Schematic of the iterative process to compute self-consistent solutions of Kohn-Sham equations. We assumed atomic unities. Quantities are defined in Equations (13,11).

Hamiltonian $\hat{H}_M$ of the system. Note that the obtained spectrum and eigenfunctions belong to the auxiliary KS system and not to the original N-particles interacting Hamiltonian $\hat{H}_{\text{HK}}$. Only the electronic density is ensured to be exactly the same in the two systems. Nevertheless, the KS Hamiltonian is employed as a good starting point for more refined methods based on many-body perturbation theory (MBPT) and discussed in the next sections. The KS approach approach breaks down in the situations discussed below.

3.2 Limitations of DFT

DFT is a powerful theoretical framework for predicting a wide range of materials properties with relatively low computational cost. However, its formalism is strictly valid for ground-state properties and is not suitable for describing excited states or systems far from equilibrium. Below, we outline some key shortcomings of DFT:

1. **Approximating $E_{\text{xc}}[n(\mathbf{r})]$:** The exact form of the exchange-correlation functional is unknown. Historically, the local-density approximation (LDA)¹⁴ functional has been

the first and most widely used functional. The LDA functional assumes that $E_{xc}(\mathbf{r})$ can be locally approximated by the exchange-correlation functional of the uniform electron gas with the same electronic density $n(\mathbf{r})$, neglecting any non-local effects. Better approximations have been developed over the years, and for the simulations employed in this thesis we used the Perdew-Burke-Ernzerhof (PBE) functional¹⁸ from the generalized gradient approximation (GGA) family of exchange-correlation energies. This functional partially captures non-local effects.

2. **Band gap underestimation and excitons:** DFT computes the spectrum of the auxiliary KS system. As such, the eigenvalues do not have direct physical meaning. For semiconductors and insulators, this implies that the KS band gap does not necessarily correspond to the true quasiparticle gap of the interacting system. In most cases, DFT underestimates the electronic band gap¹⁹. In addition, DFT cannot accurately describe polarization effects arising from electron-hole interactions, which are crucial in optical spectra. A more accurate description of electron-electron interaction beyond DFT requires MBPT²⁰⁻²³. This formalism is reviewed in section 4.
3. **Dispersion forces:** Van der Waals interactions are not captured by the DFT method. In 2D materials, Van der Waals interactions are important for the interaction between different layers and corrections have been developed to account for such forces. In this thesis, we mainly adopted the correction developed by *Grimme et al.*^{24,25}.
4. **Superconductivity:** DFT cannot describe the superconducting state. Researchers employed different strategies to address this issue, a summary of these strategies are described in this thesis in section 5. The method developed by the author is described in Chapter 3.
5. **Strongly Correlated Systems:** DFT fails to predict properties of materials with strong electron-electron correlations such as Mott insulators or transition metal oxides. Researchers, employs approaches based on DFT + mean-field theory (DMFT) or Hubbard U corrections to solve this issue^{26,27}. FeSe (Chapter 5) is a complex system that requires accounting for both superconductivity and a Hubbard-U correction.
6. **Excited States and Time-Dependence:** DFT cannot describe excited states directly. Time-dependent DFT (TD-DFT) is a theoretical framework capable of describing the dynamics of excited states but has limitations related to the exchange-correlation functional, the description of non-local many-body interactions and multi-excitations states²⁸. In this thesis, we employ MBPT approaches to predict the optical properties of excited 2D systems (Chapter 6).
7. **Finite Temperature:** DFT is a zero-temperature theory. Electronic temperature can easily be incorporated via state occupations, while nuclear contributions require explicit treatment²⁹. To account for the nuclear contributions, researchers typically employ either: (i) molecular dynamics (MD) simulations³⁰, which reproduce thermal nuclear motion

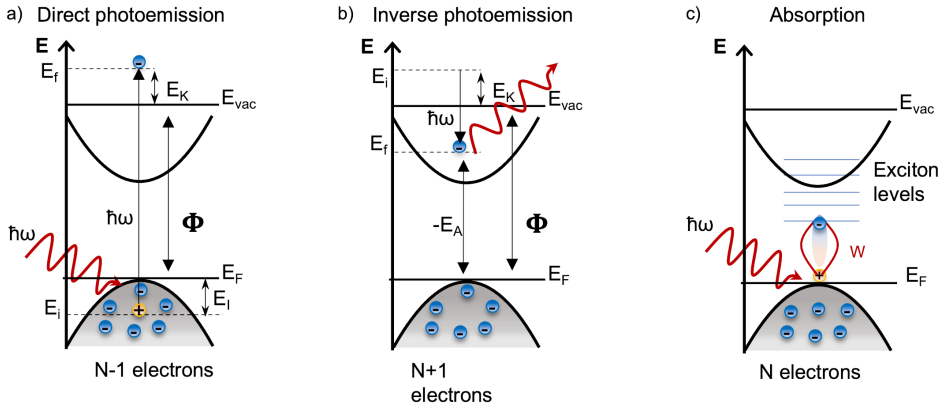


Figure 4.3 Schematic representation of typical spectroscopy experiments involving electron excitations. In (a) direct photoemission, an electron absorbs a photon and is excited via a laser pulse with energy $\hbar\omega$ from an initial energy state E_i to a final energy state E_f beyond the vacuum level E_{vac} , acquiring kinetic energy E_K . In (b) inverse photoemission, an excited electron relaxes to a lower energy state by emitting a photon. In (c) absorption the electron remains within the material, attracted by empty states through the screened Coulomb interaction W . The interaction between the excited electron and the resulting hole leads to the formation of neutral excitations (excitons), whose spectrum characterizes the material's electronic polarization response.

and yield temperature-dependent observables; (ii) approximate model Hamiltonians, such as those by Knoop et al.³¹ that provide an analytic solution using perturbation theory.

A detailed treatment of DFT can be found in the book of *Martin et al*¹³.

4 Many-Body Perturbation Theory

An extensive discussion of many-body perturbation theory is beyond the scope of this thesis, and several review and books can be found in the literature^{2,13,32–35}. Here, we set the stage by discussing the experimental and theoretical motivations to go beyond DFT. We identify the key physical quantities and phenomena required for a more accurate description of electronic levels and optical transitions in semiconductors, and show how the GW method (Section 4.4) and Bethe-Salpeter equation (Section 4.5) account for these effects.

4.1 Experimental Motivation and Theoretical Challenges in Spectroscopy

Spectroscopic measurements are pivotal for structural characterization and for studying the dynamics of electrons and holes in materials. They involve exciting a sample by incoming photons, electrons, or x-ray and measuring its response after perturbation. Excited systems can only be described by a theoretical formalism that goes beyond a ground-state prescription, and

therefore beyond DFT³². Typical spectroscopy experiments are: photoelectron spectroscopy (PES)^{36–38}, inverse photoemission (IPES)^{39–41}, and absorption^{42,43} (Fig. 4.3).

PES [Fig. 4.3.(a)] measures occupied states, whose energies lie below the Fermi level E_F , by detecting ejected electrons (photoelectrons). The initial energy E_i of the electron can be reconstructed from the photon energy $\hbar\omega$, the work function Φ and the kinetic energy of photoelectrons that reach the detector via the following relationship:

$$E_I = -E_i = \hbar\omega - E_K - \Phi, \text{ for } E_i < E_F, \quad (14)$$

where E_I is the ionization energy. In a PES experiment, the total number of electrons in the system changes from $N \rightarrow N - 1$.

IPES [Fig. 4.3.(b)] probes unoccupied states, whose energies are above E_F . In IPES, an excited electron relaxes via a radiative transition into a lower unoccupied state, emitting a photon. The final energy E_f , defines the energy needed to free an electron to the vacuum, namely the electron affinity (E_A), and can be obtained via the following relationship:

$$-E_A = E_i = E_K - \hbar\omega + \Phi, \text{ for } E_i \geq E_F. \quad (15)$$

The total number of total electrons in the system changes from $N \rightarrow N + 1$.

In PES and IPES the photoelectron is decoupled from the sample. In particular, in PES one can deduce, via energy and momentum conservations laws [Eq. (14)], the change in total energy of the sample as the electron escape into the vacuum. This change in energy is interpreted as the energy level of a *hole* (missing electron). Absorption [Fig. 4.3.(c)] involves both PES and IPES but it is more than just the concurrence of these two events: it involves electron-hole interactions. Unlike in photoemission, the electron remains within the sample, and the photoelectron and hole cannot be treated independently, as the electron is attracted to the hole via Coulomb interaction. The interaction between the photoelectron and hole leads to the formation of neutral excitations (*excitons*), which spectrum characterizes the material's electronic polarization (P) response (Section 4.5). The main theoretical challenge lies in simultaneously considering the density of states of excited electrons and holes, transition amplitudes, and the electron-hole interaction³².

The energies in Eq. (14) and Eq. (15) are the removal and addition energies of an electron from a system of N electrons. In second quantization, given the many-body eigenstates $|N\rangle$ of the N -electrons Schrödinger equation $\hat{H}_{MB}|N\rangle = E(N)|N\rangle$ we can compute the probability that PES and IPES processes occur. The relationship for the transition probabilities to go from the N to the $N \pm 1$ ($\psi_i(\mathbf{r})$) states are:

$$\left. \begin{aligned} \psi_i(\mathbf{r}) &= \langle N-1 | \hat{\psi}(\mathbf{r}) | N \rangle, \text{ for } E_i < E_F \\ \psi_i(\mathbf{r}) &= \langle N | \hat{\psi}(\mathbf{r}) | N+1 \rangle, \text{ for } E_i \geq E_F. \end{aligned} \right\} \quad (16)$$

At this point, to compute the transition probabilities in Eq. (16) it is convenient to introduce the concept of single-particle *Green's function* (G), defined as⁴⁴:

$$G(\mathbf{r}, t, \mathbf{r}', t') = -i \langle N | \hat{T} \left\{ \hat{\psi}(\mathbf{r}, t) \hat{\psi}^\dagger(\mathbf{r}', t') \right\} | N \rangle, \quad (17)$$

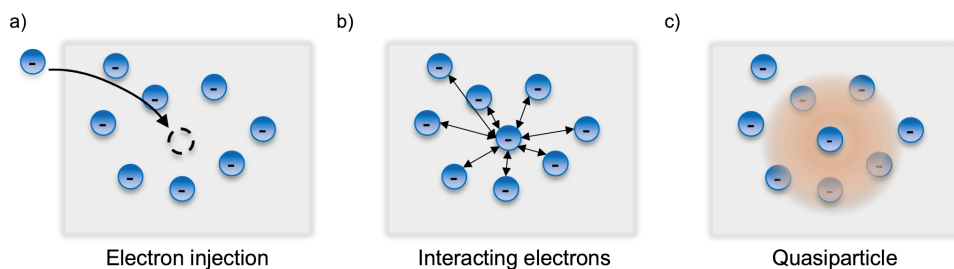


Figure 4.4 The concept of a *quasiparticle*. (a) An electron is introduced into the system. (b) As it moves through the sample, it interacts quantum mechanically with all other electrons. (c) Its motion can be effectively described by the equation of motion with that of a quasiparticle, which consists of the electron moving in an effective potential (a surrounding cloud of positive charge).

where $\hat{T}$ is the time-ordering operator which arranges the field operators according to the “later time to the left” rule. The Green’s function describes the propagation of an electron from the space-time point $(\mathbf{r}, t)$ to $(\mathbf{r}', t')$ and is thus commonly referred as the *propagator*.

The picture above assumes well-defined energy levels (*one-particle energy levels*) in the system, and PES/IPES are interpreted as a measure of the density of occupied/unoccupied states. In this view, electronic states are immutable and possess infinite lifetimes. However, this interpretation quickly breaks down. When an electron is added to or removed from the system, the remaining electrons mutually interact (we say that they “relax”), triggering a cascade of quantum interactions that renormalize their energy levels. Accounting for all these quantum interactions (in the excited state) easily becomes an intractable problem. To retain a one-particle picture, the concept of *quasiparticles* is introduced^{45–47}, leading to the notions of *quasielectrons* and *quasiholes*. The motion of quasiparticles is described by a Schrödinger-like equation with an effective potential that encapsulates all interactions (Fig. 4.4). When an electron is introduced into the system [Fig. 4.4.(a)] it immediately interacts with all other electrons [Fig. 4.4.(b)]. However, because electrons repel each other, interactions beyond the nearest neighbors are *screened* (reduced) compared to the case where particles were isolated. The net effect can be described by an effective potential, represented as a surrounding cloud of positive charge [Fig. 4.4.(c)]. Quasiparticles differ from bare electrons in that they have modified energy levels and finite lifetimes, making them a suitable framework for describing PES and IPES. In the next Sections (4.4, 4.2, 4.3), our goal will be to derive an equation of motion for a quasiparticle.

Absorption experiments are even more complex, as they involve the creation of both quasielectrons and quasiholes, which remain within the system. This necessitates an equation of motion, the Bethe-Salpeter equation (BSE)⁴⁸, to describe the bound quasielectron-quasihole pair, namely the exciton (Section 4.5).

4.2 The screened interaction

The quasiparticle picture provides a useful framework to recast the excited state into a one-particle picture. However, a crucial question remains: how can we establish a theoretical formalism to compute the cascade of quantum relaxation effects? In other words, we need a way to describe how the N -particles system responds to the addition of an electron or hole. A direct approach would require explicitly solving the time-independent Schrödinger equation for the $|N \pm 1\rangle$ state, allowing it to relax in the presence of the $|N\rangle$ system as it is done in the HF method. Instead, we adopt a *linear-response* approach, which allows us to describe the screening effect, due to Coulomb interaction $v(\mathbf{r} - \mathbf{r}')$, without solving the full $|N + 1\rangle$ many-body wavefunction and to write down the equation of motion for a quasiparticle considering how the electrostatic potential change due to the addition or removal of an electron. When an external electron or hole is introduced, the total electrostatic potential V_{tot} is modified. The relationship between the external perturbation V_{ext} and V_{tot} can be written in terms of the *dielectric matrix* ε as

$$V_{tot}(\mathbf{r}) = \int d\mathbf{r}' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}') V_{ext}(\mathbf{r}'). \quad (18)$$

The relaxation of the wavefunctions due to this perturbation induce a electronic *polarization* (P) in the system, which is directly related to the induced potential $V_{ind} = V_{tot} - V_{ext}$ and to ε via:

$$\varepsilon(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}') - \int d\mathbf{r}'' v(\mathbf{r} - \mathbf{r}'') P(\mathbf{r}'', \mathbf{r}', \omega). \quad (19)$$

The added particle $|\psi_i(\mathbf{r})|^2$ moves in an effective potential which account for: (i) the potential generated by all other charges (Hartree), (ii) the induced potential V_{ind} generated by the added particle itself, (iii) the screened exchange interaction due to the Pauli exclusion principle. Taking these effects into account leads to the Coulomb hole plus screened exchange (COHSEX) approximation^{2,49,50}

$$\left(-\frac{\nabla^2}{2m} + \int d\mathbf{r}' \rho(\mathbf{r}') v(\mathbf{r}, \mathbf{r}') + \frac{1}{2} \int d\mathbf{r}' v(\mathbf{r}', \mathbf{r}) [\varepsilon^{-1}(\mathbf{r}, \mathbf{r}') - \delta(\mathbf{r}, \mathbf{r}')] \rho(\mathbf{r}') \right) \psi_i(\mathbf{r}) - \int d\mathbf{r}' W(\mathbf{r}, \mathbf{r}') \sum_{s=1}^{\text{occ}} \psi_s^*(\mathbf{r}') \psi_s(\mathbf{r}) \psi_i(\mathbf{r}') = \epsilon_i \psi_i(\mathbf{r}), \quad (20)$$

where $W(\mathbf{r}, \mathbf{r}')$ represents the screened Coulomb interaction.

The effective potentials acting on the quasiparticle beyond the Hartree potential are collectively grouped into the *self-energy* object Σ . In the COHSEX approximation Σ is called Σ^{COHSEX} .

4.3 Hedin's equations

In the previous section, we learned that the propagation of an excited particle into the N -electrons system can be described intuitively by a quasiparticle and mathematically via the propagator G . The quantum interactions between the added particle and the remaining electrons are all grouped into the self-energy Σ and we wrote explicitly the COHSEX equation [Eq. (20)].

To go one step further, we must account for the frequency dependence of the system's response to external perturbations. Additionally, we need to include all higher-order interactions in electron-electron scattering. The mathematical framework that includes these effects is a set of five integro-differential equations derived by Hedin in his seminal 1965 work⁴⁹. Hedin's equations need to be solved self-consistently, meaning that solving for one quantity requires knowledge of the others. A useful way to visualize the structure of Hedin's equations is through a *pentagonal representation* [Fig. 4.5.(a)], where each vertex corresponds to one of the five equations, and the edges represent the functional relationships between them. A *diagrammatic approach* [Fig. 4.5.(b)] facilitates the physical interpretation of Hedin's equations. We refer to the book of *Mattuck*⁵¹ for a clear introduction to *Feynman diagrams*. Below, we outline the Hedin's equations with a comment on their physical interpretation and diagrammatic visualization (summarized in Table 4.1). We use the compact notation $1 = (\mathbf{r}_1, t_1)$ to denote a space-time coordinate and the superscript $+$ to indicate infinitesimally later time:

1. The **Dyson's equation** for G describes the propagation of an electron in an interacting system. The *exact* Green's function G is written in terms of the non-interacting one G_0 . The self-energy Σ accounts for electron-electron interactions, exchange, and correlation effects:

$$G(1, 2) = G_0(1, 2) + \int d3d4 G_0(1, 3) \Sigma(3, 4) G(4, 2). \quad (21)$$

Diagrammatically, G_0 represents the motion of an electron without interactions. G includes the effects of interactions as a sum over all possible self-energy insertions in the electron propagator.

2. The **Screened Coulomb interaction**. This equation describes how the bare Coulomb interaction v is modified by screening effects due to the presence of other electrons. The screened interaction W determines how an electron "sees" the effective potential due to other electrons.

$$W(1, 2) = v(1, 2) + \int d3d4 v(1, 3) P(3, 4) W(4, 2). \quad (22)$$

Diagrammatically, v is represented by a wavy line. W accounts for how the presence of other electrons modifies the bare Coulomb interaction and it is represented by a series of polarization bubbles.

3. The **Self-Energy equation** represents the modification of a single electron state due to interaction with other electrons. It encapsulates exchange effects and dynamic correlation effects such as quasiparticle lifetimes and satellite structures in spectral functions.

$$\Sigma(1, 2) = i \int d3d4 G(1, 4) W(1^+, 3) \Gamma(4, 2, 3). \quad (23)$$

Diagrammatically, it describes how an electron propagating in the system sees the effective potential W that is dressed by the response of all other electrons Γ . The self-energy is always inserted between two G_0 lines and modifies how electrons move.

4. The **Polarization function** P describes how the electron density responds to an external perturbation. It captures dielectric screening effects in materials.

$$P(1, 2) = -i \int d3d4 G(4, 2)G(2, 3)\Gamma(3, 4, 1). \quad (24)$$

Diagrammatically, it consists of electron-hole bubbles that illustrate how an external perturbation induces electron-hole excitations, which in turn modify W .

5. The **Vertex function** Γ describes how an external perturbation modifies the electron-electron interactions. It accounts for higher perturbation order correlation effects enabling more accurate descriptions of optical spectra.

$$\Gamma(1, 2, 3) = \delta(1, 2)\delta(1, 3) + \int d(4567) \frac{\delta\Sigma(1, 2)}{\delta G(4, 5)} G(4, 6)G(7, 5)\Gamma(6, 7, 3). \quad (25)$$

Diagrammatically, it includes multiple scattering processes going beyond mean-field approximations (higher-order scattering events).

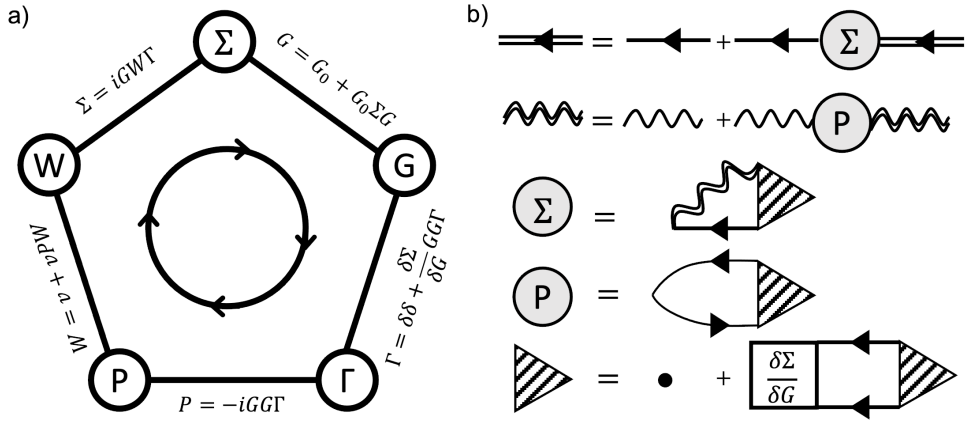


Figure 4.5 (a) Pentagonal representation of the Hedin's equations and (b) their corresponding Feynman diagrams in the order of Table 4.1.

Table 4.1 The five integro-differential Hedin's equations. All quantities are defined in Section 4.3, and the corresponding diagrams are shown in [Fig. 4.5.(b)].

Hedin's Equations		
Equation	Physical interpretation	Diagrammatic picture
Interacting propagator $G = G_0 + G_0 \Sigma G$	Propagation of an electron in an interacting system.	G_0 is represented with an arrow. It represents free propagation; G (double line) includes interaction effects as a sum over all possible self-energy insertions.
Screened Coulomb $W = v + vPW$	The screened interaction W determines how an electron experiences the effective potential.	v is a wavy line; W (double wavy line) accounts for screening and consists of polarization bubbles.
Self-Energy $\Sigma = iGW\Gamma$	Represents how a single electron state is modified due to interactions with other electrons.	Σ (light gray circle) describes how an electron propagates in an effective potential W dressed by the response function Γ .
Polarization $P(1, 2) = -iGG\Gamma$	Response of the electron density to an external perturbation (dielectric effects).	P (light gray circle) consists of electron-hole bubbles that describe how charge density is modified by an external perturbation.
Vertex function $\Gamma = \delta\delta + \frac{\delta\Sigma}{\delta G}GG\Gamma$	Describes how an external perturbation modifies electron-electron interactions. Includes higher-order correlation effects.	Γ (Triangle with stripe pattern) accounts for multiple scattering processes beyond mean-field approximations.

4.4 The GW approximation

The DFT spectrum obtained solving the KS equations [Eq. (11)] are a set of eigenvalues that belong to the KS independent one-particle system. However, there is no guarantee that the interacting system can be effectively described in a single-particle framework and that the two spectra coincide. In practice, the DFT spectrum matches well the one of the real system when electronic correlation effects can be neglected. However, for 2D materials, this is often not the case and a more accurate description of the electron-electron interaction beyond DFT is needed. State-of-the-art computational methods^{21,22,32} improve the accuracy of the electronic spectrum solving the Hedin's Eqs (21-25) under controlled approximations. The most widely and reliable approximation to Hedin's equation is the GW approximation, where the vertex is reduced to a single scattering event $\Gamma = 1$. As a result, the self-energy simplifies to $\Sigma = iGW$ which gives the method its name⁵². The GW approximation provides a systematic correction to DFT by incorporating many-body effects. Electrons are treated as *quasiparticles*, and the screened Coulomb interaction W accounts for how electrons are influenced by the electronic environment of the material. Typically, the net effect is a reduction of the repulsive interactions with other electrons and an increase of the bandgap of the material [Fig. 4.6.(a)]. Heuristically, the GW approximation can be thought of as replacing the DFT exchange-correlation potential Eq. (8) with the self-energy:

$$\Sigma(\mathbf{r}, \mathbf{r}') = iG(\mathbf{r}, \mathbf{r}')W(\mathbf{r}, \mathbf{r}'). \quad (26)$$

This leads to the quasielectron equation of motion, to be compared with Eq. (11) and (20)³:

$$\left\{ -\frac{\nabla^2}{2m} + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}[n](\mathbf{r}) \right\} \phi_i(\mathbf{r}) + \int d\mathbf{r}' \Sigma[\mathbf{r}, \mathbf{r}', \varepsilon^{GW}] \phi_i(\mathbf{r}') = \varepsilon_i^{GW} \phi_i(\mathbf{r}). \quad (27)$$

The solution of this equation yields the quasiparticle energies, which are directly comparable to experimental photoemission spectra. Typically, a non-selfconsistent GW (G_0W_0) calculation, where G and W are evaluated non-selfconsistently from DFT, is often found to provide accurate quasiparticle energies. In many cases, G_0W_0 outperforms fully self-consistent GW approaches, as self-consistency can sometimes over-correct energy levels, leading to less agreement with experiments^{21,22,32}.

4.5 Bethe-Salpeter equation

When a semiconductor is exposed to light, photons excite electrons from the valence to the conduction band, leading to empty states (holes) in the valence manifold of bands. Optical experiments probe the electronic excitation by measuring absorption, reflectance, and photoluminescence spectra. These observables can be computed via the dielectric function

³In the introduction of the COHSEX equation, we used the symbol ψ to denote a general electronic wavefunction. Here, we adopt the notation ϕ_i , as the wavefunctions in a typical DFT-GW calculation correspond to those of the KS system.

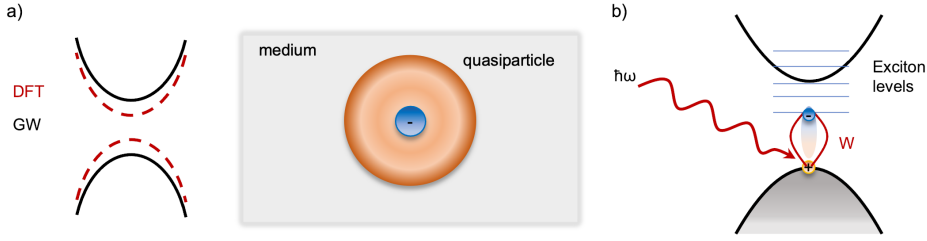


Figure 4.6 (a) On the left, a schematic of DFT and GW band structure showing the typical underestimation of the electronic band gap. On the right, a pictorial representation of a quasiparticle as an electron surrounded by an effective positive charge. (b) A laser excites the system creating excitonic energy states in the energy gap region. W is the screened Coulomb interaction.

ϵ . We discussed how GW improves significantly the accuracy of DFT by incorporating many-body effects and correcting quasiparticle energies. Hence, it considerably improves the comparison with experiments such as PES and IPES [Fig. 4.3.(a,b)]. Within the GW approximation scheme the polarization function P can be computed $P = -iGG$ and we extract from it the dielectric function ϵ and therefore absorption inverting Eq. (19)^{2,32}. This approach is known as the *Random Phase Approximation* (RPA). However, the “ GG ” product in P accounts for the independent propagation of a quasielectron and a quasihole but, it does not capture electron-hole interactions and therefore leads to a non-interacting polarization P_0 . The electron-hole interactions are crucial for describing excitons and the resulting polarization buildup in the system, as they determine the optical response of materials. This is particularly important in two-dimensional (2D) semiconductors, where electrons and holes are confined to a plane, but their electric field lines can extend into the surrounding dielectric environment²³. This geometry leads to weak dielectric screening, which in turn strengthens the Coulomb interaction between charge carriers. In this context, the strong electron-hole interaction can be understood as arising from the reduced screening of the field lines between electrons and holes, making excitonic effects dominant in the optical response. Notably, in ideal 2D systems with constant dielectric background, the exciton binding energy is enhanced by a factor of four compared to the 3D hydrogenic case, due to the modified Coulomb potential and dimensionality of the Schrödinger equation². To include electron-hole interactions, the Bethe-Salpeter equation (BSE) is employed. The BSE improves the accuracy of spectra obtained within the GW approximation including vertex corrections beyond the trivial $\Gamma = 1$. This is achieved performing a second iteration of the Hedin’s equation, keeping $\Sigma = iGW$ [Eq. (23)] and updating the polarization P [Eq. 24] with the following vertex function Γ :

$$\begin{aligned} \Gamma(1, 2, 3) = & \delta(1, 2)\delta(1, 3) \\ & + iW(1^+, 2) \int d(67)G(1, 6)G(7, 2)\Gamma(6, 7, 3). \end{aligned} \quad (28)$$

The polarization is promoted to a four-point correlation function and one ends up with the Dyson equation equation for P :

$$P(1, 2, 3, 4) = P_0(1, 2, 3, 4) + \int d(5678) P_0(1, 2, 5, 6) K(5, 6, 7, 8) P(7, 8, 3, 4). \quad (29)$$

K is the interaction kernel which accounts for the infinite series of polarization bubble-diagrams and contains an electron-hole exchange term v and the electron-hole attraction term $-W$.

$$K(1, 2, 3, 4) = \delta(1, 2)\delta(3, 4)v(1, 3) - \delta(1, 3)\delta(2, 4)W(1, 2). \quad (30)$$

Finally, it can be shown that the poles of four-point polarization function P can be mapped to an effective two-particle Hamiltonian $\hat{H}_{BSE}$ (BSE equation). As the polarization describes electron-hole excitations, the spectrum obtained by diagonalizing $\hat{H}_{BSE}$ gives direct access to the eigenvalues and eigenvectors of excitons³² [Fig.4.6.(b)] with center-of-mass momentum $\mathbf{Q}$.

In particular, we consider the electron reference frame where the exciton is formed by a conduction (c) electron with momentum $\mathbf{k}$ and a hole (v) with momentum $\mathbf{k} - \mathbf{Q}$. For the results presented in this thesis, we employ the Tamm-Dancoff approximation, which simplifies the BSE by neglecting the coupling between resonant and anti-resonant transitions. Under this approximation, the BSE is given by³²:

$$\underbrace{\left(\varepsilon_{\mathbf{c}\mathbf{k}}^{\text{GW}} - \varepsilon_{\mathbf{v}\mathbf{k}-\mathbf{Q}}^{\text{GW}} \right) A_{\mathbf{v}\mathbf{k}}^{\lambda\mathbf{Q}} + \Delta f_{\mathbf{v}\mathbf{k}} \sum_{\mathbf{k}'\mathbf{c}'\mathbf{v}'} K_{\mathbf{v}\mathbf{k}\mathbf{v}'\mathbf{c}'\mathbf{k}'}^{\text{eh},\mathbf{Q}} A_{\mathbf{v}'\mathbf{c}'\mathbf{k}'}^{\lambda\mathbf{Q}}}_{\hat{H}_{\text{BSE}}} = E^{\lambda\mathbf{Q}} A_{\mathbf{v}\mathbf{k}}^{\lambda\mathbf{Q}}, \quad (31)$$

where $\varepsilon_{\mathbf{c}\mathbf{k}/\mathbf{v}\mathbf{k}-\mathbf{Q}}^{\text{GW}}$ are the quasiparticle energies, $A_{\mathbf{v}\mathbf{k}}^{\lambda,\mathbf{Q}}$ are the BSE coefficients, and $E^{\lambda\mathbf{Q}}$ is the energy of exciton λ . The term $\Delta f_{\mathbf{v}\mathbf{k}} = (f_{\mathbf{c}\mathbf{k}} - f_{\mathbf{v}\mathbf{k}-\mathbf{Q}})$ represent the difference between electronic occupation factors. The electron-hole kernel $K_{\mathbf{v}\mathbf{k},\mathbf{v}'\mathbf{c}'\mathbf{k}'}^{\text{eh}}$ consists of two contributions: (i) an attractive term arising from the screened electron-hole interaction W , (ii) a repulsive term mediated by the bare Coulomb interaction V , which accounts for the exchange of a particle and a hole.

$$K_{\mathbf{v}\mathbf{k},\mathbf{v}'\mathbf{c}'\mathbf{k}'}^{\text{eh}} = (W_{\mathbf{v}\mathbf{k},\mathbf{v}'\mathbf{c}'\mathbf{k}'}^{\mathbf{Q}} - V_{\mathbf{v}\mathbf{k},\mathbf{v}'\mathbf{c}'\mathbf{k}'}^{\mathbf{Q}}), \quad (32)$$

$$\begin{aligned} W_{\mathbf{v}\mathbf{k},\mathbf{v}'\mathbf{c}'\mathbf{k}'}^{\mathbf{Q}} &= \langle \mathbf{v}\mathbf{k} | \hat{W} | \mathbf{v}'\mathbf{c}'\mathbf{k}' \rangle \\ &= \int d\mathbf{r} d\mathbf{r}' \phi_{\mathbf{v}\mathbf{k}-\mathbf{Q}}(\mathbf{r}) \phi_{\mathbf{c}\mathbf{k}}^*(\mathbf{r}') W(\mathbf{r}, \mathbf{r}') \phi_{\mathbf{v}'\mathbf{k}'-\mathbf{Q}}(\mathbf{r}) \phi_{\mathbf{c}'\mathbf{k}'}(\mathbf{r}'), \end{aligned} \quad (33)$$

$$\begin{aligned} V_{\mathbf{v}\mathbf{k},\mathbf{v}'\mathbf{c}'\mathbf{k}'}^{\mathbf{Q}} &= \langle \mathbf{v}\mathbf{k} | \hat{V} | \mathbf{v}'\mathbf{c}'\mathbf{k}' \rangle \\ &= 2 \int d\mathbf{r} d\mathbf{r}' \phi_{\mathbf{v}\mathbf{k}-\mathbf{Q}}(\mathbf{r}) \phi_{\mathbf{c}\mathbf{k}}^*(\mathbf{r}) V(|\mathbf{r} - \mathbf{r}'|) \phi_{\mathbf{v}'\mathbf{k}'-\mathbf{Q}}(\mathbf{r}') \phi_{\mathbf{c}'\mathbf{k}'}(\mathbf{r}'). \end{aligned} \quad (34)$$

Once the BSE is solved, one can compute the macroscopic dielectric function $\varepsilon_M(\omega)$ explicitly from the BSE eigenvalues and eigenvectors²¹:

$$\varepsilon_M(\omega) = 1 - \lim_{\mathbf{q} \rightarrow 0} v(\mathbf{q}) \sum_{\lambda} \frac{\left| \sum_{\mathbf{v}\mathbf{k}} d_{\mathbf{v}\mathbf{k}} A_{\mathbf{v}\mathbf{k}}^{\lambda,\mathbf{q}} \right|^2}{\omega - E^{\lambda\mathbf{q}} + i\eta}, \quad (35)$$

where $d_{\mathbf{v}\mathbf{k}} = \langle \mathbf{c}\mathbf{k} | e^{i\mathbf{q}\mathbf{r}} | \mathbf{v}\mathbf{k} - \mathbf{q} \rangle$ are the optical dipoles.

The BSE was first applied to solids by *Hanke* and *Sham*⁵³(1979), who calculated the absorption spectrum of bulk silicon. Since then, the BSE has been widely adopted for studying optical properties of materials and constitutes the state-of-the-art approach for *ab initio* simulations of absorption spectra. Combining the GW approximation with the BSE provides a robust theoretical framework to: (i) predict accurate band gaps, correcting the systematic underestimation of band gaps, (ii) enable the calculation of exciton binding energies and optical spectra.

The typical workflow of a G_0W_0 +BSE calculation is depicted in Fig. 4.7. The calculation starts by solving the KS equations Eq. (11), yielding the DFT eigenvalues (ϵ_i^{DFT}) and eigenvectors (ϕ_i^{DFT}). These serve as the initial input for the MBPT corrections. Using the DFT energies and wavefunctions, the non-interacting Green's function G_0 is built⁴. Simultaneously, the polarization function P_0 is computed within the RPA approximation. The dielectric function ϵ_{RPA}^{-1} is derived from P_0 and used to construct the screened Coulomb interaction W_0 . The self-energy $\Sigma = iG_0W_0$ is evaluated to correct the DFT eigenvalues, yielding quasiparticle energies $\epsilon_i^{G_0W_0}$. Finally, to capture electron-hole interactions, we solve the BSE Eq. (31) which requires: $\epsilon_i^{G_0W_0}$, the static RPA-screened Coulomb interaction W_0 and occupation factors f_i . As discussed above, solving the BSE is equivalent to solving the Dyson's equation for P , obtained updating Γ in a second Hedin iteration (Eq. 28). Lastly, we emphasize that, in principle, the updated dielectric function ϵ should be used to recompute W beyond RPA. However, this correction is typically neglected in practical calculations.

Despite its high computational cost, the GW+BSE method has become an indispensable tool in condensed matter physics and material science, particularly for studying 2D semiconductors and insulators, enabling direct comparison with experimental results.

⁴Strictly speaking, the term non-interacting is incorrect when referring to the Green's function obtained from DFT. In this context, it refers to using the KS Green's function as the zeroth-order term in a perturbative expansion.

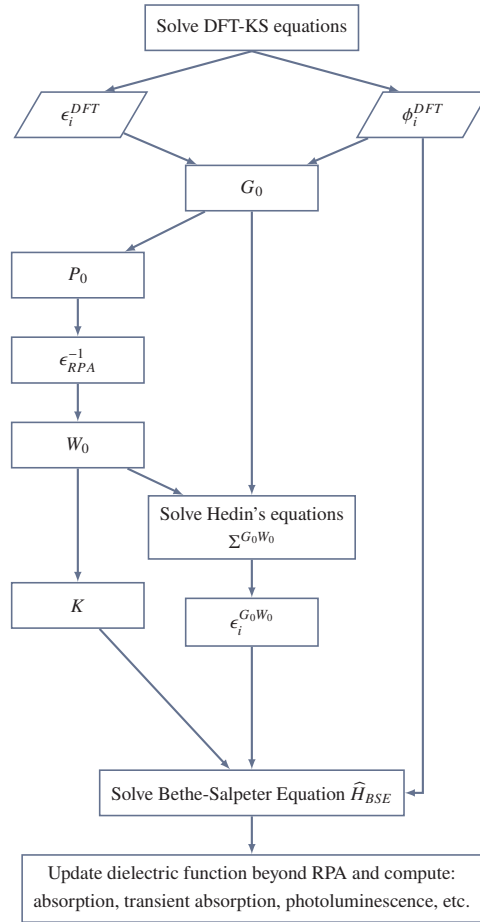


Figure 4.7 Schematic of the G_0W_0 -BSE method. This workflow allows to compute quasiparticle energies and the excitonic spectrum. This is the state-of-the-art computational methods to compute electronic and optical properties of solids from first-principles.

5 Superconductivity

Superconductivity is an intrinsically quantum phenomenon, defying the classical picture of dissipative current flow. It is one of the striking cases where quantum effects manifest at the macroscopic scale, as demonstrated by the Meissner effect⁵⁴. The microscopic theory developed by Bardeen, Cooper, and Schrieffer (BCS) back in 1957⁵⁵ was instrumental in understanding the underlying mechanism in terms of attractive interaction between electrons mediated by crystal lattice vibrations (phonons), forming Cooper pairs below a (very low) critical temperature. However, there are other complex realizations of superconductivity which cannot be explained within the BCS theory. These are referred to as *unconventional* or exotic forms of superconductivity. Examples include high-temperature superconductivity and multi-band superconductivity, where multiple bands cross the Fermi surface, leading to several superconducting instabilities^{56–59}. Further exotic forms of superconductivity can arise due to strong interactions between electrons⁶⁰, from the interplay between disorder and dimensionality⁶¹, or emerge from the proximity interaction of a conventional superconductor and a topological insulator⁶². In particular, topological superconductors^{63–66} could revolutionize the field of quantum computing by hosting quantum bits based on Majorana zero modes⁶⁷.

Modelling these unconventional aspects of superconductivity and understanding their origins requires: (a) a unified treatment of normal and superconducting properties (band structure, electron density, anomalous density), (b) a detailed description of the electronic structure (including Fermi surface nesting and inter-band interactions), and (c) the ability to model unconventional pairing mechanisms (e.g. p -wave spin-triplet). Superconducting Density Functional Theory (SCDFT)^{68,69} is a theoretical and computational⁷⁰ method that satisfies these requirements. SCDFT presents a unified way of treating normal and superconducting electron densities by combining Density Functional Theory (DFT)⁷¹, a proven successful approach for predicting the electronic structure of solids and molecules, with the Bogoliubov-de-Gennes (BdG) formalism of superconductivity^{72–74}. The BdG method is a Hartree-Fock-like mean-field approximation of the many-body Hamiltonian, which provides an equivalent description of the BCS theory generalized to real space and, therefore, can treat inhomogeneous superconductors. One of its core strengths is the ability to obtain the one-particle local density-of-states (LDOS) that can be directly linked to low-temperature Scanning Tunnelling Microscopy (STM) experiments⁷⁵.

SCDFT was originally proposed as a semi-phenomenological method, and later developed into a fully ab-initio method for conventional phonon-mediated superconductivity^{76–78}. Fully ab-initio SCDFT methods include the motion of nuclei, typically neglected in DFT. While successful in describing conventional superconductors^{79–81}, these methods fall short in modelling unconventional superconductors, where Cooper pairs are bound by other types of couplings such as electron-electron pairing⁸², or spin fluctuations⁸³. However, the original semi-phenomenological formulation of SCDFT does not impose any assumption about the pairing mechanism and therefore, can be used to model unconventional superconductors^{84,85}. The semi-phenomenological SCDFT approach has recently been implemented within multiple

scattering theory in the Korringa-Kohn-Rostoker (KKR) method (SC-KKR)^{86–90} and in the linear muffin-tin orbital method⁹¹.

This Section is organized as follows. In Sub-Section 5.1 we review the BCS theory of superconductivity, introduce the SCDFT Hamiltonian⁶⁸ and the Bogoliubov-de Gennes transformation for superconductors⁷³, and discuss our treatment of the exchange-correlation functional following Suvasini et al.⁹². In Chapter 3 we show how those theories are adapted to the linear combination of atomic orbitals (LCAO) basis set formalism and implemented in SIESTA. We generalize the BdG equations to the relativistic case and introduce our convention for spin singlet and spin triplet components of the pairing potential matrix⁹³.

5.1 Modelling superconductivity

Pre-BCS theories of superconductivity

The first phenomenological theory of superconductivity was proposed by Fritz and Heinz London in 1935⁹⁴, and treated electrons as free particles within a metal. This theory extended Maxwell's classical electromagnetism by introducing two new equations that relate the superconducting current density $\mathbf{j}_s$ to the electric ($\mathbf{E}$) and magnetic ($\mathbf{B}$) fields within the superconductor:

$$\frac{\partial \mathbf{j}_s}{\partial t} = \frac{n_s e^2}{m} \mathbf{E}, \quad (36)$$

$$\nabla \times \mathbf{j}_s = -\frac{n_s e^2}{m} \mathbf{B}, \quad (37)$$

where n_s is a phenomenological constant proportional to the concentration of superconducting carriers. The London equations explain the Meissner effect and by construction conductance without resistance. However, the predicted penetration depth of a magnetic field into a superconductor was in poor agreement with respect to experimental data⁹⁵.

A few years later, in 1950, Ginzburg and Landau⁹⁶ proposed to model superconductivity by drawing an analogy with second-order ferromagnetic phase transitions. They introduced as superconducting order parameter the (complex) wavefunction of superconducting electrons, which becomes zero above the critical temperature T_C , namely when the superconductor transitions to a normal state. The square modulus of this wavefunction is proportional to the density of superconducting electrons, in analogy with the quantum mechanical wavefunction of (normal) electrons. One of the successes of the Ginzburg–Landau theory is the classification of superconductors according to the way the Meissner state breaks down for increasing magnetic field: In Type I superconductors there is only one value of critical magnetic field H_C above which superconductivity is lost. In Type II superconductors, instead, it exists a mixed-state region between two critical field values $H_{C1} < H < H_{C2}$. Type II superconductors present vortices in this intermediate phase, and superconductivity is lost above H_{C2} . We note that the London equations can be derived as a special case of the Ginzburg-Landau theory. In addition, the Josephson effect can be predicted in the framework of the Ginzburg-Landau theory⁹⁷, even though it had not been discovered yet in 1950.

BCS theory of superconductivity

The first microscopic theory of superconductivity valid for all temperatures between zero and T_C was formulated by Bardeen, Cooper, and Schrieffer (BCS) in their seminal article “Theory of Superconductivity”⁵⁵. In BCS theory, an instability of the Fermi sea $|F\rangle$ arises when electrons experience an attractive interaction, resulting in a ground-state composed of bound electron pairs, bosonic quasiparticles, named *Cooper pairs*. In its initial formulation, the origin of the attractive electron-electron interaction was inspired by Fröhlich, who proposed that superconductivity is driven by electron-phonon processes⁹⁸.

The BCS Hamiltonian is the sum of a one-particle normal-state Hamiltonian $\mathbf{h}^0$ and a two-particle Hamiltonian $\mathbf{H}^{\text{inter}}$, an effective attractive electron-electron interaction typically arising from electron-phonon interaction⁷⁵:

$$\mathbf{H}^{\text{BCS}} = \mathbf{h}^0 + \mathbf{H}^{\text{inter}} = \sum_{\mathbf{k}, \sigma} \xi_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}, \mathbf{k}'} \mathbf{V}_{\mathbf{k}\mathbf{k}'} c_{\mathbf{k}'\uparrow}^\dagger c_{-\mathbf{k}'\downarrow}^\dagger c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow}, \quad (38)$$

where $\xi_{\mathbf{k}}$ includes all the contributions from single particle terms (i.e. non-interacting Hamiltonian), $c_{\mathbf{k}\sigma}$ and $c_{\mathbf{k}\sigma}^\dagger$ are the destruction and creation operators of an electron with momentum $\mathbf{k}$ and spin $\sigma = (\uparrow, \downarrow)$, and $\mathbf{V}_{\mathbf{k}\mathbf{k}'}$ are the electron-electron interaction matrix elements.

In superconductors, Cooper pairs condense into a ground-state characterized by a non-vanishing *anomalous charge density* $\chi_{\mathbf{k}\sigma\sigma'} = \langle c_{-\mathbf{k}\sigma} c_{\mathbf{k}\sigma'} \rangle$, defined as the average of two electron annihilation operators, which plays the role of the superconducting order parameter and represents the destruction of a Cooper pair. The anomalous charge density is a bosonic object and, hence, must satisfy the Pauli exclusion principle, namely it must be antisymmetric under exchange of the two electrons forming the Cooper pair: $\chi_{-\mathbf{k}\sigma'\sigma} = \chi_{\mathbf{k}\sigma\sigma'}$. This implies that if $\chi_{\mathbf{k}\sigma\sigma'}$ is even (odd) under the transformation $\mathbf{k} \rightarrow -\mathbf{k}$, then it has to be odd (even) under spin exchange leading to a $S = 0$ singlet state ($S = 1$, triplet state). The BCS theory only considers the $S = 0$ singlet state case and, hence, $\chi_{\mathbf{k}\sigma\sigma'} = \chi_{\mathbf{k}\downarrow\uparrow}$.

All the physical observables describing the superconducting state of the system are expressed in terms of the eigenenergies and eigenfunctions of the BCS Hamiltonian. To compute them, one would have to calculate the average of the bi-quadratic term $\mathbf{H}^{\text{inter}}$. However, this cannot be done exactly, neither numerically nor analytically. For this reason, it is convenient to apply a mean-field approximation to transform the bi-quadratic interacting term (four-fields) into a quadratic (two-fields) one. To this purpose, we define $\delta_{\mathbf{k}}$, a small deviation of $c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow}$ from its expectation value:

$$c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} = \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle + \underbrace{c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} - \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle}_{\delta_{\mathbf{k}}}. \quad (39)$$

We introduce this expression and its adjoint

$$c_{\mathbf{k}'\uparrow}^\dagger c_{-\mathbf{k}'\downarrow}^\dagger = \langle c_{\mathbf{k}'\uparrow}^\dagger c_{-\mathbf{k}'\downarrow}^\dagger \rangle + \underbrace{c_{\mathbf{k}'\uparrow}^\dagger c_{-\mathbf{k}'\downarrow}^\dagger - \langle c_{\mathbf{k}'\uparrow}^\dagger c_{-\mathbf{k}'\downarrow}^\dagger \rangle}_{\delta_{\mathbf{k}'}^\dagger} \quad (40)$$

in Eq. (38), and use

$$\begin{aligned}
 c_{\mathbf{k}'\uparrow}^\dagger c_{-\mathbf{k}'\downarrow}^\dagger c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} &= \langle c_{\mathbf{k}'\uparrow}^\dagger c_{-\mathbf{k}'\downarrow}^\dagger \rangle \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle + \langle c_{\mathbf{k}'\uparrow}^\dagger c_{-\mathbf{k}'\downarrow}^\dagger \rangle \delta_{\mathbf{k}} \\
 &\quad + \delta_{\mathbf{k}'}^\dagger \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle + \delta_{\mathbf{k}'}^\dagger \delta_{\mathbf{k}} \\
 &\approx \langle c_{\mathbf{k}'\uparrow}^\dagger c_{-\mathbf{k}'\downarrow}^\dagger \rangle \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle + \langle c_{\mathbf{k}'\uparrow}^\dagger c_{-\mathbf{k}'\downarrow}^\dagger \rangle \delta_{\mathbf{k}} \\
 &\quad + \delta_{\mathbf{k}'}^\dagger \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle \\
 &\approx \langle c_{\mathbf{k}'\uparrow}^\dagger c_{-\mathbf{k}'\downarrow}^\dagger \rangle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} + c_{\mathbf{k}'\uparrow}^\dagger c_{-\mathbf{k}'\downarrow}^\dagger \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle \\
 &\quad - \langle c_{\mathbf{k}'\uparrow}^\dagger c_{-\mathbf{k}'\downarrow}^\dagger \rangle \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle,
 \end{aligned} \tag{41}$$

where we neglect quadratic terms in δ_k^2 . The mean-field BCS Hamiltonian becomes:

$$\mathbf{H}_{\text{MF}}^{\text{BCS}} = \mathbf{h}^0 - \sum_{\mathbf{k}} \left\{ \Delta_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger + \Delta_{\mathbf{k}}^\dagger c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \right\} + E_0, \tag{42}$$

where

$$\Delta_{\mathbf{k}'} = - \sum_{\mathbf{k}} V_{\mathbf{k}\mathbf{k}'} \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle = - \sum_{\mathbf{k}} V_{\mathbf{k}\mathbf{k}'} \chi_{\mathbf{k}\downarrow\uparrow} \tag{43}$$

is the *superconducting gap function* or *pairing potential*, and

$$E_0 = \sum_{\mathbf{k}} \Delta_{\mathbf{k}} \langle c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger \rangle = \sum_{\mathbf{k}} \Delta_{\mathbf{k}} \chi_{\mathbf{k}\downarrow\uparrow}^\dagger \tag{44}$$

is a constant energy shift, which can often be neglected. Note that this approximation is exact in the limit of weak electronic correlations. The mean-field approximation breaks the U(1) gauge symmetry $c_{\mathbf{k}\uparrow} \rightarrow e^{i\phi} c_{\mathbf{k}\uparrow}$ which implies that the number of particle N is not fixed. As a consequence, the $\mathbf{H}_{\text{MF}}^{\text{BCS}}$ Hamiltonian is treated in the grand canonical ensemble formalism. However, the parity of the particle number (i.e., the number of particles modulo 2) remains a good quantum number. This implies that the ground-state of Eq. (42) is a linear combination of either even or of odd states.

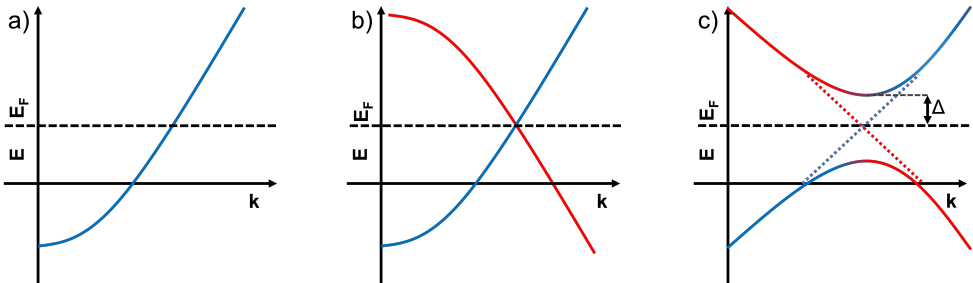


Figure 5.8 Schematic of the electron-hole coupling in a superconductor. a) normal state: parabolic-like electron band; b) Introduction of the charge-conjugated particles (holes, red band) c) The addition of the interaction term Δ opens a superconducting gap due to electron and hole excitations. E_F is the Fermi energy.

To diagonalize the mean-field Hamiltonian $\mathbf{H}_{\text{MF}}^{\text{BCS}}$ of Eq. (42) it is convenient to recast it in the Nambu basis. Then, we can apply a Bogoliubov transformation, which expresses the electron creation and annihilation operators as a linear combination of two new quasi-particle operators γ and $\gamma^\dagger$ ⁷⁵

$$c_{\mathbf{k}\uparrow} = u_{\mathbf{k}\uparrow}\gamma_{\mathbf{k}\uparrow} - v_{-\mathbf{k}\uparrow}^*\gamma_{-\mathbf{k}\downarrow}^\dagger, \quad c_{\mathbf{k}\downarrow} = u_{\mathbf{k}\downarrow}\gamma_{\mathbf{k}\downarrow} + v_{-\mathbf{k}\downarrow}^*\gamma_{-\mathbf{k}\uparrow}^\dagger, \quad (45)$$

$$c_{\mathbf{k}\uparrow}^\dagger = u_{\mathbf{k}\uparrow}^*\gamma_{\mathbf{k}\uparrow}^\dagger - v_{-\mathbf{k}\uparrow}\gamma_{-\mathbf{k}\downarrow}, \quad c_{\mathbf{k}\downarrow}^\dagger = u_{\mathbf{k}\downarrow}^*\gamma_{\mathbf{k}\downarrow}^\dagger + v_{-\mathbf{k}\downarrow}\gamma_{-\mathbf{k}\uparrow}. \quad (46)$$

The γ and $\gamma^\dagger$ operators diagonalize the Bogoliubov Hamiltonian by construction, and represent the destruction and creation of a *Bogoliubon* (or Bogoliubov quasi particle), respectively. Bogoliubons are (*almost*) neutral spin-1/2 fermions, formed by the superposition of electrons and holes excitations in a superconductor. In particular, $\gamma_{\mathbf{k}\uparrow}$ destroys an electron with momentum $\mathbf{k}$ and spin $\uparrow$ or creates an electron with momentum $-\mathbf{k}$ and spin $\downarrow$. The probability of creating a Cooper pair ($\mathbf{k}\uparrow, -\mathbf{k}\downarrow$) is proportional to $\sum_{\mathbf{k}\sigma} |v_{\mathbf{k}\sigma}|^2$ ⁹⁹. Due to particle-hole symmetry in superconductors, the spectrum of the BCS Hamiltonian is symmetric with respect to the Fermi level: if $(u_{\mathbf{k}\uparrow}u_{\mathbf{k}\downarrow}v_{-\mathbf{k}\uparrow}v_{-\mathbf{k}\downarrow})^T$ is a solution of Eq. (47) with energy $+E_{\mathbf{k}}$, then $(v_{-\mathbf{k}\uparrow}^*v_{-\mathbf{k}\downarrow}^*u_{\mathbf{k}\uparrow}^*u_{\mathbf{k}\downarrow}^*)^T$ is a solution with energy $-E_{\mathbf{k}}$.

This approach leads to an eigenvalue equation for $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$, the electron and hole components of the Nambu spinor. The Nambu spinor is an extension of the two-component Dirac spinor. It describes a four-component (particle/antiparticle, spin up/down) wave function. In terms of the Nambu spinor, the eigenvalue problem reads:

$$\begin{aligned} \mathbf{H}_{\text{MF}}^{\text{BCS}} \begin{pmatrix} u_{\mathbf{k}\uparrow} \\ u_{\mathbf{k}\downarrow} \\ v_{-\mathbf{k}\uparrow} \\ v_{-\mathbf{k}\downarrow} \end{pmatrix} &= \begin{pmatrix} \xi_{\mathbf{k}\uparrow\uparrow} & \xi_{\mathbf{k}\uparrow\downarrow} & 0 & \Delta_{\mathbf{k}} \\ \xi_{\mathbf{k}\downarrow\uparrow} & \xi_{\mathbf{k}\downarrow\downarrow} & -\Delta_{\mathbf{k}} & 0 \\ 0 & -\Delta_{\mathbf{k}}^* & -\xi_{-\mathbf{k}\uparrow\uparrow}^* & -\xi_{-\mathbf{k}\uparrow\downarrow}^* \\ \Delta_{\mathbf{k}}^* & 0 & -\xi_{-\mathbf{k}\downarrow\uparrow}^* & -\xi_{-\mathbf{k}\downarrow\downarrow}^* \end{pmatrix} \begin{pmatrix} u_{\mathbf{k}\uparrow} \\ u_{\mathbf{k}\downarrow} \\ v_{-\mathbf{k}\uparrow} \\ v_{-\mathbf{k}\downarrow} \end{pmatrix} \\ &= E_{\mathbf{k}} \begin{pmatrix} u_{\mathbf{k}\uparrow} \\ u_{\mathbf{k}\downarrow} \\ v_{-\mathbf{k}\uparrow} \\ v_{-\mathbf{k}\downarrow} \end{pmatrix}. \end{aligned} \quad (47)$$

Note that the number of degrees of freedom is now doubled with respect to the normal electronic structure problem. The Bogoliubov Hamiltonian in the mean-field approximation in the Nambu basis consists of four blocks: the particle block in the top-left corner, the anti-particle block in the bottom-right corner, and the coupling between particle and anti-particles as off-diagonal blocks. In order to be consistent with the literature, we will interchangeably use electrons (holes) as particles (anti-particles). For a given electronic state, $\mathbf{H}_{\text{MF}}^{\text{BCS}}$ describes a two level system with energies $+\xi_{\mathbf{k}}$ and $-\xi_{\mathbf{k}}$ for the electron and hole states, respectively. A superconducting gap opens when the electron and hole states are coupled by an interaction of magnitude $\Delta_{\mathbf{k}}$, as illustrated in Fig. 5.8.

Successes and limits of BCS theory of superconductivity

The bare Coulomb interaction between electrons $V(\mathbf{q}) = V(\mathbf{k} - \mathbf{k}') = \frac{4\pi e^2}{q^2}$, where $\mathbf{q}$ is the momentum transfer between two states at $\mathbf{k}$ and $\mathbf{k}'$, is always positive and, hence, cannot generate Cooper pairs. Negative terms in the Coulomb interaction arise when one considers the motion of the nuclei and the screening of the Coulomb potential $\varepsilon(\mathbf{q}, \omega)$ ⁹⁹. Electron-phonon interaction accounts for these effects, and it is included in the Hamiltonian in the form of two additional bosonic terms: the phonon dispersion $\mathbf{H}_{ph}$ and the electron-phonon interaction $\mathbf{H}_{e-ph}$. An electron moving over the background of nuclear charges polarizes the medium creating an excess of positive charge which, in turn, attracts a second electron. The electron-phonon interaction leads to attractive interaction only in the isotropic channel, where the momentum transfer mediated by the phonon is zero, which implies a constant gap function $\Delta_k = \Delta_0$, typical of a *s*-wave pairing, as we will see in Section 5.1.

Phonon-mediated interaction explains conventional superconductivity in elemental metals, such as Pb or Nb. However, it is inconclusive for most high-temperature superconductors, such as cuprates or pnictides. In these heavy-fermion superconductors (with *d*- or *f*-orbitals), electrons near the Fermi level experience a strong Coulomb repulsion. This results in an avoided overlap between the electrons forming the Cooper pairs, leading to an anisotropic pairing wavefunction. Moreover, the disagreement between the asymptotic behavior of the specific heat predicted by conventional BCS theory and experimental measurements¹⁰⁰ points to a different and unknown pairing mechanism. While phonon-mediated electron-electron interactions are the basis of conventional superconductivity, unconventional superconductivity requires interactions that could be mediated by other (quasi)particles, such as magnons and plasmons^{101,102}. However, regardless of the microscopic details of these exotic interactions, unconventional superconductors can be modelled by a non-trivial dispersion of the gap function $\Delta_{\mathbf{k}}$ and symmetry arguments, as we will see in the next section.

Nature of the pairing potential

For a system with collinear spin ($\mathbf{H}_{\uparrow\downarrow} = \mathbf{H}_{\downarrow\uparrow} = 0$) the BCS Hamiltonian in Eq. (38) is invariant under the symmetry group $\mathcal{G} = G \times \mathcal{S} \times \mathcal{K} \times U(1)$ where G is the point group of the crystal lattice symmetry, $\mathcal{S}$ is the spin representation, $\mathcal{K}$ is the time-reversal symmetry group and $U(1)$ is the gauge symmetry group related to charge conservation, which stems from the invariance of physical observables under transformation $\psi \rightarrow e^{i\phi}\psi \forall \phi \in \mathbb{C}$. *Conventional superconductors* only break the gauge symmetry $U(1)$. In *unconventional superconductors*, the symmetries of the Hamiltonian are further lowered, and this is reflected in symmetries of the gap function.

Eq. (43) defines the gap function $\Delta_{\mathbf{k}}$ in terms of the anomalous charge density $\chi_{\mathbf{k}\sigma\sigma'} = \langle c_{-\mathbf{k}\sigma} c_{\mathbf{k}\sigma'} \rangle$, inheriting the corresponding symmetry properties. In particular, the gap function must be antisymmetric under the exchange of the two electrons constituting a Cooper pair. The orbital and spin wave function of the Cooper pair must have opposite symmetry under electron exchange: a spin singlet ($S = 0$) wave function is anti-symmetric and, hence, must be

accompanied by a symmetric orbital wave function (even orbital quantum number, such as an s , d or g state). The spin wave-function of a spin-triplet state ($S = 1$) is symmetric and, hence, its orbital counterpart must be antisymmetric (l odd), as in the case of a p or f wave.

In the case of non-collinear systems or in systems with SOC, the spin operator does not commute with the Hamiltonian. This leads to a mixing of singlet and triplet contributions. To consider this, we generalize the order parameter by explicitly writing the spin index $\chi_{\mathbf{k}\sigma\sigma'} = \langle c_{-\mathbf{k}\sigma} c_{\mathbf{k}\sigma'} \rangle$. The gap function $\Delta_{\mathbf{k}}$ can be written in terms of the Pauli matrices (σ_x , σ_y , σ_z) and the identity matrix σ_0 . For spin singlet, $\Delta_{\mathbf{k}} = i d_{0,\mathbf{k}} \sigma_y$, while for spin triplet $\Delta_{\mathbf{k}} = i(\mathbf{d}_{\mathbf{k}} \cdot \boldsymbol{\sigma}) \sigma_y$, where $d_{0,\mathbf{k}}$ and $\mathbf{d}_{\mathbf{k}}$ are parametric functions of $\mathbf{k}$. This is an extension of the BCS theory which only includes the $\downarrow, \uparrow$ and $\uparrow, \downarrow$ channels. Following the Balian-Werthamer parametrization¹⁰³ we recast the BCS Hamiltonian of Eq. (38) as:

$$\mathbf{H}_{\text{MF}}^{\text{BCS}} \begin{pmatrix} u_{\mathbf{k}\uparrow} \\ u_{\mathbf{k}\downarrow} \\ v_{-\mathbf{k}\uparrow} \\ v_{-\mathbf{k}\downarrow} \end{pmatrix} = \begin{pmatrix} \xi_{\mathbf{k}\uparrow\uparrow} & \xi_{\mathbf{k}\uparrow\downarrow} & \Delta_{\mathbf{k}\uparrow\uparrow} & \Delta_{\mathbf{k}\uparrow\downarrow} \\ \xi_{\mathbf{k}\downarrow\uparrow} & \xi_{\mathbf{k}\downarrow\downarrow} & \Delta_{\mathbf{k}\downarrow\uparrow} & \Delta_{\mathbf{k}\downarrow\downarrow} \\ -\Delta_{-\mathbf{k}\uparrow\uparrow}^* & -\Delta_{-\mathbf{k}\uparrow\downarrow}^* & -\xi_{-\mathbf{k}\uparrow\uparrow}^* & -\xi_{-\mathbf{k}\uparrow\downarrow}^* \\ -\Delta_{-\mathbf{k}\downarrow\uparrow}^* & -\Delta_{-\mathbf{k}\downarrow\downarrow}^* & -\xi_{-\mathbf{k}\downarrow\uparrow}^* & -\xi_{-\mathbf{k}\downarrow\downarrow}^* \end{pmatrix} \begin{pmatrix} u_{\mathbf{k}\uparrow} \\ u_{\mathbf{k}\downarrow} \\ v_{-\mathbf{k}\uparrow} \\ v_{-\mathbf{k}\downarrow} \end{pmatrix} \\ = \varepsilon_{\mathbf{k}} \begin{pmatrix} u_{\mathbf{k}\uparrow} \\ u_{\mathbf{k}\downarrow} \\ v_{-\mathbf{k}\uparrow} \\ v_{-\mathbf{k}\downarrow} \end{pmatrix}. \quad (48)$$

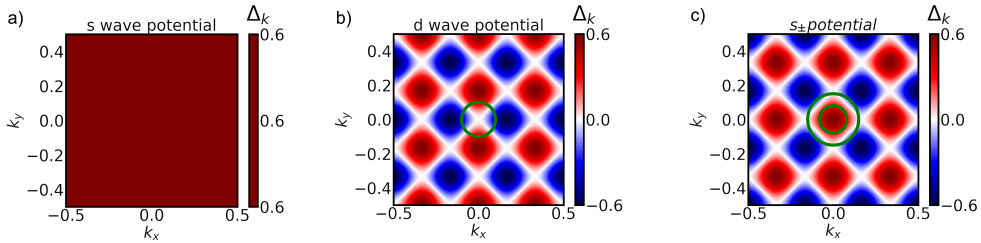


Figure 5.9 Schematic representation of the symmetry properties of the angular component of a general spin singlet ($S = 0$) pairing potential $\Delta_{\mathbf{k}}$ in the reciprocal space of a square lattice. a) s -wave (constant $\Delta_{\mathbf{k}}$); b) d -wave; c) $s_{\pm}$ -pairing. The green circle represents the Fermi surface.

In order to give a pictorial representation of the shape of the superconducting gap function for different l , we report a schematic of three different singlet contributions in Fig. 5.9: s -, d -, and $s_{\pm}$ -wave. The s -wave ($l = 0$) case, illustrated in [Fig. 5.9.(a)], occurs for constant $\Delta_{\mathbf{k}}$, and has been covered in Section 5.1. For a d -wave ($l = 2$), the gap function changes sign twice in the reciprocal space, and the regions where it drops to zero are called nodal lines. This implies that, for a given electronic dispersion, there might be regions in the $\mathbf{k}$ -space where the Fermi surface crosses the nodes of the gap function, hence suppressing the formation of Cooper pairs. Therefore, there will be regions in the band structure where a superconducting gap is opened and other where the material behaves like a metal [Fig. 5.9.(b)]. For a pairing function with

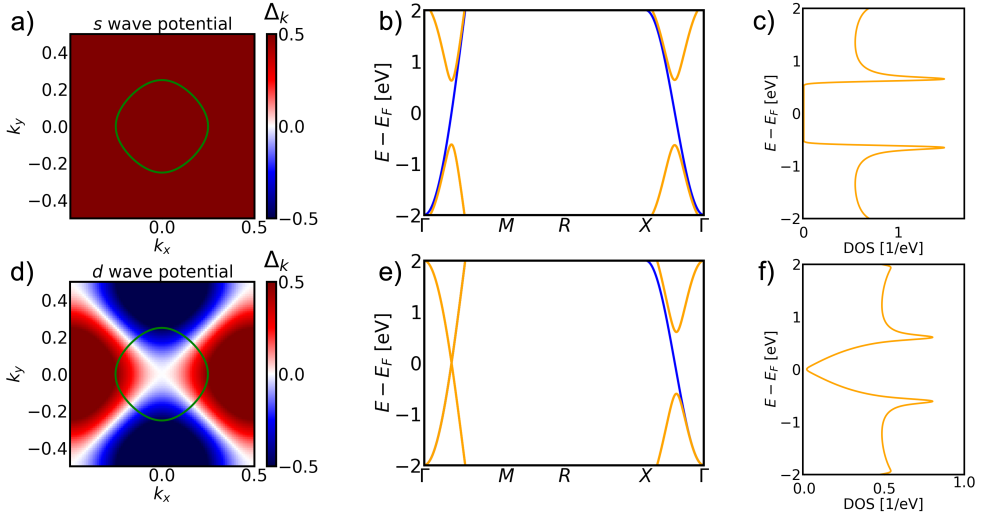


Figure 5.10 Numerical calculation for a hydrogen atom in a cubic lattice with one electron and one hole orbital interacting via a s -wave (a, b, c) and d -wave (d, e, f) gap function: a) and d) gap function dispersion and Fermi surface (green circle); b) and e) band structure in the normal (blue) and superconducting (orange) phase; c) and f) DOS in the superconducting phase.

even orbital coupling (as in the present $d = 2$ case), Cooper pairs are always suppressed at Γ because $\Delta_{\mathbf{k},\sigma\sigma'}$ is odd under inversion symmetry and, hence, $\Delta_{\mathbf{k}=\Gamma,\sigma\sigma'} = -\Delta_{\mathbf{k}=-\Gamma,\sigma\sigma'} = 0$. A notable, particular case with $l = 0$ orbital symmetry is the $s_{\pm}$ pairing, which is believed to describe the superconducting state of an FeSe monolayer¹⁰⁴. Its functional dependence is similar to a d -wave pairing, shifted by half the length of the Brillouin Zone (BZ) in the x or y direction. Its value changes sign in momentum space, but it is non-vanishing at Γ . This implies that the Fermi surface of a material with $s_{\pm}$ pairing can either cross or avoid the nodal lines [Fig. 5.9.(c)]. This picture becomes more complex when the symmetries of the underlying crystal structure are considered, as one needs to replace the point group G by the relevant crystal lattice representation (i.e.: $\mathcal{D}_{6h}$ hexagonal system, $\mathcal{D}_{4h}$ tetragonal system etc...).

To illustrate the role of the pairing potential, we present the numerical solution of the secular Eq. (47) for a fictitious system of one atom, H, in a face-centered cubic lattice, in the normal and superconducting state. We consider two distinct pairing of the superconducting state: (i) spin singlet s -wave with $\Delta_{\mathbf{k}} = \Delta_0 = 0.5$ eV and (ii) d -wave with $\Delta_{\mathbf{k}} = \Delta_0 (\cos(k_x x) + \cos(k_y y))$ [see Fig. 5.10.(a) and Fig. 5.10.(d)]. Electronic band structure and density of states (DOS) are computed within a TB model using the SISL package⁵. [Fig. 5.10.(b)] illustrates the band structure of the normal (blue) and superconducting (orange) state. An isotropic pairing opens a superconducting gap of size $\approx 2\Delta$, resulting in a U-shaped DOS [Fig. 5.10.(c)]. A d -wave pairing gives a linear dispersion along the Γ -M line [Fig. 5.10.(e)] and opens a superconducting gap along X- Γ , resulting in a V-shaped DOS [Fig. 5.10.(f)]. This can be

⁵<https://github.com/zerothi/sisl>

understood by inspecting the dispersion of the gap function in k-space [Fig. 5.10.(d)] and its intersection with the Fermi surface (green circle): The gap function vanishes in the (k_x, k_y) plane for $k_y = k_x$ and $k_y = -k_x$. As a result, the superconducting state is inhibited along $\Gamma(0, 0, 0) - M(0.5, 0.5, 0)$ path leading to observable states within the superconducting gap as reflected in the DOS.

Beyond conventional superconductivity

The open research question is: which interactions give rise to exotic pairing potentials resulting in unconventional superconductivity? In 1965 Kohn and Luttinger discussed a new possible pairing mechanism: in their seminal work⁸, they demonstrated theoretically that a system of weakly interacting fermions cooled down to very low temperatures does not need an intrinsic attractive potential to become superconducting. This is due to the long-range (radial) oscillatory behaviour of the screened Coulomb potential that couples with electron wave functions with higher angular momentum l , resulting in an effective attractive force. This work sets the basis for two new concepts: first, superconductivity might arise from interaction other than electron-phonon, and second, higher angular components of the electron wave function can be crucial for describing superconductivity. The Kohn-Luttinger theory predicts that any metal becomes a superconductor at low enough temperatures, of the order of $10^{-7}T_F$, where T_F is the Fermi temperature. However, due to the magnitude of this critical temperature, an experimental validation would not be possible.

An alternative and interesting mechanism that gives rise to unconventional superconductivity due to spin fluctuations was proposed in 1966 by Berk and Schrieffer¹⁰⁵. In magnetic materials, a spin-polarized electron can polarize the spins of the surrounding electrons in the crystal, leading to an effective attractive interaction and formation of Cooper pairs. For this class of materials it is possible to reach relative high T_C as in the case of cuprate superconductors¹⁰⁶.

The connection between symmetry and nature of superconductivity enables the classification of a special class of superconductors: topological crystalline superconductors^{67,107}. The heterostructures built from different combinations of superconductor and magnetic/non-magnetic materials or systems with vortices are of particular interest for applications in quantum computing. Indeed, near a boundary or at the vortex core, the pairing wavefunction collapses forming spatially localized states called *Andreev bound states* (ABS)¹⁰⁸. ABS play a crucial role in understanding the fundamental physics behind transport phenomena in normal metal/superconductor junctions and the arising of Majorana bound states in semiconductor-superconductor systems. In spintronics, the presence of spin-polarized ABS at the interface between a ferromagnet and a superconductor opens the door for potential innovative devices that exploit both superconductivity and spin properties^{109–111}. ABS can also be used, experimentally, to probe the phase and amplitude of the pairing potential.

In the last 30 years, theoretical and experimental works have been devoted to probing and analysing the symmetry of the superconducting energy gap function in momentum space. The interplay between the electronic dispersion in multi-band systems and the symmetry of the gap function allows for engineering new materials with desired properties such as topological

edge states and the formation of Majorana zero mode for quantum computing^{66,112}. A general implementation of superconductivity must consider the tensorial (orbital and spin) nature of the superconducting gap function. Our method sets the basis for such a description, allowing for a different coupling scheme between different pair of electron and hole orbitals.

5.2 Superconducting Density Functional Theory

In this section we review the crucial results of Oliveira, Kohn, and Gross (OKG) on the formally exact extension of density functional theory (DFT) to superconducting density functional theory (SCDFT). The starting point of SCDFT is a general DFT many-body Hamiltonian:

$$\begin{aligned} \hat{\mathbf{H}} &= \sum_{\mu,\sigma\sigma'} \int d\mathbf{r} \psi_{\mu,\sigma}^\dagger(\mathbf{r}) \left[\hat{H}^0 + \hat{H}^{e-e} + \hat{H}^{rel} \right] \psi_{\mu,\sigma'}(\mathbf{r}) \\ &+ \frac{1}{2} \sum_{\substack{\mu,\mu',\nu,\nu' \\ \sigma_1,\sigma'_1,\sigma_2,\sigma'_2}} \int d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 \psi_{\mu\sigma_1}^\dagger(\mathbf{r}_1) \psi_{\mu'\sigma'_1}^\dagger(\mathbf{r}'_1) \times \\ &\quad \Lambda^{\sigma_1\sigma'_1\sigma_2\sigma'_2}(\mathbf{r}_1, \mathbf{r}'_1, \mathbf{r}_2, \mathbf{r}'_2) \psi_{\nu'\sigma'_2}(\mathbf{r}'_2) \psi_{\nu\sigma_2}(\mathbf{r}_2) \end{aligned} \quad (49)$$

where μ is the orbital/site index, $\hat{H}^0$ is the non-relativistic one-body Hamiltonian consisting of the electron kinetic energy and potential energy V_{ext} in external fields (including the field of the nuclei), $\hat{H}^{e-e}$ is the electron-electron Coulomb interaction, and $\hat{H}^{rel}$ are first-order relativistic corrections (mass-velocity term¹¹³, spin-orbit interactions, and Darwin term^{114–116}), and Λ is the superconducting kernel which describes a two-particle potential in the most general form. The field operator $\psi_{\mu,\sigma}(\mathbf{r})$ creates an electron at $\mathbf{r}$ with spin σ . Our formulation differs from OKG⁶⁸ only in the spin indices of the superconducting term. We do not impose a singlet contribution but keep it general following the Balian-Werthamer parametrization⁹³.

Oliveira *et al.* proved that the fundamental ideas of DFT also apply to superconducting systems, namely the Hohenberg-Kohn theorems can be generalized to superconductors and the Kohn-Sham ansatz is applicable. In order to generalize the Hohenberg-Kohn theorem, one must consider the anomalous density $\chi_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = \langle \psi_\sigma(\mathbf{r}) \psi_{\sigma'}(\mathbf{r}') \rangle$ in addition to the normal charge density $\rho_{\sigma\sigma'}(\mathbf{r}) = \langle \psi_\sigma^\dagger(\mathbf{r}) \psi_{\sigma'}(\mathbf{r}) \rangle$. Then the energy of the system is a well-defined functional of the two densities, and of a universal functional $F[\rho, \chi] = E[\rho, \chi] - \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r}$. Furthermore, it is possible to map the interacting system onto a non-interacting auxiliary system (Kohn-Sham ansatz). Analogously to conventional DFT, this leads to the definition of an exchange-correlation functional $E_{xc}[\rho, \chi]$ such that the ground-state densities of the interacting and non-interacting systems are identical. The SCDFT Hamiltonian takes the form

$$\begin{aligned} \mathbf{H}_{\sigma\sigma'}^{KS} &= \int \psi_\sigma(\mathbf{r}) h_{\sigma\sigma'}^{KS}(\mathbf{r}) \psi_{\sigma'}(\mathbf{r}) d\mathbf{r} \\ &- \int \left[(\Delta_{\sigma\sigma'}^{KS})^*(\mathbf{r}, \mathbf{r}') \psi_\sigma(\mathbf{r}) \psi_{\sigma'}(\mathbf{r}') + \text{H.c.} \right] d\mathbf{r} d\mathbf{r}', \\ h_{\sigma\sigma'}^{KS}(\mathbf{r}) &= \frac{-\nabla^2}{2} \delta_{\sigma\sigma'} + V_{ext}(\mathbf{r}) + \sum_{\sigma} \int \frac{\rho_{\sigma\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E^{xc}[\rho, \chi]}{\delta \rho}, \end{aligned} \quad (50)$$

$$\Delta_{\sigma\sigma'}^{KS}(\mathbf{r}, \mathbf{r}') = -\frac{\delta E^{xc}[\rho, \chi]}{\delta \chi^*} = \sum_{\sigma} \int \Lambda^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}', \mathbf{r}_2, \mathbf{r}_2') \chi_{\sigma\sigma'}(\mathbf{r}_2, \mathbf{r}_2') d\mathbf{r}_2 d\mathbf{r}_2', \quad (51)$$

where

$$E^{xc}[\rho, \chi] = E_{xc}^{KS}[\rho] - \sum_{\sigma} \int d\mathbf{r} d\mathbf{r}' d\mathbf{x} d\mathbf{x}' \chi_{\sigma}(\mathbf{r}, \mathbf{r}')^* \Lambda^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; \mathbf{x}, \mathbf{x}') \chi_{\sigma'}(\mathbf{x}, \mathbf{x}'). \quad (52)$$

This Hamiltonian is diagonalized by the orthogonal Bogoliubov operators $\gamma, \gamma^{\dagger}$:

$$\psi_{\uparrow}(\mathbf{r}) = \sum_n \left(u_{\uparrow}^n(\mathbf{r}) \gamma_{n\uparrow} - v_{\uparrow}^{n*}(\mathbf{r}) \gamma_{n\downarrow}^{\dagger} \right), \quad (53)$$

$$\psi_{\downarrow}(\mathbf{r}) = \sum_n \left(u_{\downarrow}^n(\mathbf{r}) \gamma_{n\downarrow} + v_{\downarrow}^{n*}(\mathbf{r}) \gamma_{n\uparrow}^{\dagger} \right). \quad (54)$$

Note that in Eq. (53) the $\uparrow$ and $\downarrow$ of the γ operators do not label a spin wavefunction component index but rather subspaces. In this basis $\mathbf{H} = E_n \gamma_n^{\dagger} \gamma_n$ and the coefficients u_n and v_n satisfy the eigenvalue equations

$$\sum_{\sigma'} \left(h_{\sigma\sigma'}^{KS} u_{\sigma'}^n(\mathbf{r}) + \int \Delta_{\sigma\sigma'}^{KS}(\mathbf{r}, \mathbf{r}') v_{\sigma'}^n(\mathbf{r}') d\mathbf{r}' \right) = E_n u_{\sigma}^n(\mathbf{r}) \quad (55)$$

$$\sum_{\sigma'} \left(-h_{\sigma\sigma'}^{KS*} v_{\sigma'}^n(\mathbf{r}) - \int (\Delta_{\sigma\sigma'}^{KS})^*(\mathbf{r}, \mathbf{r}') u_{\sigma'}^n(\mathbf{r}') d\mathbf{r}' \right) = E_n v_{\sigma}^n(\mathbf{r}). \quad (56)$$

The two densities are given by the following expressions:

$$\rho_{\sigma\sigma'}(\mathbf{r}) = \sum_n \left[u_{\sigma}^n(\mathbf{r}) u_{\sigma'}^{n*}(\mathbf{r}) f(\varepsilon_n) + v_{\sigma}^{n*}(\mathbf{r}) v_{\sigma'}^n(\mathbf{r}) (1 - f(\varepsilon_n)) \right], \quad (57)$$

$$\chi_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = \sum_n \left[u_{\sigma}^n(\mathbf{r}) v_{\sigma'}^{n*}(\mathbf{r}') f(\varepsilon_n) + v_{\sigma}^{n*}(\mathbf{r}) u_{\sigma'}^n(\mathbf{r}') (1 - f(\varepsilon_n)) \right] \quad (58)$$

where f is the Fermi occupation function given by $\langle \gamma_{n\uparrow}^{\dagger} \gamma_{n\uparrow} \rangle = \langle \gamma_{n\downarrow}^{\dagger} \gamma_{n\downarrow} \rangle^6$.

A crucial aspect of unconventional superconductivity is the effect of the spin pairing on the gap function Δ . In order to keep our implementation as general as possible, we write $\chi_{\sigma\sigma'}$ in the above-mentioned Balian-Werthamer parametrization¹⁰³. In this way, the spin structure of Eq. (43) reveals two different components, one symmetric (singlet) and one antisymmetric (triplet) in space. We define three triplet components $\chi^{T_x}, \chi^{T_y}, \chi^{T_z}$ and the singlet component χ^S as

$$\chi^S(\mathbf{r}, \mathbf{r}') = \frac{\chi_{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}') - \chi_{\downarrow\uparrow}(\mathbf{r}, \mathbf{r}')}{2}, \quad (59)$$

$$\chi^{T_x}(\mathbf{r}, \mathbf{r}') = \frac{\chi_{\downarrow\downarrow}(\mathbf{r}, \mathbf{r}') - \chi_{\uparrow\uparrow}(\mathbf{r}, \mathbf{r}')}{2}, \quad (60)$$

$$\chi^{T_y}(\mathbf{r}, \mathbf{r}') = \frac{\chi_{\downarrow\downarrow}(\mathbf{r}, \mathbf{r}') + \chi_{\uparrow\uparrow}(\mathbf{r}, \mathbf{r}')}{2i}, \quad (61)$$

$$\chi^{T_z}(\mathbf{r}, \mathbf{r}') = \frac{\chi_{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}') + \chi_{\downarrow\uparrow}(\mathbf{r}, \mathbf{r}')}{2}. \quad (62)$$

⁶with spin degeneracy

The pairing potential $\Delta_{\sigma\sigma'}^{KS}$, can be decomposed in the same way. From this point onwards, we refer to $\Delta_{\sigma\sigma'}^{KS}$, as $\Delta_{\sigma\sigma'}$.

The Eliashberg theory^{78,117,118} has been successful in describing electron-phonon driven superconductivity. Phonon dynamics is included in the form of a frequency-dependent electron self-energy, giving rise to retardation effects that impact electrons. Hence, the corresponding superconducting order parameter is also frequency dependent, in contrast with a static order parameter in BCS theory.

A DFT-based theory of superconductivity without adjustable parameters was proposed by Lüders et al.⁷⁸. Here, the motion of the nuclei is included via a multi-component DFT formalism where three densities are introduced: electronic, superconducting, and the diagonal of the nuclear density matrix. In this work, a set of BdG-like Kohn-Sham equations including a universal $F[\rho, \chi, \Gamma]$ functional is derived. The most notable result is the equation that links the pairing potential with the renormalization term $\mathcal{Z}$ and the kernel $\mathcal{K}$, which can be calculated with density-functional perturbations theory (DFPT) and GW+Eliashberg theory¹¹⁷:

$$\Delta(\xi) = -\mathcal{Z}(\xi)\Delta(\xi) - \frac{1}{2} \int_{-\mu}^{\infty} d\xi' N(\xi') \mathcal{K}(\xi, \xi') \times \frac{\tanh[(\beta/2)\xi']}{\xi'} \Delta(\xi'), \quad (63)$$

where $N(\xi)$ is the density of states at energy ξ .

This formalism has been applied to elemental metals, with results that are in good agreement with experiments⁷⁶.

SCDFT in SIESTA treat the pairing potential as a semi phenomenological parameter, chosen to reproduce experimental quantities (e.g. critical temperature, superconducting gap), following the prescription of Suvasini⁹². This approach is more general, it allows for electron-phonon driven superconductivity, but it does not impose any restriction on the form of the pairing mechanism allowing to simulate unconventional superconductivity.

Authorship statement

This chapter was written by Riccardo Reho to provide the necessary theoretical background for this thesis.

Bibliography

- 1 E. Schrödinger, *Annalen der physik* **385**, 437 (1926).
- 2 F. Bechstedt, *Many-body approach to electronic excitations* (Springer, 2016).
- 3 Z. E. Musielak and B. Quarles, *Reports on Progress in Physics* **77**, 065901 (2014).
- 4 W. Pauli, *Naturwiss* **12**, 741 (1924).
- 5 D. R. Hartree, in *Mathematical Proceedings of the Cambridge Philosophical Society*, Vol. 24 (Cambridge University Press, 1928) pp. 111–132.

- 6 V. Fock, *Zeitschrift für Physik* **61**, 126 (1930).
- 7 J. C. Slater, *Physical review* **81**, 385 (1951).
- 8 W. Kohn and J. M. Luttinger, *Physical Review Letters* **15**, 524 (1965).
- 9 P. Hohenberg and W. Kohn, *Physical review* **136**, B864 (1964).
- 10 M. J. Gander and G. Wanner, *Siam Review* **54**, 627 (2012).
- 11 M. Born and W. Heisenberg, *Original Scientific Papers Wissenschaftliche Originalarbeiten* , 216 (1985).
- 12 S. Reichardt, *Many-body perturbation theory approach to Raman spectroscopy and its application to 2D materials*, Ph.D. thesis, Unilu-University of Luxembourg, Luxembourg (2018).
- 13 R. M. Martin, *Electronic structure: basic theory and practical methods* (Cambridge university press, 2020).
- 14 W. Kohn and L. J. Sham, *Physical review* **140**, A1133 (1965).
- 15 P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, *et al.*, *Journal of physics: Condensed matter* **21**, 395502 (2009).
- 16 P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. B. Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, *et al.*, *Journal of physics: Condensed matter* **29**, 465901 (2017).
- 17 A. Garcia, N. Papior, A. Akhtar, E. Artacho, V. Blum, E. Bosoni, P. Brandimarte, M. Brandbyge, J. I. Cerdá, F. Corsetti, *et al.*, *The Journal of chemical physics* **152**, 204108 (2020).
- 18 J. P. Perdew, K. Burke, and M. Ernzerhof, *Physical Review Letters* **77**, 3865 (1996).
- 19 P. Mori-Sánchez, A. J. Cohen, and W. Yang, *Physical Review Letters* **100**, 146401 (2008).
- 20 M. Rohlfling and S. G. Louie, *Physical Review B* **62**, 4927 (2000).
- 21 A. Marini, C. Hogan, M. Grüning, and D. Varsano, *Computer Physics Communications* **180**, 1392 (2009).
- 22 D. Sangalli, A. Ferretti, H. Miranda, C. Attaccalite, I. Marri, E. Cannuccia, P. Melo, M. Marsili, F. Paleari, A. Marrazzo, *et al.*, *Journal of Physics: Condensed Matter* **31**, 325902 (2019).
- 23 M. S. Hybertsen and S. G. Louie, *Physical Review B* **34**, 5390 (1986).

- 24** S. Grimme, Journal of computational chemistry **27**, 1787 (2006).
- 25** S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, The Journal of chemical physics **132** (2010).
- 26** A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Reviews of Modern Physics **68**, 13 (1996).
- 27** J. Hubbard, Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences **276**, 238 (1963).
- 28** E. Runge and E. K. Gross, Physical Review Letters **52**, 997 (1984).
- 29** N. D. Mermin, Physical Review **137**, A1441 (1965).
- 30** T. Hansson, C. Oostenbrink, and W. van Gunsteren, Current opinion in structural biology **12**, 190 (2002).
- 31** F. Knoop, N. Shulumba, A. Castellano, J. P. Alvarinhas Batista, R. Farris, M. J. Verstraete, M. Heine, D. Broido, D. S. Kim, J. Klarbring, *et al.*, Journal of Open Source Software **9** (2024).
- 32** G. Onida, L. Reining, and A. Rubio, Reviews of modern physics **74**, 601 (2002).
- 33** G. Stefanucci and R. Van Leeuwen, *Nonequilibrium many-body theory of quantum systems: a modern introduction* (Cambridge University Press, 2013).
- 34** G. Strinati, La Rivista del Nuovo Cimento (1978-1999) **11**, 1 (1988).
- 35** D. Golze, M. Dvorak, and P. Rinke, Frontiers in chemistry **7**, 377 (2019).
- 36** S. D. Kevan, *Angle-resolved photoemission: theory and current applications*, Vol. 74 (Elsevier, 1992).
- 37** W. Eberhardt and E. Plummer, Physical Review B **28**, 3605 (1983).
- 38** F. Himpsel, Advances in Physics **32**, 1 (1983).
- 39** M. Abbate, J. Goedkoop, F. De Groot, M. Grioni, J. Fuggle, S. Hofmann, H. Petersen, and M. Sacchi, Surface and Interface Analysis **18**, 65 (1992).
- 40** A. Goldmann, V. Dose, and G. Borstel, Physical Review B **32**, 1971 (1985).
- 41** J. C. Fuggle, J. E. Inglesfield, and P. Andrews, *Unoccupied electronic states: fundamentals for XANES, EELS, IPS and BIS*, Vol. 69 (Springer, 1992).
- 42** A. Aliane, S. Abboudi, C. Seladji, and B. Guendouz, Renewable and Sustainable Energy Reviews **65**, 443 (2016).
- 43** S. Koch, M. Kira, G. Khitrova, and H. Gibbs, Nature materials **5**, 523 (2006).

- 44** A. L. Fetter and J. D. Walecka, *Quantum theory of many-particle systems* (Courier Corporation, 2012).
- 45** L. D. Landau, Sov. Phys. JETP **3**, 920 (1957).
- 46** L. Landau, Soviet Physics JETP-Ussr **5**, 101 (1957).
- 47** L. Landau, Sov. Phys. JETP **8**, 70 (1959).
- 48** X. Blase, I. Duchemin, D. Jacquemin, and P.-F. Loos, The Journal of Physical Chemistry Letters **11**, 7371 (2020).
- 49** L. Hedin, Physical Review **139**, A796 (1965).
- 50** L. Hedin, Journal of Physics: Condensed Matter **11**, R489 (1999).
- 51** R. D. Mattuck, *A guide to Feynman diagrams in the many-body problem* (Courier Corporation, 2012).
- 52** L. Reining, Wiley Interdisciplinary Reviews: Computational Molecular Science **8**, e1344 (2018).
- 53** W. Hanke and L. Sham, Physical Review Letters **43**, 387 (1979).
- 54** W. Meissner and R. Ochsenfeld, Naturwissenschaften **21**, 787 (1933).
- 55** J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Physical review **108**, 1175 (1957).
- 56** F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schäfer, Physical Review Letters **43**, 1892 (1979).
- 57** D. Jérôme, A. Mazaud, M. Ribault, and K. Bechgaard, Journal de Physique Lettres **41**, 95 (1980).
- 58** C. C. Tsuei and J. R. Kirtley, Reviews of Modern Physics **72**, 969 (2000).
- 59** G. R. Stewart, Reviews of Modern Physics **83**, 1589 (2011).
- 60** L. Balents, C. R. Dean, D. K. Efetov, and A. F. Young, Nature Physics **16**, 725 (2020).
- 61** B. Sacépé, M. Feigel'man, and T. M. Klapwijk, Nature Physics **16**, 734 (2020).
- 62** S. Frolov, M. Manfra, and J. Sau, Nature Physics **16**, 718 (2020).
- 63** A. Y. Kitaev, Physics-Uspekhi **44**, 131 (2001).
- 64** W.-Y. He, B. T. Zhou, J. J. He, N. F. Q. Yuan, T. Zhang, and K. T. Law, Communications Physics **1**, 40 (2018).

- 65** J. S. Lee, B. Shojaei, M. Pendharkar, A. P. McFadden, Y. Kim, H. J. Suominen, M. Kjaergaard, F. Nichele, H. Zhang, C. M. Marcus, and C. J. Palmstrøm, *Nano Letters* **19**, 3083 (2019).
- 66** E. Prada, P. San-Jose, M. W. A. de Moor, A. Geresdi, E. J. H. Lee, J. Klinovaja, D. Loss, J. Nygård, R. Aguado, and L. P. Kouwenhoven, *Nature Reviews Physics* **2**, 575 (2020).
- 67** M. Sato and Y. Ando, *Reports on Progress in Physics* **80**, 076501 (2017).
- 68** L. N. Oliveira, E. K. U. Gross, and W. Kohn, *Physical Review Letters* **60**, 2430 (1988).
- 69** M. Suvasini and B. Gyorffy, *Physica C: Superconductivity* **195**, 109 (1992).
- 70** “The Elk Code,” <http://elk.sourceforge.net/>.
- 71** R. O. Jones, *Reviews of modern physics* **87**, 897 (2015).
- 72** N. Bogoljubov, V. V. Tolmachov, and D. Širkov, *Fortschritte der physik* **6**, 605 (1958).
- 73** N. N. Bogoljubov, *Il Nuovo Cimento* **7**, 794 (1958).
- 74** P.-G. de Gennes, *Superconductivity of Metals and Alloys*, Advanced Book Classics (Advanced Book Program, Perseus Books, Reading, Mass, 1999).
- 75** J.-X. Zhu, *Bogoliubov-de Gennes method and its applications*, Vol. 924 (Springer, 2016).
- 76** M. Marques, M. Lüders, N. Lathiotakis, G. Profeta, A. Floris, L. Fast, A. Continenza, E. Gross, and S. Massidda, *Physical Review B* **72**, 024546 (2005).
- 77** A. Sanna, in *The Physics of Correlated Insulators, Metals, and Superconductors. Lecture Notes of the Autumns School on Correlated Electrons 2017, Schriften des Forschungszentrums Jülich. Reihe Modeling and Simulation*. (Forschungszentrum Jülich GmbH, Institute for Advanced Simulation, 2017).
- 78** M. Lüders, M. Marques, N. Lathiotakis, A. Floris, G. Profeta, L. Fast, A. Continenza, S. Massidda, and E. Gross, *Physical Review B* **72**, 024545 (2005).
- 79** P. Cudazzo, G. Profeta, A. Sanna, A. Floris, A. Continenza, S. Massidda, and E. K. U. Gross, *Physical Review Letters* **100**, 257001 (2008).
- 80** L. Boeri and G. B. Bachelet, *Journal of Physics: Condensed Matter* **31**, 234002 (2019).
- 81** L. Boeri, in *Handbook of Materials Modeling*, edited by W. Andreoni and S. Yip (Springer International Publishing, Cham, 2020) pp. 73–112.
- 82** F. Schrodi, P. M. Oppeneer, and A. Aperis, *Physical Review B* **104**, L140506 (2021).
- 83** D. Scalapino, *Journal of Low Temperature Physics* **117**, 179 (1999).

- 84** W. M. Temmerman, Z. Szotek, B. L. Gyorffy, O. K. Andersen, and O. Jepsen, *Physical Review Letters* **76**, 307 (1996).
- 85** B. L. Gyorffy, Z. Szotek, W. M. Temmerman, O. K. Andersen, and O. Jepsen, *Physical Review B* **58**, 1025 (1998).
- 86** G. Csire, J. F. Annett, J. Quintanilla, and B. Újfalussy, *Physical Review B* **106**, L020501 (2022), publisher: American Physical Society.
- 87** G. Csire, B. Újfalussy, J. Cserti, and B. Györffy, *Physical Review B* **91**, 165142 (2015).
- 88** G. Csire, A. Deák, B. Nyári, H. Ebert, J. F. Annett, and B. Újfalussy, *Physical Review B* **97**, 024514 (2018).
- 89** T. G. Saunderson, J. F. Annett, B. Újfalussy, G. Csire, and M. Gradhand, *Physical Review B* **101**, 064510 (2020).
- 90** P. Rüßmann and S. Blügel, *Physical Review B* **105**, 125143 (2022).
- 91** H. Ness, I. A. Sadovskyy, A. E. Antipov, M. van Schilfgaarde, and R. M. Lutchyn, *npj Computational Materials* **8**, 23 (2022).
- 92** M. B. Suvasini, W. M. Temmerman, and B. L. Gyorffy, *Phys. Rev. B* **48**, 1202 (1993).
- 93** K. Capelle and E. Gross, *Physical Review B* **59**, 7140 (1999).
- 94** F. London and H. London, *Proceedings of the Royal Society of London. Series A - Mathematical and Physical Sciences* **149**, 71 (1935).
- 95** A. B. Pippard, *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* **216**, 547 (1953).
- 96** V.L. Ginzburg and L.D. Landau, *Journal of Experimental and Theoretical Physics* **20**, 17 (1950).
- 97** R. Sharma, *Superconductivity: Basics and Applications to Magnets*, Springer Series in Materials Science, Vol. 214 (Springer International Publishing, Cham, 2021).
- 98** H. Fröhlich, *Physical Review* **79**, 845 (1950).
- 99** M. Tinkham, *Introduction to superconductivity* (Courier Corporation, 2004).
- 100** B. White, J. Thompson, and M. Maple, *Physica C: superconductivity and its applications* **514**, 246 (2015).
- 101** I. V. Bobkova, A. M. Bobkov, A. Kamra, and W. Belzig, *Communications Materials* **3**, 95 (2022).
- 102** E. Pashitskii and V. Pentegov, *Low Temperature Physics* **34**, 113 (2008).

- 103** R. Balian and N. Werthamer, Physical review **131**, 1553 (1963).
- 104** P. J. Hirschfeld, Comptes Rendus Physique **17**, 197 (2016).
- 105** N. F. Berk and J. R. Schrieffer, Physical Review Letters **17**, 433 (1966).
- 106** S. K. M and D. J. C. S, Mat. today **11**, 14 (2008).
- 107** K. Shiozaki and M. Sato, Physical Review B **90**, 165114 (2014).
- 108** A. Andreev *et al.*, Sov. Phys. JETP **20**, 1490 (1965).
- 109** G. Csire, J. Cserti, and B. Újfalussy, Journal of Physics: Condensed Matter **28**, 495701 (2016).
- 110** R. M. Lutchyn, E. P. Bakkers, L. P. Kouwenhoven, P. Krogstrup, C. M. Marcus, and Y. Oreg, Nature Reviews Materials **3**, 52 (2018).
- 111** Y. Yao, R. Cai, T. Yu, Y. Ma, W. Xing, Y. Ji, X.-C. Xie, S.-H. Yang, and W. Han, Science Advances **7**, eabh3686 (2021).
- 112** J. M. Gambetta, J. M. Chow, and M. Steffen, npj quantum information **3**, 2 (2017).
- 113** A. Farazdel, W. M. Westgate, A. M. Simas, R. P. Sagar, and V. H. Smith, International Journal of Quantum Chemistry **28**, 61 (2009).
- 114** T. Saue, ChemPhysChem **12**, 3077 (2011).
- 115** M. Marsili, A. Molina-Sánchez, M. Palummo, D. Sangalli, and A. Marini, Physical Review B **103**, 155152 (2021).
- 116** R. Cuadrado and J. Cerdá, Journal of Physics: Condensed Matter **24**, 086005 (2012).
- 117** G. Eliashberg, Sov. Phys. JETP **11**, 696 (1960).
- 118** F. Marsiglio, Annals of Physics **417**, 168102 (2020).

Density functional Bogoliubov-de Gennes theory for superconductors implemented in the SIESTA code



Based on

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Abstract

SIESTA-BdG integrates the simultaneous solution of the Bogoliubov-de Gennes (BdG) and Density Functional Theory (DFT) equations within SIESTA, a first-principles code for material simulations using pseudopotentials and a localized basis set. This approach describes both conventional and unconventional superconducting states, as well as inhomogeneous superconductors and heterostructures. We validate SIESTA-BdG by computing superconducting charge density, band structure, superconducting gap features, and density of states for conventional (Nb, Pb) and unconventional (FeSe) superconductors, finding excellent agreement with experiments and the KKR-BdG framework. SIESTA-BdG supports modeling quantum transport in superconducting devices and includes the superconducting DFT potential of Oliveira, Gross, and Kohn approximately. This chapter is based on Reho and Wittemeier et al.¹ R. Reho and N. Wittemeier contributed equally to the theoretical foundation, and all authors contributed equally to the implementation.

1 Introduction

Superconductivity is an intrinsically quantum phenomenon, defying the classical picture of dissipative current flow. It is one of the striking cases where quantum effects manifest at the macroscopic scale, as demonstrated by the Meissner effect². The microscopic theory developed by Bardeen, Cooper, and Schrieffer (BCS) in 1957^{3,4} was instrumental in understanding the underlying mechanism in terms of attractive interaction between electrons mediated by crystal lattice vibrations (phonons), forming Cooper pairs below a (very low) critical temperature. However, there are other complex realizations of superconductivity which cannot be explained within the BCS theory. These are referred to as *unconventional* or exotic forms of superconductivity. Examples include high-temperature superconductivity and multiband superconductivity, where multiple bands cross the Fermi surface, leading to several superconducting instabilities^{5–8}. These and other exotic forms of superconductivity can arise due to strong interactions between electrons⁹, from the interplay between disorder and dimensionality¹⁰, or emerge from the proximity interaction of a conventional superconductor and a topological insulator (topological superconductivity)¹¹. In particular, topological superconductors^{12–15} could revolutionize the field of quantum computing by hosting quantum bits based on Majorana zero modes¹⁶.

Modelling and understanding the origins of effects like proximity-induced superconductivity and unconventional superconductivity requires covering one or more of the following points: (a) a realistic description of heterostructures and interfaces between normal and superconducting materials (for example, to model topological superconductors) (b) a unified treatment of normal and superconducting electronic properties to predict band structure, density of states, normal and anomalous charge density, and (c) the ability to model unconventional pairing mechanisms between electrons (e.g. p -wave spin - triplet), beyond BCS theory. Superconducting density functional theory (SCDFT)¹⁷ satisfies these requirements: it combines density functional theory (DFT)^{18,19}, which successfully predicts structural and electronic properties of solids, with the Bogoliubov-de Gennes (BdG) formalism^{20–22}, which is a Hartree-Fock-like mean-field approximation of the many-body Hamiltonian generalizing the BCS theory³ to treat inhomogeneous superconductors. SCDFT allows for a general form of the pairing interaction and, hence, can describe normal/superconductor interfaces and unconventional superconductors^{23,24}, in addition to conventional ones^{25–27}.

In SCDFT, a non-local superconductive effective potential (depending on both normal and anomalous charge densities) replaces the standard DFT one (Section 2.1 and Appendix A). Then, the energy functional's minimization with respect to both normal and anomalous densities leads to the BdG equations. SCDFT is formally an exact theory. However, it does not give a prescription for the construction of the superconducting coupling (kernel) λ . In this work, we follow the semi-phenomenological approach of Suvasini *et al*^{28,29}, where the superconducting kernel is assumed to be *local* and the explicit functional dependence on the normal (ρ) and anomalous (χ) densities is replaced by *site-dependent constants* (Section 2.1),

namely we neglect the dynamical update of the superconducting kernel due to quasiparticle interactions (such as magnons or phonons).

Semi-phenomenological SCDFT has been recently implemented within multiple scattering theory in the Korringa-Kohn-Rostoker (KKR) approximation (KKR-BdG)^{30,31} to study conventional superconductors³¹, proximity-induced superconductivity^{32–34}, and the formation of Yu-Shiba-Rusinov states (YSR)^{35–37}. A different approach, combining dynamical mean field theory (DMFT) and the quasiparticle self-consistent GW approximation, has been recently developed and implemented in the Questaal code³⁸ and successfully used to model (un)conventional superconductors^{38–40}. In Questaal, the superconducting properties are extracted from pairing susceptibilities in the particle-particle channel, computed with the Bethe-Salpeter equation.

In this paper, we present the theoretical description and software implementation of semi-empirical SCDFT in the SIESTA DFT method and code^{41,42}, which we will refer to as SIESTA-BdG. SIESTA is a well-documented, open source code with an exhaustive set of tutorials¹, and a large community of developers and users. SIESTA uses a basis of strictly localized orbitals, which leads to sparse matrices which can be diagonalized using highly efficient linear algebra algorithms: SIESTA has a native interface for the ScaLAPACK, MRRR and ELPA solvers. These solvers and recently developed GPU-accelerated interface in ELPA can also be used in SIESTA-BdG. In addition, the ELSI library allows simultaneous parallelization over k-points, orbitals, and spins, which is particularly useful given the extremely dense sampling of the Brillouin Zone required to capture the (sub)meV energy scales characterizing the superconducting gap. All these features make SIESTA-BdG an ideal choice for studying superconductivity in systems consisting of several hundreds of atoms such as interfaces, or heterostructures.

In SIESTA-BdG, the specific value of the superconducting coupling can be taken from experiment, simulations (electron-phonon DFT, strong correlation model, ...), or chosen to explore the properties of the system as a function of the input parameters. Then, one can perform a self-consistent calculation of both normal and superconducting (*anomalous*) charge densities to compute the pairing potential and superconducting properties, such as local density of states (directly comparable with scanning tunnelling microscopy experiments), shape and size of the superconducting gap, quasiparticle spectrum, electron and hole wave functions, Fermi surface, and electron momentum distribution function (Section 2.2). SIESTA-BdG can be employed to analyse the role that different atomic orbitals play in the formation of Cooper pairs by selectively “activating” the pairing between specific orbitals. This feature is useful to investigate the mechanism behind exotic forms of superconductivity. SIESTA-BdG is implemented using the spin - orbit coupling (SOC) formalism present in SIESTA⁴³, so that SOC and related effects (such as topology and topological superconductivity) can be fully described in synergy with normal state properties. Hence, within SIESTA, one can compute the full spectrum of structural, electronic, magnetic, and topological properties of both normal and superconducting materials.

¹<https://github.com/siesta-project> and <https://www.youtube.com/@siestaproject>

Quantum electron transport can also be computed using the same software package, ensuring a coherent description of all these properties for the whole simulation workflow. The SIESTA-BdG method is an ideal starting point for superconducting quantum transport calculations using non-equilibrium Green's functions techniques (NEGF), because the strictly localized basis sets used in SIESTA make it easy to define local Hamiltonians and local Green's functions. Indeed, the SIESTA package comes with a set of routines and utilities that implement methods to compute quantum transport properties in normal state device, namely *TRANSIESTA*^{44,45}. In this work, we show how the SIESTA-BdG method can be applied to study superconducting quantum transport in a (5,5) armchair carbon nanotube (CNT) using NEGF methods in a one-particle framework⁴⁶⁻⁵⁰. We compute the normal and *Andreev* transmission and reflection functions for an artificial N-S junction.

The manuscript is organized as follows. In Section 2 we adapt the Bogoliubov-de Gennes formalism²¹ to linear combination of atomic orbitals (LCAO) methods, present the SIESTA-BdG implementation, three different self-consistency schemes to solve the SIESTA-BdG equations, and two methods for the initialization of the superconducting pairing potential and coupling. In Section 3 we present SIESTA-BdG simulations for conventional (Nb) and unconventional superconductors (FeSe), and validate them against experimental and/or theoretical simulations with KKR-BdG. In Section 4, we formulate electron transport in the presence of superconductivity within the SIESTA-BdG method and discuss the foreseen impact on the field. In the appendices we discuss the spin generalized superconducting DFT formalism (Appendix A), computational strategies to perform SIESTA-BdG simulations (Appendix B) including efficiency, accuracy, SIESTA-BdG solution methods, initialization of the superconducting potential, and computational details. Adaptation of scattering theory for transport in superconductors to the SIESTA-BdG formalism is covered in Appendix C.

2 SIESTA-BdG

2.1 Bogoliubov-de Gennes equations in a localized basis set

In the SIESTA-BdG method, the spin generalized Kohn-Sham BdG equations - reviewed in Appendix A - are written in terms of the SIESTA linear combination of atomic orbitals (LCAO) basis set⁴¹. An atomic orbital ϕ_μ is identified by an atom label (I) and its quantum numbers (l, m, n), collected in a super-index $\mu = \{I, l, m, n\}$ which labels the basis orbitals in the unit cell:

$$\varphi_\mu^\alpha(\mathbf{r}) = \varphi_{I l m n \alpha}(\mathbf{r}) = \varphi_{I l m n}(\mathbf{r}) \otimes |\alpha\rangle \quad (1)$$

with α the spin index. The electron $u_i^\alpha(\mathbf{r})$ and hole $v_i^\alpha(\mathbf{r})$ eigenfunctions in the LCAO basis set can still be grouped into four-component Nambu spinors $\Psi_i(\mathbf{r}) = (u_i^\uparrow(\mathbf{r}) \ u_i^\downarrow(\mathbf{r}) \ v_i^\uparrow(\mathbf{r}) \ v_i^\downarrow(\mathbf{r}))^T$, and read:

$$u_i^\alpha(\mathbf{r}) = \sum_\mu \varphi_\mu(\mathbf{r}) u_{i\mu}^\alpha, \quad v_i^\alpha(\mathbf{r}) = \sum_\mu \varphi_\mu^*(\mathbf{r}) v_{i\mu}^\alpha \quad (2)$$

where $u_{i\mu}^\alpha$ and $v_{i\mu}^\alpha$ are the expansion coefficients, and i the index of the superconducting bands (Bogoliubon excitation state).

SIESTA solves the DFT problem using periodic boundary conditions. Non-periodic systems (molecules, tubes, slabs, interfaces, ...) are modelled using the supercell approach. Assuming a lattice periodic pairing potential, it is convenient to write and solve the BdG eigenvalue problem in the reciprocal space of the simulation cell. Exploiting the Bloch theorem, the electron and hole wavefunction can be expanded in Bloch waves

$$\begin{aligned} u_i^\alpha(\mathbf{k}, \mathbf{r}) &= \sum_{\mu, \mathbf{R}} e^{i\mathbf{k}(\mathbf{R}+\tau_\mu)} \varphi_\mu(\mathbf{r}) u_{i\mu}^\alpha(\mathbf{k}) \\ v_i^\alpha(\mathbf{k}, \mathbf{r}) &= \sum_{\mu, \mathbf{R}} e^{i\mathbf{k}(\mathbf{R}+\tau_\mu)} \varphi_\mu^*(\mathbf{r}) v_{i\mu}^\alpha(\mathbf{k}) \end{aligned} \quad (3)$$

where the sum runs through all orbitals in space, given by the lattice vectors $\mathbf{R}$ and orbitals positions τ_μ in the unit cell, and $\mathbf{k}$ is the crystal momentum of the supercell. Writing the BdG equations in the LCAO basis is crucial to reveal the contribution of specific orbitals to superconductivity, explain complex interactions between different bands (multi-band superconductors), and analyse competing superconducting phases as those breaking time-reversal symmetry or related to different spin configurations⁵¹. The relevant equations for the SIESTA-BdG method in $\mathbf{k}$ -space are:

1. the BdG Hamiltonian $\hat{\mathbf{H}}_{\text{BdG}}$

$$\hat{H}_{\text{BdG}, \mu\nu}^{\alpha, \beta}(\mathbf{k}) = \sum_{\nu, \mathbf{R}} e^{i\mathbf{k}(\mathbf{R}+\tau_\nu-\tau_\mu)} \hat{H}_{\text{BdG}, \mu\nu}^{\alpha, \beta} \quad (4)$$

2. the eigenvalue problem

$$\begin{aligned} \sum_{\mu\alpha} \begin{pmatrix} \mathbf{h}_{\nu\mu}^{\text{KS}\beta\alpha}(\mathbf{k}) - \mu S_{\nu\mu}(\mathbf{k}) \delta_{\beta\alpha} & \Delta_{\nu\mu}^{\beta\alpha}(\mathbf{k}) \\ -\Delta_{\nu\mu}^{*\beta\alpha}(-\mathbf{k}) & -\mathbf{h}_{\nu\mu}^{\text{KS}* \beta\alpha}(-\mathbf{k}) + \mu S_{\nu\mu}(\mathbf{k}) \delta_{\beta\alpha} \end{pmatrix} \\ \begin{pmatrix} u_{i\mu}^\alpha(\mathbf{k}) \\ v_{i\mu}^\alpha(\mathbf{k}) \end{pmatrix} = \varepsilon_i \sum_{\mu\alpha} S_{\nu\mu}(\mathbf{k}) \delta_{\beta\alpha} \begin{pmatrix} u_{i\mu}^\alpha(\mathbf{k}) \\ v_{i\mu}^\alpha(\mathbf{k}) \end{pmatrix}, \end{aligned} \quad (5)$$

where $\mathbf{h}^{\text{KS}}$ is the normal state Kohn-Sham Hamiltonian, $\Delta_{\nu\mu}^{\beta\alpha}(\mathbf{k})$ is the superconducting pairing potential, $S_{\nu\mu}(\mathbf{k})$ the overlap matrix at $\mathbf{k}$ and μ the chemical potential,

3. the normal and anomalous densities

$$\rho_{\mu\nu}^{\alpha\beta}(\mathbf{k}) = \sum_i f(\varepsilon_i(\mathbf{k})) u_{i\mu}^{*\alpha}(\mathbf{k}) u_{i\nu}^\beta(\mathbf{k}) \quad (6)$$

$$\begin{aligned} &+ \sum_i \bar{f}(\varepsilon_i(-\mathbf{k})) v_{i\mu}^\alpha(-\mathbf{k}) v_{i\nu}^{*\beta}(-\mathbf{k}) \\ \chi_{\mu\nu}^{\alpha\beta}(\mathbf{k}) &= \sum_i f(\varepsilon_i(\mathbf{k})) u_{i\nu}^\beta(\mathbf{k}) v_{i\mu}^{*\alpha}(\mathbf{k}) \\ &+ \sum_i \bar{f}(\varepsilon_i(-\mathbf{k})) u_{i\mu}^\alpha(-\mathbf{k}) v_{i\nu}^{*\beta}(-\mathbf{k}) \end{aligned} \quad (7)$$

where $f(\varepsilon_i)$ and $\bar{f}(\varepsilon_i) = 1 - f(\varepsilon_i)$ are the occupation functions,

4. the pairing potential $\Delta_{\mu\nu}^{\alpha\beta}(\mathbf{k})$:

$$\Delta_{\mu\nu}^{\alpha\beta}(\mathbf{k}) = - \sum_{l=0,1,2,3} \sum_{\gamma} i\sigma_l^{\alpha\gamma} \sigma_2^{\gamma\beta} \times \int_{\text{BZ}} d\mathbf{k}' \lambda_l^{\mu\nu}(\mathbf{k} - \mathbf{k}') \chi_{\mu\nu}^l(\mathbf{k}') \quad (8)$$

where σ_l are the Pauli matrices, $\lambda_l^{\mu\nu}$ are the orbital projected superconducting couplings. We denote as λ the matrix with elements $\lambda_l^{\mu\nu}$.

The above equations are only valid under the assumption that the pairing potential is lattice periodic. Superconductors with spatially non-uniform pairing potential need to be modelled using a supercell approach. This is the case of Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) phase of a superconductor⁵², which is characterized by Cooper pairs with finite momentum.

Even though the superconducting coupling λ is local, it can have an explicit dependence on the atomic orbitals in real-space, which can be used to initialize the simulations (Sections 2.3 and B). The pairing potential Δ is updated in the self-consistent steps via 8 (Section 2.2) and it acquires a non-trivial wave vector $\mathbf{k}$ -dependence. Hence, the SIESTA-BdG formalism allows one to compute non-isotropic superconducting band gap and superconductors with multiple $\mathbf{k}$ -dependent gaps (multiband superconductors).

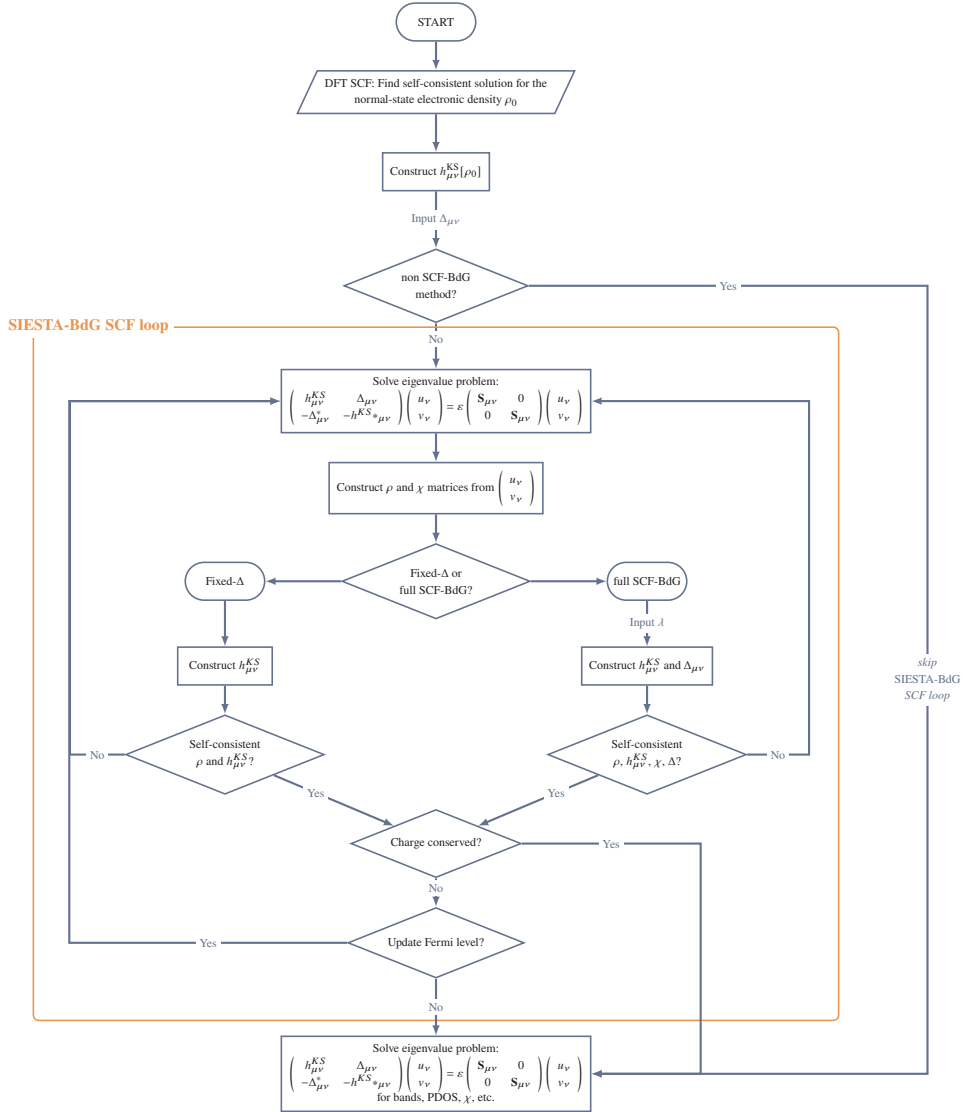


Figure 2.1 Schematic of the iterative process to compute self-consistent solutions of the SIESTA-BdG secular equation. During the update step within the SIESTA-BdG SCF loop the density or the Hamiltonian is mixed.

In the following, the quantities computed in real and reciprocal space are denoted with a $\mathbf{R}$ or $\mathbf{k}$ superscript, respectively (e.g. $\mathbf{H}^{\mathbf{R}}, \mathbf{H}^{\mathbf{k}}$). The matrix elements of any function in real space $g(\mathbf{r})$ can be written in the LCAO basis as $g_{\mu,\nu}^{\mathbf{R}} = \sum_{\mathbf{R}'} \int_{\text{UC}+\mathbf{R}'} d^3\mathbf{r} \phi_{\mu}^*(\mathbf{r}) g(\mathbf{r}) \phi_{\nu}(\mathbf{r} - \mathbf{R})$.

2.2 SIESTA-BdG SCF Solution Methods

Preliminary to SIESTA-BdG simulations, we perform a normal state DFT calculation to compute the electronic Hamiltonian $\mathbf{h}^{\text{KS}}$ and normal state density ρ . The converged $\mathbf{h}^{\text{KS}}$ is used to construct the BdG Hamiltonian $\mathbf{H}_{\text{BdG},\mu\nu}^{\text{R}}$ by introducing a pairing potential Δ to break charge conservation and enable the superconducting phase. In SIESTA-BdG, Δ and λ can be initialized in the orbital or real space representation, as discussed in Section 2.3. Then, the SIESTA-BdG Hamiltonian and (normal and anomalous) densities can be computed by solving the eigenvalue problem [Eq. (5)] either directly (*non SCF-BdG*) or by performing a self-consistent field cycle (SCF) on only the normal density (*fixed- Δ*) or both the normal and anomalous densities (*full SCF-BdG*).

For a given choice of Δ or λ full self-consistency should also include the chemical potential in addition to the densities. The number of electrons is given by a weighted sum over all states, using a (chemical potential dependent) occupation function as the weighting factor. For normal-state calculations, only the occupation function depends on the chemical potential (μ) while for SIESTA-BdG calculations, μ explicitly enters the eigenvalue problem. This means that a change in μ requires one to solve the eigenvalue problem again to find new solutions, making the process more complex. To compute μ we follow the approach by Suvasini et al.²⁹ where μ is updated in an outer loop that repeats the SCF cycle until the correct number of particles is reached²⁹. The user can skip this loop to reduce computational costs. In this case, the total number of electrons might not match the number of electrons in the normal state, but experience shows that the deviation is small for typical values of the pairing potential²⁹. The SIESTA-BdG solution methods are illustrated in Fig. 2.1 and described below.

Non SCF-BdG: The $\mathbf{H}_{\text{BdG}}^{\text{R}}$ Hamiltonian is constructed and diagonalized [Eq. (4)]. No SIESTA-BdG SCF loop is performed; therefore, $\mathbf{h}^{\text{KS}}$ is not updated in the presence of Δ . The resulting eigenvalues and eigenvectors are post-processed to calculate electronic band structure, density of states, normal and anomalous charge density. The underlying assumption is that superconductivity is a small perturbation of $\mathbf{h}^{\text{KS}}$ and the normal state density. The *non SCF-BdG* method has a significantly lower computational cost compared to *fixed- Δ* and *full SCF-BdG*, as the latter two methods perform an additional SCF cycle using the four-component Nambu spinors $\Psi_i(\mathbf{r})$.

Fixed- Δ : The $\mathbf{H}_{\text{BdG}}^{\text{R}}$ Hamiltonian is diagonalized in the presence of a fixed pairing potential Δ . At every step of the SIESTA-BdG SCF cycle, the Kohn-Sham Hamiltonian ($\mathbf{h}^{\text{KS}}$), the normal (ρ) and the anomalous (χ) densities are updated. Self-consistency is ensured on the normal-state part ($\mathbf{h}^{\text{KS}}, \rho$) of the SIESTA-BdG Hamiltonian. The underlying assumption is that the perturbations induced on the superconducting properties due to the anomalous charge are negligible, namely the initial guess for Δ is good enough to model the superconducting system and does not need to be updated in the SCF cycle via Eq. (8). In particular, for bulk Nb the difference between *fixed- Δ* and *non SCF-BdG* in the density of states are negligible for values of the pairing potential Δ smaller than ~ 100 meV (Appendix B).

Full SCF-BdG: is an implementation of the full self-consistent field SIESTA-BdG scheme. The superconducting couplings λ and the external pairing potential $d_{\text{ext}}^i(\mathbf{r}, \mathbf{r}')$ [Eq. (A15)]

must be specified in the input. The external pairing potential is needed to ensure a non-zero anomalous density in the first SCF step, and is set to zero thereafter [see discussion after Eq. (A15)]. At each SCF step, $\mathbf{h}^{\mathbf{KS}}$, ρ , χ and $\Delta = \sum_i (d_{\text{ext}}^i(\mathbf{r}) - \lambda^i(\mathbf{r}) \chi^i(\mathbf{r})) \sigma_i i \sigma_2$ are updated. Analogously to normal-state simulations, Δ and χ can be mixed using generalized SIESTA algorithms. Convergence can be achieved on Δ , on χ , or on both of them simultaneously.

2.3 Initialization of the pairing potential and superconducting coupling

Depending on the solution method, either the superconducting coupling λ (*full SCF-BdG*) or the pairing potential Δ (*non SCF-BdG* and *fixed- Δ*) is a semi-empirical parameter. Their initial values can be expressed either in terms of the LCAO atomic orbitals (*orbital representation*) or as a modulation in real space of a superconducting strength parameter $\bar{\lambda}$ or $\bar{\Delta}$ (*superconducting strength representation*) by a function $g(\mathbf{r})$, i.e. $\Delta(\mathbf{r}) = \bar{\Delta}g(\mathbf{r})$. Note that, when working in this representation, we use a bold symbol to indicate real-space matrices with orbital projected matrix elements (as λ) and italics for real space functions $\lambda(\mathbf{r})$. The *orbital representation* is ideal for investigating the nature of the superconducting interaction by selectively coupling specific orbitals. The user can directly specify the matrix elements of the pairing potential ($d_{\mu\nu}^{i\mathbf{R}}$) for any superconducting channel (i). The full pairing potential matrix is constructed using the orbital representation of Eq. (A16):

$$\begin{aligned} \Delta_{\mu\nu}^{\mathbf{R}} &= \sum_{i=0,1,2,3} d_{\mu\nu}^{i\mathbf{R}} \sigma_i i \sigma_2 \\ &= \sum_{i=0,1,2,3} \left(d_{\text{ext},\mu\nu}^{i\mathbf{R}} - \lambda_i^{\mathbf{R}\mu\nu} \chi_{\mu\nu}^{i\mathbf{R}} \right) \sigma_i i \sigma_2 \end{aligned} \quad (9)$$

If the symmetries of the gap function are known, then the initial guess for Δ can be constructed as a matrix respecting those symmetries. For instance, one can specify a pairing exclusively between electrons and holes occupying the same orbital on the same atom (*intra-orbital*, diagonal Δ), or between different electron and hole orbitals belonging to the same atom (*on-site*, block-diagonal Δ), or couple all the orbitals of all atoms (*full overlap*, full Δ matrix), as illustrated in Fig. 2.2. The flexibility of the *orbital representation* has been used to identify the orbitals responsible for unconventional superconductivity in FeSe (Section 3.2).

The *superconducting strength representation* has a more intuitive physical meaning, as the superconducting pairing is defined on the SIESTA real-space grid. In this case, the user can choose among the different options depending on the knowledge of the physical properties and symmetries of the materials to be studied. The computed physical observables (for instance, χ) mainly depends on the spatial basis overlap $S_{\mu\nu}^{\mathbf{R}}$ and not on $g(\mathbf{r})$, as illustrated in Appendix B for bulk Pb. The current implementation includes the following options for the modulation function $g(\mathbf{r})$:

- *Gaussians*: $g(\mathbf{r}; \mathbf{x}, \sigma) = e^{-|\mathbf{r}-\mathbf{x}|^2/(2\sigma^2)}$, with center $\mathbf{x}$ and width σ .

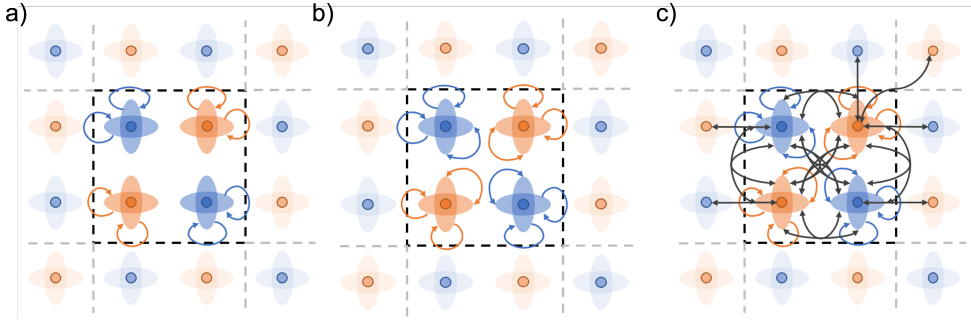


Figure 2.2 Initialization of the superconducting pairing in the *orbital representation*: Schematic representation of coupling between orbitals in the (a) intra-orbital, (b) on-site, and (c) full overlap pairing.

- *Spherical wells*: $g(\mathbf{r}; \mathbf{x}, \sigma) = \theta(|\mathbf{r} - \mathbf{x}|; \sigma, \eta)$ with center $\mathbf{x}$ and radius σ . The shape θ can be a Heaviside step function (hard well) or a Fermi-Dirac function with broadening η (soft well).
- *Plane waves*: $g(\mathbf{r}; \mathbf{k}, \phi) = \cos(\mathbf{k}\mathbf{r} + \phi)$, where $\mathbf{k}$ is the wave vector and ϕ is the phase of the wave at $\mathbf{x} = 0$.
- any combination of the above

Gaussian and spherical wells can be centred at any point within the unit cell and have arbitrary widths, potentially extending beyond the unit cell boundary. The lattice periodicity is automatically imposed. Plane waves can be used to represent fully delocalized interactions. Superpositions of multiple waves can be used to create pairing potentials with different symmetries. The versatility of the initial choice can be used to model complex systems with inhomogeneous superconducting potential.

3 Results

3.1 Bulk Niobium

Bulk Niobium is a good system for validating the SIESTA-BdG method, as several theoretical^{29,31} and experimental^{54–56} results are available in the literature for comparison. We computed the superconducting state DOS using the *full SCF-BdG* method and compared the SIESTA-BdG result with the JuKKR code³¹ and experimental data from STM measurements⁵⁴ (Fig. 3.3). There is good agreement between the two codes: both predict a DOS with two peaks at $\sim \pm 2$ meV (main coherence peaks), characteristic of conventional superconductors, and denoted U-shaped gap. In addition, the two codes predict visible gap anisotropy, as revealed by the multiple peaks in the DOS for low enough smearing temperatures. The two approaches differ in the position of the innermost peaks, the relative shift is about ± 0.2 meV, which can be

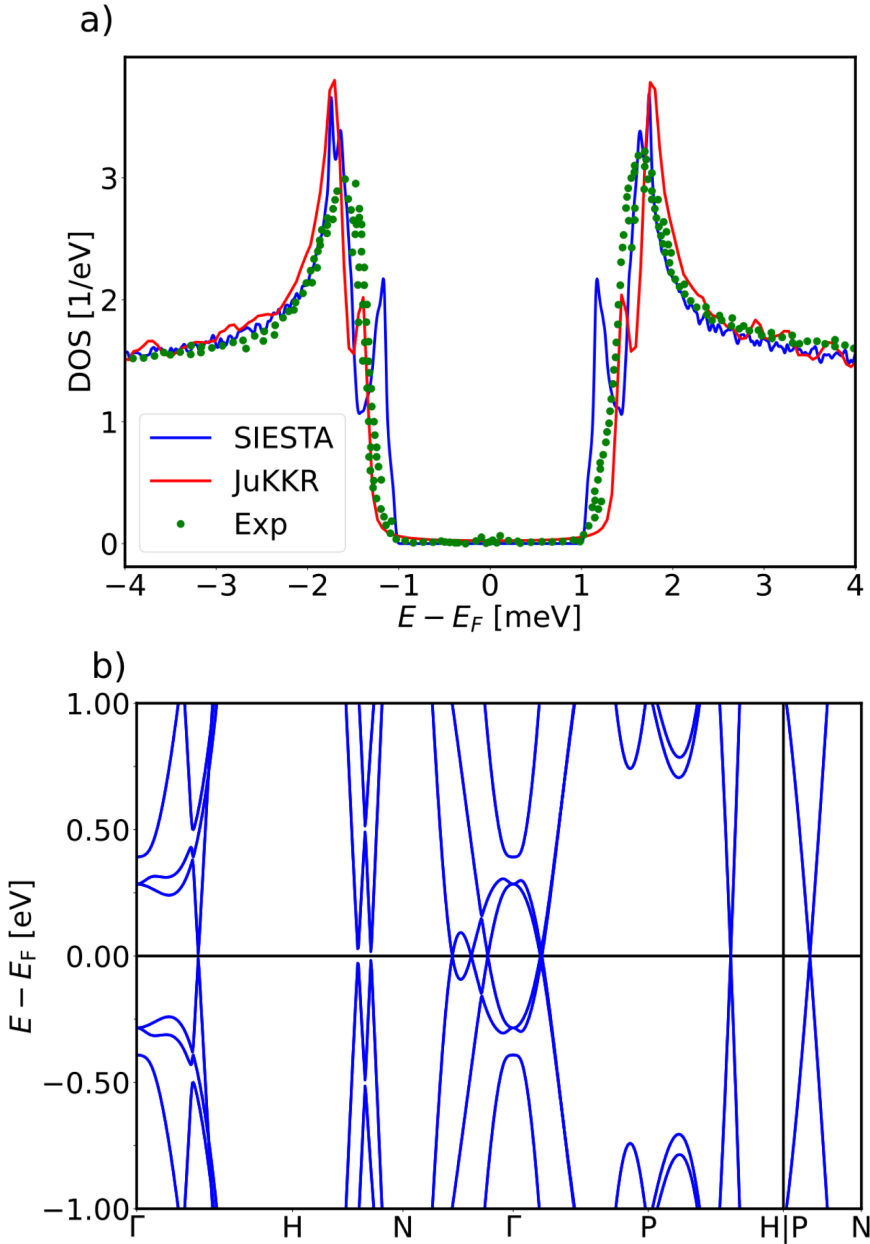


Figure 3.3 Bulk Nb: (a) Density of States (DOS) comparison among *full SCF-BdG* SIESTA, JuKKR^{31,53} and STM measurements⁵⁴, showing good agreement between simulations and experiment. For SIESTA-BdG we set $\lambda = 0.188 \text{ eV} \cdot V_{\text{sphere}}$ with a spherical ($r = 1.4136 \text{ \AA}$) square well potential and a smearing temperature $T = 0.1 \text{ K}$. In the JuKKR code a value of $\lambda = 1.11 \text{ eV}$ was used³¹. (b) Superconducting band structure with visible particle-hole symmetry.

explained by differences in the assumptions underlying the two codes. The overall gap shape also matches the one from the experiment. The missing gap anisotropy in the experimental data could be due to temperature (smearing), SIESTA-BdG predicts an additional gap anisotropy (i.e. each main coherence peak splits in two) compared to JuKKR, possibly due to the finer sampling of the energy axis in our calculation.

3.2 Bulk FeSe

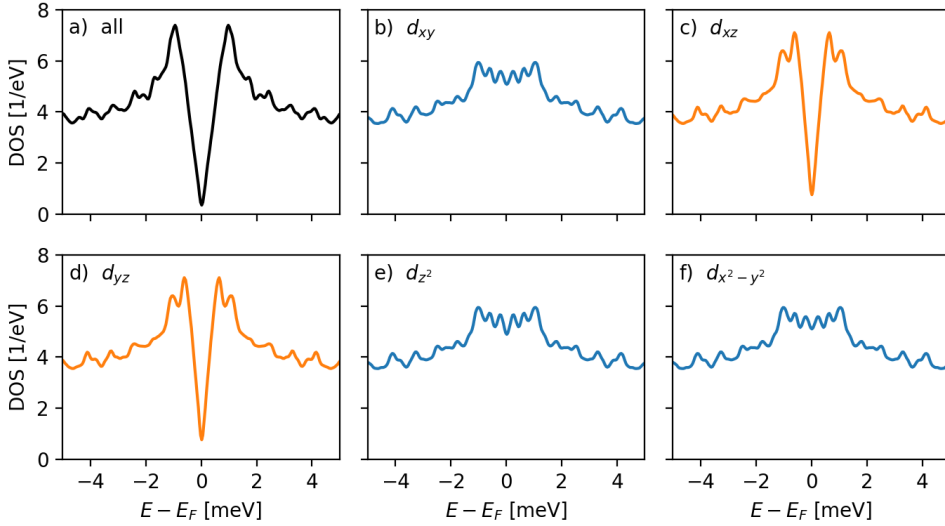


Figure 3.4 DOS of FeSe, an unconventional superconductor, for different pairing potentials calculated with the SIESTA-BdG method: (a) isotropic pairing ($\Delta(\mathbf{r}) = 3$ meV), (b-f) pairing potential limited to a different Fe- d orbital ($\Delta_{d_\nu d_\nu} = 3$ meV). The simulations with isotropic pairing (a) reproduce the size and shape of the experimentally observed superconducting gap⁵⁷. The superconducting gap emerges only if the pairing potential is applied to the d_{xz} (c) or d_{yz} (d) orbitals.

The origin and character of high-temperature superconductivity in FeSe (and other iron-based superconductors) are currently debated^{58–60}. It has been suggested that FeSe is an unconventional d -wave superconductor^{61–63} driven by pairing interaction in the $3d_{xz}$ and $3d_{yz}$ orbitals of iron⁶⁴. Experimental evidence suggests that FeSe does not possess long-range magnetic order. Even at low temperatures (4 K), spin fluctuations are significant⁵¹. These fluctuations occur primarily between two magnetic phases: Néel (or checkerboard) and staggered dimer. In the Néel magnetic structure, the magnetic moments of neighbouring iron atoms are antiparallel. In the following, we report results for the Néel magnetic structure. The simulation of the nematic phase would require very large supercells in periodic boundary conditions, which is beyond the scope of this work.

The superconducting gap of FeSe in the Néel phase is V shaped and of the order of $\sim 1 - 10$ meV at the coherence peaks, depending on the experimental conditions⁵⁷. To model the superconducting state we use the *non SCF-BdG* method and initialize the pairing potential with a constant ($\Delta(\mathbf{r}) = \bar{\Delta} = 3$ meV). The correct V shape of the superconducting gap emerges from our calculations (Fig. 3.4.a). This indicates that orbital symmetries are sufficient to predict the conventional or unconventional nature of the superconducting gap.

To analyse the role of different orbitals in enabling superconductivity, we restrict the pairing interaction to specific orbitals: We use the *orbital representation* method (Section 2.3) and assign non-zero values to matrix elements corresponding to a specific Fe-3d orbital (Fe-3d_{xz}, Fe-3d_{yz}, ...) at a time. We observe that imposing a pairing potential exclusively between 3d_{xz} or 3d_{yz} orbitals opens a V-shaped gap [Fig. 3.4 (b-f)]. We can therefore identify those orbitals as responsible for unconventional superconductivity in FeSe. The superconducting gap is smaller than the one computed with isotropic pairing among *all* orbitals because the pairing interaction is limited to a subset of all orbitals, reducing the pairing potential's average strength. No superconducting gap emerges if the pairing interaction is restricted to any of the other Fe-3d orbitals.

4 Quantum Transport within the SIESTA-BdG formalism

4.1 The formalism

The SCDF formalism maps the many-body problem, including the pair interaction giving rise to Cooper pairs, onto an equivalent non-interacting problem described by one-particle wave functions. In this auxiliary system, many aspects of quantum transport can be described in one-particle frameworks in a Landauer-based conductivity approach. As is commonly done in DFT approaches, the KS wavefunctions are assumed to be a good approximation to the one-particle wavefunction of the interacting many-body system^{48–50,65}. However, any current described in such a one-particle framework is fundamentally a one-particle current. As such, Cooper pair currents are not described.

In a non-superconducting device, the current through any electrode e at temperature T_e and chemical potential μ_e is given by⁶⁶

$$I_e = \frac{e}{h} \int_{-\infty}^{\infty} d\varepsilon \int_{\text{BZ}} d\mathbf{k} \sum_{e' \neq e} T_{ee'} [f_e(\varepsilon) - f_{e'}(\varepsilon)] \quad (10)$$

where $T_{ee'}$ is the transmission function between two electrodes e and e' , and $f_e(\varepsilon)$ is the occupation function for the electrode e . The energy and $\mathbf{k}$ dependence of the quantities is implicit.

In the case of superconducting electrodes or devices, the single-particle current can be carried either by the electrons or holes. The transmission ($T_{ee'}$) and reflection probabilities

(R_e) become 2x2 matrices

$$R_e \rightarrow \begin{pmatrix} R_e^{pp} & R_e^{hp} \\ R_e^{ph} & R_e^{hh} \end{pmatrix} \quad T_{ee'} \rightarrow \begin{pmatrix} T_{ee'}^{pp} & T_{ee'}^{hp} \\ T_{ee'}^{ph} & T_{ee'}^{hh} \end{pmatrix} \quad (11)$$

with R_e^{pp} (R_e^{hh}) the reflection probability for electrons (holes) in lead e to scatter back into electronic (hole) states on the same electrode, and R_e^{ph} (R_e^{hp}) the reflection probability for an electron (hole) in lead e to scatter into hole (electron) states in the same lead (Andreev reflection). Similarly, the four components of $T_{ee'}$ describe the scattering probabilities between electron and hole states in lead e and electron and hole states in e' (normal and anomalous transmission). The transmission and reflection functions can be calculated using the Green's function formulation of quantum transport^{66,67}. Using all four functions (see Appendix C for additional details), the current through any (normal) electrode can be written as⁶⁸

$$I_e = \frac{2e}{h} \int_{-\infty}^{\infty} d\varepsilon \int_{\text{BZ}} d\mathbf{k} \left\{ \sum_{e' \neq e} T_{ee'}^{pp} [f_e(\varepsilon) - f_{e'}(\varepsilon)] \right. \\ - T_{ee'}^{hh} [\bar{f}_e(\varepsilon) - \bar{f}_{e'}(\varepsilon)] \\ + \sum_{e' \neq e} T_{ee'}^{ph} [f_e(\varepsilon) - \bar{f}_{e'}(\varepsilon)] \\ - T_{ee'}^{hp} [\bar{f}_e(\varepsilon) - f_{e'}(\varepsilon)] \\ \left. + [R_e^{hp} + R_e^{ph}] [f_e(\varepsilon) - \bar{f}_e(\varepsilon)] \right\} \quad (12)$$

where $\bar{f}_e(\varepsilon)$ is the occupation of hole states in the electrode e . Moving to the low-bias limit $f_e(\varepsilon) = f(\varepsilon) - \frac{\partial f}{\partial \varepsilon}(\varepsilon)[\mu_e - \mu]$ (μ the reference chemical potential w.r.t to which the electrode potentials are shifted) and invoking particle-hole symmetry, the expression for the current can be rewritten as:

$$I_e \approx \frac{2e}{h} \int_{\text{BZ}} d\mathbf{k} \sum_{e' \neq e} T_{ee'}^{pp}(\mu) [\mu_{e'} - \mu_e] \\ + \sum_{e' \neq e} T_{ee'}^{ph}(\mu) [2\mu - \mu_{e'} - \mu_e] + 2R_e^{hp}(\mu) [\mu - \mu_e] \quad (13)$$

In this formula three different components of the current can be identified: (i) a *normal* component which depends on electron-electron (hole-hole) transmission (T^{pp} , T^{hh}), (ii) an *anomalous* component which depends on electron-hole (hole-electron) transmission (T^{ph} , T^{hp}), and (iii) an *Andreev* contribution which depends solely on the Andreev reflections (R^{hp} , R^{ph}). Particle conservation requires that the currents flowing in all electrodes sum up to zero (Kirchhoff's current law⁶⁹): $\sum_e I_e = 0$ ^{48,70}. This condition uniquely determines the chemical potential μ : The current is not proportional to the pairwise differences in the electrode chemical potentials, and explicitly depends on the electrode chemical potentials. This is an important difference with respect to a normal-state device.

Eq. (12) is valid for computing the current of any normal electrode with a superconducting device. However, it is not suitable for a superconducting electrode e , as it does not account for

the contributions of Cooper pair currents. Arguments on how to properly compute currents under non-equilibrium conditions and in superconducting electrodes are given in^{48,50,70} and references therein.

A non-zero conductance at zero applied voltage (zero-bias conductance) can only arise due to Andreev (or anomalous) terms in this formalism. In a bulk superconductor, no reflections occur, and the anomalous transmission is equal to zero. Thus, the zero-bias conductance in any bulk superconductor is zero. Only in the presence of a scattering region can Andreev reflections (or anomalous transmission) occur and lead to a non-zero conductance. This, of course, does not imply a finite resistance of the bulk superconductor, since Cooper pair currents are not included in the description.

The SIESTA-BdG method, due to the strictly localized basis set, constitute an ideal starting point for quantum transport calculations using non-equilibrium Green's functions techniques (NEGF) on open quantum systems with superconducting components, such as superconductor junctions and topological superconductor devices. The chemical potential in the leads does not change as a consequence of the interaction with the scattering region⁶⁶.

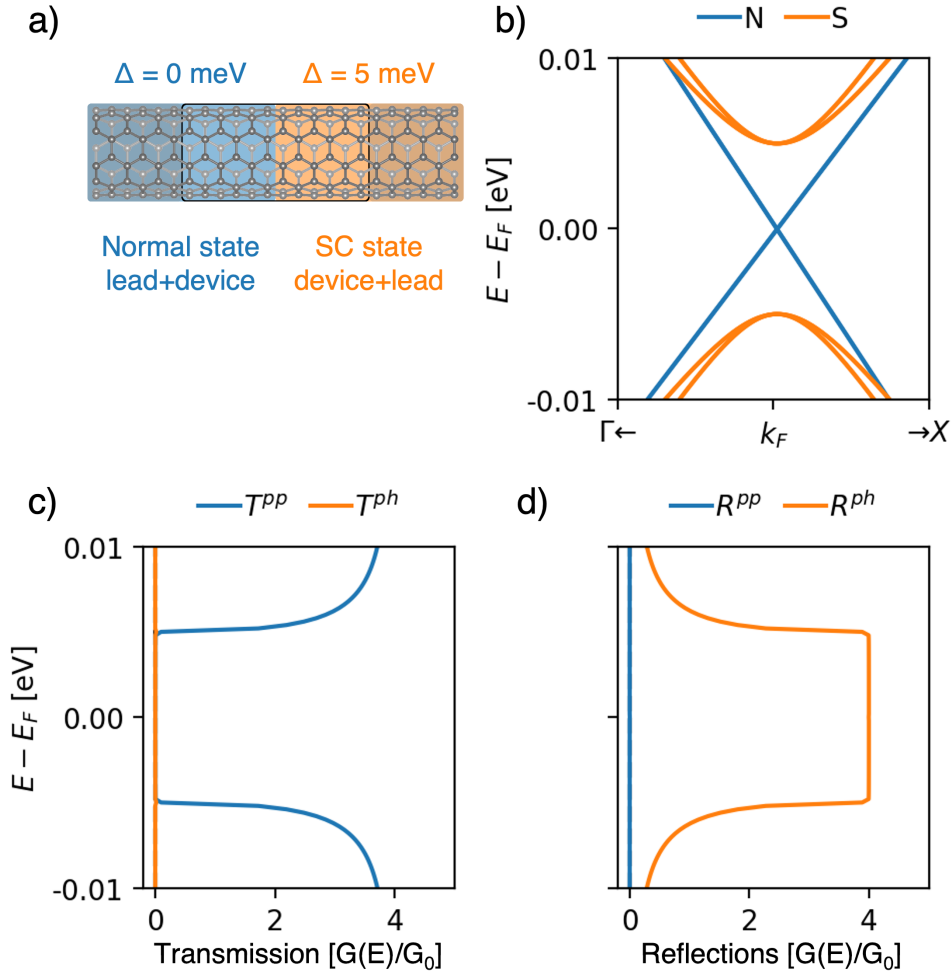


Figure 4.5 Normal-Superconductor (N-S) junction in an (5,5) carbon nanotube. The normal ($\Delta = 0$ meV) and superconducting ($\Delta = 5$ meV) regions are indicated in blue and orange, respectively. (a) Simulation cell for transport simulations displaying scattering region and leads (shaded area) (b) Electronic band structure of the scattering region of the N-S (5, 5) carbon nanotube junction. (c) Transmission and (d) reflection in quantum conductance units G_0 . Within the superconductor gap, all electrons in the normal electrode participate in Andreev reflections (R^{eh}). For energies larger than the superconducting gap, the N-S junction behaves like a normal metal. At the superconducting gap there is a smooth transition between the two regimes.

To showcase the possible application of the SIESTA-BdG method in the quantum transport formalism, we consider a (5,5) armchair carbon nanotube (CNT) as a transport system. Signatures of superconductivity have been observed in different types of carbon nanotubes: (a) 4 Å single-wall carbon nanotubes at $T_C \approx 15$ K (Meissner effect)⁷¹, (b) multi-wall nanotubes

with 10 nm outer tube at $T_C \approx 12$ K (sudden drop of DOS below T_C)⁷², and (c) ropes of single-wall carbon nanotubes at 0.55 K (drop of resistance)⁷³. However, it is difficult to reliably create superconductivity in one-dimensional nanostructures due to low DOS and quantum fluctuations⁷⁴. If realized and stabilized, superconducting carbon nanotubes could be ideal one-dimensional leads for nanoelectronics.

We construct an N-S junction within a (5,5) nanotube by selectively applying the pairing potential to part of the scattering region and right electrode. Our transport device consists of 3 rings of the (5,5) nanotube (scattering region) which are contacted by the same nanotube on each side (electrodes, each 3 rings wide), thus forming an infinite tube. We use the Hamiltonian obtained from a periodic calculation neglecting the coupling with the infinite leads. We then use the Green's function formulation of quantum transport⁶⁶ to obtain the transmission and reflection probabilities. We apply the *non SCF-BdG* method and neglect any changes in the electronic structure of the leads due to the superconducting pairing (Landauer assumption). Therefore, the resulting N-S junction possesses a negligible barrier for the electrons and electron-electron back-scattering should be close to non-existent. Thus, our N-S junction is expected to behave like an ideal N-S junction, allowing for Andreev reflections that can lead to non-vanishing reflection coefficients. Furthermore, we use an isotropic superconducting pairing with a strength of 5 meV.

In the normal state, the band structure of a (5,5) armchair CNT near the Fermi level [blue lines in Fig. 4.5.(a)] is described by four linear bands (two per spin channel). In the superconducting state [orange lines, Fig. 4.5.(a)], a band gap opens up at the Fermi level. The band dispersion becomes parabolic, and the number of bands is doubled. In addition, Fig. 4.5 shows the different transmission and reflection functions for the N-S junction between a normal state CNT and superconducting CNT. The Andreev reflections R^{ph} and normal transmission T^{PP} [Fig.s 4.5.(b,c)] become significant at the edge of the superconducting gap where electron and hole states hybridize in the scattering region because of the pairing potential. Deep within the gap, the anomalous transmission T^{ph} and the normal reflection R^{PP} are zero, and all incoming states are perfectly reflected (Fig.s 4.5.(b.d)). These results exactly replicate the expected behaviour for a barrier-free N-S junction⁷⁵.

Conclusions and Outlook

In this work we present SIESTA-BdG, a method to calculate the superconducting properties of materials and its implementation in the open-source SIESTA code⁴². SIESTA-BdG implements the semi-phenomenological SCDFT formalism of Suvasini²⁹ in localized basis sets (equations 5 and 8). We show that SIESTA-BdG can accurately predict both conventional and unconventional superconductors.

We propose three solution methods to solve the DFT-BdG secular equation(5): *non SCF-BdG*, *fixed- Δ* and *full SCF-BdG*, which mainly differ in the treatment of self-consistency of the superconducting density and Hamiltonian. We present different options for initializing the superconducting coupling/pairing, which is a parameter in this method. We sustained our

discussion with three test cases: Nb, Pb and FeSe bulk, which demonstrate the robustness and accuracy of our implementation. We critically compared our results with experiments and KKR-BdG simulations, finding excellent quantitative agreement (Section 3). We introduced and discussed optimization schemes such as the adaptive Brillouin Zone sampling, the tetrahedron method, parallelization over $\mathbf{k}$ -points and real space initialization of the pairing potential that are indispensable for an accurate description of the superconducting state. We conclude the manuscript with a perspective on the simulation of quantum transport for superconductors by combining the SIESTA-BdG with the NEGF formalism of Ref. ^{44,45}. As a proof of concept, we compute transmission and reflection probabilities of a normal/superconducting junction in a carbon nanotube.

The limitations of SIESTA-BdG are related to the ignorance of the exact form of the superconducting coupling (λ) or pairing (Δ), namely the magnitude and phase of the superconducting interaction is unknown. One can make an estimate using full SCDFT for conventional superconductors, or refer to theories that model the superconducting coupling strength itself^{76,77}. As a guideline to initialize the pairing potential/coupling, we suggest using first the *superconducting strength representation* with a constant modulation function to acquire familiarity with the system and, then, test more specific real-space initializations. When the symmetries of the system are known, it might be easier to impose them directly in the matrix elements of the pairing potential (*orbital representation*, Section 2.2). Exploring the consequences of the initialization of the superconducting parameter (different solution methods, new or more complex real space initialization, etc.) needs to be addressed case-by-case, as it is material specific.

The applicability of our approach is vast, heterostructures and complex device configurations being prime candidates that could benefit from this novel implementation, given SIESTA's inherent optimal scaling. In perspective, SIESTA-BdG framework can be interfaced with existing SCDFT codes, mapping the non-local SCDFT potential into an approximate local one and/or extended to a non-local superconducting potential to allow for SCDFT calculations. SIESTA-BdG is the basis for the description of transport in superconducting systems: In general, the SCDFT formalism maps the many-body problem, including the pair interaction giving rise to Cooper pairs, onto an equivalent non-interacting problem described by one-particle wavefunctions. In this auxiliary system, transport is described by a one-particle framework (e.g. scattering matrix formalism or Green's function formalisms⁷⁸), as opposed to other Many-Body formalism which focuses on the two-particle superconducting response functions^{39,40,79}. The current implementation will provide a useful tool to further investigate and understand exotic forms of superconductivity and related emerging physics such as unconventional superconductivity, proximity induced superconductivity, topological superconductivity, interplay between magnetism and superconductivity.

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Authorship statement

This chapter is based on Reho and Wittemeier et al.¹ R. Reho and N. Wittemeier contributed equally to the theoretical foundation, and all authors contributed equally to the implementation. RR took the lead in writing the manuscript. PO and ZZ assessed the correctness of the manuscript. ZZ, as the last author, secured funding.

Data availability statement

The data that support the findings of this study are openly available on Materials Cloud.

5 Appendices

A Spin generalized Superconducting DFT

The SCDFT Hamiltonian $\hat{H}_{\text{BdG}}(\mathbf{r}, \mathbf{r}')$ ¹⁷ consists of four blocks describing particles (top-left), antiparticles (bottom-right), and particle/antiparticle coupling Δ (off-diagonal)²:

$$\hat{H}_{\text{BdG}}(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} \hat{h}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') & \Delta(\mathbf{r}, \mathbf{r}') \\ \Delta^*(\mathbf{r}, \mathbf{r}') & -\hat{h}^*(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') \end{pmatrix} \quad (\text{A1})$$

To extend the 2×2 SCFDT Hamiltonian to the 4×4 fully relativistic case (i.e. including SOC), we follow the SIESTA formalism⁴²:

$$\hat{H}_{\text{BdG}, \alpha\beta}(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} \hat{h}_{\alpha\beta}^{KS}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') & \Delta_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \\ -\Delta_{\alpha\beta}^*(\mathbf{r}, \mathbf{r}') & -\hat{h}_{\alpha\beta}^{*KS}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') \end{pmatrix} \quad (\text{A2})$$

with spin indices α and β , and

$$\hat{h}^{KS}(\mathbf{r}) = \left(-\nabla^2 + \hat{V}^H - \mu \right) \mathbb{1}_2 + \hat{V}^{\text{KB}} + \hat{V}^{\text{SO}} + \hat{V}^{\text{XC}} \quad (\text{A3})$$

the 2×2 fully relativistic electronic Kohn-Sham Hamiltonian. The latter includes the kinetic energy ∇^2 , the Hartree potential $\hat{V}^H$, the chemical potential μ , the Kleinman–Bylander scalar-relativistic pseudo-potential $\hat{V}^{\text{KB}}$, the spin - orbit term $\hat{V}^{\text{SO}}$, and the exchange-correlation potential $\hat{V}^{\text{XC}}$. The relativistic contributions to the pairing potential Δ are neglected. The minus sign in the bottom-left block of Eq. (A2) arises from the anticommutation rules of the spin indices: $-\Delta_{\alpha,\beta}^* = \Delta_{\beta,\alpha}^*$. Writing explicitly the spin dependence, it reads:

$$\hat{H}_{\text{BdG}}(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} \hat{h}_{\uparrow\uparrow}^{KS}(\mathbf{r}) & \hat{h}_{\uparrow\downarrow}^{KS}(\mathbf{r}) & \Delta_{\uparrow\uparrow}(\mathbf{r}, \mathbf{r}') & \Delta_{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}') \\ \hat{h}_{\downarrow\uparrow}^{KS}(\mathbf{r}) & \hat{h}_{\downarrow\downarrow}^{KS}(\mathbf{r}) & \Delta_{\downarrow\uparrow}(\mathbf{r}, \mathbf{r}') & \Delta_{\downarrow\downarrow}(\mathbf{r}, \mathbf{r}') \\ -\Delta_{\uparrow\uparrow}^*(\mathbf{r}, \mathbf{r}') & -\Delta_{\uparrow\downarrow}^*(\mathbf{r}, \mathbf{r}') & -\hat{h}_{\uparrow\uparrow}^{*KS}(\mathbf{r}) & -\hat{h}_{\uparrow\downarrow}^{*KS}(\mathbf{r}) \\ -\Delta_{\downarrow\uparrow}^*(\mathbf{r}, \mathbf{r}') & -\Delta_{\downarrow\downarrow}^*(\mathbf{r}, \mathbf{r}') & -\hat{h}_{\downarrow\uparrow}^{*KS}(\mathbf{r}) & -\hat{h}_{\downarrow\downarrow}^{*KS}(\mathbf{r}) \end{pmatrix} \quad (\text{A4})$$

²We interchangeably use the term electrons (holes) and particles (anti-particles).

The spin generalized Kohn-Sham BdG equations are, then:

$$\int d\mathbf{r}' \widehat{H}_{\text{BdG}}(\mathbf{r}, \mathbf{r}') \begin{pmatrix} u_i^\uparrow(\mathbf{r}') \\ u_i^\downarrow(\mathbf{r}') \\ v_i^\uparrow(\mathbf{r}') \\ v_i^\downarrow(\mathbf{r}') \end{pmatrix} = \varepsilon_i \begin{pmatrix} u_i^\uparrow(\mathbf{r}) \\ u_i^\downarrow(\mathbf{r}) \\ v_i^\uparrow(\mathbf{r}) \\ v_i^\downarrow(\mathbf{r}) \end{pmatrix}. \quad (\text{A5})$$

The eigenfunctions of the BdG Hamiltonian are four-component Nambu spinors $\Psi_i(\mathbf{r}) = (u_i^\uparrow(\mathbf{r}) u_i^\downarrow(\mathbf{r}) v_i^\uparrow(\mathbf{r}) v_i^\downarrow(\mathbf{r}))^T$, where $u_i^\alpha(r)$ and $v_i^\alpha(r)$ are the electron and hole components. In the superconducting ground state (ε_0) all Cooper pairs are in the same energy level. The eigenenergies ε_i above the ground state correspond to Bogoliubons, namely quasiparticles consisting of a linear combination of excited electrons and holes. The BdG equations (A2) satisfy particle-hole symmetry¹⁶. Namely, if $(u_i^\uparrow(\mathbf{r}) u_i^\downarrow(\mathbf{r}) v_i^\uparrow(\mathbf{r}) v_i^\downarrow(\mathbf{r}))^T$ is an eigenvector with solution ε_i , then $(v_i^\uparrow(\mathbf{r}) v_i^\downarrow(\mathbf{r}) u_i^\uparrow(\mathbf{r}) u_i^\downarrow(\mathbf{r}))^{*T}$ leads to an equivalent solution with eigenvalue $-\varepsilon_i$.

In analogy with Kohn-Sham DFT, one can define single particle (V) and pairing (Δ) effective potentials in terms of a superconducting exchange-correlation functional $\Omega_{xc}[\rho, \chi]$, which is a functional of both the normal $\rho(\mathbf{r})$ and the anomalous $\chi(\mathbf{r}, \mathbf{r}')$ charge densities :

$$V[\rho, \chi](\mathbf{r}) = V^H(\mathbf{r}) + V^{KB}(\mathbf{r}) \quad (\text{A6})$$

$$+ V^{SO}(\mathbf{r}) + \frac{\delta \Omega_{xc}[\rho, \chi]}{\delta \rho(\mathbf{r})}$$

$$\Delta[\rho, \chi](\mathbf{r}, \mathbf{r}') = d^0(\mathbf{r}, \mathbf{r}') i\hat{\sigma}_2 + \quad (\text{A7})$$

$$\sum_{j=1,2,3} d^j(\mathbf{r}, \mathbf{r}') \hat{\sigma}_j i\hat{\sigma}_2$$

$$d^i[\rho, \chi](\mathbf{r}, \mathbf{r}') = d_{\text{ext}}^i(\mathbf{r}, \mathbf{r}') \quad (\text{A8})$$

$$- \frac{\delta \Omega_{xc}[\rho, \chi]}{\delta \chi^{*i}(\mathbf{r}, \mathbf{r}')} \quad \text{with } i = 0, 1, 2, 3$$

where $\hat{\sigma}_i$ are the Pauli matrices, d^i are the singlet ($i = 0$) and triplet ($i = 1, 2, 3$) spin components in the Balian-Werthamer (BW) representations⁸⁰, and $d_{\text{ext}}^i(\mathbf{r}, \mathbf{r}')$ is an external pairing potential introduced, formally, to break the charge symmetry of the system. In practice, the SIESTA-BdG implementation builds the BdG Hamiltonian from $d_{\text{ext}}^i(\mathbf{r}, \mathbf{r}')$ in the first self-consistent field iteration. The resulting anomalous density is used to build the pairing potential in the successive step and $d_{\text{ext}}^i(\mathbf{r}, \mathbf{r}')$ is set to zero thereafter. For this reason, $d_{\text{ext}}^i(\mathbf{r}, \mathbf{r}')$ is missing in equation(8).

In the BW representation, the singlet and triplet spin components of the anomalous charge density are

$$\chi^0(\mathbf{r}, \mathbf{r}') = \frac{\chi^{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}') - \chi^{\downarrow\uparrow}(\mathbf{r}, \mathbf{r}')}{2} \quad (\text{A9})$$

$$= \frac{\chi^{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}') + \chi^{\uparrow\downarrow}(\mathbf{r}', \mathbf{r})}{2},$$

$$\chi^1(\mathbf{r}, \mathbf{r}') = \frac{\chi^{\downarrow\downarrow}(\mathbf{r}, \mathbf{r}') - \chi^{\uparrow\uparrow}(\mathbf{r}, \mathbf{r}')}{2} \quad (\text{A10})$$

$$= \frac{\chi^{\uparrow\uparrow}(\mathbf{r}', \mathbf{r}) - \chi^{\downarrow\downarrow}(\mathbf{r}', \mathbf{r})}{2},$$

$$\chi^2(\mathbf{r}, \mathbf{r}') = \frac{\chi^{\downarrow\downarrow}(\mathbf{r}, \mathbf{r}') + \chi^{\uparrow\uparrow}(\mathbf{r}, \mathbf{r}')}{2i} \quad (\text{A11})$$

$$= \frac{\chi^{\downarrow\downarrow}(\mathbf{r}', \mathbf{r}) + \chi^{\uparrow\uparrow}(\mathbf{r}', \mathbf{r})}{-2i},$$

$$\chi^3(\mathbf{r}, \mathbf{r}') = \frac{\chi^{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}') + \chi^{\downarrow\uparrow}(\mathbf{r}, \mathbf{r}')}{2} \quad (\text{A12})$$

$$= \frac{\chi^{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}') - \chi^{\uparrow\downarrow}(\mathbf{r}', \mathbf{r})}{2}.$$

The BW parametrization is useful to study the properties of χ under parity transformation $\mathbf{r} \rightarrow \mathbf{r}'$. χ is a fermionic object and, hence, must satisfy the Pauli exclusion principle, namely it must be antisymmetric under exchange of the two electrons forming the Cooper pair: $\chi^{\beta\alpha}(\mathbf{r}', \mathbf{r}) = -\chi^{\alpha\beta}(\mathbf{r}, \mathbf{r}')$. This implies that if $\chi^{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ is even (odd) under the parity transformation, then it has to be odd (even) under spin exchange leading to a $S = 0$ singlet state ($S = 1$, triplet state).

The normal and anomalous densities that minimize the energy functional $E[\rho, \chi]$ are¹⁷

$$\begin{aligned} \rho(\mathbf{r}) &= \sum_{\alpha, i} f(\varepsilon_i) |u_i^\alpha(\mathbf{r})|^2 \\ &\quad + \sum_{\alpha, i} \bar{f}(\varepsilon_i) |v_i^\alpha(\mathbf{r})|^2 \\ \chi^{\alpha\beta}(\mathbf{r}, \mathbf{r}') &= \sum_i f(\varepsilon_i) u_i^\alpha(\mathbf{r}') v_i^{*\alpha}(\mathbf{r}) \\ &\quad + \sum_i \bar{f}(\varepsilon_i) u_i^\alpha(\mathbf{r}) v_i^{*\beta}(\mathbf{r}') \end{aligned} \quad (\text{A13})$$

where $f(\varepsilon_i)$ is the occupation function of the i^{th} Bogoliubon, and $\bar{f}(\varepsilon_i) = 1 - f(\varepsilon_i)$. In contrast to conventional DFT, the sum over α , and i in Eq. (A13) extends over all states and is not limited by the Fermi level. Furthermore, the contribution of the uv^* terms in χ is expected to be non-zero only in an energy region close to the Fermi surface²².

In SCDFT, $\Omega_{xc}[\rho, \chi]$ is written in terms of a superconducting kernel which is, in general, a non-local pairing interaction dependent on four spatial (and spins) variables: $\lambda[\rho, \chi](\mathbf{r}, \mathbf{r}'; \mathbf{r}_1, \mathbf{r}_1')$. In this work, we use Suvasini²⁹ assumption of a local superconducting kernel $\lambda(\mathbf{r})$. As a consequence, the exchange-correlation functional reduces to

$$\Omega_{xc}[\rho, \chi] = \Omega_{0,xc}[\rho] + \int \sum_i d\mathbf{r} \chi^{i*}(\mathbf{r}) \lambda^i(\mathbf{r}) \chi^i(\mathbf{r}) \quad (\text{A14})$$

with $\Omega_{0,xc}$ the Kohn-Sham exchange-correlation potential, and

$$d^i(\mathbf{r}) = d_{\text{ext}}^i(\mathbf{r}) - \lambda^i(\mathbf{r}) \chi^i(\mathbf{r}) \quad (\text{A15})$$

which is expanded in its tensor form in the BW representation as

$$\begin{aligned} \Delta(\mathbf{r}) &= \sum_{i=0,1,2,3} d^i(\mathbf{r}) \sigma_i i \sigma_2 \\ &= \sum_{i=0,1,2,3} [d_{\text{ext}}^i(\mathbf{r}) - \lambda^i(\mathbf{r}) \chi^i(\mathbf{r})] \sigma_i i \sigma_2 \end{aligned} \quad (\text{A16})$$

B SIESTA-BdG simulations in practice

Convergence of SIESTA-BdG simulations

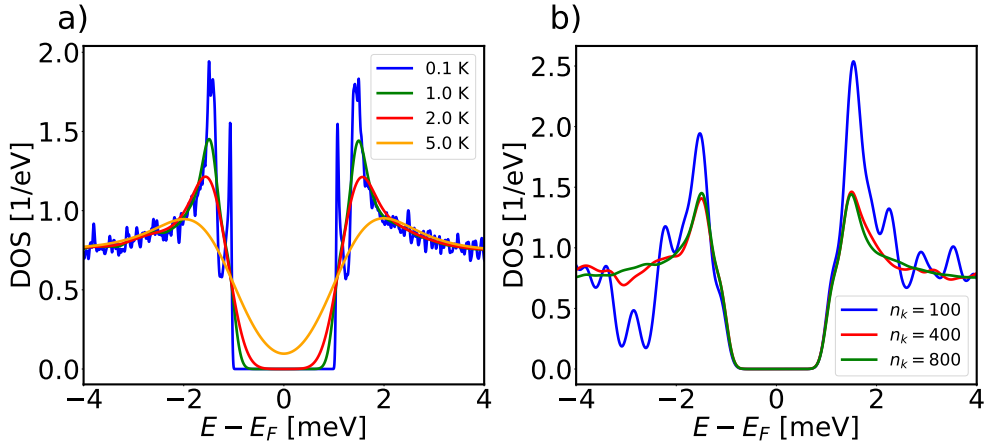


Figure B1 Convergence of SIESTA-BdG calculations for bulk Niobium. a) Dependence of the DOS on smearing temperature at fixed $800 \times 800 \times 800$ k-grid. Gap anisotropy is only resolved when the smearing temperature is on the order of 0.1 K or lower. b) DOS dependence on k-grid size ($n_k \times n_k \times n_k$) with a smearing temperature $T = 1.0$ K: an extremely dense sampling ($n_k = 800$) is required to converge the tails of the gap and resolve the coherence peaks.

A rigorous convergence study of simulation parameters is required for the SIESTA-BdG method. This concerns the real-space grid cutoff, the SCF cycle tolerances, the k-grid for the SCF cycle and DOS/PDOS, and the smearing of electron/hole occupations.

The cutoff value of the real-space grid is typically the same order of magnitude as for normal-state SIESTA simulations, as it mostly depends on the choice of the pseudopotentials and on the desired accuracy of the representation of physical quantities (density, potential, charge) on the SIESTA real-space grid.

SCF tolerances for *non SCF-BdG* and *fixed- Δ* are similar to fully-relativistic normal state calculations, namely 10^{-5} for the density matrix and 10^{-4} eV for the Hamiltonian). *Full*

SCF-BdG calculations require stricter SCF tolerance compared to normal state calculations by one to two orders of magnitude.

The $\mathbf{k}$ -grid for the SCF cycles can be converged in steps: first, for the normal metal phase, then the superconducting-state DOS is converged (using the normal-state SCF $\mathbf{k}$ -grid), and finally the SCF $\mathbf{k}$ -grid is further refined against the shape and size of the superconducting gap.

The smearing temperature and DOS/PDOS sampling of the Brillouin zone need to be pushed beyond the usual converged values for normal-state SIESTA simulations. The smearing temperature is related to the Fermi-Dirac occupation function for electrons and holes, as usually defined in first-principles DFT simulations. The smaller the smearing temperature, the higher the energy resolution in the DOS. The DOS can vary greatly with the smearing temperature, as illustrated in Fig. B1.(a). Therefore, the DOS is a good quantity to be used for converging the smearing temperature. As a rule of thumb, setting the temperature to about one-tenth of the superconducting gap usually ensures accurate simulations.

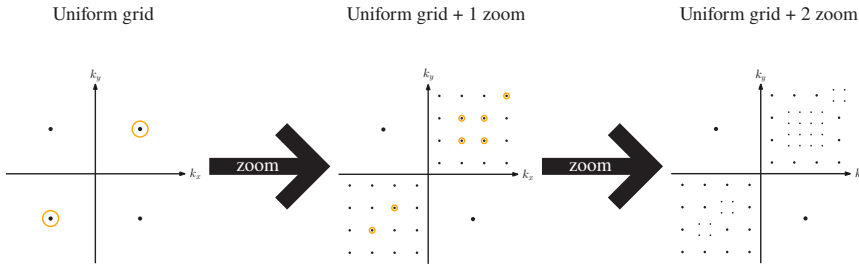


Figure B2 Schematic illustration of the adaptive Brillouin Zone sampling scheme. Starting with a coarse grid, the algorithm determines the points that contribute to the DOS in the region of interest (points circled in orange). To enhance the sampling, the contributing points are replaced by a denser grid (we "zoom" in on the interesting region). This procedure can be repeated to iteratively improve the sampling.

In order to obtain smooth and converged DOS/PDOS it is necessary to use hundreds to thousands of $\mathbf{k}$ -points in each direction. An under-converged sampling results in noisy DOS, which manifests most clearly in the tails that border the superconducting gap, as illustrated in Fig. B1.(b) for the DOS of bulk Nb computed with different $\mathbf{k}$ -grids. Performing SIESTA-BdG DOS/PDOS simulations at such extremely dense sampling of the Brillouin Zone requires the use of the strategies for efficient sampling described in Section B.

We extended the two parallelization strategies present in SIESTA, over orbitals and over $\mathbf{k}$ -points, to also work for the SIESTA-BdG calculations with Nambu spinors, structuring our algorithm analogously to the one already present in SIESTA⁴².

Strategies for efficient sampling of the Brillouin Zone.

The parallelization techniques allow one to deal with numerous $\mathbf{k}$ -points by distributing the work among more processors. Another approach is reducing the number of $\mathbf{k}$ -points needed.

For normal state calculations, the tetrahedron method has been shown to be effective in accurately calculating integrals over the Brillouin Zone with relatively few points⁸¹. In a typical SIESTA-BdG calculation, the region of interest is limited to a few meV around the Fermi energy and the linear interpolation of the tetrahedron method fails to capture the rapid variations happening at these small energy scales. Therefore, we adopted a different strategy, we use an adaptive sampling scheme where a dense sampling grid is only used in the regions of the Brillouin Zone close to the Fermi surface and a coarse grid everywhere else. We implemented this as an iterative procedure, schematically illustrated in Fig. B2, using the following steps:

1. diagonalize the BdG Hamiltonian $\mathbf{H}^k$ and find all the eigenvalues using an initial uniform grid in $\mathbf{k}$ -space,
2. identify which points have at least one eigenvalue that lies in a user-specified energy range,
3. replace all these points by denser sub-grids centred on the points,
4. diagonalize the Hamiltonian and find the eigenvalues using these new points,
5. repeat steps 2 to 4 until the desired accuracy in the density of states is reached.

As an illustration of the effectiveness of this procedure, we compute the DOS of bulk Nb using the adaptive sampling and compare with the DOS computed with a uniform $800 \times 800 \times 800$ k -grid [Fig. B1.(b)]. The results can be seen in Fig. B3. The adaptive procedure starts with a $100 \times 100 \times 100$ grid and at each iteration (repeated three times) contributing points were replaced by a $2 \times 2 \times 2$ sub-grid. This procedure allows one to effectively reach the uniform $800 \times 800 \times 800$ sampling but only in a small energy window around the Fermi energy. The adaptive grid reproduces the smooth DOS at a fraction of the computational cost.

Limit of applicability of non-SCF BdG solution method

To investigate the differences in results between using the *non SCF-BdG* and *fixed- Δ* approaches, the density of states (DOS) of bulk Niobium was computed for different magnitudes of the pairing potential Δ using both methods. For each magnitude, a real-space initialization of touching hard spheres was used. The results of the two approaches were compared by integrating the absolute differences between the curves. This difference was divided by the integral of the DOS of fixed- Δ over the same energy range to get a relative integrated difference. The results can be seen in Fig. B4. The differences in the DOS remain small (less than 2%) up to a Δ of 100 meV. This is consistent with earlier statements that the superconducting pairing potential is a small perturbation. For large values of Δ (≥ 1 eV) the difference become significant. This however lies beyond the reasonable strength for Niobium and most known superconductors. Nevertheless, we stress that one should verify which of the approaches is sufficient for the system under study.

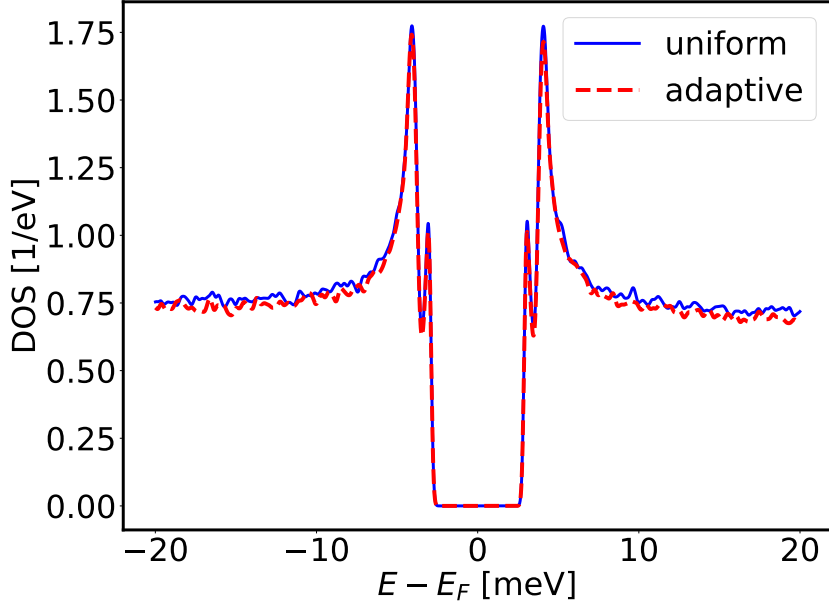


Figure B3 The DOS of bulk Niobium computed with a uniform $800 \times 800 \times 800$ $\mathbf{k}$ -grid and an adaptive grid. Δ has been set to 5 meV. The adaptive grid was generated starting from a $100 \times 100 \times 100$ uniform grid and using, for three iterations, a $2 \times 2 \times 2$ sub-grid

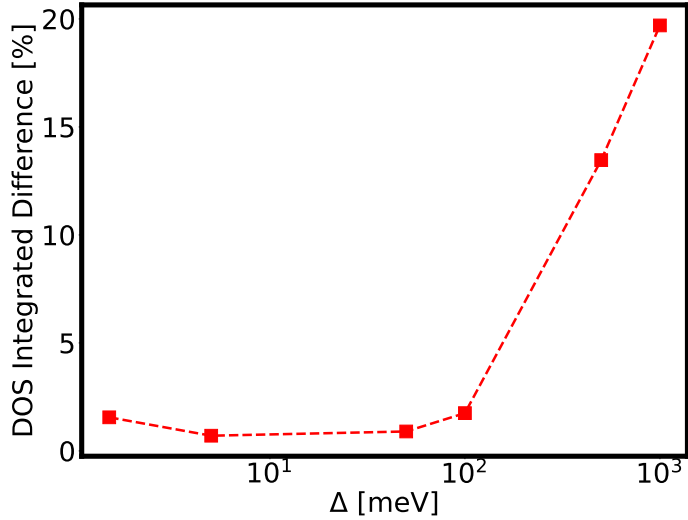


Figure B4 The relative integrated difference in the DOS of bulk Niobium for *non SCF-BdG* and *fixed- Δ* calculations with different magnitudes of the pairing potential Δ .

Comparing SCF-BdG solution methods and real space initializations

In this Section, we use bulk Pb to compare the three different SIESTA-BdG SCF solution methods introduced in Section 2.2. We work in the *superconducting strength representation* of Section 2.3. For the *full SCF-BdG* method, we also compare different ways of specifying the superconducting coupling $\lambda(\mathbf{r})$.

Bulk Pb is a conventional *s*-wave superconductor, where the pairing potential arises from electron-phonon interactions^{82–86}. The superconducting gap of lead is U-shaped, the density of states inside the superconducting gap is flat and rises sharply at the edges of the gap (coherence peaks)⁸³. The size of the superconducting gap has been measured between 2.3 and 2.5 meV, depending on the crystal orientation^{82,83}.

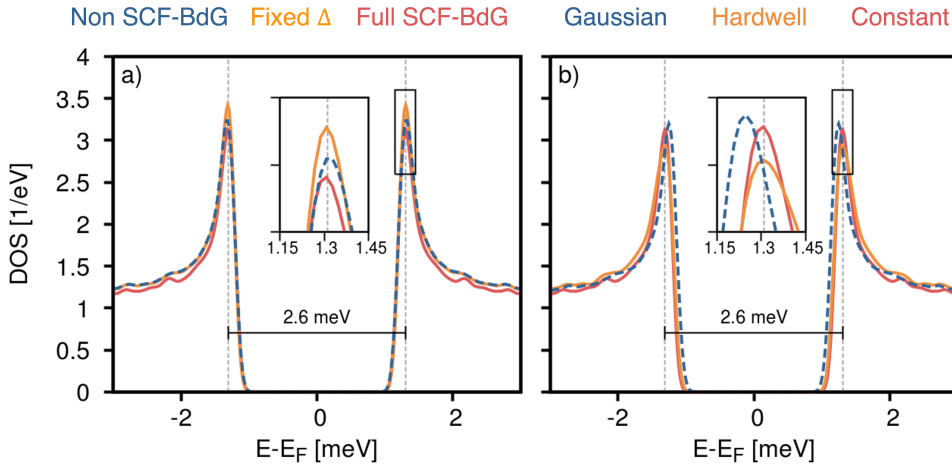


Figure B5 DOS of bulk Pb calculated with the SIESTA-BdG method with smearing temperature 0.01 meV. (a) Comparison of solution methods *non SCF-BdG*, *fixed-Δ*, and *full SCF-BdG*, assuming isotropic pairing $\Delta(\mathbf{r}) = \bar{\Delta} = 1.25$ meV; $\lambda(\mathbf{r}) = \bar{\lambda} = 0.315$ eV·V_{UC}. (b) Comparison between real-space initialization methods within the *full SCF-BdG* approach (constant, touching spherical hardwells, atom-centered Gaussian ($\sigma = 0.3$ Å)).

Based on this knowledge, we use a singlet-pairing potential with a strength of $\bar{\Delta} = 1.25$ meV (half of the gap size). We assume this potential to be uniform and isotropic in real space, i.e., in matrix form, the pairing potential can be written as

$$\Delta_{\mu\nu}(\mathbf{R}) = \bar{\Delta} \begin{pmatrix} 0 & S_{\mu\nu}(\mathbf{R}) \\ -S_{\mu\nu}(\mathbf{R}) & 0 \end{pmatrix} \quad (\text{B1})$$

where $S_{\mu\nu}(\mathbf{R})$ is the overlap matrix.

We perform calculations with all three solution methods (*non SCF-BdG*, *fixed-Δ*, and *full SCF-BdG*) to obtain the DOS for the superconducting phase of Pb. For the *full SCF-BdG* method in Fig. B5.(a), we define λ isotropic in space and tune its strength to obtain a gap with

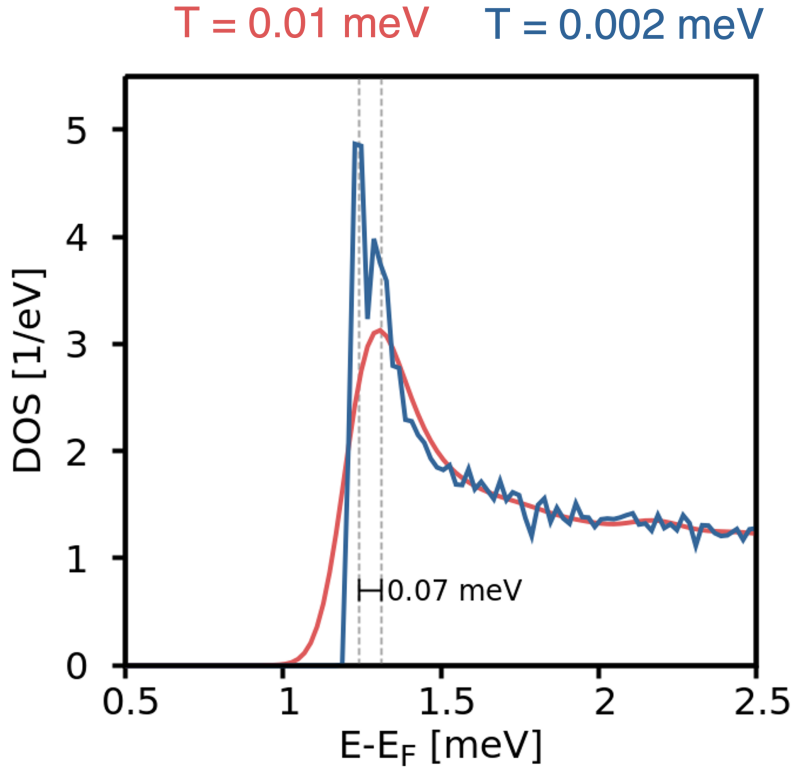


Figure B6 DOS of bulk Pb calculated with *full SCF-BdG* with smearing temperature 0.01 meV (red) and 0.002 meV (blue) using the constant real-space initialization method as in Fig. B5.(c). The plot shows that the computed coherence peak splitting (0.07 meV) agrees well with the experimental one 0.1 meV.

the same width as for the two other methods finding $\bar{\lambda} = 0.315 \text{ eV} \cdot V_{UC}$, where V_{UC} is the unit cell volume. The resulting superconducting gap confirms the experiment in shape and magnitude [Fig. B5.(a)] irrespective of the solution method used. The coherence peaks at the edge of the gap are sharp, and the density of states forms a small plateau between these peaks. Simulations with a smearing temperatures of 0.002 meV allow us to predict a splitting of the coherence peak of 0.07 meV, which agrees well with the experimentally observed one (0.1 meV) (Fig. B6).

To assess the influence of the real-space initialization of the superconducting coupling $\lambda(\mathbf{r})$, we calculate the pairing potential $\Delta(\mathbf{r})$ and the anomalous density $\chi(\mathbf{r})$ of bulk lead using the *full SCF-BdG* approach and the following initializations: (i) *constant* $\lambda(\mathbf{r}) = \bar{\lambda}$, (ii) touching *spherical hardwell* $\lambda(\mathbf{r}) = \bar{\lambda}$ if $|\mathbf{r} - \mathbf{r}_{Pb}| < 1.704 \text{ \AA}$, and (iii) *Gaussian* shape $\lambda(\mathbf{r}) = \bar{\lambda} e^{-|\mathbf{r} - \mathbf{r}_{Pb}|^2 / (2\sigma^2)}$; $\sigma = 0.3 \text{ \AA}$, as illustrated in Fig. B7. In each case, we tune the parameter $\bar{\lambda}$ to obtain a gap with approximately 2.56 meV width [Fig. B5.(b)], resulting in $\bar{\lambda}/V_{UC} = 0.315 \text{ eV}$, 0.350 eV, and 3.69 eV for (i), (ii), and (iii), respectively.

Despite the differences in the functional form of the superconducting coupling, the computed physical properties (DOS and anomalous charge) are qualitatively similar, indicating that the physically relevant information is included in the overlap matrix, namely in the projection of λ and/or Δ on the orbitals close to the Fermi level. The width of the superconducting gap is the same by construction. The extension of the anomalous charge and the spatial representation of Δ , instead, depend on the choice of $\bar{\lambda}$ and the specific radius of the modulation function. The case that differ most is the Gaussian initialization, as those functions are more sharply localized on the atoms.

Computational Details

SIESTA and SIESTA-BdG: The simulations for bulk Nb, Pb, and FeSe were performed with PBE⁸⁷ functional, norm-conserving pseudopotentials from the Pseudo-Dojo database⁸⁸, and the default SIESTA double- ζ polarized (DZP) basis set⁴¹. The crystal structure of each system was relaxed with a maximum stress tolerance of 0.01 GPa for bulk Pb and 0.1 GPa for bulk Nb respectively.

For bulk Nb, the KS equations were solved using $T = 0.1 \text{ K}$, a $120 \times 120 \times 120 \text{ k-grid}$, and a mesh cutoff of 600 Ry. Structural relaxation was performed with $T = 1 \text{ meV}$, and a $40 \times 40 \times 40 \text{ k-grid}$. The DOS was sampled on a $400 \times 400 \times 400 \text{ k-grid}$ and then refined iterating the Adaptive Brillouin Zone sampling three times with a $2 \times 2 \times 2 \text{ sub-grid}$. A spherical square well potential with a constant value of $\lambda = 0.188 \text{ eV} \cdot V_{\text{sphere}}$ inside the sphere was used (radius $r = 1.4136 \text{ \AA}$) to solve the SIESTA-BdG equations.

For bulk Pb, the KS equations were solved using $T = 1 \text{ K}$, a $60 \times 60 \times 60 \text{ k-grid}$, and a mesh cutoff of 2000 Ry. The DOS was sampled on a $300 \times 300 \times 300 \text{ k-grid}$ and then refined with a $3 \times 3 \times 3 \text{ sub-grid}$.

The FeSe simulations are converged for a smearing temperature of 0.5 meV, a $29 \times 29 \times 29 \text{ k-grid}$ for KS-equations, and a mesh cutoff of 1300 Ry. The DOS was sampled on a $480 \times 480 \times 120 \text{ k-grid}$.

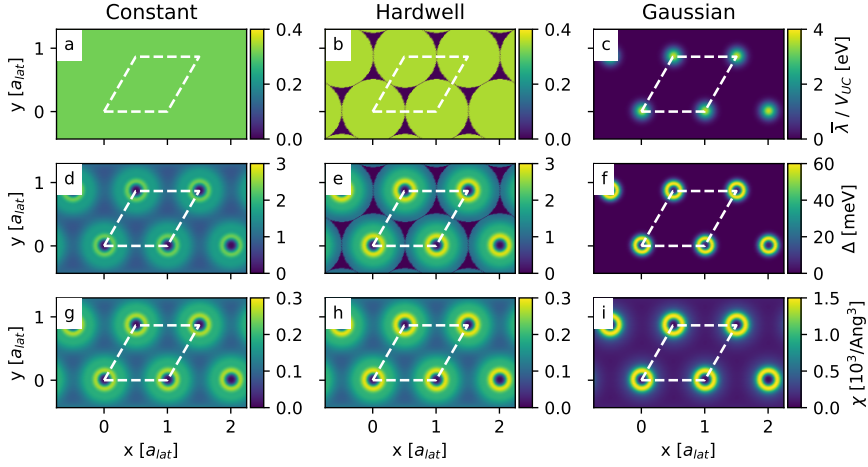


Figure B7 Real-space visualization of (a – c) the superconducting coupling parameter $\lambda(\mathbf{r})$, (d – f) the pairing potential $\Delta(\mathbf{r})$, and (g – i) the anomalous density $\chi(\mathbf{r})$ for bulk Pb. These quantities are computed for different initializations of $\lambda(\mathbf{r})$ in the *full SCF-BdG* solution method. The columns correspond to different initialization: (a) constant, (b) touching spherical hardwell ($R = 1.704 \text{ \AA}$), and (c) Gaussian shape ($\sigma = 0.3 \text{ \AA}$). The intensity of each quantity is represented as a colour gradient. The dashed parallelogram indicates the unit cell of Pb with atoms centred on the corners.

Quantum transport: We solve the KS equations using a smearing temperature of 1 meV, a $1 \times 1 \times 151$ $\mathbf{k}$ -grid, and a mesh cutoff of 800 Ry. The simulations are performed with the LDA functional as parameterized by Perdew and Zunger⁸⁹ and norm-conserving fully relativistic pseudopotentials from the Pseudo-Dojo database⁸⁸. The atomic positions were calculated according to the structure of an ideal nanotube with lattice constant $2.46 \text{ \AA}$. We perform a SIESTA-BdG calculation using the *non SCF-BdG* method with a pairing of 5 meV in the superconducting section of the scattering region and the right electrode, and set the superconducting pairing to 0 in the normal conductor section. While it is well known that the superconducting order parameter decays as a power law in low-dimensional nanostructures^{90,91}, we enforce a sharp decay here for a proof of concept. In order to calculate the quantum conductance, we use a custom Python script (Supplementary Material).

C Scattering theory for quantum transport with the SIESTA-BdG formalism

The relationship between current and voltage in superconductors is fundamentally different from that encountered in normal conductors. In a non-superconducting device, the current

through any electrode is given by

$$I_e = \int_{-\infty}^{\infty} d\varepsilon [M_e(\varepsilon) - R_e(\varepsilon)] f_e(\varepsilon) - \sum_{e' \neq e} T_{ee'}(\varepsilon) f_{e'}(\varepsilon) \quad (C1)$$

where $\mathbf{M}(\varepsilon)$ is the number of channels in the electrode e at energy ε , $\mathbf{R}(\varepsilon)$ is the reflection function, $\mathbf{T}_{e,e'}(\varepsilon)$ is the transmission function between two electrodes e and e' , and $f_e(\varepsilon)$ is the occupation function for the electrode e . Each electrode has its own chemical potential (μ_e) and temperature (T_e). The $\mathbf{k}$ dependence of all quantities here is implicit.

The transmission and reflection functions are directly related to the scattering matrix $\mathbf{s}_{ee'}(\varepsilon)$:

$$T_{ee'}(\varepsilon) = \text{Tr} \left\{ \mathbf{s}_{ee'}^\dagger(\varepsilon) \mathbf{s}_{ee'}(\varepsilon) \right\} \quad (C2)$$

$$R_e(\varepsilon) = M_e(\varepsilon) - \text{Tr} \left\{ \mathbf{s}_{ee}^\dagger(\varepsilon) \mathbf{s}_{ee}(\varepsilon) \right\}$$

Furthermore, the unitarity of the scattering matrix implies $M_e = R_e + \sum_{e' \neq e} T_{ee'}$ ⁶⁶. This relationship allows us to rewrite the current as a sum of pairwise currents.

$$I_{e,e'} = \int_{-\infty}^{\infty} d\varepsilon T_{ee'}(\varepsilon) [f_e(\varepsilon) - f_{e'}(\varepsilon)] \quad (C3)$$

$$I_e = \sum_{e' \neq e} I_{e,e'}$$

In the low-bias limit the difference in the Fermi-occupation function of the electrodes is proportional to the difference in their chemical potential and the pairwise currents are written as.

$$I_{e,e'} \approx T_{ee'}(\mu)(\mu_{e'} - \mu_e) \quad (C4)$$

In other words, the current is proportional to the applied bias.

In the case of superconducting electrodes or devices, the transmission and reflection probabilities become 2×2 matrices [Eq. (11)]⁴⁸.

We obtain the reflection and transmission probabilities using Green's function techniques, adopting an approach similar to the generalized Fisher-Lee relation⁹².

$$T_{ee'}^{\alpha\beta}(\varepsilon) = \text{Tr} \left\{ \mathbf{s}_{ee'}^{\alpha\beta}(\varepsilon) \mathbf{s}_{ee'}^{\alpha\beta}(\varepsilon)^\dagger \right\} \quad (C5)$$

$$R_{ee'}^{\alpha\beta}(\varepsilon) = \text{Tr} \left\{ \mathbf{s}_{ee'}^{\alpha\beta}(\varepsilon) \mathbf{s}_{ee'}^{\alpha\beta}(\varepsilon)^\dagger \right\} \quad (C6)$$

$$s_{ee'}^{\alpha\beta} = -\delta_{\alpha\beta} \delta_{ee'} M_e^\alpha(\varepsilon) \quad (C7)$$

$$+i\mathbf{\Gamma}_e^{1/2}(\varepsilon) \mathbf{G}(\varepsilon + i0^+) \mathbf{\Gamma}_{e'}^{1/2}(\varepsilon)$$

$$\mathbf{G}(\varepsilon + i0^+) = (\varepsilon + i0^+) \mathbf{S} - \mathbf{H} - \sum_e \mathbf{\Sigma}_e(\varepsilon) \quad (C8)$$

where $\Gamma_e(\varepsilon) = i \left[\Sigma_e(\varepsilon) - \Sigma_e^\dagger(\varepsilon) \right]$ is the electrode broadening matrix, $\Sigma_e(\varepsilon)$ is the electrode self-energy, $\mathbf{G}(\varepsilon + i0^+)$ is the retarded Green's function of the open quantum system, and $M_e^\alpha(\varepsilon)$ is the number of electrode channels.

The electrode self-energies are calculated using the Lopez-Sancho/Lopez-Sancho algorithm⁹³. The number of channels $M_e^\alpha(\varepsilon)$ is determined in a separate calculation of the bulk electrodes.

These additional scattering probabilities have to be taken into account when calculating the current through any electrode. Taking into account the opposite charge of electrons and holes, the current through the electrode e is given by:

$$\begin{aligned}
 I_e = \frac{e}{h} \int_{-\infty}^{\infty} \bigg\{ & \underbrace{\left[M_e(\varepsilon) - R_e^{pp}(\varepsilon) + R_e^{hp}(\varepsilon) \right]}_{\text{electronic contribution}} f_e(\varepsilon) \\
 & - \underbrace{\sum_{e' \neq e} \left[T_{ee'}^{pp}(\varepsilon) - T_{ee'}^{hp}(\varepsilon) \right]}_{\text{electronic contribution}} f_{e'}(\varepsilon) \\
 & - \underbrace{\left[M_e(\varepsilon) - R_e^{hh}(\varepsilon) + R_e^{ph}(\varepsilon) \right]}_{\text{hole contribution}} \bar{f}_e(\varepsilon) \\
 & - \underbrace{\sum_{e' \neq e} \left[-T_{ee'}^{hh}(\varepsilon) + T_{ee'}^{ph}(\varepsilon) \right]}_{\text{hole contribution}} \bar{f}_{e'}(\varepsilon) \bigg\} d\varepsilon.
 \end{aligned} \tag{C9}$$

Here, $\bar{f}(\varepsilon) = 1 - f(\varepsilon)$ is the occupation function of the hole-like states in the electrode. As in a normal metal, the unitarity of the scattering matrix links the number of electrode channels to the reflection and transmission functions⁶⁸:

$$M_e(\varepsilon) = R_e^{pp}(\varepsilon) + R_e^{ph}(\varepsilon) \tag{C10}$$

$$\begin{aligned}
 & + \sum_{e' \neq e} [T_{ee'}^{pp}(\varepsilon) + T_{ee'}^{ph}(\varepsilon)] \\
 & = R_e^{hh}(\varepsilon) + R_e^{hp}(\varepsilon) \\
 & + \sum_{e' \neq e} [T_{ee'}^{hh}(\varepsilon) + T_{ee'}^{hp}(\varepsilon)].
 \end{aligned} \tag{C11}$$

Using these identities, we can rewrite the current through electrode I_e [Eq. (12)] as

$$\begin{aligned}
 I_e = \frac{e}{h} \int_{-\infty}^{\infty} \bigg\{ & [R_e^{hp}(\varepsilon) + R_e^{ph}(\varepsilon)][f_e(\varepsilon) - \bar{f}_e(\varepsilon)] \\
 & + \sum_{e' \neq e} [T_{ee'}^{pp}(\varepsilon) + T_{ee'}^{hh}(\varepsilon)][f_e(\varepsilon) - f_{e'}(\varepsilon)] \\
 & + \sum_{e' \neq e} T_{ee'}^{hp}(\varepsilon)[\bar{f}_e(\varepsilon) - f_{e'}(\varepsilon)] \\
 & + T_{ee'}^{ph}(\varepsilon)[f_e(\varepsilon) - \bar{f}_{e'}(\varepsilon)] \bigg\} d\varepsilon
 \end{aligned} \tag{C12}$$

where $\bar{f}_e(\varepsilon)$ is the occupation of hole states in the electrode e . Moving to the low-bias limit ($f_e(\varepsilon) = f(\varepsilon) - \frac{\partial f}{\partial \varepsilon}(\varepsilon)[\mu_e - \mu]$), and invoking particle-hole symmetry allows us to rewrite the expression of the current as [Eq. (13)]:

$$\begin{aligned}
 I_e \approx \frac{e}{h} \sum_{e' \neq e} & T_{ee'}^{pp}(\mu)[\mu_{e'} - \mu_e] \\
 & + \sum_{e' \neq e} T_{ee'}^{hp}(\mu)[\mu_{e'} + \mu_e - 2\mu] \\
 & + 2R_e^{hp}(\mu)(\mu_e - \mu)
 \end{aligned} \tag{C13}$$

Bibliography

- 1** R. Reho, N. Wittemeier, A. Kole, P. Ordejón, and Z. Zanolli, arXiv preprint arXiv:2406.02022 (2024).
- 2** W. Meissner and R. Ochsenfeld, *Naturwissenschaften* **21**, 787 (1933).
- 3** J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Physical review* **108**, 1175 (1957).
- 4** J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Physical Review* **106**, 162 (1957).
- 5** F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schäfer, *Physical Review Letters* **43**, 1892 (1979).
- 6** D. Jérôme, A. Mazaud, M. Ribault, and K. Bechgaard, *Journal de Physique Lettres* **41**, 95 (1980).
- 7** C. C. Tsuei and J. R. Kirtley, *Reviews of Modern Physics* **72**, 969 (2000).
- 8** G. R. Stewart, *Reviews of Modern Physics* **83**, 1589 (2011).
- 9** L. Balents, C. R. Dean, D. K. Efetov, and A. F. Young, *Nature Physics* **16**, 725 (2020).
- 10** B. Sacépé, M. Feigel'man, and T. M. Klapwijk, *Nature Physics* **16**, 734 (2020).
- 11** S. Frolov, M. Manfra, and J. Sau, *Nature Physics* **16**, 718 (2020).
- 12** A. Y. Kitaev, *Physics-Uspekhi* **44**, 131 (2001).
- 13** W.-Y. He, B. T. Zhou, J. J. He, N. F. Q. Yuan, T. Zhang, and K. T. Law, *Communications Physics* **1**, 40 (2018).
- 14** J. S. Lee, B. Shojaei, M. Pendharkar, A. P. McFadden, Y. Kim, H. J. Suominen, M. Kjaergaard, F. Nichele, H. Zhang, C. M. Marcus, and C. J. Palmstrøm, *Nano Letters* **19**, 3083 (2019).
- 15** E. Prada, P. San-Jose, M. W. A. de Moor, A. Geresdi, E. J. H. Lee, J. Klinovaja, D. Loss, J. Nygård, R. Aguado, and L. P. Kouwenhoven, *Nature Reviews Physics* **2**, 575 (2020).
- 16** M. Sato and Y. Ando, *Reports on Progress in Physics* **80**, 076501 (2017).
- 17** L. N. Oliveira, E. K. U. Gross, and W. Kohn, *Physical Review Letters* **60**, 2430 (1988).
- 18** P. Hohenberg and W. Kohn, *Physical review* **136**, B864 (1964).
- 19** W. Kohn and L. J. Sham, *Physical review* **140**, A1133 (1965).
- 20** N. Bogoljubov, V. V. Tolmachov, and D. Širkov, *Fortschritte der physik* **6**, 605 (1958).
- 21** N. N. Bogoljubov, *Il Nuovo Cimento* **7**, 794 (1958).

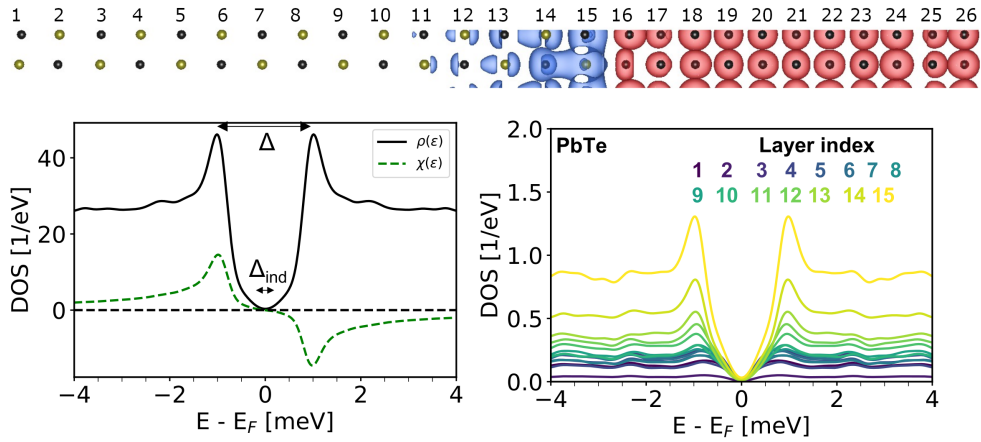
- 22** P. G. DeGennes, *Superconductivity of Metals and Alloys*, (W. A. Benjamin, New York) (1966).
- 23** W. M. Temmerman, Z. Szotek, B. L. Gyorffy, O. K. Andersen, and O. Jepsen, *Physical Review Letters* **76**, 307 (1996).
- 24** B. L. Gyorffy, Z. Szotek, W. M. Temmerman, O. K. Andersen, and O. Jepsen, *Physical Review B* **58**, 1025 (1998).
- 25** P. Cudazzo, G. Profeta, A. Sanna, A. Floris, A. Continenza, S. Massidda, and E. K. U. Gross, *Physical Review Letters* **100**, 257001 (2008).
- 26** L. Boeri and G. B. Bachelet, *Journal of Physics: Condensed Matter* **31**, 234002 (2019).
- 27** L. Boeri, in *Handbook of Materials Modeling*, edited by W. Andreoni and S. Yip (Springer International Publishing, Cham, 2020) pp. 73–112.
- 28** M. Suvasini and B. Gyorffy, *Physica C: Superconductivity* **195**, 109 (1992).
- 29** M. B. Suvasini, W. M. Temmerman, and B. L. Gyorffy, *Phys. Rev. B* **48**, 1202 (1993).
- 30** G. Csire, B. Újfalussy, J. Cserti, and B. Györffy, *Physical Review B* **91**, 165142 (2015).
- 31** P. Rüßmann and S. Blügel, *Physical Review B* **105**, 125143 (2022).
- 32** P. Rüßmann and S. Blügel, *arXiv preprint arXiv:2208.14289* (2022).
- 33** Y. Zhang, J. Huang, C. Zhang, P. Wang, Z. Wang, T. Wang, Z. Xing, and D. Xing, *Physical Review B* **102**, 064503 (2020).
- 34** C. Li, Y.-F. Zhao, A. Vera, O. Lesser, H. Yi, S. Kumari, Z. Yan, C. Dong, T. Bowen, K. Wang, *et al.*, *Nature Materials* **22**, 570 (2023).
- 35** B. Nyári, A. Lászlóffy, L. Szunyogh, G. Csire, K. Park, and B. Ujfalussy, *Physical Review B* **104**, 235426 (2021).
- 36** K. Park, B. Nyari, A. Laszloffy, L. Szunyogh, and B. Ujfalussy, *New Journal of Physics* **25**, 033022 (2023).
- 37** A. Lászlóffy, B. Nyári, L. Szunyogh, K. Park, and B. Ujfalussy, *Physical Review B* **107**, 224515 (2023).
- 38** D. Pashov, S. Acharya, W. R. Lambrecht, J. Jackson, K. D. Belashchenko, A. Chantis, F. Jamet, and M. van Schilfgaarde, *Computer Physics Communications* **249**, 107065 (2020).
- 39** S. Acharya, D. Pashov, and M. van Schilfgaarde, *Physical Review B* **105**, 144507 (2022).
- 40** S. Acharya, M. I. Katsnelson, and M. van Schilfgaarde, *npj Quantum Materials* **8**, 24 (2023).

- 41** J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, *Journal of Physics: Condensed Matter* **14**, 2745 (2002).
- 42** A. Garcia, N. Papior, A. Akhtar, E. Artacho, V. Blum, E. Bosoni, P. Brandimarte, M. Brandbyge, J. I. Cerdá, F. Corsetti, *et al.*, *The Journal of chemical physics* **152**, 204108 (2020).
- 43** R. Cuadrado and J. Cerdá, *Journal of Physics: Condensed Matter* **24**, 086005 (2012).
- 44** M. Brandbyge, J.-L. Mozos, P. Ordejón, J. Taylor, and K. Stokbro, *Physical Review B* **65**, 165401 (2002).
- 45** N. Papior, N. Lorente, T. Frederiksen, A. García, and M. Brandbyge, *Computer Physics Communications* **212**, 8 (2017).
- 46** H. Ness, I. A. Sadovskyy, A. E. Antipov, M. van Schilfgaarde, and R. M. Lutchyn, *npj Computational Materials* **8**, 23 (2022).
- 47** H. Ness and M. Van Schilfgaarde, arXiv preprint arXiv:2309.06984 (2023).
- 48** C. J. Lambert, *Journal of Physics: Condensed Matter* **3**, 6579 (1991).
- 49** F. Taddei, S. Sanvito, J. H. Jefferson, and C. J. Lambert, *Physical Review Letters* **82**, 4938 (1999).
- 50** G. Stefanucci, E. Perfetto, and M. Cini, *Physical Review B* **81**, 115446 (2010).
- 51** Q. Wang, Y. Shen, B. Pan, X. Zhang, K. Ikeuchi, K. Iida, A. D. Christianson, H. C. Walker, D. T. Adroja, M. Abdel-Hafiez, X. Chen, D. A. Chareev, A. N. Vasiliev, and J. Zhao, *Nature Communications* **7**, 12182 (2016).
- 52** R. Casalbuoni and G. Nardulli, *Reviews of Modern Physics* **76**, 263 (2004).
- 53** P. Rüßmann and S. Blügel, “Density functional Bogoliubov-de Gennes analysis of superconducting {Nb} and {Nb}(110) surfaces,” (2021).
- 54** L. Schneider, *Realizing topological boundary modes in bottom-up constructed magnetic nanostructures on superconducting surfaces*, Ph.D. thesis, Universität Hamburg, Hamburg (2021).
- 55** D. K. Finnemore, T. F. Stromberg, and C. A. Swenson, *Phys. Rev.* **149**, 231 (1966).
- 56** V. Karasik and I. Y. Shebalin, *SOV PHYS JETP* **30**, 1068 (1970).
- 57** S. Kasahara, T. Watashige, T. Hanaguri, Y. Kohsaka, T. Yamashita, Y. Shimoyama, Y. Mizukami, R. Endo, H. Ikeda, K. Aoyama, T. Terashima, S. Uji, T. Wolf, H. von Löhneysen, T. Shibauchi, and Y. Matsuda, *Proceedings of the National Academy of Sciences* **111**, 16309 (2014).

- 58 J. K. Glasbrenner, I. I. Mazin, H. O. Jeschke, P. J. Hirschfeld, R. M. Fernandes, and R. Valentí, *Nature Physics* **11**, 953 (2015).
- 59 C.-L. Song, Y.-L. Wang, P. Cheng, Y.-P. Jiang, W. Li, T. Zhang, Z. Li, K. He, L. Wang, J.-F. Jia, *et al.*, *Science* **332**, 1410 (2011).
- 60 P. J. Hirschfeld, *Comptes Rendus Physique* **17**, 197 (2016).
- 61 J. Paglione and R. L. Greene, *Nature Physics* **6**, 645 (2010).
- 62 S.-H. Baek, D. V. Efremov, J. M. Ok, J. S. Kim, J. van den Brink, and B. Büchner, *Nature Materials* **14**, 210 (2015).
- 63 P. Massat, D. Farina, I. Paul, S. Karlsson, P. Strobel, P. Toulemonde, M.-A. Méasson, M. Cazayous, A. Sacuto, S. Kasahara, T. Shibauchi, Y. Matsuda, and Y. Gallais, *Proceedings of the National Academy of Sciences* **113**, 9177 (2016).
- 64 P. Zhang, T. Qian, P. Richard, X. P. Wang, H. Miao, B. Q. Lv, B. B. Fu, T. Wolf, C. Meingast, X. X. Wu, Z. Q. Wang, J. P. Hu, and H. Ding, *Physical Review B* **91**, 214503 (2015).
- 65 H. Ness and M. van Schilfgaarde, (2023), 10.48550/ARXIV.2309.06984.
- 66 S. Datta, *Electronic Transport in Mesoscopic Systems*, 1st ed. (Cambridge University Press, 1995).
- 67 J. Ferrer, C. J. Lambert, V. M. García-Suárez, D. Z. Manrique, D. Visontai, L. Oroszlany, R. Rodríguez-Ferradás, I. Grace, S. W. D. Bailey, K. Gillemot, H. Sadeghi, and L. A. Algharagholi, *New Journal of Physics* **16**, 093029 (2014).
- 68 C. J. Lambert and R. Raimondi, *Journal of Physics: Condensed Matter* **10**, 901 (1998).
- 69 S. Kirchhoff, *Annalen der Physik* **140**, 497 (1845).
- 70 S. Datta, P. F. Bagwell, and M. P. Anantram, (1996).
- 71 Z. K. Tang, L. Zhang, N. Wang, X. X. Zhang, G. H. Wen, G. D. Li, J. N. Wang, C. T. Chan, and P. Sheng, *Science* **292**, 2462 (2001).
- 72 I. Takesue, J. Haruyama, N. Kobayashi, S. Chiashi, S. Maruyama, T. Sugai, and H. Shinohara, *Physical Review Letters* **96**, 057001 (2006).
- 73 M. Kociak, A. Yu. Kasumov, S. Guéron, B. Reulet, I. I. Khodos, Yu. B. Gorbatov, V. T. Volkov, L. Vaccarini, and H. Bouchiat, *Physical Review Letters* **86**, 2416 (2001).
- 74 K.-i. Sasaki, J. Jiang, R. Saito, S. Onari, and Y. Tanaka, *Journal of the Physical Society of Japan* **76**, 033702 (2007).
- 75 G. E. Blonder, M. Tinkham, and T. M. Klapwijk, *Physical Review B* **25**, 4515 (1982).

- 76** Y. in't Veld, M. I. Katsnelson, A. J. Millis, and M. Rösner, 2D Materials (2023).
- 77** M. Simonato, M. Katsnelson, and M. Rösner, Physical Review B **108**, 064513 (2023).
- 78** G. Stefanucci, E. Perfetto, and M. Cini, Physical Review B **81**, 115446 (2010).
- 79** S. Acharya, D. Pashov, F. Jamet, and M. van Schilfgaarde, Symmetry **13**, 169 (2021).
- 80** R. Balian and N. Werthamer, Physical review **131**, 1553 (1963).
- 81** P. E. Blöchl, O. Jepsen, and O. K. Andersen, Physical Review B **49**, 16223 (1994), publisher: American Physical Society.
- 82** B. L. Blackford and R. H. March, Physical Review **186**, 397 (1969).
- 83** G. I. Lykken, A. L. Geiger, K. S. Dy, and E. N. Mitchell, Physical Review B **4**, 1523 (1971).
- 84** R. Heid, K.-P. Bohnen, I. Yu. Sklyadneva, and E. V. Chulkov, Physical Review B **81**, 174527 (2010).
- 85** I. Yu. Sklyadneva, R. Heid, P. M. Echenique, K.-B. Bohnen, and E. V. Chulkov, Physical Review B **85**, 155115 (2012).
- 86** A. Sirohi, P. Saha, S. Gayen, A. Singh, and G. Sheet, Nanotechnology **27**, 285701 (2016).
- 87** J. P. Perdew, K. Burke, and M. Ernzerhof, Physical Review Letters **77**, 3865 (1996).
- 88** M. van Setten, M. Giantomassi, E. Bousquet, M. Verstraete, D. Hamann, X. Gonze, and G.-M. Rignanese, Computer Physics Communications **226**, 39 (2018).
- 89** J. P. Perdew and A. Zunger, Physical Review B **23**, 5048 (1981).
- 90** J. González and E. Perfetto, Physical Review B **76**, 155404 (2007).
- 91** J. González and E. Perfetto, Journal of Physics: Condensed Matter **20**, 145218 (2008).
- 92** H. Boumrar, M. Hamidi, H. Zenia, and S. Lounis, Journal of Physics: Condensed Matter **32**, 355302 (2020).
- 93** M. L. Sancho, J. L. Sancho, and J. Rubio, Journal of Physics F: Metal Physics **14**, 1205 (1984).

Proximity - Induced Superconductivity in PbTe/Pb heterostructures from first principles



Based on

R. Reho, A. R. Botello-Méndez, Z. Zanolli, “Proximity induced superconductivity in PbTe/Pb via first principles”, arXiv:2412.01749 (2024), under review in Phys. Rev. B.

Abstract

Semiconductor–superconductor hybrid devices have been proposed as promising platforms for detecting and analyzing Majorana zero modes, which find applications in topological quantum computing. In this work, we solve the Kohn-Sham Density Functional Theory and Bogoliubov–de Gennes equations to describe the normal and superconducting properties of a PbTe/Pb heterostructure. We resolve a proximity–induced superconducting gap on the PbTe side. The hybridization between PbTe and Pb causes the emergence of a soft Bardeen–Cooper–Schrieffer–like superconducting gap. We compute the anomalous charge density in real space, estimating its decay length and showing that the pairing potential is anisotropic. Contrary to the models that predict Majorana zero modes in these interfaces, we find a significantly large Schottky barrier in the normal state preventing the emergence of zero modes. Our findings strengthen the understanding of the physics governing PbTe/Pb hybrid devices and their viability for Majorana zero modes applications. This chapter is based on Reho et al¹. RR conducted the first-principles simulations and developed the necessary routines in the SIESTA and sisL codes. RR also took the lead in writing the manuscript.

1 Introduction

PbTe/Pb planar Josephson junctions² have been proposed as viable platforms for topological superconductivity, due to their resilience to charged impurities, wide electron mobility, and excellent crystalline quality^{3,4}. PbTe's narrow bandgap and large Landé g -factor, combined with Pb's relatively wide superconducting gap ($\Delta \sim 3\text{meV}$) and critical temperature ($T_C \sim 7\text{K}$), make these materials advantageous compared to conventional InAs-Al and InSb-Al heterostructures (HS)^{5,6}.

Several nanoscale heterostructures have been proposed as platforms for hosting Majorana Zero modes (MZMs)^{7–12}. A common feature across these systems is the crucial role of interfacial proximity effects.

To host MZMs, a semiconductor–superconductor (SM–SC) interface must meet several key requirements^{13,14}: (i) strong spin-orbit coupling and significant Zeeman energy gap (V_Z) in the semiconductor, (ii) s -wave superconductor, (iii) proximity induced superconductivity, and (iv) the heterostructure chemical potential must lie within the SM's Zeeman gap and the SC gap. When the applied Zeeman field exceeds the critical value $V_C = \sqrt{\Delta^2 + \mu^2}$ the system transitions into a topological phase, hosting MZMs at its ends^{15–17}. Experiments confirmed that superconductors can induce a superconducting gap in topological insulators (TIs), with the proximity effect decaying exponentially as the TI film thickness increases^{18,19}.

Theoretical works showed that proximity induced superconductivity is possible for SC–TI heterostructures, emphasizing the importance of accounting for the details of the chemical and physical properties at the interface^{20,21}. These findings emphasize the need to employ *ab initio* methods to describe the interfacial properties of PbTe/Pb heterostructures (HS).

*Cole et al.*²² developed a minimal model to describe the density of states (DOS) in a generic SM–SC heterostructure and investigated how the SC–coupling strength and the height of the interface barrier affect the shape of the SC gap. They identified a hard U-shaped superconducting gap as indicative of a strong SC–coupling regime, where the superconductor overshadows the semiconductor's electronic properties. Conversely, a soft Bardeen–Cooper–Schrieffer-like gap corresponds to a weak SC–coupling regime, where low-energy states of the HS are predominantly of semiconductor character. Weak SC–coupling is, therefore, desirable for achieving topological superconductivity^{23,24}.

We investigate from first-principles proximity effects in a PbTe/Pb HS, focusing on the conditions required for MZMs to emerge. All our findings are obtained using the recently implemented SIESTA-BdG method^{25,26}, which solves the Kohn-Sham Density Functional Theory and Bogoliubov–de Gennes equations to describe on the same footing the normal and superconducting properties. We discuss how the electrostatic environment at the interface is critical for the emergence of MZMs. We find significant band bending at the interface, leading to charge transfer from PbTe to Pb, and affecting the position of the chemical potential. In the superconducting state we observe a soft BCS-like SC gap, indicating a weak SC–coupling between PbTe and Pb. We predict a proximity-induced superconducting gap in PbTe and a softening of Pb SC gap (with respect to bulk). We show that the superconducting anomalous

charge density ($\chi(\mathbf{r})$) emerging at the interface is anisotropic. Our findings are robust against lattice deformations (strain) and applied electric field. In particular, the induced SC gap at the interface is resilient under lattice strain.

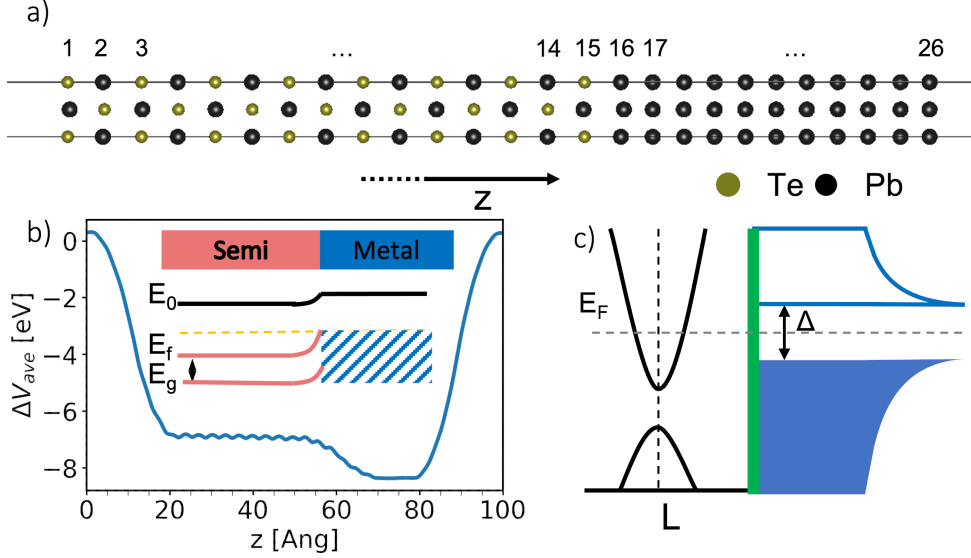


Figure 1.1 (a) Side view of the relaxed (4, -5) PbTe/Pb heterostructure stacked along the [001] direction. (b) Average electrostatic potential (ΔV_{ave}) across the interface with a schematic of the energy alignment between a semiconductor and a metal. (c) Schematic energy alignment between a semiconductor and a superconductor, representative of PbTe/Pb. The optimal alignment for the emergence of Majorana Zero Modes occurs when the semiconductor gap and the superconductor gap align in energy.

2 PbTe/Pb Heterostructure: Normal state

PbTe and Pb {001} planes are not commensurate. Hence, in order to build the HS, it is necessary to introduce strain into the unit cell of both materials. We employ 15 PbTe and 11 Pb layers, which ensures that the DOS in the central region of PbTe (layers 6–7 Fig 1.1.(a)) and Pb [layers 21–22 Fig 1.1.(a)] matches the corresponding bulk values. We examined a range of strain from $\sim 1\%$ to $\sim 9\%$ on the PbTe side, and $\sim -8\%$ to ~ -0.4 on the Pb side, relaxing the atomic positions for each configuration. We denote strain in the HS with a pair of numbers referring to strain on PbTe and Pb, respectively. In the following, we focus on the HS with 4% strain on PbTe and -5% strain on Pb, namely (4, -5).

In the normal state, the bands [Fig. 2.2.(a)] cross the Fermi level, resulting in a metallic heterostructure with visible band splitting (mostly near the M point) due to hybridization between PbTe and Pb states. To prove this, we remove the interaction between PbTe and Pb by

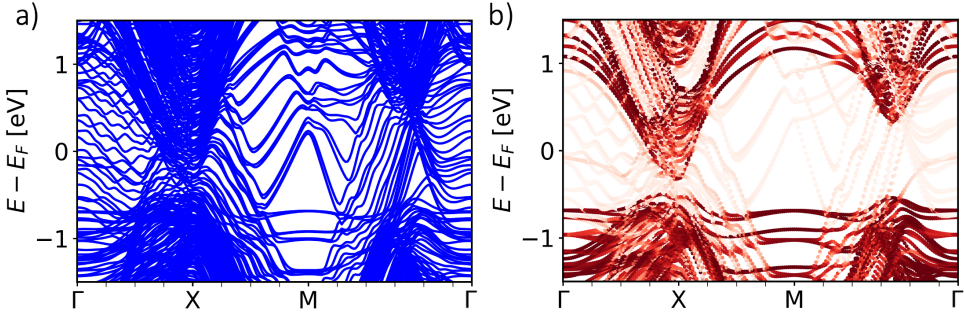


Figure 2.2 (a) PbTe/Pb normal state band structure. The bands cross the Fermi level, resulting in a metallic heterostructure. (b) Normal state bands with the coupling between the PbTe and Pb sides of the heterostructure set to zero. The color intensity represents the contribution from the PbTe orbitals.

setting their coupling to zero in the Kohn Sham Hamiltonian. The resulting band structure [Fig. 2.2.(b)] does not exhibit any splitting. We highlight the PbTe contribution to the electronic structure with dark red points in [Fig. 2.2.(b)], proving that the states near the Fermi energy predominantly belong to the semiconductor.

The interaction between the two materials leads to variation in chemical bonds and relative atomic positions near the interface, along with charge transfer from PbTe to Pb. Using Mulliken charge analysis²⁷, we compute the variation of charge ΔQ on PbTe (Q_{PbTe}) and Pb (Q_{Pb}) in the HS with respect to their freestanding nominal values. We find a depletion of charge on PbTe indicating an electron transfer from the PbTe to the Pb side of the HS (Table D1 and Fig.D1).

When a metal comes in contact with a semiconductor, their energy level align, creating a potential energy barrier (Schottky barrier) at the interface due to the difference in their work functions [Fig. 1.1(b)]. We calculate from first-principles the average electrostatic potential ($\Delta V_{ave}(z)$)²⁸, namely the spatial average of all electrostatic interactions in the system. The average is performed layer-by-layer, and it quantifies the band alignment in heterostructure. To create an environment favourable to the emergence of MZMs¹⁵, it would be desirable to have a $\Delta V_{ave} \sim 0$ eV so that the electronic states participating in the superconducting proximity effect are close to the SOC splitted bands of PbTe at L [Fig. 1.1.(c) and Appendix B, Fig. B3].

We predict, instead, a significant difference in the average electrostatic potential across the interface $\Delta V_{ave} \sim 1.2$ eV, with the PbTe side being higher in energy than the Pb side [Fig. 1.1(b)].

We studied the robustness of these findings against strain and the presence of an external electric field. Our results indicate that ΔV_{ave} and the normal state electronic DOS near the Fermi level are not significantly affected by varying strain [Table 2.1 and Fig. 2.3.(a)]. We compute the excess charge ΔQ and observe that it slightly increases by increasing strain on PbTe (Table D1), substantiating the conclusion that the electrostatic environment close to the interface does not change under lattice deformations. Furthermore, the shape and magnitude

of the DOS is not affected by the electric field [Fig. 2.3(b)]. The magnitude of the applied electric fields are all considerably above the electrical breakdown point of bulk PbTe which can be estimated to be $6.4 \times 10^{-6} \text{ V/\AA}^{29}$, while its sign and direction are chosen to offset the difference in electrostatic potential at the interface ΔV_{ave} .

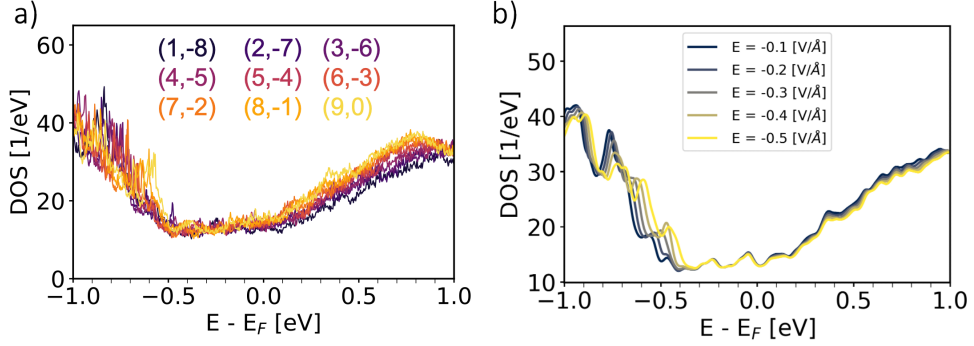


Figure 2.3 PbTe/Pb normal state DOS for different (a) strain and (b) applied electric field across the interface, represented with different colors.

Table 2.1 Difference in average electrostatic potential ΔV_{ave} across the interface of the PbTe/Pb HS for different strain. The (4, -5) HS is highlighted in bold.

strain (PbTe/Pb) [%]	ΔV_{ave} [eV]
1.0%/-7.7%	1.36
2.0%/-6.8%	0.84
3.0%/-5.9%	0.93
4.0%/-5.0%	1.20
5.0%/-4.0%	1.08
6.0%/-3.2%	1.10
7.0%/-2.3%	1.17
8.0%/-1.3%	1.22
9.0%/-0.4%	1.30

3 PbTe/Pb heterostructure: Superconducting state

We used the SIESTA-BdG method to compute the superconducting DOS of bulk Pb (Appendix B) and PbTe/Pb heterostructures. We demonstrate that a proper initialization of the superconducting pairing potential is essential to avoid unphysical results (Appendix C, Fig. C1). Moreover, we demonstrate how the SIESTA-BdG method can be used to investigate various pairing mechanisms and their effects on the superconducting density of states (SC-DOS). Computational details and geometrical aspects of the HS are presented in the Section 4.

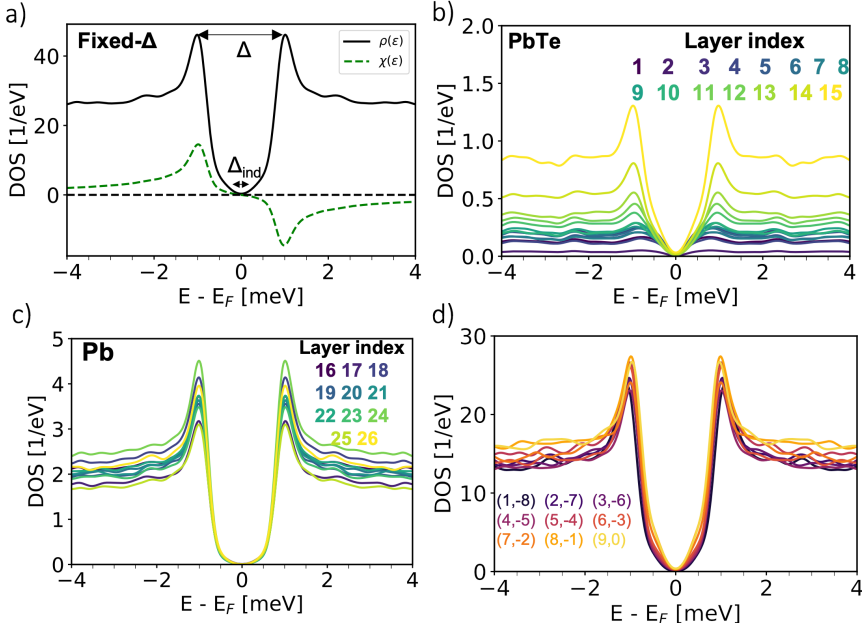


Figure 3.4 Superconducting DOS (SC-DOS, $\rho(\epsilon)$, black continuous line) and anomalous DOS (ADOS, $\chi(\epsilon)$, dashed green line) for the (4, -5) PbTe/Pb HS. Two distinct energy ranges are resolved within the soft BCS-like SC gap: the difference between the two main coherence peaks Δ and the induced SC-gap Δ_{ind} , where the SC-DOS vanishes. The dashed black line serves as a reference for zero DOS. (a) SC-DOS projected on individual PbTe (b) and Pb (c) layers, and for the PbTe/Pb HS for different strain values (d).

More than fifty years ago, experimental measures^{30,31} of bulk Pb revealed an anisotropic U-shaped SC-DOS with two superconducting gaps of width $\sim 2.34 - 2.5$ and $\sim 2.7 - 2.8$ meV depending on the crystal orientation. Each coherence peak is split in two, with an energy separation of $\sim 0.1 - 0.2$ meV. Splitting of the coherence peaks in bulk Pb has been theoretically predicted with SIESTA-BdG²⁵ and KKR-BdG methods³², and is further discussed in Appendix B.

The HS, exhibits a *soft* U-shaped gap with coherence peaks $\Delta = 2.0$ meV far apart and an induced gap $\Delta_{ind} = 0.6$ meV [Fig. 3.4.(a)].

The soft gap originates from anisotropies in the superconducting gap across different layers of the heterostructures, as it can be evidenced from the BdG spectrum (Fig. D2). Indeed, due to heterostructuring, the electrostatic environment of Pb atoms changes layer-by-layer, leading to multiple superconducting gaps at different $\mathbf{k}$ -points in the BdG spectrum. We find that the anomalous density of states (ADOS, $\chi(\epsilon)$) is dominated by the singlet components (Cooper pair with total spin zero), while the triplet components (Cooper pair with total spin one) are negligible. The shape of the total DOS is determined by the induced gap in the PbTe side of the heterostructure, as indicated by the projected density of states [Fig. 3.4.(b)]. The

low energy states inside the SC gap are predominantly of PbTe character, hence the HS is in the weak coupling regime²². The hybridization between Pb and PbTe “poisons” the SC gap, leading to a soft BCS-like superconducting density of states (SC-DOS $\rho(\epsilon)$). The Pb side of the heterostructure retains its U-shape but the coherence peaks are less sharp and smaller in magnitude than bulk Pb [Fig. 3.4.(c)]. In our simulations, the soft-BCS gap at the SM-SC interface is due to structural relaxation of the atomic structure and states hybridization, as we do not include magnetic, thermal, or dissipative broadening effects³³. We find that strain only slightly affects the shape of the SC DOS in the HS [Fig. 3.4.(d)].

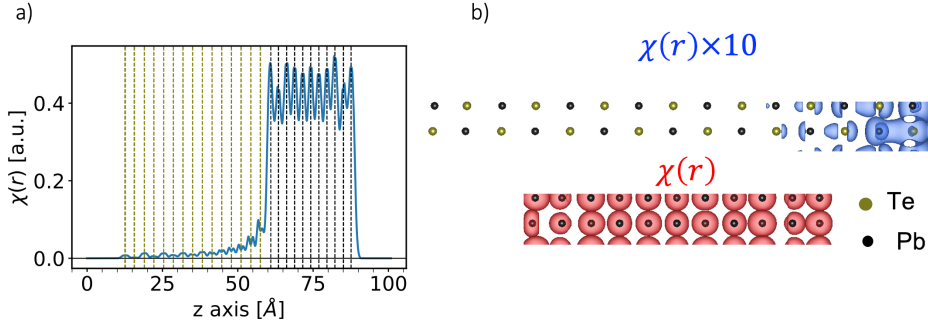


Figure 3.5 (a) Anomalous density of states $\chi(\mathbf{r})$ along the z-axis in real space. Vertical dashed lines represent the layer position in the PbTe (olive) and Pb (black) regions of the heterostructure. (b) 3D visualization of the anomalous DOS near the interface region. We set the isosurface level to a fixed value (1.7×10^{-7} 1/Bohr³), which indicate regions where $\chi(\mathbf{r})$ is constant. To enhance visualization, the isosurface on the PbTe side of the heterostructure (blue) is set to a value 10 times smaller than the Pb side (red).

From the computed anomalous charge density $\chi(\mathbf{r})$, we explain the SC-gap dependence from the position along the heterostructure. On the Pb side, $\chi(\mathbf{r})$ oscillates around a constant value with maxima at the Pb atomic positions [Fig. 3.5.(a)]. The oscillations are likely due to the finite size of the simulated system. On the PbTe side, $\chi(\mathbf{r})$ decays from the interface towards the surface. We fitted an exponential function to $\chi(\mathbf{r})$ and calculated an effective superconducting coherence length of $\xi \sim 14$ Å. Note that ξ is a result of an effective pairing potential that describes the average build-up of anomalous charge densities in the superconductor.

As discussed above, the superconducting gap $\Delta(\mathbf{k})$ exhibits anisotropy in $\mathbf{k}$ -space, meaning its magnitude varies across different $\mathbf{k}$ -points. The anomalous charge density is directly related to the pairing potential by the following expression:

$$\Delta_{\mu\nu}^{\alpha\beta}(\mathbf{k}) = - \sum_{l=0,1,2,3} \sum_{\gamma} i\sigma_l^{\alpha\gamma} \sigma_2^{\gamma\beta} \times \int_{\text{BZ}} d\mathbf{k}' \lambda_l^{\mu\nu}(\mathbf{k} - \mathbf{k}') \chi_{\mu\nu}^l(\mathbf{k}').$$

We visualize the anomalous charge density in [Fig. 3.5.(b)], where the isosurface level indicate regions with constant $\chi(\mathbf{r})$. To enhance visualization, the isosurface on the PbTe side

of the heterostructure [blue regions in Fig. 3.5.(b)] is set to a value 10 times smaller. The anomalous charge density penetrates in the PbTe region, it is enhanced at the interface, and it is highly anisotropic. On the Pb side of the HS, the anomalous density is homogenous in the central region (layers 21–22) similar to bulk Pb, while it deforms around the interface and the vacuum region. Therefore, the pairing potential in the HS is not isotropic.

4 Computational methods

To model the PbTe/Pb interface, we computed its electronic structure using density functional theory (DFT) as implemented in the SIESTA code^{26,34}, including spin-orbit coupling and the PBE exchange-correlation functional³⁵. We employed optimized norm-conserving Vanderbilt pseudopotentials (ONCVSP³⁶) in PSML format³⁷ from PseudoDojo database³⁸. The Kohn-Sham equations were solved using standard double-zeta polarized basis sets of localized atomic orbitals on a $60 \times 60 \times 1$ Monkhorst-Pack grid. Real space integral were evaluated on grids with a cut-off energy of 2000 Ry for the SC state calculations and 500 Ry for the normal state ones. The Fermi-Dirac occupation function was smoothed using an electronic temperature of 0.1 meV, to ensure that the broadening of the electronic states is well below the size of the superconducting gap. All crystal structures were relaxed using the FIRE algorithm with a force threshold of 0.005 eV/Å and a maximum stress tolerance of 0.5 meV/Å³.

The superconducting properties of PbTe/Pb were modeled using the SIESTA-BdG method²⁵. In this approach a semi-empirical superconducting pairing potential is introduced on top of the self-consistent Kohn-Sham Hamiltonian describing the normal state. We employed the *fixed- Δ* solution method, where the BdG Hamiltonian is diagonalized in the presence of a fixed pairing potential Δ . Multiple SCF steps are performed. Self-consistency is achieved on the normal state Hamiltonian, assuming that perturbations induced by the self-consistent update of the anomalous charge are negligible. In the *fixed- Δ* solution method, the pairing potential Δ is a semi-empirical parameter. The initial value of the pairing potential is expressed, in real space via a superconducting strength parameter $\bar{\Delta}$ as $\Delta(\mathbf{r}) = \bar{\Delta}g(\mathbf{r})$, with $g(\mathbf{r})$ a general function. We refer to this approach as the *superconducting strength representation*. This real-space approach is useful to model heterostructures such as the one studied in this work. In the case of the (4,-5) PbTe/Pb HS we initialize the superconducting pairing potential as touching spherical hardwells with radius $r = 1.58$ Å and strength $\bar{\Delta} = 1.50$ meV around Pb atoms.

Our approach utilizes an effective pairing potential that describes the average build-up of anomalous charge densities in the superconductor, providing a robust framework for interpreting the physical phenomena. Therefore, we do not expect large variations on the superconducting properties of the HS as the Pb thickness changes, even though finite-size effects can significantly influence the SC-DOS in planar Josephson junctions.^{39–41} Thus, our approach is suitable to estimate the superconducting penetration depth.

We computed the triplet components of the SC-DOS and anomalous DOS as outlined in the SIESTA-BdG work²⁵, finding that their values are negligibly small.

5 Conclusion

We used a combined Kohn–Sham and Bogoliubov–de Gennes approach to investigate the semiconductor–superconductor (SM–SC) heterostructure composed of PbTe and Pb, focusing on the interfacial properties and the potential applicability of this system for detecting Majorana Zero Modes (MZMs)^{15,17,42}. We discussed the (normal state) metallization of the heterostructure driven by strong hybridization between PbTe and Pb states at the interface. We predict a significant difference in electrostatic potential at the interface, which poses a challenge in achieving the necessary energy alignment between the SM Zeeman gap and SC gap. These findings remain robust against strain and electric field.

In the superconducting state, a soft BCS–like superconducting gap is computed, indicating a weak superconducting coupling between the two systems²². Moreover, we predicted proximity–induced superconductivity in the PbTe region of the heterostructure. We resolved the superconducting density of states layer by layer, revealing that the induced SC gap is enhanced near the interface, with a softened SC gap on the Pb side. We analyzed the shape and decay of the anomalous charge density $\chi(\mathbf{r})$, revealing an anisotropic pairing potential. We observed a weak superconducting coupling regime at the interface, which prevents the superconductor to overscreen the HS properties. The weak regime favours the device’s tunability with gate and bias voltages, creating a route to get the desirable energy alignment between the two materials. Our findings strengthen the understanding of the physics governing PbTe/Pb hybrid devices and their potential application in hosting Majorana Zero Modes (MZMs).

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Authorship statement

This chapter is based on the work of Reho et al.¹. RR conducted the first-principles simulations and developed the necessary routines within the SIESTA and sisL codes. RR also took the lead in writing the manuscript. ABM contributed to the physical interpretation and provided

feedback on the manuscript. ZZ, as the last author, secured funding for the project and assessed the correctness of the manuscript.

6 Appendices

A Geometrical aspect of the HS

We constructed the PbTe/Pb HS, stacking 15 layers slab of PbTe cell and 11 layers of Pb along the [001] direction. The HS extends infinitely in the x and y directions. Periodic replicaes are separated by 26 Å vacuum along the z-axis. The PbTe slab was constructed by rotating the in-plane conventional cell by 45 degrees and reconstructing its primitive cell. The Pb slab was constructed by repeating the conventional cell along the [001] direction 12 times and removing one layer to achieve 11 layers of Pb. Farey sequences⁴³ were employed to identify commensurate cells for the full heterostructure. This method inherently introduces strain in the system. We considered several strained configurations of the PbTe/Pb heterostructure. The strain on each side of the heterostructure is defined as:

$$\text{strain} = \frac{a_{\text{hs}} - a_{\text{rlx},i}}{a_{\text{rlx},i}} \quad i = \text{Pb, PbTe} \quad (\text{A1})$$

where a_{hs} is the lattice parameter of the heterostructure while $a_{\text{rlx},i}$ is the relaxed lattice parameter of the constituent materials.

B Bulk Pb and bulk PbTe

We present the crystal structure and electronic properties of bulk Pb and PbTe, emphasizing the orbitals' contribution to the electronic states near the Fermi level. The interaction and hybridization between these states are critical for the proximity-induced superconductivity effect at the PbTe/Pb interface.

Bulk Pb

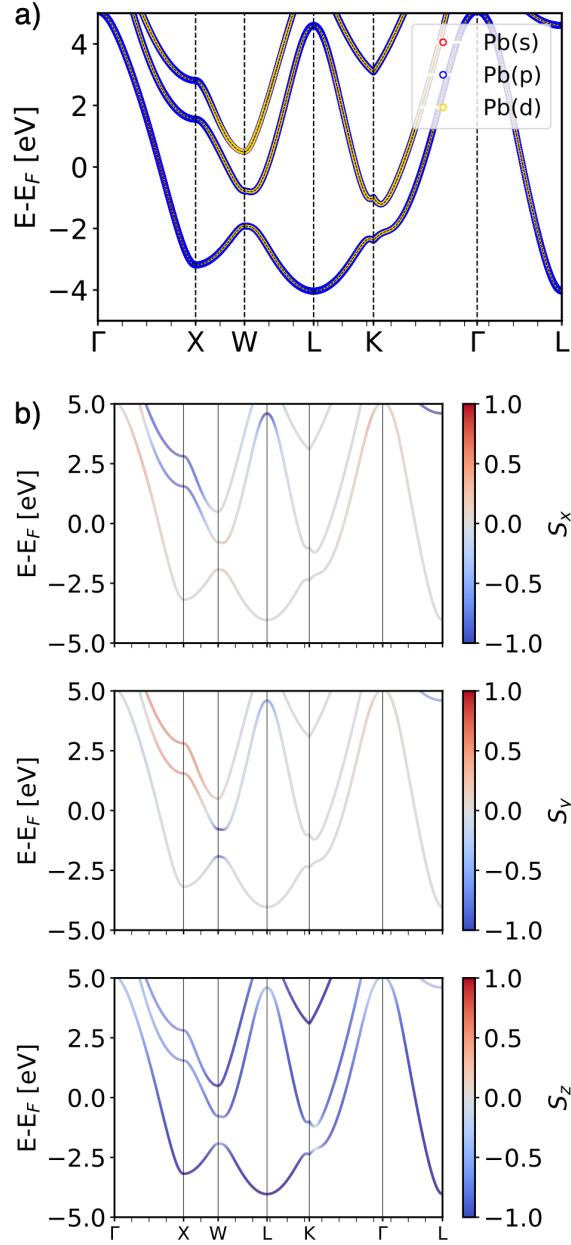


Figure B1 Orbital (a) and spin (b) projected bands structure of bulk Pb in the normal state. In (a) we observe that the electronic states crossing the Fermi level are p and d orbitals. In (b) we observe a spin flip at W for S_x and S_y spin orientations.

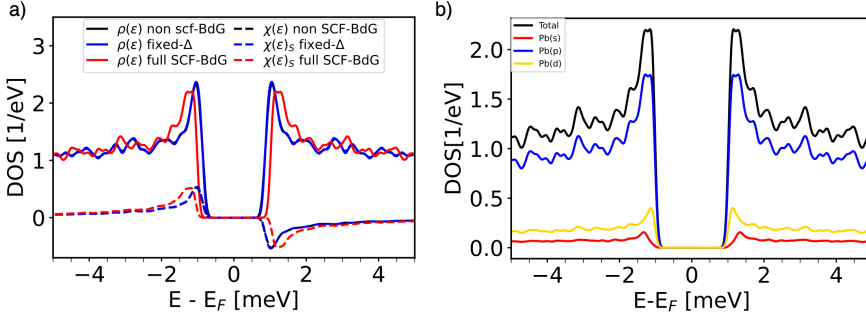


Figure B2 (a) SC-DOS (continuous lines) and ADOS (dashed lines) of bulk Pb computed with the solution methods: *non SCF-BdG* (black), *Fixed- Δ* (blue), and *Full SCF-BdG* (red). The *Full SCF-BdG* method reveals a small splitting of the main coherence peaks. (b) Orbital contribution to the DOS using the *Full SCF-BdG* method, showing that the main contributions from *p* and *d* orbitals, as indicated by the orbitals crossing the Fermi level. Similar results are found using the other two solution methods.

The space group of Pb is $Fm\bar{3}m$. Structural relaxation yielded a primitive lattice vector of $a_{prim} = 3.547 \text{ \AA}$ ($a_{conv} = 5.016 \text{ \AA}$). Pb behaves as a metal with an orbital character dominated by *d* and *p* orbitals close to the Fermi level at the high-symmetry points *W* and *K* [Fig. B1.(a)]. The total spin moment is zero, in agreement with bulk Pb being not magnetic. We investigate the spin projection for the electronic states close to the Fermi level, as those are relevant for the formation of Cooper pairs. The spin-projected band structure [Fig. B1.(b)] show that the spin components S_x and S_y change sign at *W* (spin flip).

We modeled the superconducting state using the SIESTA-BdG code²⁵, employing three solution methods: *non SCF-BdG*, *Fixed- Δ* , and *full SCF-BdG*. All three solution methods predict a conventional U-shaped SC gap of ~ 3 meV (Fig. B2). We initialize the pairing potential in the *superconducting strength representation* (on a real-space grid) as touching spherical hardwells with radius $r = 1.58 \text{ \AA}$. In the *non SCF-BdG* and *fixed- Δ* methods, the initial strength of the superconducting pairing potential is $\bar{\Delta} = 1.50$ meV. In the *full SCF-BdG* method, instead, the initial value of the superconducting coupling is $\lambda(r) = 80.3$ eV. We computed the orbital projected superconducting density of states (Fig. B2) and conclude that Pb *p* and *d* are the dominant electronic states close to the Fermi level, and hence relevant for the superconducting properties. The *full SCF-BdG* predicts that the coherence peak at $\sim \pm 1.8$ meV displays a small splitting. This splitting is physical and has been experimentally measured in bulk Pb^{30,31}, and found to be $\sim 0.1 - 0.2$ meV depending on the crystal direction. Simulations with the KKR-BdG method have analyzed the gap anisotropy and identified three superconducting gaps³². In our earlier work²⁵, we report two superconducting gaps in bulk Pb, consistent with these findings. Accurately resolving the splitting of the coherence peak requires an extremely low smearing temperature ($T = 0.002$ meV). We note that the coherence peak splitting is only predicted within the *full SCF-BdG* method: the splitting is not present when the SC-DOS is computed with the *fixed- Δ* and *non scf-BdG* methods.

Bulk PbTe

The space group of PbTe is $Fm\bar{3}m$. Structural relaxation yielded a primitive lattice vector of $a_{prim} = 4.578 \text{ \AA}$ (to be compared with the experimental value $4.568 \text{ \AA}$ ^{44,45}). PbTe is a semiconductor. Our calculations predict its spin-orbit coupling gap to be 0.023 eV in the ground state⁴⁶. The magnitude of the gap varies with strain and can reach hundreds of meV⁴⁶ as showed in Table B1. The states close to the Fermi level are predominantly composed of Te p -orbitals in the valence manifold (with minor contributions from Pb s, p, d -orbitals) and Pb p -orbitals in the conduction manifold [Figs. B3.(a,b)]. Near the Fermi level at L , the $S_x S_y$ spin components of the bands change sign while we observe a spin flip along the S_z component. For energies 1.5 eV above the Fermi level, we observe a $\sim 0.5 \text{ eV}$ SOC splitting in the S_x and S_y components [Fig. B3.(b)].

Table B1 Electronic gap (ΔE_L) of PbTe as a function of its in-plane lattice parameter. The configuration that matches the value of the lattice parameter for the (4,-5) PbTe/Pb HS is highlighted in bold.

Lattice parameter [$\text{\AA}$]	ΔE_L [eV]
4.39	0.251
4.44	0.224
4.49	0.147
4.53	0.069
4.58	0.023
4.63	0.058
4.67	0.107
4.72	0.149
4.76	0.181

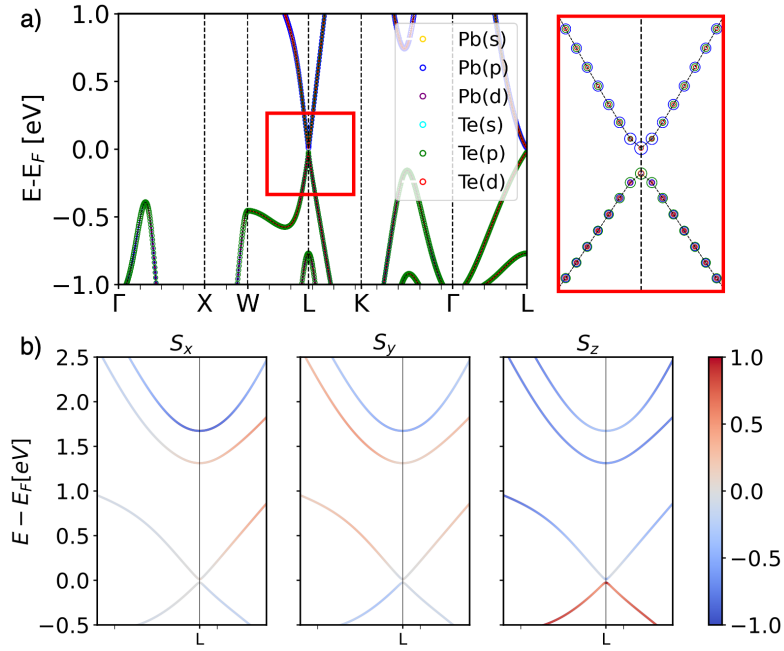


Figure B3 Electronic band structures for PbTe bulk. (a) Orbital projected band structure. The inset shows an energy region close to the Fermi level. (b) Spin projected band structure. Positive and negative spins are depicted in red and blue, respectively.

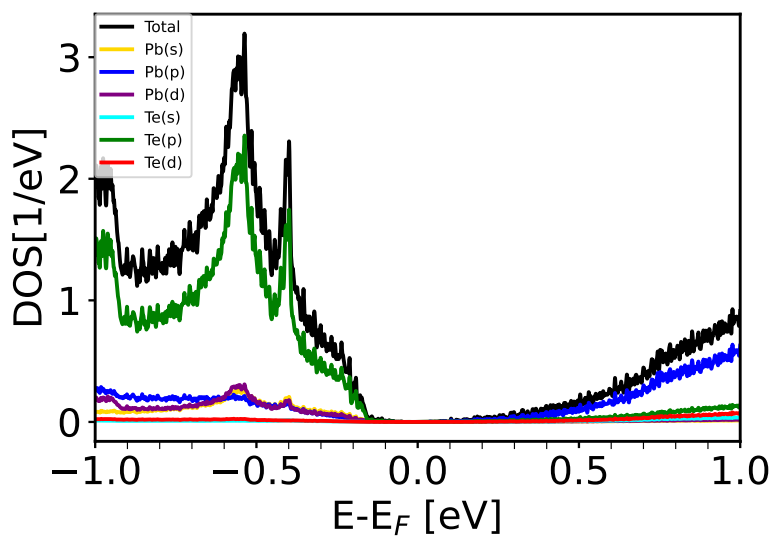


Figure B4 Projected DOS of bulk PbTe. Near the Fermi level, the valence band is predominantly influenced by Te p orbitals, whereas the conduction band shows a substantial contribution from Pb p orbitals

C Initialization of the Pairing Potential and Its Impact on the Superconducting Properties

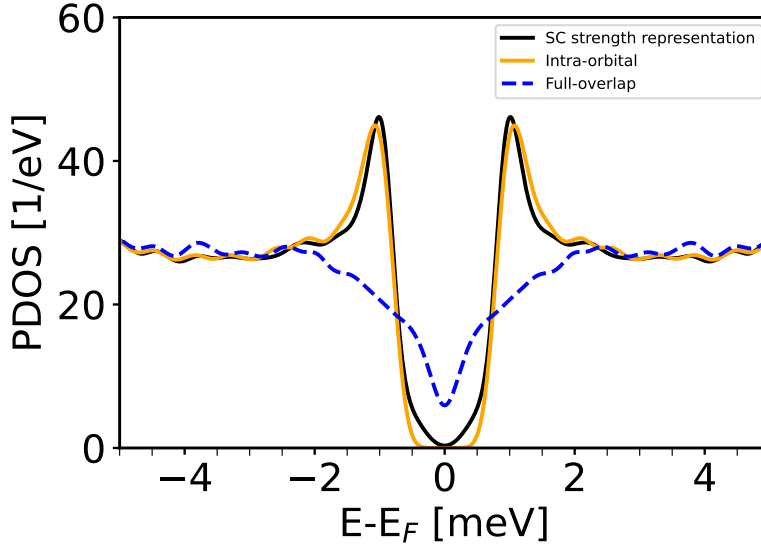


Figure C1 The SC-DOS, $\rho(\varepsilon)$, of the (4,-5) PbTe/Pb HS is computed using the *superconducting strength representation method* (solid black line) and the *orbital representation method*. In the orbital representation, we evaluate intra-orbital coupling (solid orange line) and full-overlap coupling (dashed blue line). When pairing occurs between electrons and holes within the same orbital on the same atom (intra-orbital), a conventional U-shaped gap emerges. In contrast, when superconducting coupling involves interactions between different orbitals across different atoms (superconducting strength representation or full-overlap), the hard superconducting gap becomes softened.

In the SIESTA-BdG method one can employ different methods for solving the BdG equations and different approaches for initializing the pairing potential Δ ²⁵. We tested multiple initializations of the pairing potential. In the main text, we report results obtained within the superconducting strength representation for all simulations.

We compared the superconducting strength and orbital representation (*intra-orbital* coupling or *full-overlap*) for the PbTe/Pb heterostructure (Fig. C1). The intra-orbital coupling lacks the interactions between different orbitals that can be captured by the superconducting strength representation, making it more localized. As a result, the *intra-orbital* coupling misses the hybridization and coupling between states belonging to the PbTe and Pb sides of the heterostructure, leading to a U-shaped DOS. However, when we excessively couple states belonging to different orbitals and atoms (full-overlap), the superconducting gap closes. Therefore, initializing the pairing potential in real-space as touching sphere hardwells is a physically intuitive and reasonable approach.

D Additional figures and tables

This section presents additional figures and tables related to the PbTe/Pb HS. We performed a Mulliken charge analysis and calculated the excess charge ΔQ under different strain conditions, finding that ΔQ remains robust against strain variations. (Table D1). A layer-by-layer decomposition of ΔQ (Fig. D1) reveals charge depletion on the PbTe side of the interface, with a corresponding accumulation on the Pb side.

Fig. D2 shows the BdG spectrum of the (4,-5) PbTe/Pb HS. The SC gap $\Delta(\mathbf{k})$ is anisotropic, as evidenced by the variations in the width of the splitting of the BdG dispersion along the Brillouin Zone

Table D1 Excess of charge ΔQ computed for different strain. Positive (negative) values of ΔQ denote the acceptor (donor) character of the layer. We compare the excess of charge on the PbTe side (ΔQ_{PbTe}) of the heterostructure, with the one on the Pb side (ΔQ_{Pb}). The (4, -5) HS is highlighted in bold.

strain (PbTe/Pb) [%]	ΔQ_{PbTe} [1/e]	ΔQ_{Pb} [1/e]
1.0%/-7.7%	-0.096	0.096
2.0%/-6.8%	-0.098	0.098
3.0%/-5.9%	0.101	0.101
4.0%/-5.0%	-0.103	0.103
5.0%/-4.0%	-0.107	0.107
6.0%/-3.2%	-0.106	0.106
7.0%/-2.3%	-0.109	0.109
8.0%/-1.3%	-0.114	0.114
9.0%/-0.4%	-0.119	0.119

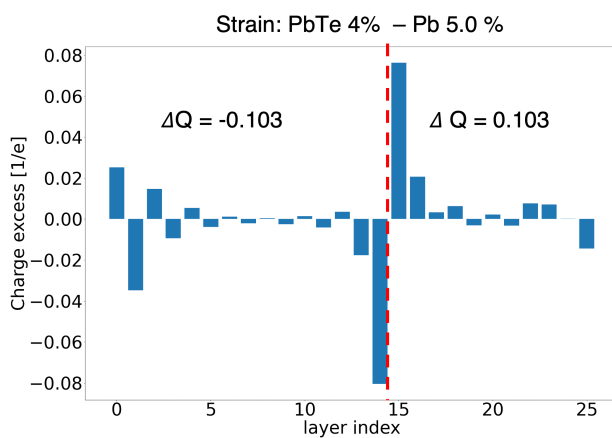


Figure D1 Mulliken charge analysis for (4,-5) PbTe/Pb HS. Layer-by-layer excess charge. Positive (negative) values of ΔQ denote the acceptor (donor) character of the layer. The red dashed line denote the separation between the PbTe and Pb side of the heterostructure. The sum of the excess charge on the PbTe and Pb side ΔQ is reported in the plot.

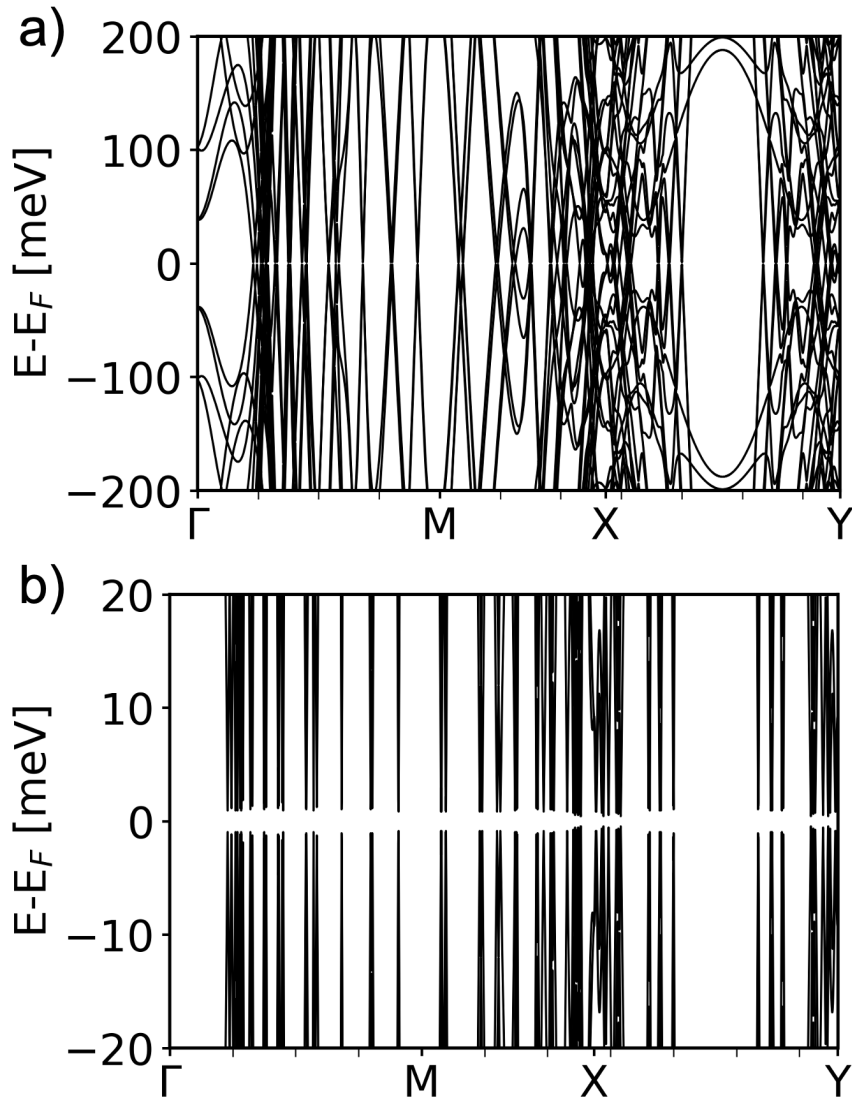


Figure D2 BdG spectrum for the (4,-5) PbTe/Pb HS. The right panel displays the superconducting states dispersion in a narrower energy range.

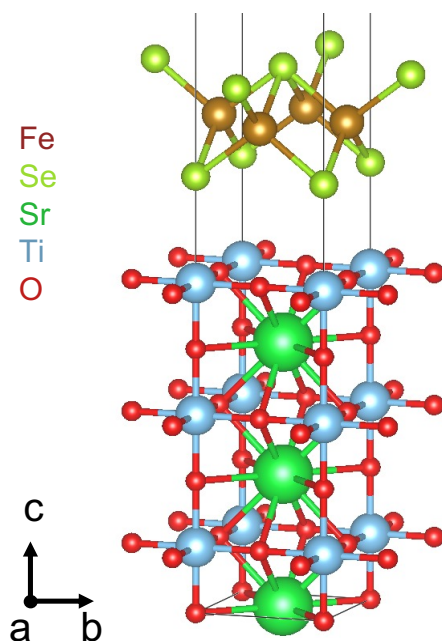
Bibliography

- 1 R. Reho, A. Botello-Méndez, and Z. Zanolli, arXiv preprint arXiv:2412.01749 (2024).
- 2 R. Li, W. Song, W. Miao, Z. Yu, Z. Wang, S. Yang, Y. Gao, Y. Wang, F. Chen, Z. Geng, *et al.*, Nano Letters **24**, 4658 (2024).
- 3 G. Springholz, G. Bauer, and G. Ihninger, Journal of crystal growth **127**, 302 (1993).
- 4 G. Grabecki, J. Wróbel, T. Dietl, E. Janik, M. Aleszkiewicz, E. Papis, E. Kamińska, A. Piotrowska, G. Springholz, and G. Bauer, Physica E: Low-dimensional Systems and Nanostructures **34**, 560 (2006).
- 5 S. C. Ten Kate, M. F. Ritter, A. Fuhrer, J. Jung, S. G. Schellingerhout, E. P. Bakkers, H. Riel, and F. Nichele, Nano Letters **22**, 7049 (2022).
- 6 Y. Jiang, S. Yang, L. Li, W. Song, W. Miao, B. Tong, Z. Geng, Y. Gao, R. Li, F. Chen, *et al.*, Physical Review Materials **6**, 034205 (2022).
- 7 F. Yang, F. Qu, J. Shen, Y. Ding, J. Chen, Z. Ji, G. Liu, J. Fan, C. Yang, L. Fu, *et al.*, Physical Review B—Condensed Matter and Materials Physics **86**, 134504 (2012).
- 8 M.-X. Wang, C. Liu, J.-P. Xu, F. Yang, L. Miao, M.-Y. Yao, C. Gao, C. Shen, X. Ma, X. Chen, *et al.*, Science **336**, 52 (2012).
- 9 S.-Y. Xu, N. Alidoust, I. Belopolski, A. Richardella, C. Liu, M. Neupane, G. Bian, S.-H. Huang, R. Sankar, C. Fang, *et al.*, Nature Physics **10**, 943 (2014).
- 10 J.-P. Xu, C. Liu, M.-X. Wang, J. Ge, Z.-L. Liu, X. Yang, Y. Chen, Y. Liu, Z.-A. Xu, C.-L. Gao, *et al.*, Physical Review Letters **112**, 217001 (2014).
- 11 G. Yue, C. Zhang, E. D. Huemiller, J. H. Montone, G. R. Arias, D. G. Wild, J. Y. Zhang, D. R. Hamilton, X. Yuan, X. Yao, *et al.*, Physical Review B **109**, 094511 (2024).
- 12 Z. Huang, Z. Zhang, and P. Cui, Physical Review B **109**, 224516 (2024).
- 13 Z. Cao, D. E. Liu, W.-X. He, X. Liu, K. He, and H. Zhang, Physical Review B **105**, 085424 (2022).
- 14 C. Payá, S. D. Escribano, A. Vezzosi, F. Peñaranda, R. Aguado, P. San-Jose, and E. Prada, Physical Review B **109**, 115428 (2024).
- 15 E. Prada, P. San-Jose, M. W. A. de Moor, A. Geresdi, E. J. H. Lee, J. Klinovaja, D. Loss, J. Nygård, R. Aguado, and L. P. Kouwenhoven, Nature Reviews Physics **2**, 575 (2020).
- 16 R. Aguado, La Rivista del Nuovo Cimento **40**, 523 (2017).
- 17 V. Mourik, K. Zuo, S. M. Frolov, S. Plissard, E. P. Bakkers, and L. P. Kouwenhoven, Science **336**, 1003 (2012).

- 18** Y. Wang, W. Song, Z. Cao, Z. Yu, S. Yang, Z. Li, Y. Gao, R. Li, F. Chen, Z. Geng, *et al.*, Proceedings of the National Academy of Sciences **121**, e2406884121 (2024).
- 19** P. Dong, X. Hou, J. He, Y. Zhang, Y. Ding, X. Zeng, J. Wang, Y. Wu, K. Watanabe, T. Taniguchi, *et al.*, Physical Review B **109**, L140503 (2024).
- 20** P. Rüßmann and S. Blügel, arXiv preprint arXiv:2208.14289 (2022).
- 21** K. Park, G. Csire, and B. Ujfalussy, Physical Review B **102**, 134504 (2020).
- 22** W. S. Cole, S. Das Sarma, and T. D. Stanescu, Physical Review B **92**, 174511 (2015).
- 23** N. Read and D. Green, Physical Review B **61**, 10267 (2000).
- 24** A. Y. Kitaev, Physics-uspekhi **44**, 131 (2001).
- 25** R. Reho, N. Wittemeier, A. H. Kole, P. Ordejón, and Z. Zanolli, Phys. Rev. B **110**, 134505 (2024).
- 26** A. Garcia, N. Papior, A. Akhtar, E. Artacho, V. Blum, E. Bosoni, P. Brandimarte, M. Brandbyge, J. I. Cerdá, F. Corsetti, *et al.*, The Journal of chemical physics **152**, 204108 (2020).
- 27** R. S. Mulliken, The Journal of chemical physics **23**, 1833 (1955).
- 28** A. Baldereschi, S. Baroni, and R. Resta, Physical Review Letters **61**, 734 (1988).
- 29** L.-M. Wang, in *2006 25th International Conference on Microelectronics* (IEEE, 2006) pp. 576–579.
- 30** B. L. Blackford and R. H. March, Physical Review **186**, 397 (1969).
- 31** G. I. Lykken, A. L. Geiger, K. S. Dy, and E. N. Mitchell, Physical Review B **4**, 1523 (1971).
- 32** T. G. Saunderson, J. F. Annett, B. Újfalussy, G. Csire, and M. Gradhand, Physical Review B **101**, 064510 (2020).
- 33** S. Takei, B. M. Fregoso, H.-Y. Hui, A. M. Lobos, and S. Das Sarma, Physical Review Letters **110**, 186803 (2013).
- 34** J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, Journal of Physics: Condensed Matter **14**, 2745 (2002).
- 35** J. P. Perdew, K. Burke, and M. Ernzerhof, Physical Review Letters **77**, 3865 (1996).
- 36** D. Hamann, Physical Review B **88**, 085117 (2013).
- 37** A. García, M. J. Verstraete, Y. Pouillon, and J. Junquera, Computer Physics Communications **227**, 51 (2018).

- 38** M. van Setten, M. Giantomassi, E. Bousquet, M. Verstraete, D. Hamann, X. Gonze, and G.-M. Rignanese, *Computer Physics Communications* **226**, 39 (2018).
- 39** U. A. Aceves Rodriguez, F. S. M. Guimarães, and S. Lounis, *Nanomaterials* **14**, 254 (2024).
- 40** H. Yamazaki, G. Csire, N. Kucska, N. Shannon, H. Takagi, and B. Ujfalussy, *arXiv preprint arXiv:2404.09784* (2024).
- 41** A. Shanenko, M. Croitoru, and F. Peeters, *Physical Review B—Condensed Matter and Materials Physics* **75**, 014519 (2007).
- 42** C. Nayak and F. Wilczek, *Nuclear Physics B* **479**, 529 (1996).
- 43** I. Niven, H. S. Zuckerman, and H. L. Montgomery, *An introduction to the theory of numbers* (John Wiley & Sons, 1991).
- 44** D. R. Lide, *CRC handbook of chemistry and physics*, Vol. 85 (CRC press, 2004).
- 45** W. D. Lawson, *Journal of Applied Physics* **22**, 1444 (1951).
- 46** P. Aguado-Puente, S. Fahy, and M. Grüning, *Physical Review Research* **2**, 043105 (2020).

The crucial role of substrate in FeSe/STO: new insights to interface-driven superconductivity from first-principles



Based on

R. Reho, N. Wittemeier, A. H. Kole, A. R. Botello-Méndez, Z. Zanolli, “The crucial role of substrate in FeSe/STO: new insights to interface-driven superconductivity from first-principles”, arXiv:2503.15025 (2025)

Abstract

We investigate the superconducting properties of monolayer FeSe, both freestanding (ML FeSe) and on SrTiO₃ (STO), by simultaneously solving the Kohn-Sham Density Functional Theory and Bogoliubov–de Gennes equations. Our results demonstrate that the substrate profoundly alters both the normal-state and superconducting properties of FeSe. We identify proximity-induced superconductivity in the interfacial TiO₂ layer of STO, due to hybridization between Fe *d* and O *p* orbitals. This hybridization results in a fivefold increase in the superconducting gap width and confines superconducting states to the *M* point in the Brillouin Zone. This is in contrast to ML FeSe, where superconductivity emerges at both the Γ and *M* points. Furthermore, the substrate modifies the orbital character of the states responsible for superconductivity, which change from Fe d_{z^2} in ML FeSe to Fe d_{xz}/d_{yz} in FeSe/STO. In both systems, we demonstrate an anisotropic superconducting gap with multiple coherence peaks, originating at different k-points in the Brillouin Zone. Additionally, in FeSe/STO, we identify emerging states unique to the superconducting phase arising from electron-hole hybridization at *M*, in agreement with experiments. Our findings highlight the decisive impact of substrate (hybridization, strain, charge transfer, magnetic order) on the superconducting properties of FeSe. We suggest potential pathways for engineering novel high-temperature FeSe-based superconductors by leveraging interfacial interactions in substrates with high electron affinity. This chapter is based on Reho et al¹. RR conducted the first-principles simulations and developed the necessary routines in the SIESTA and sisL codes. RR also took the lead in writing the manuscript.

1 Introduction

Monolayer (ML) FeSe on SrTiO₃ (FeSe/STO) features high critical temperature ($T_C \sim 40\text{--}100$ K) making it appealing for both fundamental research and development of next-generation quantum devices^{2–4}. The electronic dispersion of FeSe is highly sensitive to factors such as magnetic configurations, structural changes (strain) and the dielectric environment (doping and dipole interactions)⁵. The presence of a substrate affects all the above properties which, in turn, directly influence the superconducting pairing mechanism⁶. Experiments on FeSe/STO proved the conventional BCS-like s -wave nature of the superconducting pairing potential⁷. Zhang *et al.*⁸ reported two anisotropic superconducting gaps driven by Fe d_{xz}/d_{yz} (20 meV wide) and Fe d_{xy} (26 meV wide), reflecting the multiorbital nature of the Fermi surface and the orbital-dependent pairing in iron chalcogenides. Currently, it is still unclear whether FeSe/STO exhibits single or double coherence peaks⁹, the interplay between its magnetic and electronic properties is not fully understood, the agreement between theoretical predictions and experiments is incomplete, and the origin of high T_C is unknown.

Tight-binding models of FeSe ML and FeSe/STO successfully describe specific experiments but lack general applicability^{2,9} and are restricted to a normal state description. State-of-the-art theoretical studies^{10–12} combine dynamical mean field theory (DMFT) and the quasiparticle self-consistent GW approximation to describe the superconducting instability of FeSe/STO from the spin and charge response of the system. These studies explain the dependence of the critical temperature on doping and Fe-O interaction. This method includes electron correlations and requires careful parameter tuning.

In this work, we simultaneously solve the Kohn-Sham Density Functional Theory (DFT) and Bogoliubov–de Gennes (BdG) equations^{13,14} to analyze and interpret both the normal and superconducting states of ML FeSe and FeSe/STO. Our findings highlight the significant impact of the substrate on the superconducting (SC) phase of FeSe, and emphasize how interface-driven superconductivity can be leveraged to enhance superconductivity in FeSe. In the normal state, metallicity in ML FeSe arises from an electron pocket at M and a hole pocket along the $\Gamma - X$. In contrast, in FeSe/STO, the hole pocket shifts to lower energies within the valence band. This difference influences the mechanism behind superconductivity. In the superconducting phase, we predict proximity-induced superconductivity on the interfacial O atoms and a fivefold widening of the SC gap in FeSe/STO compared to ML FeSe. We elucidate the origins of superconducting coherence peaks in the superconducting density of states (SC-DOS) of both system, identifying univocally the real-space orbitals and momentum vector $\mathbf{k}$ associated with these peaks. We characterize the Bogoliubov–de Gennes spectrum and predict an anisotropic, momentum-dependent superconducting gap $\Delta(\mathbf{k})$ for both system. We analyze the changes in electronic dispersion between freestanding ML FeSe and FeSe/STO, identifying the dominant roles of Fe d and O p orbitals in shaping the Fermi surface. We conclude that FeSe and FeSe/STO act as fundamentally different materials, as substrate hybridization, interfacial interactions and charge transfer play a crucial role in shaping the microscopic superconducting mechanism. This behaviour can be generalized to the whole

family of iron superconductors. Substrate engineering presents a promising approach to design superconductors with enhanced T_C .

2 Results

2.1 Structural properties

In the following, we focus on the tetragonal phase of ML FeSe, in view of comparing it with Fe/STO¹. The primitive unit cell of FeSe consists of two Fe and two Se atoms. The Fe atoms form two tetragonal sub-lattices, offset relative to each other [Fig. 2.1.(a)]. The Se atoms form tetrahedra centered on the Fe atoms. After structural relaxation, the lattice parameter of ML FeSe is 3.71 Å and the Se-Se distance is 1.44 Å. FeSe is usually grown by molecular beam epitaxy (MBE) on the TiO₂ terminated surface of STO⁹. For this reason, we first modeled STO as a six-layer slab and performed a full relaxation (atoms and unit cell), obtaining a lattice constant of 3.92 Å. The atomic positions of the FeSe/STO heterostructure were then relaxed while keeping the STO lattice fixed, resulting in 5.7% strain on FeSe ML. The FeSe/STO heterostructure was constructed by placing the bottom Se atom of FeSe directly above the top Ti atom of the STO substrate. After relaxation, the Se-Ti distance was 2.95 Å [Fig. 2.3.(a)].

2.2 Magnetic instabilities

FeSe, both in its bulk and ML forms, exhibits a complex energy landscape characterized by multiple competing magnetic configurations. The lowest-energy magnetic state of bulk FeSe is theoretically predicted to be the staggered dimer phase¹⁵. However, long-range magnetic order is not observed in experiments. Indeed, bulk FeSe is a nematic quantum-disordered paramagnet, interpolating between the checkerboard antiferromagnetic (CB-AFM) and stripe AFM phases, both in the low ($T = 4$ K) and high temperature ($T = 110$ K) regimes¹⁶. For bulk and ML FeSe, we computed first-principles total energies of various magnetic configurations (Appendix A). In both cases, we found three low-energy competing magnetic configurations: staggered trimer, staggered dimer, and single stripe, followed by two CB-AFM phases (in- and out-of-plane) with similar total energies, approximately 68 meV above the lowest-energy configurations. We find that only the band structure of the out-of-plane CB phase [Fig. 2.1.(a)] resembles the ARPES electronic dispersion^{5,17}. For this reason, we focus on the CB phase despite its higher total energy compared to the other phases.

¹While single crystal FeSe undergoes a tetragonal-to-orthorhombic phase transition below 90K⁶, we expect that the symmetry of the STO surface (D_4) will stabilize the tetragonal FeSe phase of FeSe in FeSe/STO⁶

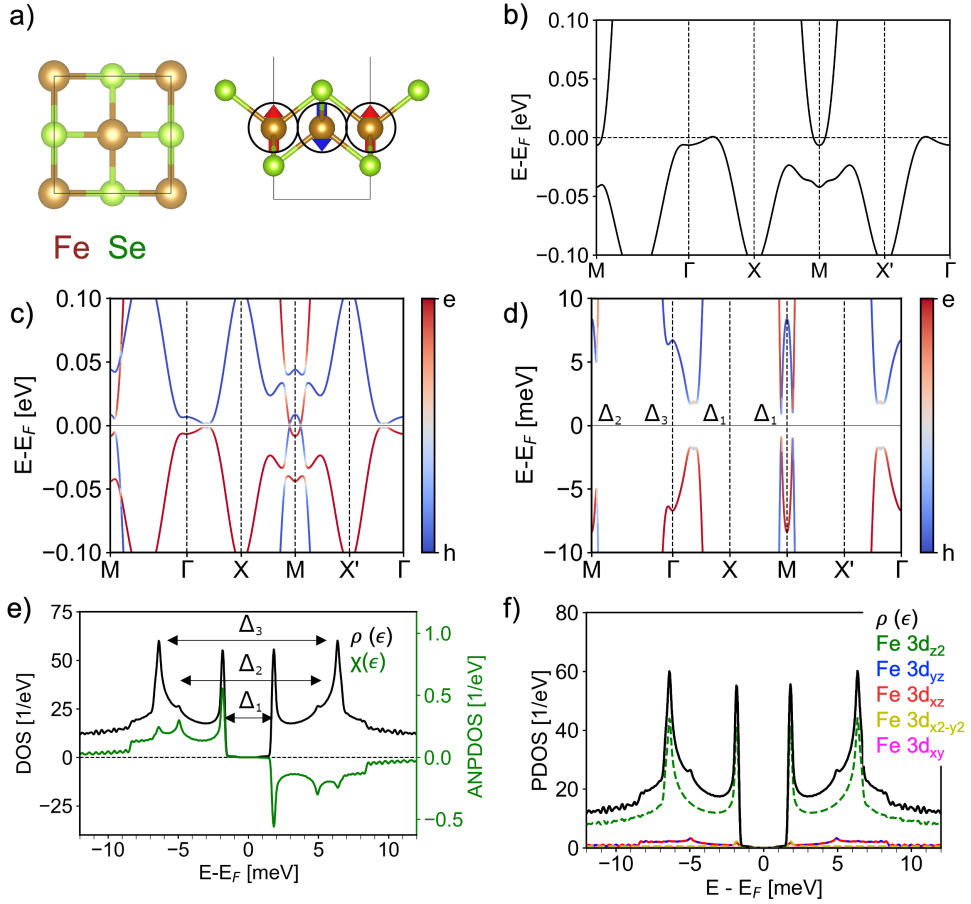


Figure 2.1 ML FeSe in the CB-AFM magnetic phase. (a) Top and side view of a unit cell of ML FeSe, with red and blue arrows representing spin directions and black circles illustrating the initialization of the superconducting pairing potential. (b) Normal state band structure. (c) Superconducting band structure projected on the electron (red) and hole (blue) components of the BdG spectrum. In (d) we report a narrower energy range around the SC gap. (e) SC-DOS ($\rho(\epsilon)$, black) and anomalous SC-DOS ($\chi(\epsilon)$, green) exhibiting superconducting gaps with widths $\Delta_1 = 3.6$, $\Delta_2 = 10.0$, and $\Delta_3 = 12.8$ meV. (f) SC-DOS projected over Fe orbitals.

2.3 Normal State Electronic Properties

The normal state band structure of ML FeSe features an electron pocket at M , a hole pocket along the $\Gamma - X$ high-symmetry line, and a relative maximum in the highest occupied valence band along the $\Gamma - M$ line [Fig. 2.1.(b)]. Analysis of the Mulliken populations¹⁸ reveals that FeSe acquires 0.13 electrons (per unit cell) from STO in the FeSe/STO heterostructure. As a result, the hole pocket along the $\Gamma - X$ direction is pushed below the Fermi-level, and the top valence band becomes flatter [Fig. 2.3.(b)].

The origin of metallicity in FeSe changes due to the interaction with the substrate: in the freestanding ML, metallicity is associated with the electron and a hole pocket, while in FeSe/STO only to the electron pocket at M . Analysis of the Fermi surfaces (Fig. C4) facilitate the visualization of these concepts: In FeSe ML, the hole pocket along $\Gamma - X$ is clearly visible in Fig. C4.(a), while the relative maxima along $\Gamma - M$ lies tens of meV lower in energy. In FeSe/STO, instead, the hole pocket near Γ disappears. At M , the electron pocket of FeSe/STO has a more pronounced hyperbolic shape with respect to FeSe ML [Fig. C4.(b)]. This will have consequences in the superconducting behaviour of the two materials.

Orbital projected band structures of FeSe and FeSe/STO [Fig. 2.2] show that the orbitals associated to the electron pocket at M are Fe d_{xz} , d_{yz} , and, to a lesser extent, d_{xy} . In FeSe/STO [Fig. C3] a hole pocket associated to interfacial O p_x/p_y states emerges at M . In the superconducting phase of FeSe/STO, the Fe d states hybridize with O p_x and O p_y and are responsible for the opening of the superconducting gaps at M , as predicted by Acharya et al.^{10–12}.

2.4 Superconducting state

In order to model the superconducting phase, we solve the SIESTA–BdG equations using the *fixed- Δ* approach¹³. We initialize the superconducting pairing potential $\Delta(\mathbf{r})$ in the *superconducting strength representation*. In this approach, the pairing potential is expressed, in real space, via a superconducting strength parameter $\bar{\Delta}$.

In ML FeSe, we initialize $\Delta(\mathbf{r})$ with spheres centered on the Fe atoms, each with $\bar{\Delta} = 15$ meV [Fig. 2.1.(a)]. The BdG spectrum [Fig. 2.1.(b, c)], the SC–DOS $\rho(\varepsilon)$ and anomalous DOS $\chi(\varepsilon)$ [Fig. 2.1.(d)] reveal several superconducting gaps/coherence peaks at energies ± 1.8 (Δ_1), ± 5 (Δ_2), and ± 6.4 meV (Δ_3). The orbital projected SC–DOS [Fig. 2.1.(f)] shows that the superconducting states are mostly dominated by the Fe $3d_{z^2}$ and, to a minor extent, by $3d_{xz}$ and $3d_{yz}$ orbitals. We identify the nature of the coherence peaks from the superconducting [Fig. 2.1.(d)] and orbital-projected normal state (Fig.2.2) band structures: The Δ_1 coherence peaks originate from Fe d_{z^2} along $X - M$ (close to M) and to d_{xz}/d_{yz} along $\Gamma - X$ [Figs. 2.2.(a, b, c)]. Δ_2 originates from Fe d_{xz} and d_{yz} along $M - \Gamma$ close to M [Fig. 2.2.(a, b)]. Δ_3 originates from Fe d_{z^2} along $\Gamma - M$ close to Γ [Fig. 2.2.(c)]. The Δ_1 and Δ_2 peaks exhibit strong electron-hole coupling, as evidenced by the band inversion between electrons (red) and holes (blue) at the corresponding gap [Fig. 2.1.(d)]. From the band structure, we observe a strong anisotropy in the momentum-resolved superconducting gap structure, i.e., $\Delta(\mathbf{k}_1) \neq \Delta(\mathbf{k}_2)$. We note that the type of Fe orbitals associated with superconductivity and the nature of superconductivity in bulk FeSe differs from ML FeSe: We have recently showed¹³ that the superconducting gap of bulk FeSe is V-shaped, and is due to Fe d_{xz} and d_{yz} only, in agreement with experiments¹⁹. FeSe ML, instead, features a U-shaped gap with multiple coherence peaks, mostly due to d_{z^2} and, in minor part, to d_{xz} and d_{yz} orbitals.

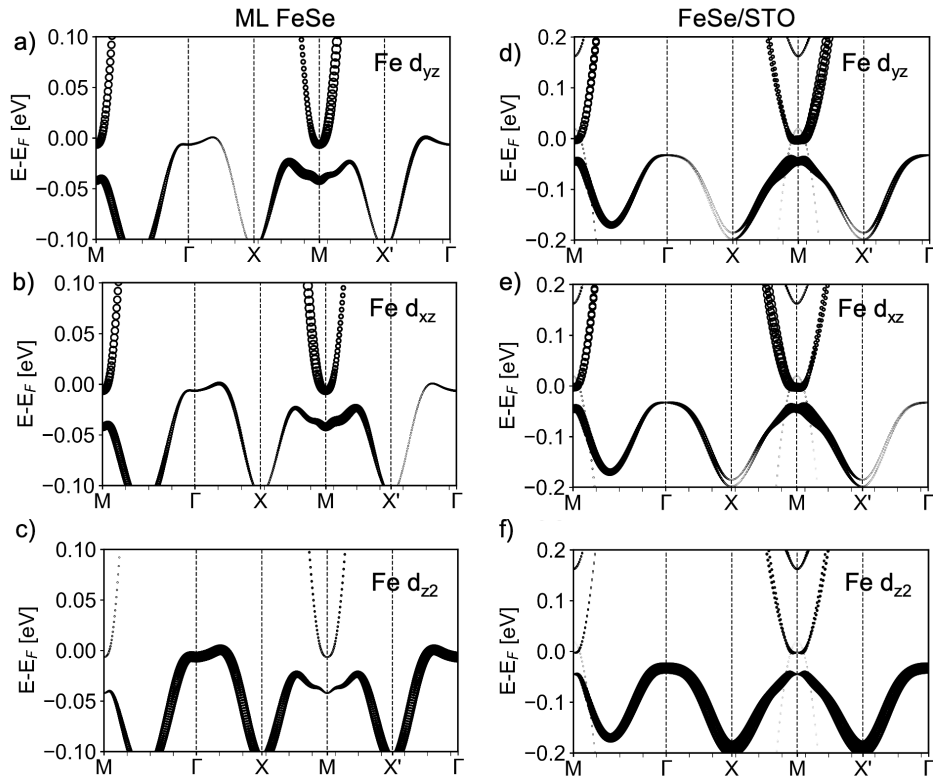


Figure 2.2 Normal state electronic band structures of (a-c) FeSe ML and (d-f) FeSe/STO projected on selected Fe orbitals. The projection over all orbitals is reported in Appendix Figs. C1 and C3

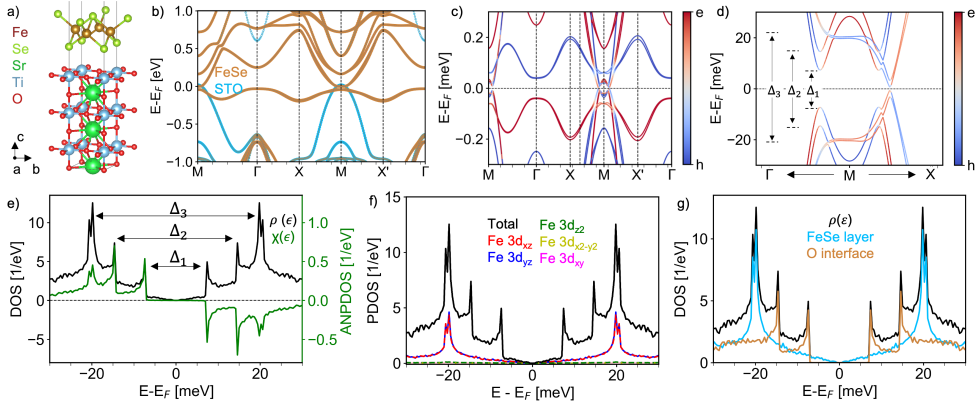


Figure 2.3 FeSe/STO with a TiO_2 -terminated surface, FeSe is in the checkerboard AFM magnetic phase: (a) atomistic model (side view). (b) Electronic band structure projected on FeSe (light brown) and STO (light blue). (c,d) Superconducting band structure in two different energy ranges. The color scheme highlights contributions from electron-like (red) and hole-like (blue) components of the BdG spectrum. (e) SC-DOS ($\rho(\varepsilon)$, black) and anomalous SC-DOS ($\chi(\varepsilon)$, green) with superconducting gap widths $\Delta_1 = 16.0$, $\Delta_2 = 28.6$, and $\Delta_3 = 40.0$ meV. (f,g) Total (black) and projected SC-DOS over (f) orbitals, and (g) FeSe layer (light brown) and interfacial O atoms (light blue).

FeSe/STO exhibits three pronounced peaks at ± 8 (Δ_1), ± 14.3 (Δ_2), and ± 20 meV (Δ_3) in the SC-DOS [Fig. 2.3.(e)]. The superconducting band structure [Fig. 2.3.(d)] shows several gaps of different sizes near M , along the $M - X$ and $M - \Gamma$ directions, demonstrating that $\Delta(\mathbf{k})$ is anisotropic. The normal-state band structure [Fig. 2.3.(b)] and the projected SC-DOS [Fig. 2.3.(g)] allow us to attribute the Δ_1 and Δ_2 peaks/gaps to the STO substrate and, more specifically, to the interfacial O p_x and p_y states [Figs. C3.(g,h)]. Therefore, we deduce that superconductivity has been induced by proximity on the oxygen atoms. The Δ_3 peak is, instead, due to Fe and originates along the $M - \Gamma$ line close to M . By comparing with FeSe ML, we deduce that the Fe-related SC-gap at M broadens and changes in orbital character from d_{z^2} to d_{xz} and d_{yz} , [Fig. 2.3.f] in FeSe/STO due to coupling with the substrate. The hybridization between FeSe and the substrate, combined with particle-hole symmetry, leads to the emergence of new bands in the BdG spectrum [Figs. 2.3.(c,d)] that are not present in the normal state dispersion [Figs. 2.3.(b)]. These new bands are at Γ (~ 250 meV below E_F), and M (~ 15 – 30 , 70 and ~ 180 meV below E_F) originating from the hybridization of Fe d_{z^2} and O p_z (at Γ) and Fe d_{xz} and d_{yz} with O p_x and p_y (at M). The energy range of these bands corresponds to the experimentally observed “replica bands”²⁰. In our simulations, replica bands originate from: (i) the superconducting pairing potential which couples the interfacial region between FeSe and STO, and (ii) particle-hole symmetry which mirrors the normal-state conduction states in the valence manifold. Our results qualitatively agree with ARPES measurements of FeSe/STO^{2,3,9}. Differences might be due to the semi-phenomenological nature of the SIESTA-BdG method: the initialization of the pairing potential results in an energy shift of the coherence peaks (Appendix B).

3 Discussion

In this study, we investigated the superconducting properties of ML FeSe, employing a combined Kohn–Sham and Bogoliubov–de Gennes approach. We analyzed two cases: freestanding FeSe (ML FeSe) and FeSe on a TiO₂–terminated STO substrate (FeSe/STO).

For both systems, we predicted an anisotropic superconducting gap $\Delta(\mathbf{k})$ [Figs. 2.3.(d) and 2.1.(d)]. We identified the nature of the superconducting coherence peaks and attributed their origin to specific regions in the Brillouin Zone: In freestanding FeSe, superconductivity is due to states around Γ and M points. In FeSe/STO, superconductivity originates from states around the M point only.

In addition, we identified the specific atoms and orbitals that are responsible for superconductivity: We observed a change in the orbital character of the Fe states responsible for superconductivity from d_{z^2} (ML FeSe) to d_{xz}/d_{yz} (FeSe/STO). In FeSe/STO, Fe d and O p orbitals strongly hybridize near the Fermi energy at the M point [Figs. 2.3.(b)] giving rise to two coherence peaks ($\Delta_{1/2}$, mostly contributed by O) and a higher-energy one (Δ_3 , mostly contributed by Fe). Remarkably, we observed proximity-induced superconductivity in the interfacial TiO₂ layer.

Our analysis of the normal-state band structure of the two materials allowed us to shed light on the different mechanisms behind their superconductivity: In ML FeSe, metallicity originates from an electron pocket at M and a hole pocket along the $\Gamma - X$ line. In FeSe/STO, instead, the hole pocket shifts to lower energies in the valence band. Therefore, the superconducting mechanism is intrinsically different in two cases: In ML FeSe, Cooper pairs can either form at $\sim \Gamma$ and $\sim M$ (difference between electron and hole crystal momentum $Q = 0$), or can scatter between M and Γ ($Q \neq 0$). In FeSe/STO, instead, Cooper pairs formation is only possible at M ($Q = 0$).

In both ML FeSe and FeSe/STO, we found multiple competing magnetic configurations. In this work, we focused on the checkerboard antiferromagnetic phase because its band structure best resembles ARPES measurements¹⁷. The impact of different magnetic configurations on the superconducting phase remains an open question, with the possibility that superconductivity may be favored in a specific direction when using the single stripe configuration with different spin alignments along the x and y axes. Future studies could investigate the superconducting state under different magnetic configurations to provide deeper insights into its behavior, or explore the potential for topological superconductivity in FeSe systems coupled with magnetic impurities and strong spin-orbit coupling, such as the recently observed zero energy states at the edges of line defects in Fe(Se, Te)²¹.

Our findings emphasize the role of hybridization with the substrate in determining the superconducting properties of FeSe. Hybridization between Fe and the substrate triggers proximity-induced superconductivity in STO. We suggest that heterostructures consisting of FeSe and substrates, including elements with high electron affinity, will promote charge transfer and facilitate Cooper pair formation in the substrate, opening the way to engineering novel FeSe-based superconductors operating at high temperatures.

4 Methods

4.1 First-principles ground state simulations

All simulations were performed using the SIESTA method^{14,22}, with the PBE²³ functional, norm-conserving pseudopotentials from the Pseudo-Dojo database²⁴, and the default SIESTA double- ζ polarized (DZP) basis set with an orbital cutoff radii of 272 meV. Simulations were converged for a mesh-cutoff of 1300 Ry. In FeSe/STO we account for the correlation effects between Fe and the interfacial oxygen atoms by applying a Hubbard correction U of 0.1 eV to the Fe d states^{25,26}. This value of U allows us to reproduce reasonably the band dispersion observed in ARPES^{4,16}, in particular the position of the highest occupied state at Γ , as illustrated in Fig. C2). All calculations include SOC.

To solve the KS-equations, we employed a $101 \times 101 \times 1$ and $16 \times 16 \times 1$ $\mathbf{k}$ -grid for ML FeSe and FeSe/STO, respectively. The Fermi-Dirac occupation function was smoothed out using an electronic temperature of 10 meV in the normal state for both freestanding FeSe and FeSe/STO. This value has been lowered to 0.1 meV for the superconducting state simulations to ensure that the broadening of the electronic states is well below the size of the superconducting gap. The crystal structures were relaxed with a maximum force tolerance of 0.005 eV/Å.

4.2 SIESTA-BdG method

The superconducting properties were modeled using the SIESTA-BdG method¹³. In this approach, a semi-empirical superconducting pairing potential is introduced on top of the self-consistent Kohn-Sham Hamiltonian describing the normal state. We used the *fixed- Δ* method with the superconducting pairing potential initialized in real space (*superconducting strength representation*) as touching spherical hardwells. We used hardwells with radius $\mathbf{r} = 1.32$ Å ($\mathbf{r} = 1.39$ Å) and strength $\bar{\Delta} = 15.0$ meV ($\bar{\Delta} = 73.0$ meV) around the Fe atoms for ML FeSe (FeSe/STO). We used a radius of $\mathbf{r} = 1.5$ Å and $\bar{\Delta} = 11.0$ meV for the interfacial oxygen atoms. For a discussion on the initialization of different pairing potential see Supporting Information B. The superconducting DOS were sampled with a uniform $350 \times 350 \times 1$ and $301 \times 301 \times 1$ $\mathbf{k}$ -grid, and refined with one iteration of the adaptive-grid scheme with a $3 \times 3 \times 1$ subgrid for ML FeSe and FeSe/STO, respectively.

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MCIN/AEI/10.13039/501100011033 and by the ERDF, A way of making Europe. NW further acknowledges funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Grant Agreement No. 754558 (PREBIST – COFUND). ICN2 is supported by the Severo Ochoa programme from Spanish MINECO (Grant no. CEX2021-001214-S) and by Generalitat de Catalunya (CERCA program and Grant No. 2021SGR01519). This work was sponsored by NWO-Domain Science for the use of supercomputer facilities. We also acknowledge that the results of this research have been achieved using the Tier-0 PRACE Research Infrastructure resource Discoverer based in Sofia, Bulgaria (OptoSpin project id. 2020225411). This project has received funding from the European Union's Horizon Europe research and innovation program under Grant Agreement No 101130384 (QUONDENSATE).

Authorship statement

This chapter is based on the work of Reho et al.¹. RR conducted the first-principles simulations and developed the necessary routines within the SIESTA and sisL codes. RR also took the lead in writing the manuscript. NW initiated the project by performing the magnetic configuration analysis and conducting the initial tests for superconductivity simulations. AHK provided feedback on the generation of input files and offered technical support to ensure data reproducibility. ABM contributed to the physical interpretation and provided feedback on the manuscript. ZZ, as the last author, secured funding for the project and assessed the correctness of the manuscript.

6 Appendices

A Magnetic order

Over the last decade, the ground state of FeSe has been hotly debated in the literature. Magnetic frustration and spin fluctuations make it difficult to describe this system with the Heisenberg or Ising models. Recently, *Glasbrenner et al.*¹⁵ performed a detailed analysis, based both on first principles and model calculations establishing the Staggered Dimer (SD) as the most stable configuration for this system. Our first-principles *ab-initio* analysis confirms their result. In Fig. A1 we show the computed total energies for the Single Stripe (SS), Staggered Trimer (ST), Staggered Dimer, in-plane (IP) and out-of-plane (OOP) CheckerBoard (CB), FerroMagnetic (FM) and non magnetic (NM) configurations. We report the difference in total energies ΔE with respect to the ground state (E_{min}) in Figs A1 and A2 and Table A1.

Two different basis sets were tested: Double-Zeta Polarized (DZP) with orbital-confining cutoff radii (PAO.EnergyShift) of 272 meV and 25 meV. The first choice leads to physically correct energetic ordering, and therefore our calculations are performed with this basis set.

The low-energy magnetic configurations for ML FeSe are ST, SS, and SD, with the ST only 0.231 meV below the SD. This energy difference is below the 0.5 meV/Fe accuracy of our

simulations, hence, we conclude that the three configurations are iso-energetic. We report our results in Fig. A2 and Table A1.

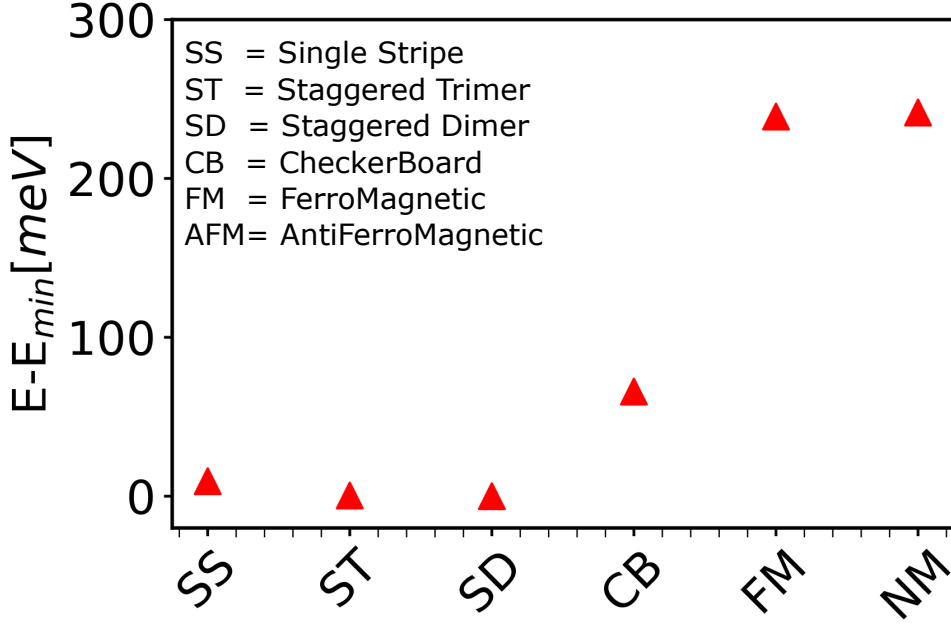


Figure A1 Energetic magnetic ordering for FeSe bulk. The lowest energy magnetic state is the Staggered Dimer configuration.

B Initialization of the Pairing Potential and Its Impact on the Superconducting Properties

In the SIESTA-BdG method, one can employ different approaches for solving the BdG equations and initializing the pairing potential Δ ¹³. We explored multiple initialization schemes for the pairing potential in both ML FeSe and FeSe/STO. In the main text, we focus on results obtained using the *fixed- Δ* method to solve the SIESTA-BdG equations, initialized within the *superconducting strength representation*. The *fixed- Δ* algorithm solves the Bogoliubov–de Gennes equations ensuring self-consistency in the normal Hamiltonian and density while holding Δ constant during the SIESTA–BdG scf steps. At every scf step the normal state Hamiltonian, the normal and the anomalous densities are updated. The *superconducting strength representation* initializes Δ in real space by specifying an initial guess for the pairing strength, $\bar{\Delta}$ (when no risk of confusion arise, we simply write Δ).

For ML FeSe, we analysed the shape and magnitude of the SC–DOS $\rho(\varepsilon)$ while varying the initial value of $\bar{\Delta}$. As shown in Fig. B1, $\rho(\varepsilon)$ is zero for $\bar{\Delta} = 0$, indicating the absence of superconductivity. A transition from a non-gapped to fully gapped SC–DOS occurs as $\bar{\Delta}$

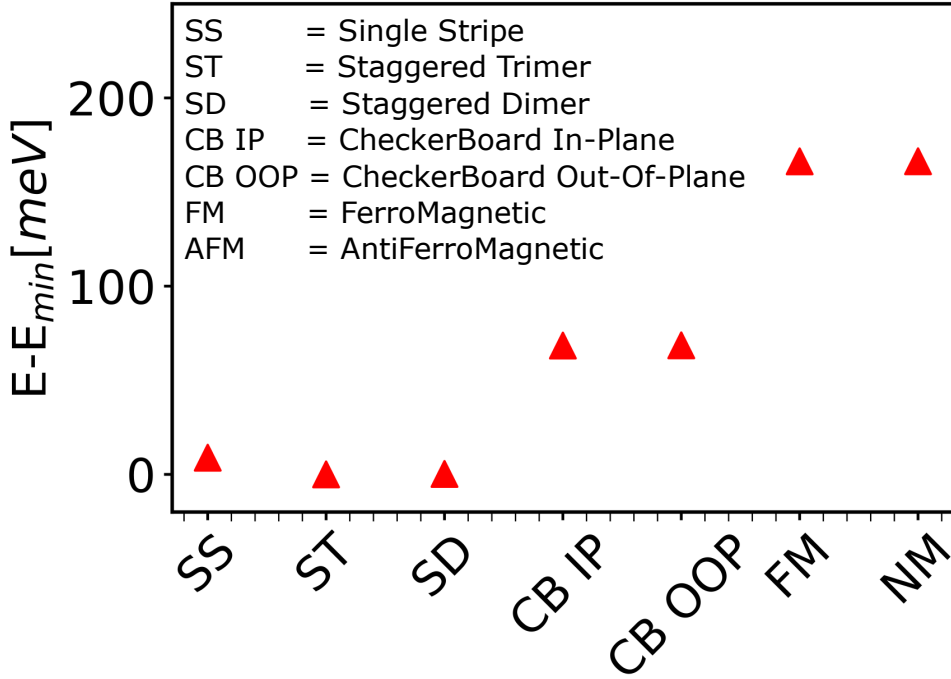


Figure A2 Energetic magnetic ordering for ML FeSe.

increases from 3 to 5 meV. Namely, $\bar{\Delta} < 5$ meV is too small to describe superconductivity in ML FeSe. For $\bar{\Delta} = 5$ meV, the double peaks around ± 8 meV merge into a single peak. Further increases in $\bar{\Delta}$ result in broader coherence peaks, reflecting the enhanced value of the superconducting pairing potential. Experimentally, different values for the superconducting gap width have been reported, with $\bar{\Delta} = 15$ meV in⁹. The BdG spectrum and SC-DOS (Figs. B2 and B1) does not, qualitatively, change for $\bar{\Delta}$ close to 15 meV. Therefore, we employed $\bar{\Delta} = 15$ meV for the SIESTA-BdG simulations presented in the main text.

For FeSe/STO, the interpretation of the SC-DOS is more complex. Our results indicate that only the states near the FeSe/STO interface contribute significantly to $\rho(\epsilon)$ close to the Fermi level, regardless of the spatial initialization of the pairing potential. In order to assess this stament, we first initialize the pairing potential $\bar{\Delta}$ uniformly across the unit cell (Fig. B4) with values ranging from 0 to 24 meV. The SC-DOS is metallic for $\bar{\Delta} = 0$. As $\bar{\Delta}$ increases, two peaks are clearly distinguishable and their separation widens. At $\bar{\Delta} = 0$ meV, we observe a pair of coherence peaks at ± 4.5 meV, which we attribute to the gaps in flat degenerate bands near the Fermi level in the normal state of FeSe/STO [Fig. 2.3.(b)]. These peaks primarily originate from Fe d orbitals. As $\bar{\Delta}$ increases, a second pair of coherence peaks emerges starting at $\bar{\Delta} = 6$ meV. This second pair, associated with interfacial O p -orbitals, becomes broader with increasing $\bar{\Delta}$, while the first pair remains unchanged. Thus, the constant initialization

Table A1 Difference in total energies $\Delta E = E - E_{\min}$, of ML FeSe and FeSe/STO with different magnetic configurations. The minimal energies are highlighted in bold.

ML FeSe	$\Delta E [meV]$
SS	8.868
ST	0.000
SD	0.231
CB IP	68.453
CB OOP	68.557
FM	166.314
NM	166.357
Bulk FeSe	$\Delta E [meV]$
SS	9.418
ST	0.424
SD	0.000
CB	65.846
FM	238.971
NM	241.511

of the pairing potential indicates that both Fe and oxygen play a role in the superconducting coupling, although the exact peak positions are not quantitatively accurate.

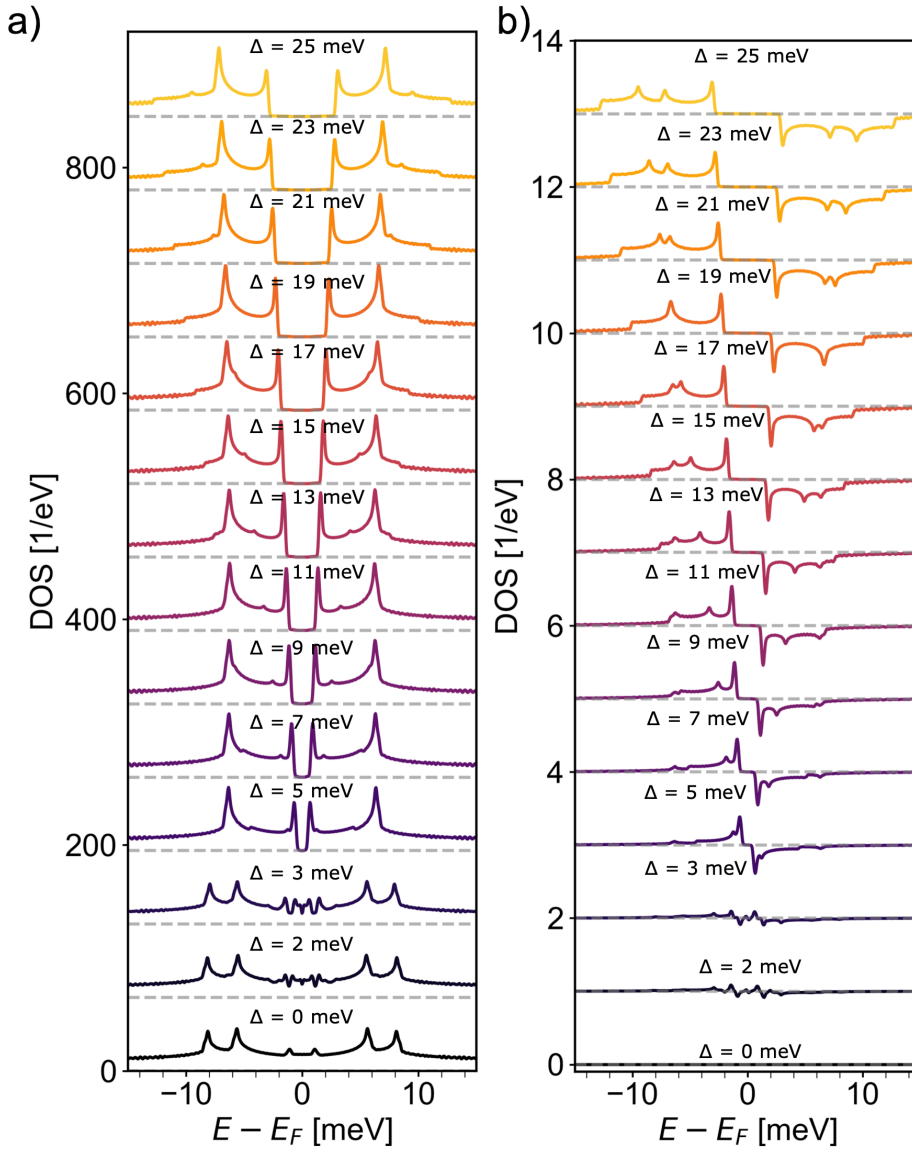


Figure B1 (a) SC-DOS and (b) anomalous DOS (right) for ML FeSe varying the initial value of Δ from 0 to 25 meV. The superconducting pairing potential is initialized only on the Fe atoms.

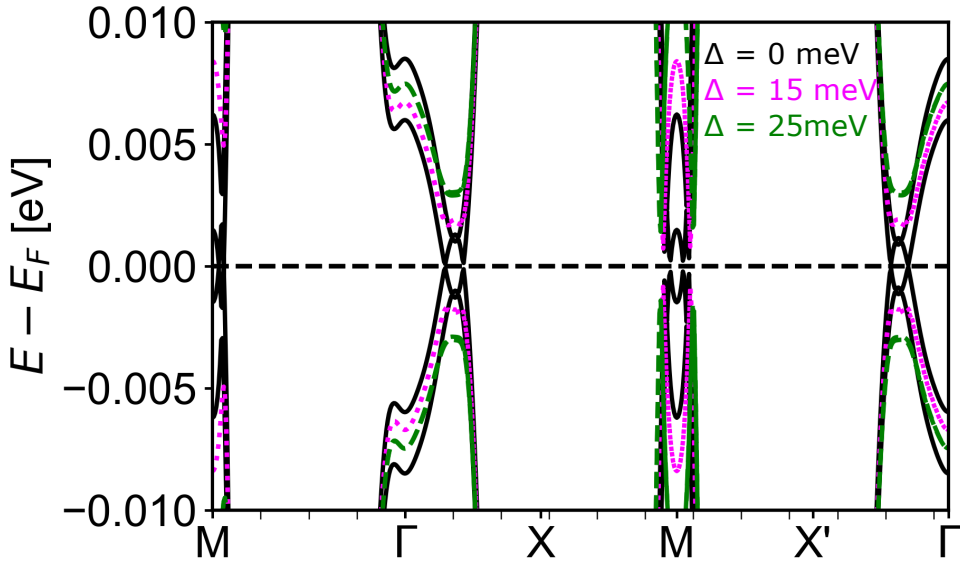


Figure B2 Superconducting band structure of ML FeSe with $\Delta = 0$ (black), 15 (magenta), or 25 (green) meV. The superconducting pairing potential is initialized only on the Fe atoms.

Furthermore, the SC-DOS does not completely drop to zero regardless of the value of $\bar{\Delta}$ while the anomalous DOS does. We interpret this behavior as follows: the first pair of coherence peaks arises from intrinsic electronic properties (coupling to STO), while the second is driven by the superconducting pairing potential, as evidenced by the trends in $\chi(\epsilon)$. The BdG spectrum near the high-symmetry point M (Fig. B3) provides further insights. Along the $M - X'$ path (left) and the $M - X$ path (right), we observe a widening separation between electron and hole states as $\bar{\Delta}$ increases, except for states near the Fermi level. Notably, a gap-closing feature appears along the $M - X'$ path, which is absent along $M - X$. This suggests a breaking of inversion symmetry in the system. A value of $\bar{\Delta} = 24$ meV is not sufficient to fully open the gap for FeSe/STO. Our tests indicate that at least a value of 45 meV is needed. For the reasonings above, we initialized the pairing potential $\bar{\Delta}$ only on the Fe atoms of the ML and the interfacial oxygen atoms. We tested that, qualitatively, no differences arise if the superconducting pairing potential is initialized uniformly across the unit cell or only on the Fe and interfacial Oxygen atoms. We also tested the case where the superconducting pairing potential is initialized as touching spheres on the Fe atoms (Fig. B5).

For FeSe/STO, we report the SC-DOS and anomalous DOS for different values of $\bar{\Delta}$ from 0 meV up to 300 meV, with the superconducting pairing initialized on the Fe interfacial oxygen atoms (Fig.s B6 and B7). These results show that for a higher value $\bar{\Delta}$ the SC-DOS becomes gapped.

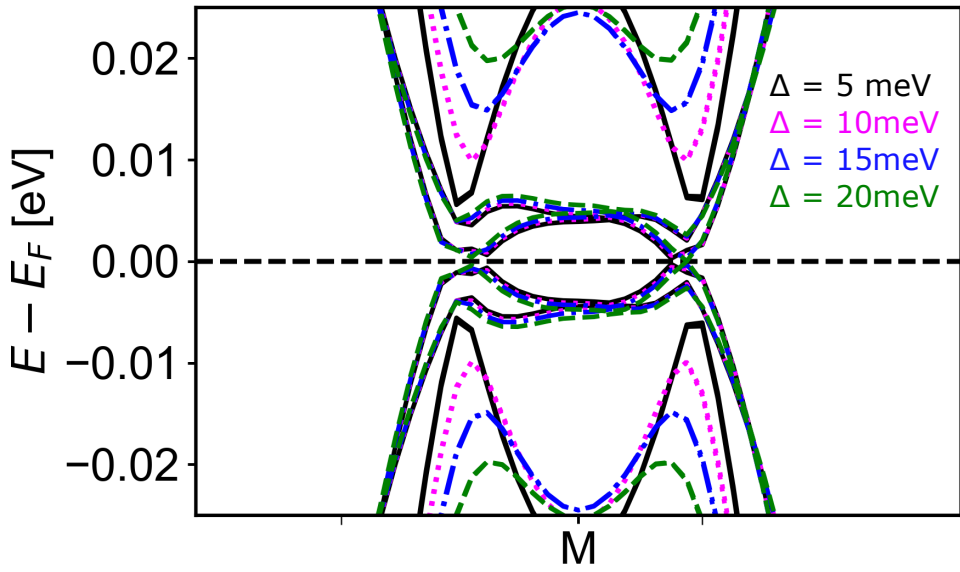


Figure B3 Superconducting band structure of FeSe/STO with $\Delta = 0$ (black), 10 (magenta), 15 (blue), or 20 (green) meV. The superconducting pairing potential is initialized on the Fe atoms and the oxygen atoms of the TiO_2 terminated surface.

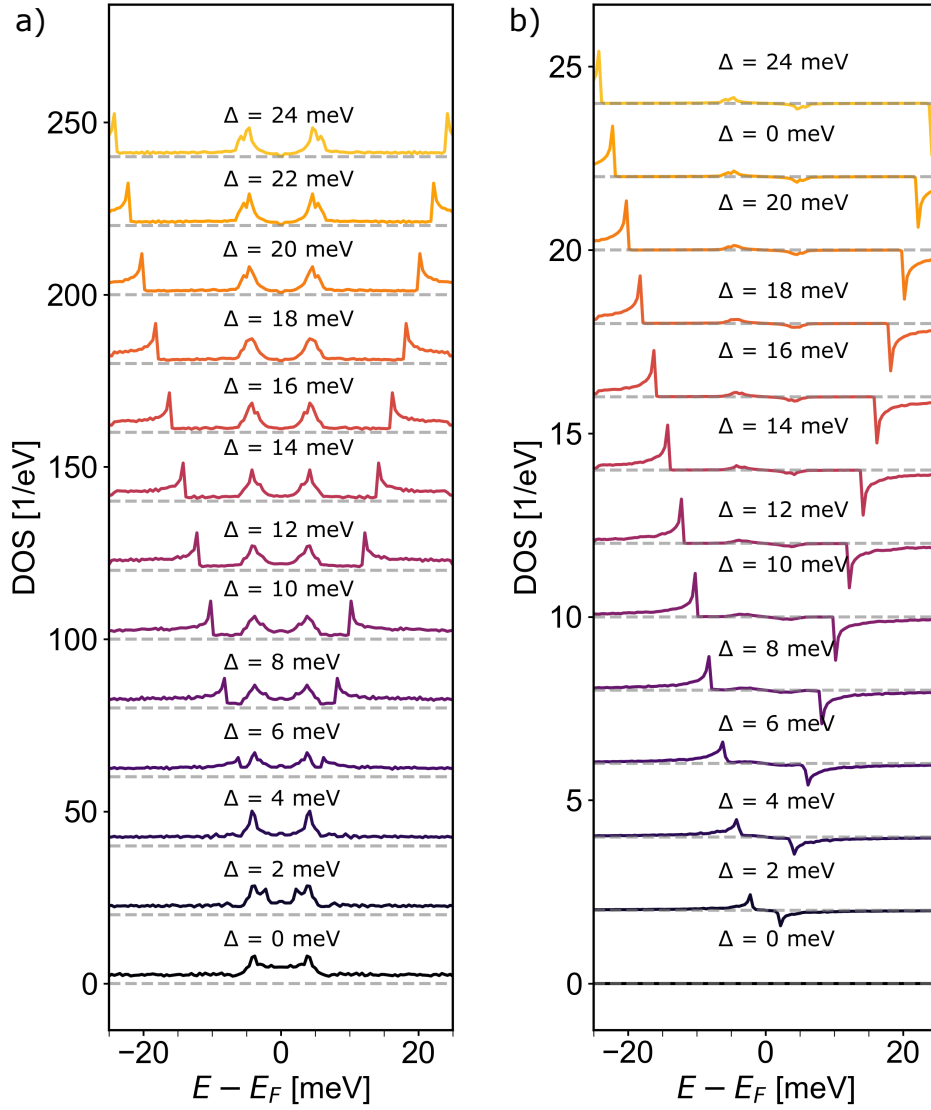


Figure B4 (a) SC-DOS and (b) anomalous DOS (right) for FeSe/STO obtained by varying Δ from 0 meV to 24 meV. The superconducting pairing potential is initialized in the whole unit cell with a constant value.

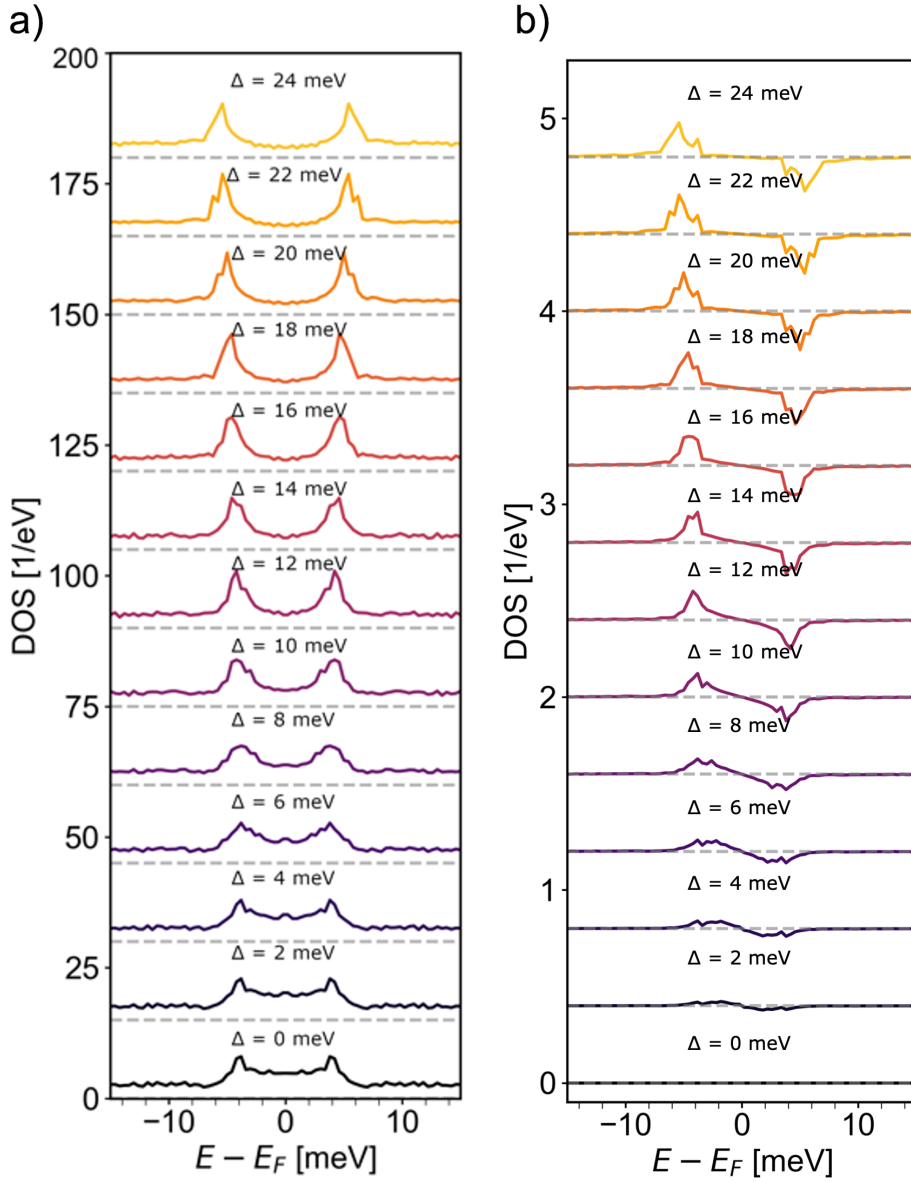


Figure B5 (a) SC-DOS and (b) anomalous DOS (right) for FeSe/STO by obtained by varying Δ from 0 to 24 meV. The superconducting pairing potential is initialized only on the Fe atoms.

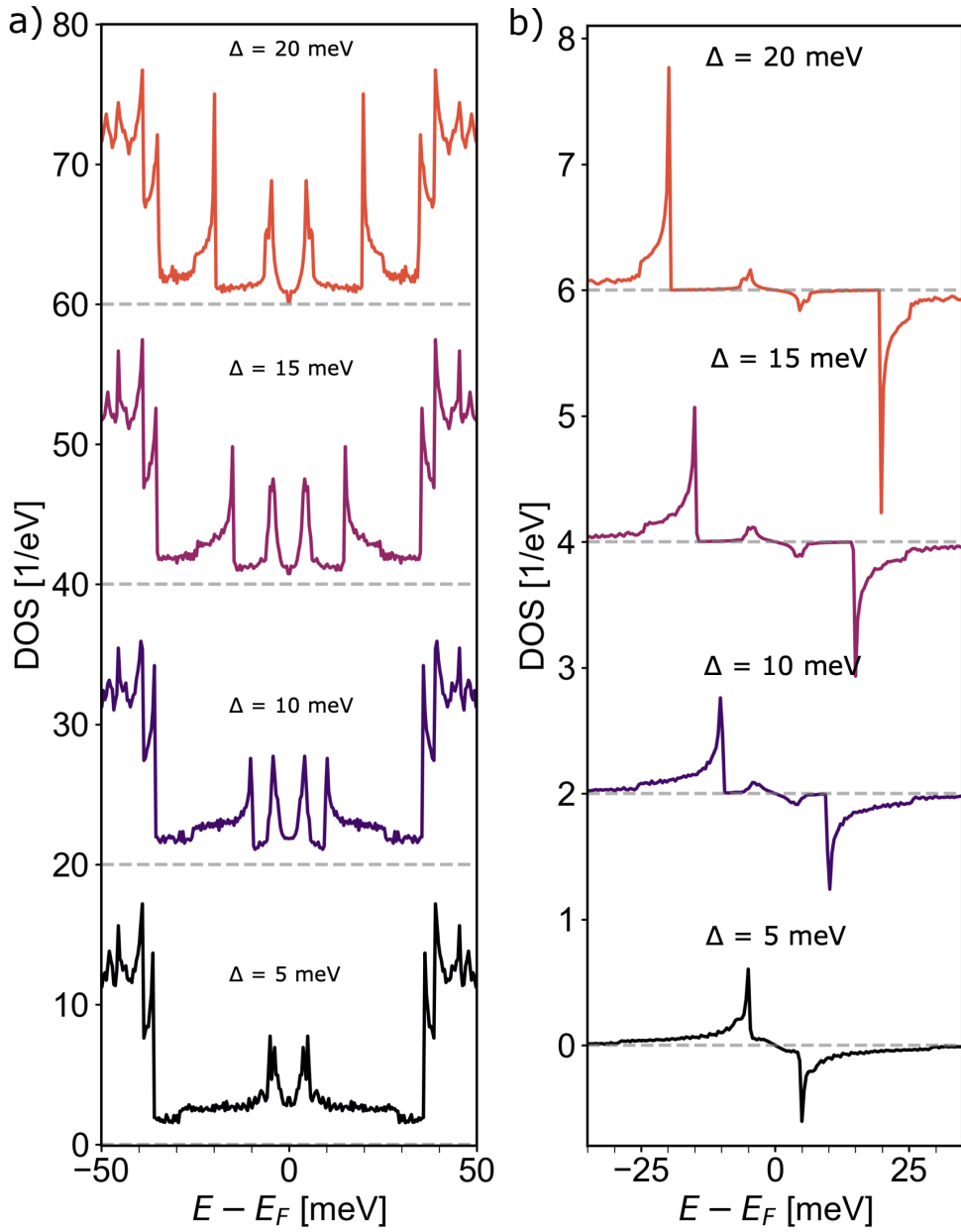


Figure B6 (a) SC-DOS and (b) anomalous DOS (right) for FeSe/STO varying Δ from 0 meV to 24 meV. The superconducting pairing potential is initialized only on the Fe atoms and the oxygen atoms of the TiO_2 terminated surface.

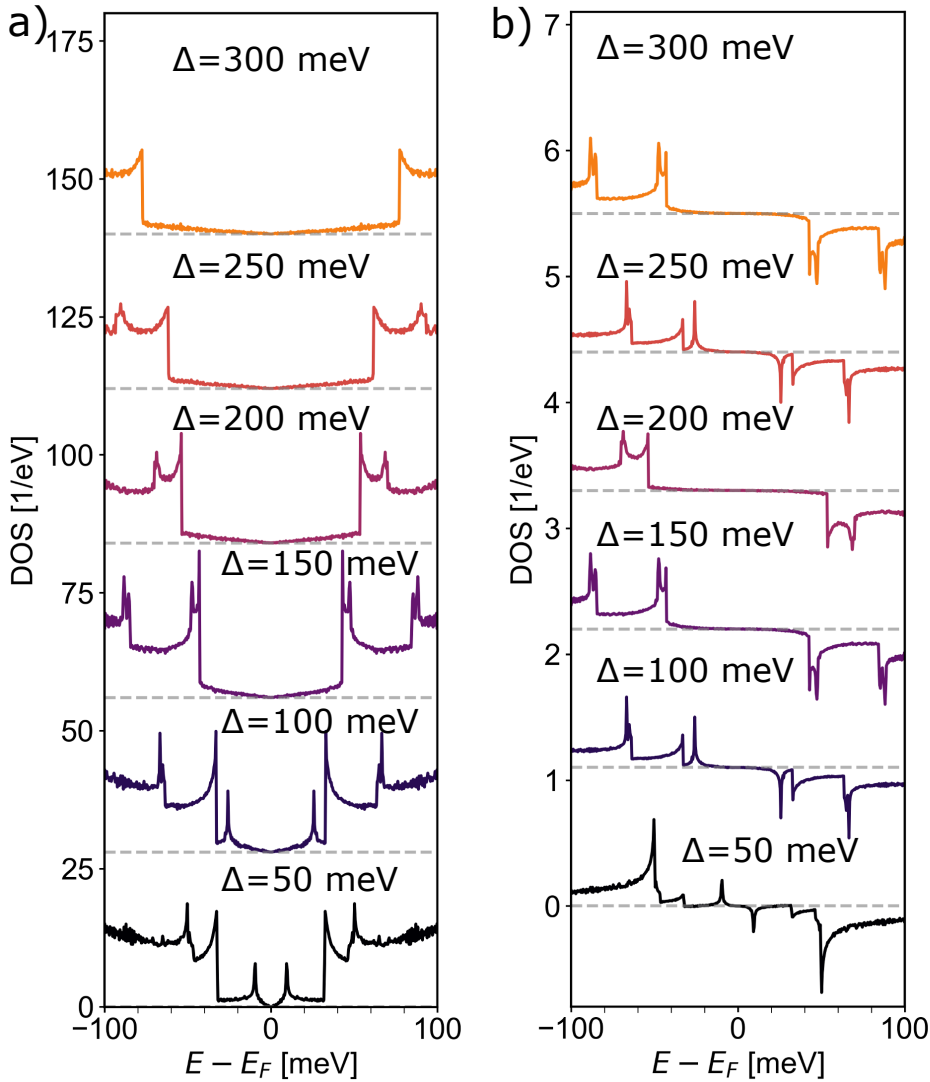


Figure B7 (a) SC-DOS and (b) anomalous DOS (right) for FeSe/STO varying Δ from 0 meV to 24 meV. The superconducting pairing potential is initialized only on the Fe atoms and the oxygen atoms of the TiO_2 terminated surface.

C Supplementary Electronic Structure Analysis of ML FeSe and FeSe/STO

In this section, we present supplementary figures that support the discussion in the main text. We compute the orbital-projected band structure of ML FeSe (Fig. C1) and FeSe/STO (Fig. C3). We show the Fermi surfaces of ML FeSe and FeSe/STO (Fig. C4). We examine the changes in the electronic dispersion of FeSe/STO as a function of the Hubbard U parameter

(Fig. C2). We compare our results with ARPES data⁹ and employ a value of $U = 0.1$ eV for the simulations performed in the main text.

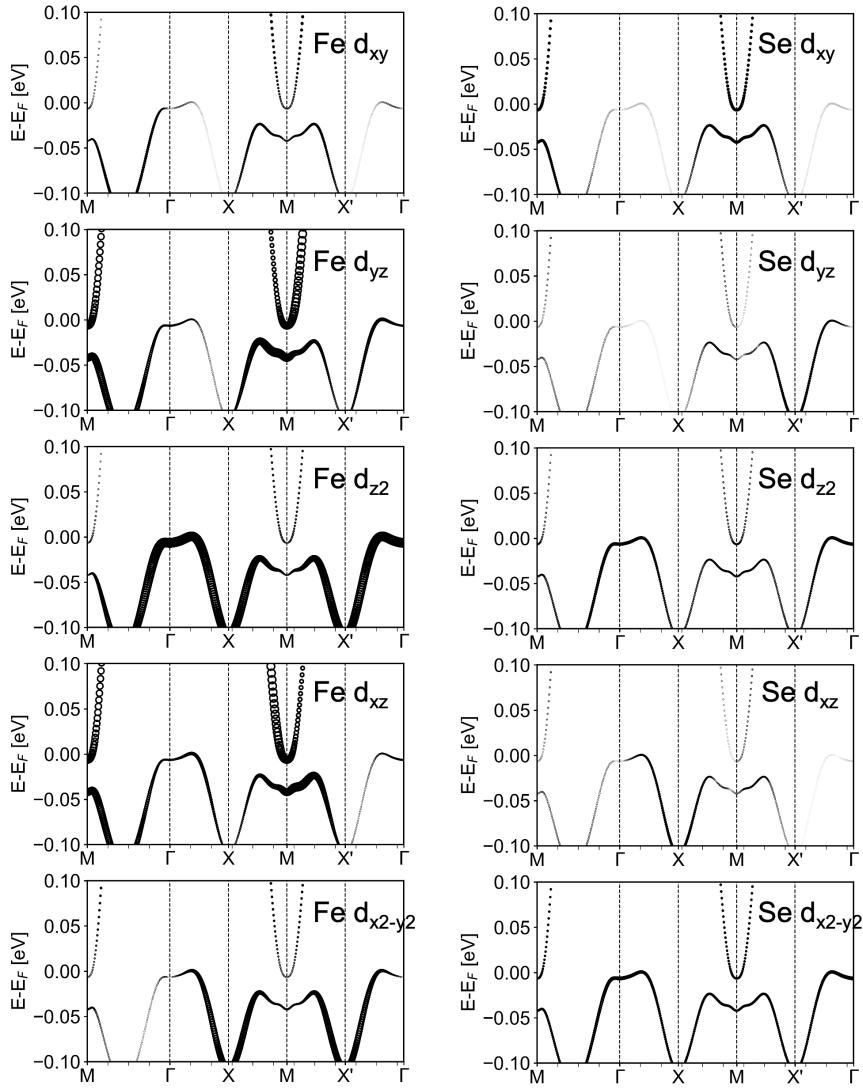


Figure C1 Electronic band structure of ML FeSe, projected on Fe(left) or Se(right) d orbitals.

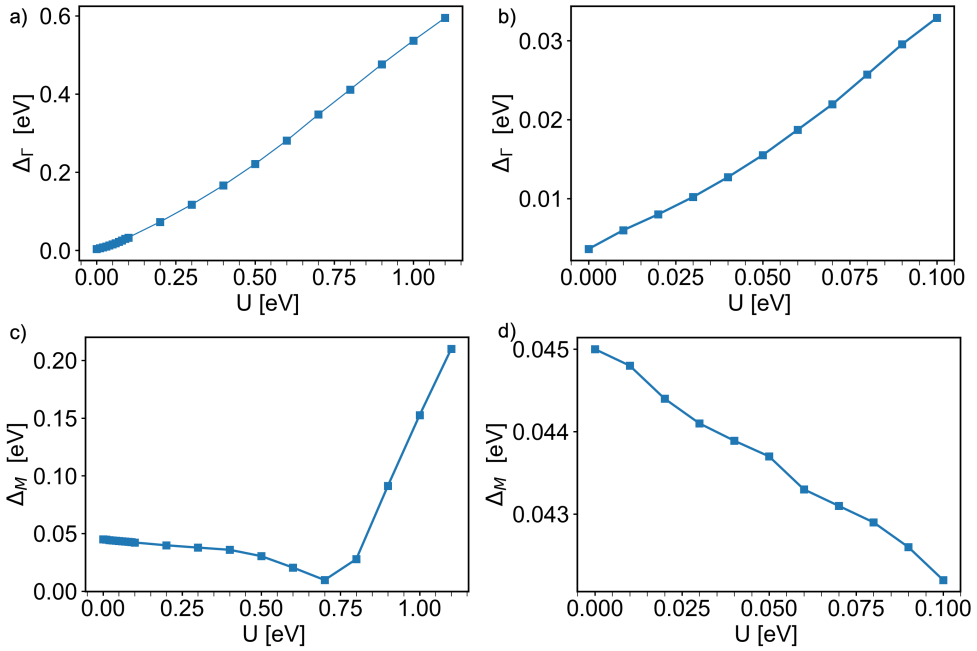


Figure C2 Convergence of the Hubbard U parameter towards ARPES results: (a) Energy difference between E_F and the last occupied state at Γ , Δ_Γ (b zoom-in) and (c,d) M , Δ_M , as a function of the Hubbard U term.

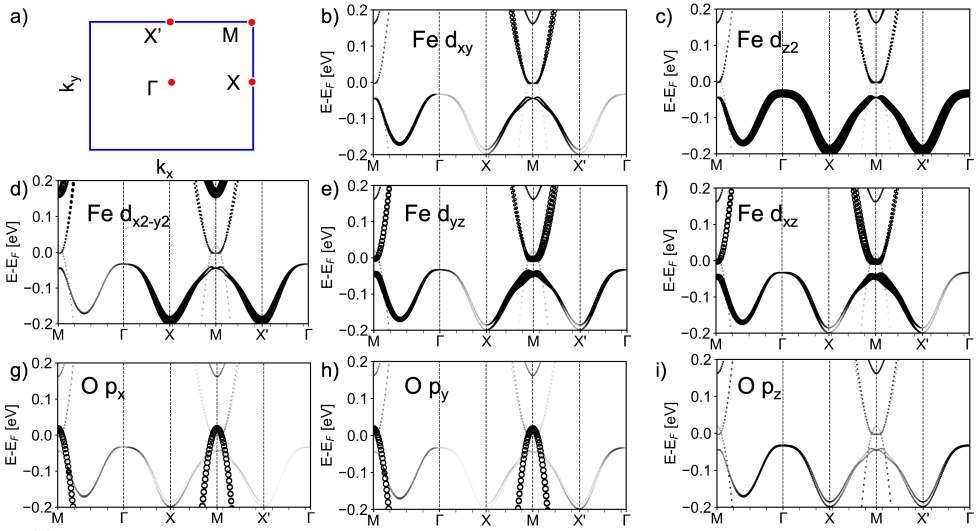


Figure C3 FeSe/STO: Schematic representation of the Brillouin Zone and its high-symmetry points. (a) Normal state electronic band structure projected on (b–f) d orbitals of Fe and (g–i) p -orbitals of O.

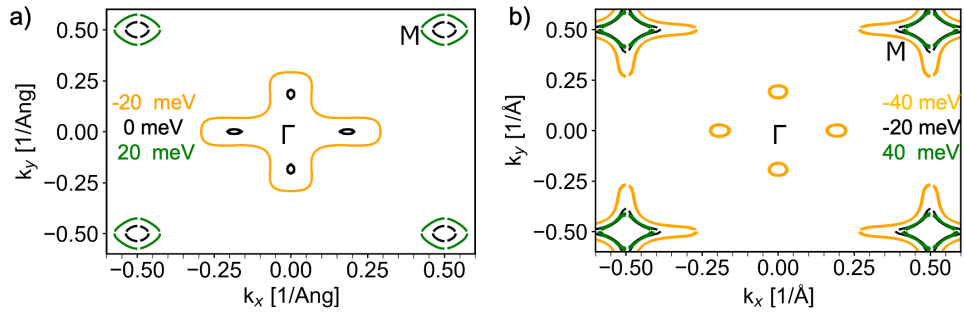


Figure C4 Fermi surfaces of (a) FeSe ML and (b) FeSe/STO in the normal state. The surfaces are shown as constant-energy cuts in the (E, k_x, k_y) frame. Energy values and corresponding colors are indicated in the legend.

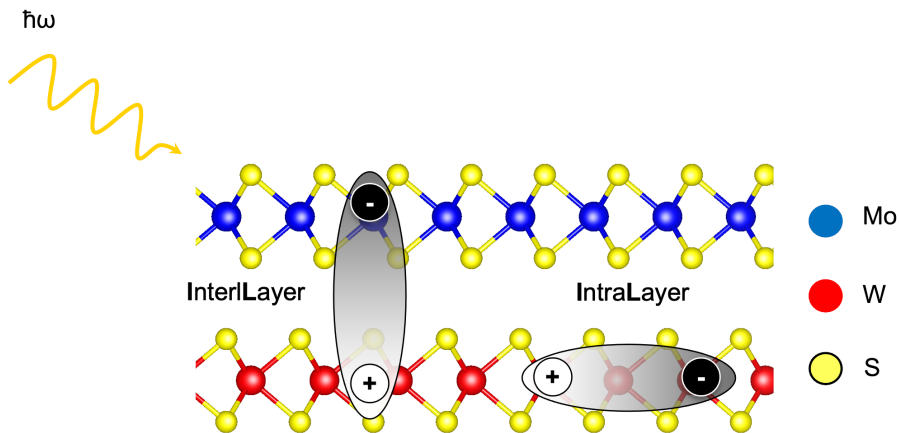
Bibliography

- 1 Riccardo Reho, Arnold H Kole, Nils Wittemeier, Andrés R Botello-Méndez, and Zeila Zanolli. The crucial role of substrate in fese/sto: new insights to interface-driven superconductivity from first-principles. *arXiv preprint arXiv:2503.15025*, 2025.
- 2 Qing-Yan Wang, Zhi Li, Wen-Hao Zhang, Zuo-Cheng Zhang, Jin-Song Zhang, Wei Li, Hao Ding, Yun-Bo Ou, Peng Deng, Kai Chang, et al. Interface-induced high-temperature superconductivity in single unit-cell fese films on sr tio3. *Chinese Physics Letters*, 29(3):037402, 2012.
- 3 Dennis Huang and Jennifer E Hoffman. Monolayer fese on sr tio3. *Annual Review of Condensed Matter Physics*, 8:311–336, 2017.
- 4 Wenhao Zhang, Zhi Li, Fangsen Li, Huimin Zhang, Junping Peng, Chenjia Tang, Qingyan Wang, Ke He, Xi Chen, Lili Wang, et al. Interface charge doping effects on superconductivity of single-unit-cell fese films on sr tio 3 substrates. *Physical Review B*, 89(6):060506, 2014.
- 5 Fawei Zheng, Zhigang Wang, Wei Kang, and Ping Zhang. Antiferromagnetic fese monolayer on sr tio3: the charge doping and electric field effects. *Scientific reports*, 3(1):2213, 2013.
- 6 Amalia I Coldea and Matthew D Watson. The key ingredients of the electronic structure of fese. *Annual Review of Condensed Matter Physics*, 9(1):125–146, 2018.
- 7 Zhiyuan Wei, Shaozhi Li, Bo Liu, Xiupeng Sun, Yinqi Hu, Shuai Sun, Shuting Peng, Yang Luo, Linwei Huai, Jianchang Shen, et al. Particle-hole mixed bogoliubov quasiparticles and cooper instability in single-unit-cell fese/sr tio3 films. *Communications Materials*, 5(1):118, 2024.
- 8 Y Zhang, JJ Lee, RG Moore, W Li, M Yi, M Hashimoto, DH Lu, TP Devereaux, D-H Lee, and Z-X Shen. Superconducting gap anisotropy in monolayer fese thin film. *Physical Review Letters*, 117(11):117001, 2016.
- 9 Xu Liu, Lin Zhao, Shaolong He, Junfeng He, Defa Liu, Daixiang Mou, Bing Shen, Yong Hu, Jianwei Huang, and XJ Zhou. Electronic structure and superconductivity of fese-related superconductors. *Journal of Physics: Condensed Matter*, 27(18):183201, 2015.
- 10 Swagata Acharya, Dimitar Pashov, Francois Jamet, and Mark van Schilfgaarde. Electronic origin of t_c in bulk and monolayer fese. *Symmetry*, 13(2):169, 2021.
- 11 Swagata Acharya, Dimitar Pashov, and Mark Van Schilfgaarde. Role of nematicity in controlling spin fluctuations and superconducting t_c in bulk fese. *Physical Review B*, 105(14):144507, 2022.
- 12 Swagata Acharya, Mikhail I Katsnelson, and Mark van Schilfgaarde. Vertex dominated superconductivity in intercalated fese. *npj Quantum Materials*, 8(1):24, 2023.

- 13 R. Reho, N. Wittemeier, A. H. Kole, P. Ordejón, and Z. Zanolli. Density functional bogoliubov-de gennes theory for superconductors implemented in the siesta code. *Phys. Rev. B*, 110:134505, Oct 2024.
- 14 Alberto Garcia, Nick Papior, Arsalan Akhtar, Emilio Artacho, Volker Blum, Emanuele Bosoni, Pedro Brandimarte, Mads Brandbyge, Jorge I Cerdá, Fabiano Corsetti, et al. Siesta: Recent developments and applications. *The Journal of chemical physics*, 152(20):204108, 2020.
- 15 J. K. Glasbrenner, I. I. Mazin, Harald O. Jeschke, P. J. Hirschfeld, R. M. Fernandes, and Roser Valentí. Effect of magnetic frustration on nematicity and superconductivity in iron chalcogenides. *Nature Physics*, 11(11):953–958, November 2015.
- 16 Qisi Wang, Yao Shen, Bingying Pan, Xiaowen Zhang, K Ikeuchi, K Iida, AD Christianson, HC Walker, DT Adroja, M Abdel-Hafiez, et al. Magnetic ground state of fese. *Nature communications*, 7(1):12182, 2016.
- 17 ZF Wang, Huimin Zhang, Defa Liu, Chong Liu, Chenjia Tang, Canli Song, Yong Zhong, Junping Peng, Fangsen Li, Caina Nie, et al. Topological edge states in a high-temperature superconductor fese/srtio3 (001) film. *Nature materials*, 15(9):968–973, 2016.
- 18 Robert S Mulliken. Electronic population analysis on lcao–mo molecular wave functions. i. *The Journal of chemical physics*, 23(10):1833–1840, 1955.
- 19 Shigeru Kasahara, Tatsuya Watashige, Tetsuo Hanaguri, Yuhki Kohsaka, Takuya Yamashita, Yusuke Shimoyama, Yuta Mizukami, Ryota Endo, Hiroaki Ikeda, Kazushi Aoyama, et al. Field-induced superconducting phase of fese in the bcs-bec cross-over. *Proceedings of the National Academy of Sciences*, 111(46):16309–16313, 2014.
- 20 JJ Lee, FT Schmitt, RG Moore, S Johnston, Y-T Cui, W Li, M Yi, ZK Liu, M Hashimoto, Ya Zhang, et al. Interfacial mode coupling as the origin of the enhancement of t_c in fese films on srtio3. *Nature*, 515(7526):245–248, 2014.
- 21 Cheng Chen, Kun Jiang, Yi Zhang, Chaofei Liu, Yi Liu, Ziqiang Wang, and Jian Wang. Atomic line defects and zero-energy end states in monolayer Fe(Te,Se) high-temperature superconductors. *Nature Physics*, 16(5):536–540, May 2020. Publisher: Nature Publishing Group.
- 22 José M Soler, Emilio Artacho, Julian D Gale, Alberto García, Javier Junquera, Pablo Ordejón, and Daniel Sánchez-Portal. The siesta method for ab initio order-n materials simulation. *Journal of Physics: Condensed Matter*, 14(11):2745, 2002.
- 23 John P Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. *Physical Review Letters*, 77(18):3865, 1996.

- 24 Michiel J van Setten, Matteo Giantomassi, Eric Bousquet, Matthieu J Verstraete, Don R Hamann, Xavier Gonze, and G-M Rignanese. The pseudodojo: Training and grading a 85 element optimized norm-conserving pseudopotential table. *Computer Physics Communications*, 226:39–54, 2018.
- 25 AI Liechtenstein, Vladimir I Anisimov, and Jan Zaanen. Density-functional theory and strong interactions: Orbital ordering in mott-hubbard insulators. *Physical Review B*, 52(8):R5467, 1995.
- 26 Eric Bousquet and Nicola Spaldin. J dependence in the lsda+ u treatment of noncollinear magnets. *Physical Review B—Condensed Matter and Materials Physics*, 82(22):220402, 2010.

Excitonic response in TMD heterostructures from first-principles: impact of stacking, twisting, and interlayer distance



Based on

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Abstract

Van der Waals heterostructures of two-dimensional transition metal dichalcogenides provide a unique platform to engineer optoelectronic devices tuning their optical properties via stacking, twisting, or straining. Using *ab initio* many-body perturbation theory, we predict the electronic and optical (absorption and photoluminescence spectra) properties of MoS₂/WS₂ and MoSe₂/WSe₂ heterobilayers with different stacking and twisting. We analyze the valley splitting and optical transitions, and we explain the enhancement or quenching of the inter- and intra-layer exciton states. We fully include transitions within the entire Brillouin Zone, contrary to predictions based on continuum models which only consider energies near the *K* point. As a result, we predict an interlayer exciton with significant electron density in both layers and a mixed intralayer exciton distributed over both MoSe₂ and WSe₂ in a twisted Se-based heterostructure. We propose that it should be possible to produce an inverted order of the excitonic states in some MoSe₂/WSe₂ heterostructures, where the energy of the intralayer WSe₂ exciton is lower than that in MoSe₂. We predict the variability across different stacking of the exciton peak positions (~100 meV) and the exciton radiative lifetimes, from pico- to nano-seconds, and even micro-seconds in twisted bilayers. The control of exciton energies and lifetimes paves the way towards applications in quantum information technologies and optical sensing. This chapter is based on Reho et al¹. RR conducted the first-principles simulations and developed the necessary routines in the YAMBO and YAMBOPY codes. RR also took the lead in writing the manuscript.

1 Introduction

Transition metal dichalcogenides (TMDs) can host strong light-matter interaction and enhanced excitonic effects, making them ideal for next-generation optical devices². TMD monolayers (MLs) can be further stacked into van der Waals heterostructures (vdW HS)^{3–5} with added functionalities. Their electronic and optical properties strongly depend on layer thickness (Δt), interlayer distance (Δd), stacking and twist angle^{6–8}. Achieving experimental control on these features is complex^{9,10}: encapsulation affects thickness and interlayer distance, and the dielectric environment influences transport and other properties. Therefore, theoretical models are essential for isolating effects and guiding experimental design. In addition, for small twist angles, TMDs HS display regions which are misaligned and other with local atomic registry (AA', AA, AB and SP, Fig. 1). In general, the changes of these degrees of freedom occur simultaneously. This makes it experimentally difficult to disentangle them.

Heterostructures of TMDs with different transition metal atoms typically show a type II band alignment, which leads to the formation of interlayer excitons (IL), in addition to intralayer (IN) ones¹¹. Understanding how IN and IL exciton energies and intensities are affected by the above degrees of freedom is essential to control and exploit them for quantum information technologies^{12–14}. The energetics, intensity and dynamics of bright IN excitons can be probed via photoluminescence (PL) or time-resolved photoluminescence (TRPL)^{11,13,15}. Establishing a correspondence between observed peaks and individual monolayers is usually done by analogy with exciton energies in the freestanding MLs. However, this approach has limited predictive power as it neglects the vdW interaction between layers and the resulting electrostatic environment (screening). *Ab initio* many-body perturbation theory (Ai-MBPT) formalism, instead, allows for unambiguous identification of the spatial and spectral origin of each excitonic transition. The first *ab-initio* calculations of PL and absorption by IL and IN excitons in a TMD vdW HS were done by Torun et al¹⁶, but with a focus on the AA' stacking only. The same year, Gillen et al.¹⁷ computed absorption spectra of Se-based AA', AA, AB HS using the Bethe-Salpeter Equation (BSE).

In this work, we systematically analyze the variation of the electronic and optical properties of MoX_2/WX_2 (with $X = \text{S/Se}$) vdW HS with interlayer distance, stacking and twisting, using Ai-MBPT^{18,19}. We have updated the PL implementation in the YAMBO code, following the general formalism of Melo and Marini²⁰ and incorporated the approaches and formalism developed in Refs.^{21,22}. These theories provide a framework for a full *ab-initio* description of the coupled out-of-equilibrium dynamics of photons, phonons, and electrons at different level of approximation. The dynamics of the carriers following light excitation can either be described in real-time or as a noncoherent thermalized exciton population. We implemented the computation of the lesser component of the electron-hole Green's function, L , which gives access to PL and transient absorption^{19,20}. We find that, under sufficient compression along the stacking direction, the excitonic ground state originates from an emerging transition at Γ . This is due to enhanced orbital overlap in the vdW gap. In-plane compressive (respectively, tensile) strain results in an increase (respectively, decrease) of the first and second bright exciton

energies. We predict that absorption and PL spectra can be unequivocally attributed to specific stacks/twists, as the corresponding energy ordering of exciton energies are of the order of ~ 100 meV. The absorption and PL spectra of twisted $\text{MoSe}_2/\text{WSe}_2$ heterostructures is particularly interesting as it hosts new emergent features: flat bands, an IL exciton with significant electron density contribution in both layers, two degenerate IN excitons localized on each of the ML, suppression of IN WSe_2 exciton, and reversed excitonic order. The $\text{MoSe}_2/\text{WSe}_2$ twisted heterostructure is promising for applications in photovoltaics, as the computed exciton lifetimes reach $0.4 \mu\text{s}$, namely several order of magnitudes larger than typical values^{23,24}.

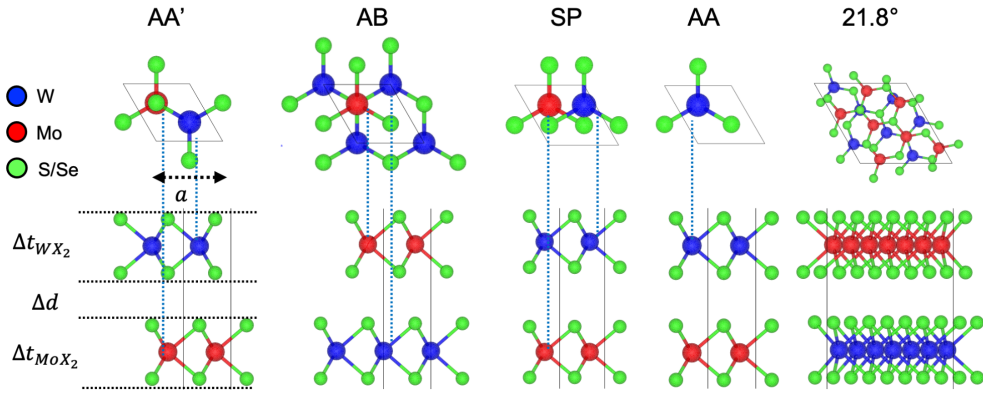


Figure 1 Top and side views of vdW HS with lattice parameter a , van der Waals gap Δd , and monolayer thickness Δt_{YX_2} with $Y = \text{W}, \text{Mo}$ and $X = \text{S}, \text{Se}$. Relaxed structural parameters are reported in Table B1.

2 Theoretical Methods

The ground state properties are computed by solving the Kohn-Sham (KS) equations within the density functional theory (DFT) formalism using the Quantum Espresso (QE) code^{25,26}. All structural relaxations were performed including spin - orbit Coupling (SOC), semiempirical van der Waals correction D2²⁷, and Se semicore states in the pseudopotential. The inclusion of Se semicore states is essential to predict the direct band-gap of MLs. Usually, the 3s and 3p Se states are assumed to be frozen in the core because of the large energy separation from 3d states. However, the spatial overlap of the corresponding wavefunctions is nonnegligible. Freezing the semicore states results in an unphysical shift of the extrema of the conduction and valence bands, and indirect band-gap for both MoSe_2 and WSe_2 MLs phases (Appendix A).

To obtain quantitative predictions of the electronic structure, we computed corrections to DFT energies using the GW method²⁸ in the plasmon-pole approximation for all $\mathbf{k}$ -points in the Brillouin Zone (BZ)²⁹. We employed the stochastic integration and the 2D cut-off of the Coulomb potential³⁰ to compute the screening W . Neutral excitations are computed from the BSE for electron-hole interactions in the Ai-MBPT formalism^{18,19}. To obtain the exciton energies and wavefunctions, we solve the BSE in the Tamm-Dancoff approximation including

local field effects³¹. The BSE can be recast into an eigenvalue equation

$$\left(\varepsilon_{\mathbf{c}\mathbf{k}}^{\text{GW}} - \varepsilon_{\mathbf{v}\mathbf{k}}^{\text{GW}}\right) A_{\mathbf{v}\mathbf{c}\mathbf{k}}^{\lambda} + \sum_{\mathbf{k}'\mathbf{c}'\mathbf{v}'} K_{\mathbf{v}\mathbf{c}\mathbf{k}}^{\text{eh}} A_{\mathbf{v}'\mathbf{c}'\mathbf{k}'}^{\lambda} = E_{\lambda} A_{\mathbf{v}\mathbf{c}\mathbf{k}}^{\lambda} \quad (1)$$

where $\varepsilon_{\mathbf{c}\mathbf{k}/\mathbf{v}\mathbf{k}}^{\text{GW}}$ are quasiparticle band energies, $A_{\mathbf{v}\mathbf{c}\mathbf{k}}^{\lambda}$ are the BSE coefficients and E_{λ} the energy of exciton λ . The optical absorption is computed from the imaginary part of the polarizability function $\alpha_{2\text{D}}(\omega)$, given by

$$\alpha_{2\text{D}}(\omega) = \frac{1}{A_{\text{uc}}} \sum_{\lambda} \frac{|\mu_{\lambda}|^2}{\omega - E_{\lambda} + i\eta} \quad (2)$$

where A_{uc} is the area of the unit cell.^{19,32} The exciton transition dipole, μ_{λ} , is defined in terms of the electronic dipoles as $\mu_{\lambda} = \sum_{\mathbf{c}\mathbf{v}\mathbf{k}} A_{\mathbf{c}\mathbf{v}\mathbf{k}}^{\lambda} d_{\mathbf{c}\mathbf{v}\mathbf{k}}$, with $d_{\mathbf{c}\mathbf{v}\mathbf{k}} = \langle \mathbf{v}\mathbf{k} | e\mathbf{r} | \mathbf{c}\mathbf{k} \rangle$, e the electron charge and $\mathbf{r}$ the one-body position operator.

The PL spectra are computed as in Ref.²⁰, analogously to Refs^{16,21,22,33}. Here, we neglect the exciton-phonon coupling. Note that, the interaction between excitons and phonons helps to overcome the momentum mismatch between the electron and hole, and leads to changes in the spectra. State of the art calculations on the exciton-phonon coupling in Photoluminescence^{21,22} are beyond the scope of the paper. They will be exceedingly heavy, as they require to compute the excitonic energies and wave-functions at finite momentum, as well as the electron-phonon matrix elements. In this approximation, the intensity of the emission spectra I^{PL} is

$$I^{\text{PL}}(\omega) = \frac{\omega^3 n_r(\omega)}{\pi^2 \hbar c^3} \sum_{\lambda} \Im \left[\frac{|\mu_{\lambda}|^2}{\omega - E_{\lambda} + i\eta} \right] e^{-\frac{E_{\lambda} - E_{\min}}{k_B T_{\text{exc}}}} \quad (3)$$

where, $E_{\min}$ the minimum energy of the exciton dispersion, $n_r(\omega) \approx 1$ the refractive index for a free-standing 2D material, $i\eta$ an infinitesimally small imaginary number, and k_B the Boltzmann constant. We assume a low-density thermalized initial population of excitons. This can be modelled by a Bose distribution function, which parametrically depends on the exciton temperature T_{exc} ^{16,34–36}. The excited state dynamics is described by the exciton radiative lifetimes $\tau_{\lambda}(0)$ in the optical limit ($\mathbf{q} \rightarrow 0$)^{23,24,37}:

$$\tau_{\lambda}(0) = \frac{\hbar^2 c A_{\text{uc}}}{4\pi e^2 E_{\lambda} \mu_{\lambda}^2}. \quad (4)$$

To visualize exciton wavefunctions (Ψ) or identify IN or IL cases, one often chooses a “chemically reasonable” position for the hole (e.g. on the electrophilic chalcogen) and examines the electron part of Ψ . In the HS in particular, this choice is delicate and potentially arbitrary, e.g. which layer’s chalcogen should we choose? To analyze electron and hole localization within the heterostructure we define the probability $P(\text{IN})$ that a transition is intralayer using the integrals

$$P^{\lambda, \leq}(\text{IN}) = \int_{z_{\text{c}} \text{ and } z_{\text{h}} \leq z_0} |\Psi^{\lambda}(\mathbf{r}_{\text{e}}, \mathbf{r}_{\text{h}})|^2 d\mathbf{r}_{\text{e}} d\mathbf{r}_{\text{h}} \quad (5)$$

where $\Psi^{\lambda} = \sum_{\mathbf{v}\mathbf{c}\mathbf{k}} A_{\mathbf{v}\mathbf{c}\mathbf{k}}^{\lambda} |\mathbf{v}\mathbf{k}\rangle |\mathbf{c}\mathbf{k}\rangle$ is the exciton wavefunction, and $\mathbf{r}_{\text{e}}, \mathbf{r}_{\text{h}}$ denote electron and hole coordinates, respectively, with the z coordinate normal to the heterostructure. The threshold

z_0 is set halfway between the two layers. The $<$ and $>$ in Eq. (5) denote that integration is done for z_h smaller or greater than the threshold z_0 . It follows that $P^{\leq}(\text{IL}) = 1 - P^{\leq}(\text{IN})$ and $P(\text{IL}) = P^{<}(\text{IL}) + P^{>}(\text{IL})$ give the interlayer transition probabilities. Their values are reported in Tables E1 and E2. The $P(\text{IN})$ defined above is unequivocal in this sense and can distinguish IN and IL for each layer and in a quantitative fashion. The implementation of Eq. (4) and other post-processing to reproduce the main results of this work are available in the author's forked repository of the YAMBOPY Python library¹.

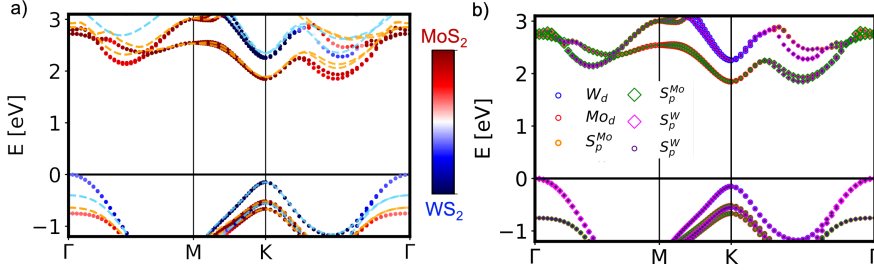


Figure 2 GW electronic band structure of the AB stacked MoS₂/WS₂ HS projected over the (a) MoS₂ (red) and WS₂ (blue) layers or (b) individual atomic orbitals Y^M_b (b orbital of atom Y in layer M). The orange and light blue dashed lines denote the GW bands of the individual MLs. The diamond-shaped symbols in panel (b) highlight the contribution from the orbitals of the chalcogen atoms close to the vdW gap.

3 Computational details

All calculations have been performed with fully relativistic pseudopotentials from PseudoDojo including the s, p and d semicore shells³⁸. The ground state properties have been computed with Quantum Espresso²⁵ relaxing the structures with the Broyden (BFGS³⁹) algorithm and the inclusion of spin orbit coupling and vdW corrections^{27,40}, a plane wave kinetic energy cutoff of 120 Ry, and the PBE⁴¹ exchange correlation functional. Atomic forces and pressure were converged to better than 10^{-7} Ry/a.u. and 0.5 kbar, respectively. With this choice, the total energies are converged to within less than 1 meV per unit cell.

The GW correction and excitonic properties have been computed on a $30 \times 30 \times 1$ grid with 12 Å of vacuum for the MLs and 20 Å of vacuum for the HS. We employed the stochastic integration and the 2D cut-off of the Coulomb potential described in Ref.³⁰ to reduce the needed size of the reciprocal space grid. We included 500 unoccupied bands for the MLs, 900 for the S-based HS, 1200 for the Se-based aligned HS and 1600 for the twisted MoSe₂/WSe₂ to compute the screening and the BSE kernel. The values of the kinetic energy cut-off for the response functions and the exchange energy were converged to ensure precision better than ~50 meV. Unless otherwise stated, we employed a $T_{\text{exc}} = 400$ K for the exciton population,

¹<https://github.com/rreho/yambopy>

which allows us to stay within the low exciton density approximation (2) and clearly resolve the emission peaks in PL, which inevitably depend on the number of available exciton states.

4 Results

4.1 Ground state properties

All MLs and HS were fully relaxed (atoms and cell) with stresses and forces below 0.5 kbar and 10^{-5} Ry/a.u.. The lattice parameters (3.191 Å and 3.327 Å for S- and Se-based HS, respectively), remained unchanged in the other stackings. The most stable configuration is AA', followed by AB, SP and AA (Table 1). In the AA stacking the metal atoms belonging to different MLs are on top of each other, resulting in electrostatic repulsion, increased total energy and increased interlayer distance Δd . The layer thickness Δt is not affected by the stacking (Table B1). The twisted Se-based heterostructure has been constructed by rotating it 21.8° relative to the AA stacking configuration, with the rotation axis positioned above two hollow sites. This results in an atomic arrangement intermediate between AA and AB stacking, with 42 atoms in the moiré unit cell. During relaxation of the twisted Se-based HS, instead, the layer spacing shrinks significantly, resulting in enhanced pressure along the stacking direction and higher total energy. The twisted heterostructure could give indications on the physics emerging in misaligned configurations, as the periodically repeated unit cell is larger and the resulting electrostatic potential more complex than the un-twisted cases.

Table 1 Total energy differences per bilayer unit cell (ΔE , meV) and interlayer distance (Δd , Å) of TMD HS.

		AA'	AB	SP	AA	Twisted
MoS ₂ /WS ₂	ΔE	0	3	21	75	//
	Δd	3.040	3.026	3.523	3.633	//
MoSe ₂ /WSe ₂	ΔE	0	4	26	105	980
	Δd	3.137	3.138	2.253	3.721	2.954

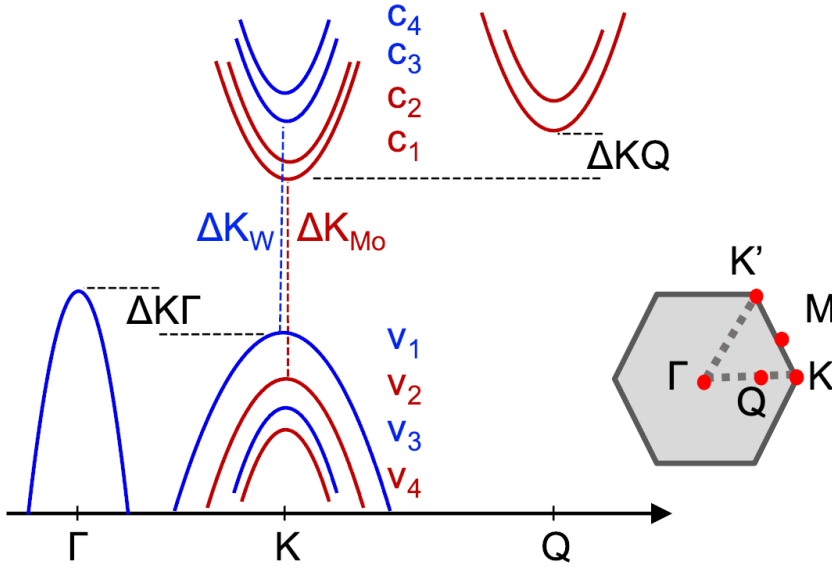


Figure 3 Schematic of a vdW HS band structure representing the layer projected bands (same color convention as in [Fig. 2(a)] and the valley splittings ΔKQ and $\Delta K\Gamma$. $\Delta K_{Mo}/\Delta K_W$ label the energy difference at K between bands belonging to the same monolayer ($c_1 - v_2$ and $c_3 - v_1$, respectively). Note that $c_1 - c_2$ and $c_3 - c_4$ are degenerate at K .

4.2 GW electronic band structure

A quantitative description of the electronic band structure allows one to determine the spatial origin of optical transitions and the direct/indirect nature of each system. This is especially important in phonon assisted processes where multiple electron scatterings might occur from K to Q and vice versa.

In Fig. 2 we analyze the GW band structure for the specific case of MoS_2/WS_2 in the AB stacking. All GW band structures are reported in Appendix C and Fig. C1. The bands are projected either on layers [Fig. 2(a)], as schematically represented in Fig. 3, or on specific atomic orbitals [Fig. 2(b)]. The orbital projection shows the effect of the MLs hybridization and screening in the HS. The HS band structure is more complex than a simple superposition of those of the constituent layers [orange and light blue dashed lines in Fig. 2(a)]: the valence and conduction band edges display a type II alignment at K , with a reduced fundamental gap at K ($\Delta K = 2.058$ eV) with respect to the MLs, leading to the formation of IL excitons. The GW gap of TMD MLs and HS ranges between $\sim 1.2 - 2.5$ eV and increases with the atomic number of the chalcogen atom, while it is less sensitive to the transition metal (Table C1).

The electronic states close to K either belong to WS_2 or MoS_2 layers [Figs. 2(a) and 3]. Specifically, they belong to p and d orbitals of sulfur and metal atoms, respectively [Fig. 2(b)]. We denote ΔK_M , $M = (Mo, W)$ the layer-specific GW gaps (topmost valence to

lowest conduction band belonging to W/Mo). These determine the continuum energy level of IN excitons and their binding energy (BE). We predict that due to interlayer screening the $\Delta K_{\text{Mo/W}}$ gap in a vdW HS is considerably lower than the monolayer one, except for the AA' MoS₂/WS₂ HS (Tables C1 and D1).

All systems display a similar orbital projected band structure (Fig. C1) since they share the same crystal symmetry. The differences are due to the details of the stacking: The spatial overlap between out-of-plane p and d orbitals from each layer affects the valley splitting at high symmetry points of the conduction ($\Delta K_Q = E_Q - E_K$) and valence ($\Delta K_\Gamma = E_K - E_\Gamma$) bands and the SOC splitting at K [Fig. 2(b)]. Going from the most stable (AA') to the less stable (AA) structure, the energy overlap between the second and third valence band (involving p and d orbitals from both layers) increases (Table C1), pushing upwards the valence band at the K point and resulting in a direct gap for the AA structure ($\Delta K_\Gamma > 0$). The Se-based HS exhibit direct gap, except for the twisted one. The variations in the band structure influence the IL and IN exciton energies; however, these are not the only determinants of the absorption peaks (see Sec. 4.3.b). The many-body Kernel, as described by Eq. (1), introduces additional complexity through screening effects that differ with each stacking configuration.

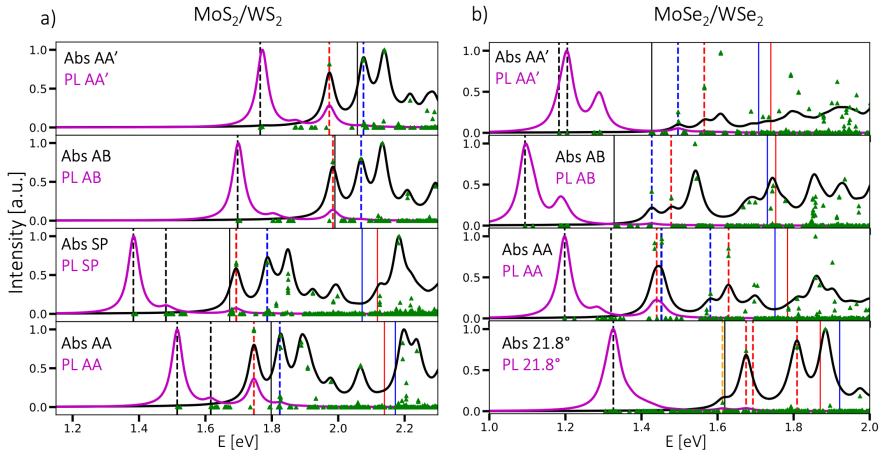


Figure 4 MoS₂/WS₂ and MoSe₂/WSe₂ absorption (black) and PL (magenta) spectra and oscillator strengths (green triangles). Spectra are arranged from top to bottom based on decreasing structural stability. Vertical dashed lines indicate the excitonic peak energies with their corresponding character: IL in black, IN-Mo in red, IN-W in blue, and IN(Mo+W) in orange. Vertical solid lines indicate the electronic gaps at K of the full HS (ΔK , black) and of the projected bands for the individual Mo (ΔK_{Mo} , red) and W layers (ΔK_{W} , blue).

The computed GW gap of S-based HS agree with the literature within ~ 10 meV, while the Se-based gaps are red-shifted by about $\sim 100 - 200$ meV^{4,42–46}. This discrepancy is within the typical accuracy of GW/BSE simulations and can be attributed to specific simulation choices: relaxation with SOC, full Se semicore pseudopotential, vdW correction, and use of the RIM-W

2D Coulomb potential integration method³⁰, which leads to increased screening with respect to previous simulations.

4.3 Optical properties of HS

In this section, we present the absorption and emission spectra of vdW HS. In particular, we discuss the IL excitons and the change in their energy onset upon varying the interlayer distance Δd . We distinguish between symmetry forbidden dark IL excitons and “gray” excitons, which have very small transition dipoles due to the reduced overlap between the hole and electron wavefunctions. We number the excitonic peaks with IX_N (where $N = 1, 2, \dots$). The binding energy (BE) is defined as $BE = \Delta K - IX_N$ for interlayer excitons and $BE = \Delta K_{\text{Mo/W}} - IX_N$ for intralayer excitons.

Spectra: Fig. 4 shows the PL and absorption spectra [Eq. (2)] for different HS stackings. For the stacking that are closer in total energy (AA', AB, AA SP), we predict a systematic energy ordering of the spectra; from $AA' \rightarrow AB \rightarrow AA \rightarrow SP$ for S-based HS and $AA' \rightarrow AA \rightarrow AB$ for Se-based HS. This is marked by the IL (black dashed lines, $v_1 - c_1$ transition) and IN (red/blue dashed lines, $v_2 - c_2$ and $v_1 - c_4$, respectively) excitons. The AA and twisted stackings exhibit quite a different structure (as indicated by the higher total energy) and cannot be directly compared to the above. The absorption spectra of $\text{MoSe}_2/\text{WSe}_2$ in the AA stacking [black continuous line, Fig. 4(b)] shows two absorption peaks for two intralayer excitons: one (red dashed line) localized on the MoSe_2 layer and the other (blue dashed line) on the WSe_2 layer. These transitions are independent but very close in energy. Both have significant and similar oscillator strengths (green triangles). The broadening chosen for visualization is the same for all plots, which, in this case, results in a merging of the two peaks into a single dome. The vdW HS bright exciton peaks (Table 2) are red shifted with respect to the constituent MLs (Table E3), except for the AA' (stable) and AB stacking of the S-based HS. The BEs of the IN excitons are considerably smaller (~ 100 meV) in the vdW HS Table 2 with respect to the MLs Table E3. Thus, it is not straightforward to determine the layer localization of HS excitons simply comparing with the MLs.

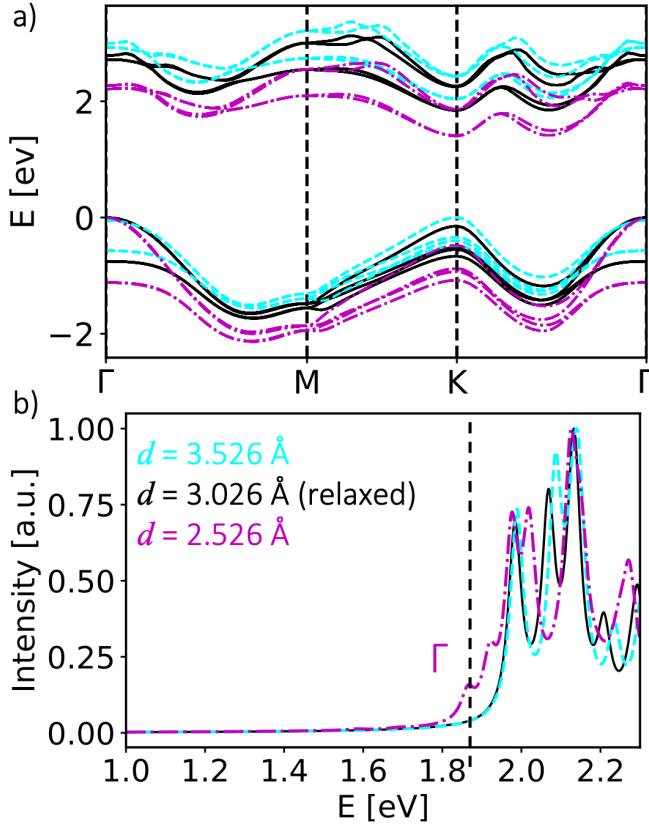


Figure 5 GW band structure (a) and BSE absorption spectrum (b) for MoS₂/WS₂ vdW HS in the AB stacking varying the interlayer distance. The black line corresponds to the relaxed HS ($\Delta d = 0$), while cyan and magenta correspond to systems that differ in interlayer spacing by ± 0.5 Å, respectively. Bands are aligned by their last valence state at Γ . The gap closes strongly with compression, and becomes direct under expansion.

In the twisted HS the reduced interlayer distance and rotation compensate each other. As a consequence, exciton positions are close to those of the MLs. Moreover, the IN-W exciton around ~ 1.8 eV is quenched, and it shows a small oscillator strength. We expect this to be a result of the compression along the stacking direction.

The magnitude of the $\Delta K_{\text{Mo/W}}$ gaps varies among different stacking, the binding energy of the IL and IN excitons are close in magnitude (Table 2), again except for the twisted HS which has a larger binding energy. This is probably due to the fact that variations in the energy gaps and the contributions stemming from the many-body Kernel [as described in Eq. (1)] counterbalance one another.

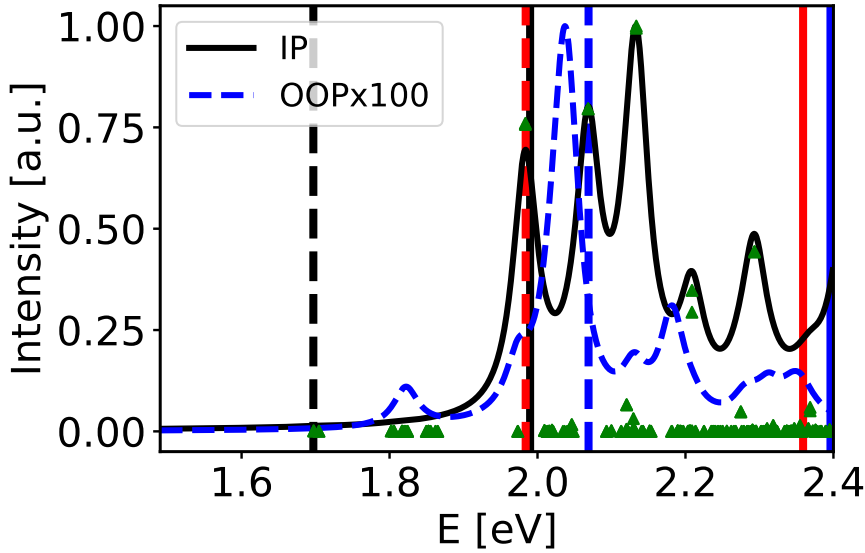


Figure 6 Absorption spectra of MoS_2/WS_2 (AB stacking) computed with in-plane (IP, black) or out-of-plane (OOP, blue) distribution of dipoles. The black continuous line indicates the electronic gap, while the dashed lines indicate the exciton peak (Mo in red, W in blue). Green triangles represent the oscillator strength. Both spectra are rescaled to 1, but the OOP one is 100 times smaller than the IP.

Interlayer excitons: In all vdW HS (Fig. 4) we identify a dark and “gray” IL exciton states below the first IN-Mo and IN-W peaks. Our results predict a reversed intralayer exciton order, with respect to the monolayers, around ~ 1.4 eV in the $\text{MoSe}_2/\text{WSe}_2$ AA’ and AB stacking, with the IN-W exciton lower in energy than IN-Mo. This unexpected reversed exciton order can be explained by the energy discrepancy in the electronic properties of the parent MLs (Sec. 4.2). Note that the exciton order is very sensitive to the computational choices (SOC, pseudopotentials, van der Waals correction) employed for structural relaxation.

The electron distribution of the IL exciton in TMD HS does not reside only in the vacuum region between the two layers, contrary to predictions based on continuum models. We understand this as a consequence of the nature of the exciton wavefunction, which formally contains contributions from all the $\mathbf{k}$ -points in the Brillouin Zone. Such electron distribution cannot be described in models that compute the optical properties only in proximity to the high-symmetry point K .

Our results show that IL excitons of the twisted HS have a significant electron density weight in both layers (Table E2). Moreover, for the same system, we predict an exciton state just below the electronic gap, indicated in orange [Fig. 4(b)], featuring mixed intralayer MoSe_2 (v_2 - c_2) and WSe_2 (v_1 - c_4) transitions. We label this state IN(Mo+W). Analogously, not all the IN excitons have an electronic distribution highly localized within one layer (Tables E2 and E1). An example of this can be seen in the AB stacking of $\text{MoSe}_2/\text{WSe}_2$, where the probability of IN localization, denoted as $P(\text{IN-W})$ [Eq. (5)], is only 20.21%.

To assess the dependence of the exciton peaks on the interlayer distance Δd , we consider the specific case of MoS₂/WS₂ in the AB stacking (Fig. 5). We varied Δd by $\pm 0.5 \text{ \AA}$ and inspected the effects on the band structure and absorption. Increasing Δd the bands blueshift by about $\sim 200 \text{ meV}$, but absorption peaks blueshift by only $\sim 6 \text{ meV}$. This implies that c-axis tensile strain has a relatively weak effect on the position of the peaks.

Decreasing Δd the bands redshift by $\sim 400 \text{ meV}$, the system is in an unfavourable configuration with high stresses and pressure. Absorption changes drastically, with new peaks arising between 1.8 and 1.9 eV [Fig. 5(b)]. In particular, the enhanced overlap between the p_z orbitals due to vertical compression results in a new bright transition at Γ at 1.86 eV. The lack of inversion symmetry in vdW HS results in a $\sim 10 \text{ meV}$ splitting of the c_1/c_2 bands. The effect of the splitting propagates to the absorption and emission spectra [Eq. (1)] where the first poles of the BSE equation with low oscillator strength [green triangles Figs 4(a) and 4(b)] are IL excitons, with energy splitting of the order of the SOC splitting⁴⁷. This effect is more pronounced in Se-based HS due to Se larger atomic mass and SOC. In addition, MoS₂/WS₂ in the SP stacking displays two dark IL exciton state groups separated by 0.098 eV. Se-based vdW HS, instead, display two distinct IL excitons in the AA' and AA stacking. Furthermore, we observe that all systems have clusters of dark BSE equation poles below the first bright peak whose energy, shape, and spread varies with the different stacking.

Dark and “gray” IL excitons: The darkness of excitons can be due to symmetry as in MLs but also to the interlayer nature, which implies very small overlap between the hole and electron wavefunctions. The latter excitons are “gray”, but not dipole forbidden. To discern the dark IL exciton, one can either inspect the dipole matrix elements (Table E5) or move the electric field polarization out of plane (schematically represented in Fig. E1). Considering again the AB alignment of MoS₂/WS₂ as a prototypical example, we see that varying the electric field direction, the forbidden IL exciton at $\sim 1.8 \text{ eV}$ becomes bright, with the IN excitons being weaker than the in-plane (IP) configuration (Fig. 6). In particular, we observe that, among the series of IL excitons below the fundamental gap, the first one remains dark in the out-of-plane (OOP) configuration while the second one becomes bright. This is due to different spin indices of the bands involved in the formation of the exciton states. The first IL exciton of the series comes from a transition between $v_1 - c_1$ (spin - down/spin - up), while the second one from $v_1 - c_2$ (spin - down/spin - down). Note that in Fig. 6 we rescaled the maximum absorption to 1 for both IP and OOP configuration, however, in absolute value, the OOP one is around two orders of magnitude weaker due to the smaller out-of-plane dipole.

Detailed exciton energies and transitions for the various systems are listed in Table 2. In Appendix E we report the absorption plots for IP and OOP electric field direction for all systems, along with information on the relevant energetic transitions.

Table 2 Interlayer exciton (IL), intralayer exciton (IN-M) and binding energies (BE) for the vdW HS.

System	Stacking	IX ₀ exciton			IX ₁ exciton			IX ₂ exciton		
		E [eV]	BE [eV]	IL/IN	E [eV]	BE [eV]	IL/IN	E [eV]	BE [eV]	IL/IN
MoS ₂ /WS ₂	AA'	1.765	0.292	IL	1.973	0.368	IN-Mo	2.079	0.323	IN-W
	AB	1.697	0.293	IL	1.984	0.375	IN-Mo	2.069	0.327	IN-W
	SP	1.383	0.290	IL	1.693	0.379	IN-Mo	1.786	0.332	IN-W
	AA	1.515	0.283	IL	1.746	0.393	IN-Mo	1.827	0.345	IN-W
MoSe ₂ /WSe ₂	AA'	1.205	0.222	IL	1.496	0.204	IN-W	1.565	0.175	IN-Mo
	AB	1.094	0.235	IL	1.427	0.305	IN-W	1.478	0.275	IN-Mo
	AA	1.198	0.252	IL	1.435	0.349	IN-Mo	1.587	0.164	IN-W
	21.8°	1.305	0.314	IL	1.613	Mo: 0.308 W: 0.257	IN-Mo and IN-W	1.675	0.246	IN-Mo

5 Photoluminescence and exciton radiative lifetimes

Photoluminescence gives a quantitative description of the states involved in the creation of the IL exciton and their recombination time, which is crucial for any technological application, such as solar energy conversion devices^{48–52}.

Exciton population is tuned by changing the T_{exc} (in K or meV) in the Bose distribution. For very small exciton population at $T_{\text{exc}} = 5$ K, the PL intensity peaks at the lowest dark exciton state. In emission, we see that higher exciton states are populated and emit from the energy positions of the BSE poles (Fig. 7).

Fixing the exciton temperature T_{exc} at 400 K, we inspect the information carried by the PL spectra among different stacking (Fig. 4). In analogy to the IP vs OOP electric field configuration described in Sec. 4.3, the emission spectra show that not all dark IL excitons are the same in nature. Again, we can distinguish between dark (symmetry forbidden) and “gray” (small electron/hole overlap) IL excitons. Interestingly, PL allows analyzing further the BSE poles, and it carries complementary information with respect to the absorption spectra (both IP and OOP). Varying the direction of the electric field reveals the relative intensity of the exciton peaks in relation to the excitation direction. Meanwhile, PL serves as a distinct method to identify the most prominent interlayer (IL) emission peaks beneath the fundamental gap, among the series of BSE poles. For example, in the AA' stacking (both S- and Se- based HS) we have two BSE poles around 1.77/1.19 eV, but only the second one is bright in emission. The PL spectra for the Se-based 21.8° twisted HS is rather unique. IL excitons are not peaked at K but between Γ and M (see Supplementary Information). Note that, in addition to IL excitons, PL is peaked also for poles belonging to IN excitons.

The exciton radiative lifetimes can be modulated extensively across several orders of magnitude by varying factors such as the number of layers, stacking configurations, and temperature^{23,24,53,54}, as confirmed by our results illustrated in Fig. E2. Longer lifetimes are interesting, for instance, for photovoltaic applications⁴⁹.

In MLs, the dark exciton states are long-lived (~ 1 Ms) attributable to the low exciton oscillator strength, suggesting a low probability of re-emission upon occupation (Appendix Fig. D2). Bright excitons possess lifetimes in the picosecond range, aligning with values reported in similar studies^{23,24}. In vdW HS, we observe a significant change in the order of magnitude of the lifetimes depending on the stacking. The IL exciton lifetimes are in the

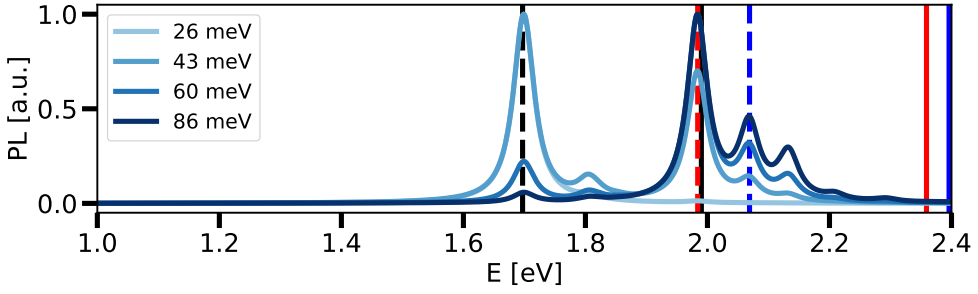


Figure 7 PL spectra of MoS₂/WS₂ (AB stacking) as a function of the excitonic population $k_B T_{\text{exc}} = 26, 43, 60, 86$ meV. The vertical continuous and dashed lines are defined as in Fig. 6. The maximal PL intensity is rescaled to unity for each temperature.

pico/nanosecond range, with a couple of exceptional transitions in the microsecond range for the AA stacking. The IN exciton lifetimes are all within the picosecond range, except for the mixed IN excitons of Se-based twisted vdW HS around 1.62 eV. Moreover, the 21.8° stacking shows a long-lived ground state IL exciton with lifetime $0.428\mu\text{s}$. The order of magnitude of the lifetime is inversely proportional to the exciton dipole strength [Eq. (4)]. IL excitons are characterized by an out-of-plane dipole moment. Its strength depends on the distance and especially on the overlap between the constituent electron and hole wave functions. A reduced overlap leads to a reduction of the exciton dipole strength and in turn an increase of its lifetime. The order of magnitude of these excitons radiative lifetimes aligns quite well with available experiments which report, for the IL exciton lifetime, a value of 40ps in MoS₂/WS₂ and 1.8ns in MoSe₂/WSe₂ ^{15,55–58}. To sum up, we show that there are IL excitons with ultralong lifetime of the order of μs and that PL is a useful tool to identify stackings and investigate the nature of IL excitons in vdW HS.

6 Conclusion

We compute the electronic band structure, absorption spectra and photoluminescence for MoS₂/WS₂, MoSe₂/WSe₂ vdW heterostructures in different stacking configurations and compare to the constituent MLs. We discuss the shift and variations of the exciton peaks, order, and lifetimes with different stacking, and analyze the sensitivity of these results to the geometrical relaxation and the inclusion of semicore states in the pseudopotentials. We show that in vdW HS, the intralayer excitons have electron density spread in both layers. This feature is enhanced in the Se-based twisted HS where the mixed intralayer exciton has an electron density distributed over both MoSe₂ and WSe₂. In addition, the twisted HS has a peculiar IL exciton with the electron density spread in both layers. We discuss on the difference between spin - forbidden dark interlayer excitons and “gray” excitons, whose darkness is the result of a reduce spatial overlap between the electron and hole wavefunctions. We show that “gray” excitons become bright when the dipoles are excited in the stacking direction. Furthermore,

we show that the emission spectra obtained with our implementation of the PL spectra within the Ai-MBPT formalism in the YAMBO code can bring additional insight into the nature of “gray” excitons.

Our findings highlight the potential to use absorption and emission as characterization tools for HS stacking. The tunability of excitonic properties in vdW TMD heterostructures enables controlled localization, energy tuning, and coupling of interlayer excitons, allowing their use as qubits for quantum logic operations.

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Authorship statement

This chapter is based on the work of Reho et al.¹. RR conducted the first-principles simulations and developed the necessary routines within the YAMBO and YAMBOPY codes. RR also took the lead in writing the manuscript. ABM, MJV and Davide Sangalli (DS) contributed to the physical interpretation and provided feedback on the manuscript. DS provided technical support for the code implementation of photoluminescence in the YAMBO code. ZZ, as the last author, secured funding for the project and assessed the correctness of the manuscript.

7 Appendices

A The role of Se semicore states and van der Waals correction

The treatment of the potential generated by the electronic states of Selenium (atomic number $Z = 34$) is critical for the assessment of the direct/indirect gap nature of TMDs MLs and, in general, of semiconductors and semimetals⁵⁹. In the pseudopotential approach, core electrons are considered to be frozen. If only partial Se semicore states $3d^{10}4s^24p^4$ are included in the pseudopotential, then we find an unphysical indirect GW band gap for the TMDs monolayers. Including semicore $3s^23p^6$ states and relaxing the structure with van der Waals corrections provided the correct direct band structure. As an example, we provide a table of the relaxed lattice parameter a for WSe₂ using different pseudopotentials, with/without van der Waals correction (Table A1). In Fig. C2 we show these effects for the GW band structure of MoSe₂ and WSe₂. The shift in energy is also reflected in the position of the exciton peaks in absorption. Coincidentally, the position of the first exciton for WSe₂ with partial semicore pseudopotentials is ~ 1.63 eV and closer to the experimental value than the one reported in the main text, ~ 1.520 eV. Moreover, employing partial semicore pseudopotentials, the MoSe₂ IX₀ exciton (at 1.52 eV) is lower in energy than the WSe₂ IX₀ exciton. Since full semicore pseudopotential lead to the correct band structure for the MLs, we employ full semicore pseudopotentials throughout this study for consistency. We understand this difference as an increased screening due to the treatment of the Coulomb potential as a truncated potential in a slab geometry³⁰.

Table A1 Effects of Se semicore states and van der Waal correction in WSe₂ relaxed structural parameters (lattice parameter a and thickness Δt), and GW electronic bandgap.

a [Å]	Δt [Å]	vdW	Semicore	ΔK gap [eV]	GW gap
3.323	3.360	No	Partial	2.178	Indirect
3.323	3.360	Yes	Partial	2.253	Indirect
3.338	3.251	Yes	Full	1.934	Direct

B Structural properties of ML and HS

Relaxed structural parameters (lattice parameter a , layer thickness Δt and $\Delta t_{\text{Mo/W}}$, and van der Waals gap Δd) of MLs and HS are reported in Table B1.

C GW band structures for TMD HS

For each system, we report the orbital-projected band structure in Fig. C1. Our findings indicate that all systems exhibit a type II band alignment, with the primary composition of the first four conduction and valence bands being the d-orbitals of the metals and the p-orbital of the chalcogen atom. Although the orbital projections vary only slightly among the systems, the

Table B1 Relaxed lattice parameter a , distance Δd between layers, and layer thickness $\Delta t_{\text{Mo/W}}$ for the vdW HS and TMDs MLs.

System	Stacking	a [Å]	Δd [Å]	Δt_{Mo} [Å]	Δt_{W} [Å]
MoS ₂	//	3.194	//	3.129	//
WS ₂	//	3.195	//	//	3.129
MoSe ₂	//	3.317	//	3.301	//
WSe ₂	//	3.338	//	//	3.251
MoS ₂ /WS ₂	AA'	3.191	3.040	3.116	3.132
	AA	3.191	3.633	3.117	3.131
	AB	3.191	3.026	3.116	3.130
	SP	3.191	3.523	3.116	3.131
MoSe ₂ /WSe ₂	AA'	3.327	3.137	3.329	3.342
	AA	3.327	3.721	3.328	3.342
	AB	3.327	3.138	3.328	3.342
	SP	3.327	3.253	3.328	3.343
	21.8°	8.780	2.954	3.280	3.333

ΔKQ and the $\Delta K\Gamma$ splittings are strongly influenced by the different stacking configurations, as reported in the main text and in Table C1.

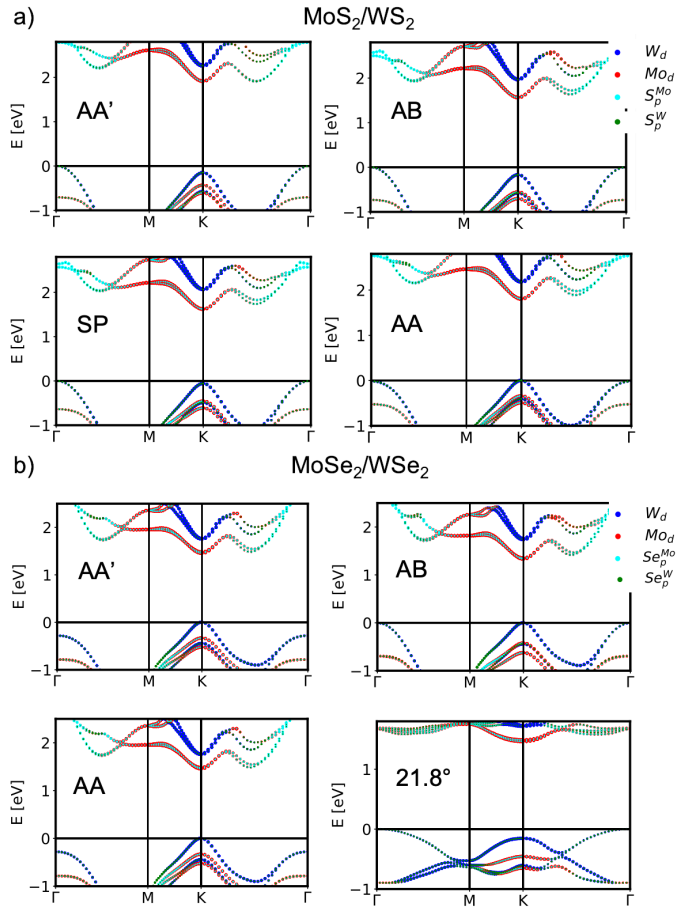


Figure C1 Orbital projected GW band structure of MoS_2/WS_2 (a) and $\text{MoSe}_2/\text{WSe}_2$ (b) for different stackings. The size of the dots is weighted by the relative orbital contribution.

Table C1 GW Energy differences ΔK , ΔK_{Mo} and ΔK_{W} , energy valley offsets ($\Delta K\Gamma = E_K - E_\Gamma$, $\Delta KQ = E_Q - E_K$) and spin - orbit coupling splitting at K for different stacking of MoS_2/WS_2 and $\text{MoSe}_2/\text{WSe}_2$ (all in eV).

System	stacking	ΔK	ΔK_{Mo}	ΔK_{W}	$\Delta K\Gamma$	ΔKQ	$\Delta K_{v_1v_2}$	$\Delta K_{v_2v_3}$	$\Delta K_{v_3v_4}$	$\Delta K_{c_2c_1}$	$\Delta K_{c_3c_2}$	$\Delta K_{c_4c_3}$
MoS_2/WS_2	AA'	2.058	2.341	2.403	-0.150	0.000	0.283	0.142	0.033	0.008	0.336	0.015
	AB	1.990	2.359	2.397	-0.149	0.009	0.369	0.142	0.117	0.008	0.336	0.011
	SP	1.673	2.072	2.118	-0.060	0.122	0.398	0.033	0.124	0.009	0.435	0.011
	AA	1.798	2.139	2.172	0.021	0.094	0.341	0.066	0.086	0.010	0.365	0.008
$\text{MoSe}_2/\text{WSe}_2$	AA'	1.427	1.748	1.706	0.028	0.030	0.331	0.018	0.079	0.027	0.383	0.011
	AB	1.329	1.753	1.731	0.006	0.090	0.424	0.018	0.183	0.019	0.383	0.025
	AA	1.452	1.784	1.751	0.281	0.030	0.331	0.113	0.079	0.027	0.272	0.011
	21.8°	1.619	1.921	1.870	-0.156	0.159	0.302	0.150	0.045	0.025	0.226	0.015

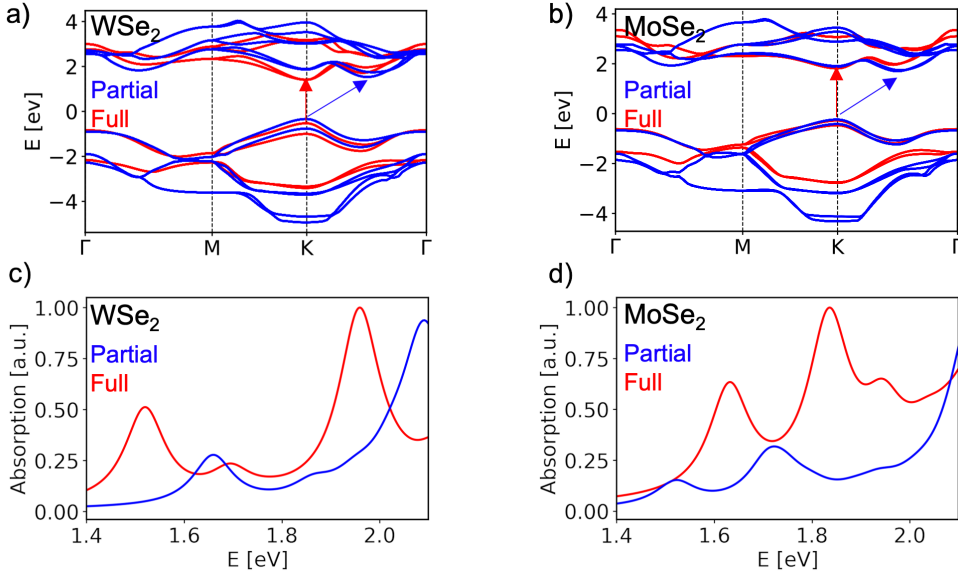


Figure C2 GW (a,b) band structures and absorption (c,d) spectra for WSe_2 and MoSe_2 MLs with full semicore (red) or partial semicore (blue) pseudopotentials. The inclusion of semicore states and relaxing the structures with SOC correctly give a direct gap band structure.

D Absorption and Emission Spectra of TMD Monolayers

The absorption and emission spectra [Eq. (1) and Eq. (2)] of the MLs (Fig. D1), confirm the high exciton binding energy attributed to diminished dielectric screening in the 2D limit. We observe a prominent emission peak at the first exciton eigenstate of the BSE Hamiltonian [Eq. (1)]. This peak coincides with the position of the first finite oscillator strength (green triangles) and is dark in absorption due to optical selection rules (spin forbidden). MoSe_2 has a dark exciton degenerate with the first bright peak, confirming previous reports^{11,60}. The computed excitonic peaks (labeled as IX_N , where $N = 1, 2, \dots$), align closely with experimental data for the S-based MLs³⁴ (Table E3). The results for Se-based MLs are further from

experimental findings⁶¹ (e.g. the energy of the first exciton peak in WSe₂ is about 100–200 meV lower) due to the underestimation of the electronic energy gap (Sec. 4.2).

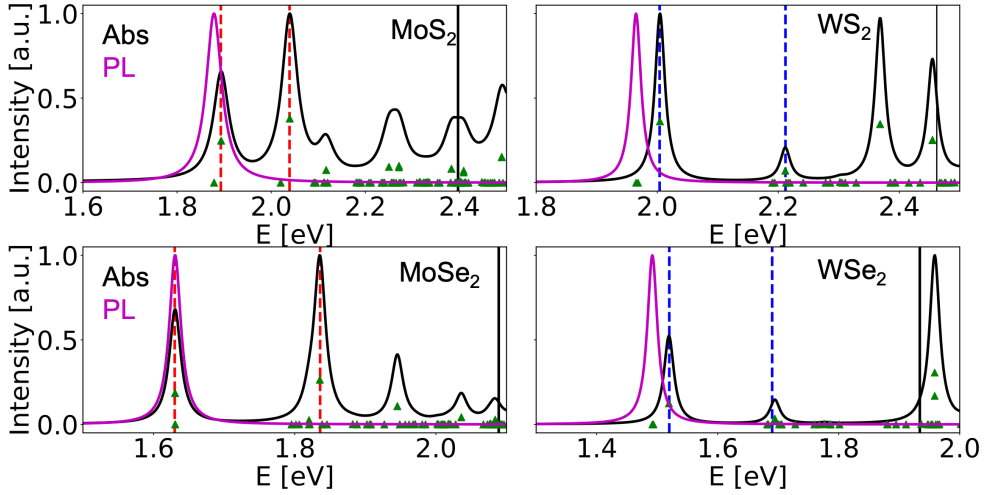


Figure D1 Absorption (black) and PL(magenta, $T_{\text{exc}} = 5K$) plots for different MLs. The black continuous vertical lines indicate the GW electronic gap while the dashed vertical lines indicate the excitonic peaks (Mo in red, W in blue). Green triangles represent the oscillator strength.

Table D1 Energy valley splittings and GW gap for the MLs.

ML	ΔK gap [eV]	$\Delta K\Gamma$ [eV]	ΔKQ [eV]
MoS ₂	2.397	0.122	0.184
WS ₂	2.462	0.252	0.028
MoSe ₂	2.089	0.345	0.144
WSe ₂	1.934	0.312	0.309

E Optical absorption of TMD heterostructures

We present a comprehensive table (Table E4) detailing the most significant transitions observed in the BSE spectra, which manifest in both absorption (IP and OOP) and photoluminescence (PL). Fig. E1 shows a schematic of the IP and OOP setup. Fig. E3 displays the IP and OOP absorption spectra for the systems under investigation, and the normalized exciton dipoles are reported in Table E5.

Analysis indicates that the strongest peaks in the OOP configuration do not appear in the IP configuration, and the most prominent IP peaks are diminished in the OOP configuration. To elucidate these findings, we have employed dashed and continuous lines in Figs. E3 and 4 to denote relevant excitonic transitions, thereby underscoring their significance within the scope of this discussion. To quantify the differences between “dark” excitons (dark in both

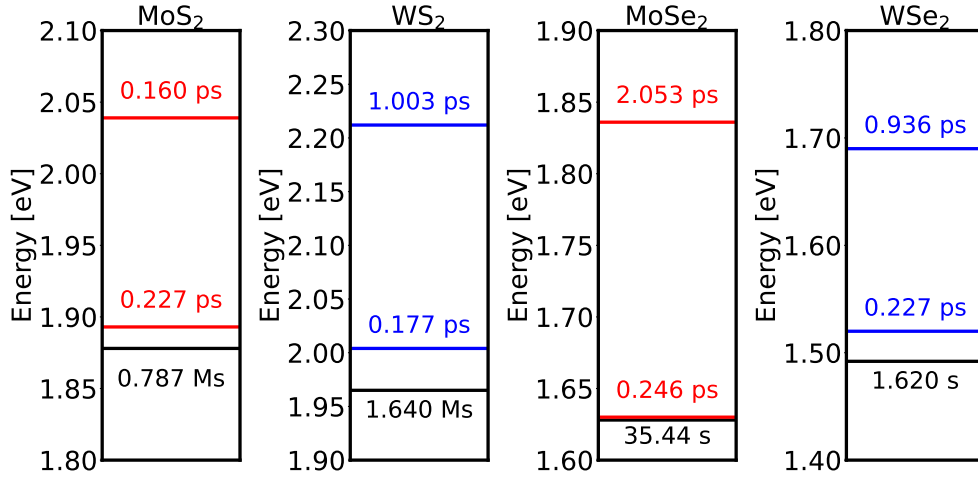


Figure D2 Lifetimes of the monolayers for IL dark states (black line) and IN-Mo/IN-W bright states (red and blue lines).

IP and OOP configurations) and “gray” excitons (dark in the IP configuration but bright in the OOP configuration, or vice versa), we present the excitonic dipole strengths of selected transitions in Table E5.

In particular, Fig. 4(b) highlights various excitonic features in the twisted heterostructure: interlayer (IL) excitons are marked with dashed vertical black lines, the mixed intralayer IN(Mo+W) state is indicated in orange, and the first three intralayer IN-Mo excitonic states are also delineated. Notably, no bright intralayer W (IN-W) excitons are observed. Additionally, Fig. E3(b) introduces new transitions following the same color coding, with an observable IN-W exciton in the twisted configuration at 1.578 eV.

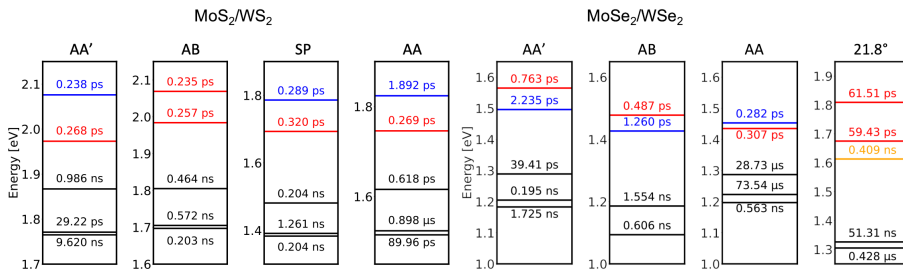


Figure E2 Energies and lifetimes of the vdW HS for dark IL states (black line) and bright IN-Mo/IN-W states (red and blue lines). The orange line denotes the mixed IN+Mo/W state for the 21.8° twist stacking.

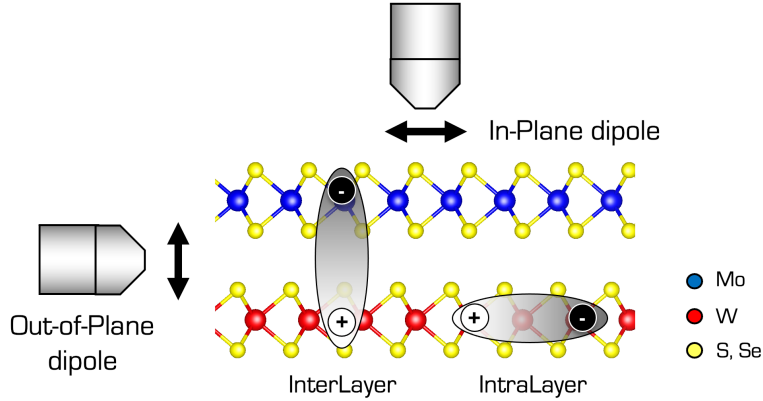


Figure E1 Schematic of a prototypical experimental setup showing a detector (gray) capturing either in-plane (IP) or out-of-plane (OOP) light excitations. The ball and stick model depicts a Se-based vdW HS.

Table E1 GW gap, exciton, and binding energies (in eV) and IN/IL coefficients for different stackings of MoS₂/WS₂.

Stacking	ΔK [eV]	IX0	P(IL)	IX1	P(IN-Mo)	IX2	P(IN-W)
AA'	1.960	1.670 (0.290)	97.81%	1.889 (0.366)	94.06%	2.057 (0.255)	54.74%
AA	1.798	1.515 (0.283)	99.2%	1.746 (0.393)	99.7%	1.827 (0.345)	65.24%
AB	1.727	1.194 (0.533)	99.2%	1.496 (0.618)	98.3%	1.639 (0.475)	99.0%
SP	1.673	1.383 (0.290)	99.14%	1.693 (0.379)	80.15%	1.786 (0.332)	97.26%

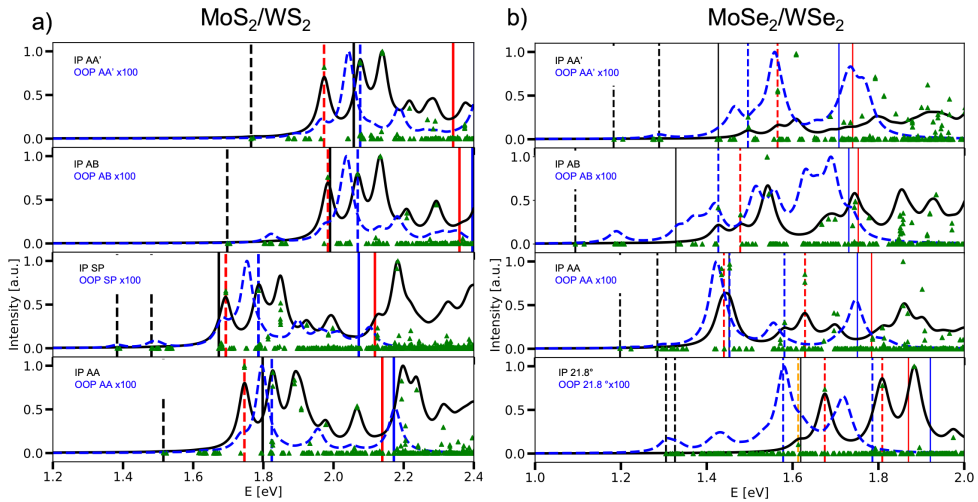


Figure E3 Absorption spectra for (a) MoS₂/WS₂ and (b) MoSe₂/WSe₂ HS, computed IP or OOP distribution of dipoles. Oscillator strengths are represented by green triangles. Dashed lines in black, red, and blue highlight the IP transition character at the *K* point, corresponding to IL, IN-Mo, IN-W transitions, respectively. Vertical solid lines in black, red, and blue delineate the electronic bandgap along with gaps between Mo and W projected bands at *K*.

Table E2 GW gap, exciton and binding energies (in eV) and IL/IN coefficient for different stackings of MoSe₂/WSe₂.

Stacking	ΔK [eV]	IX0	P(IL)	IX1	P(IN-)	IX2	P(IN-)
AA'	1.427	1.205(0.222)	97.70%	1.496(0.204)	57.91%(W)	1.565(0.175)	84.38%(Mo)
AA	1.452	1.198(0.252)	96.98%	1.435(0.349)	99.6%(Mo)	1.587(0.164)	59.06%(W)
AB	1.329	1.094(0.235)	98.71%	1.427(0.3049)	20.21%(W)	1.478(0.275)	86.16%(Mo)
21.8°	1.619	1.305(0.314)	52.63%	1.613(0.308/0.257)	40.31%(W)	1.675(0.246)	25.63%(Mo)

Table E3 Exciton (IX_N), PL peaks and binding energy (BE) for the different MLs.

ML	IX ₁ [eV]	BE [eV]	IX ₂ [eV]	BE [eV]	PL [eV]
MoS ₂	1.893	0.504	2.039	0.358	1.878
WS ₂	2.004	0.458	2.212	0.250	1.965
MoSe ₂	1.630	0.459	1.836	0.253	1.630
WSe ₂	1.520	0.414	1.694	0.240	1.492

Table E4 Transition table for Interlayer exciton (IL) and intralayer exciton (IN-X) for all vdW HSs. We report the pronounced peaks for IP and OOP electric field direction depicted in Fig. E3. A slash symbol in the binding energy indicates that the transition is above the electronic gap.

MoS ₂ /WS ₂ AA'			MoSe ₂ /WSe ₂ AA'		
E [eV]	BE [eV]	Transition (K point)	E [eV]	BE [eV]	Transition (K point)
1.765	0.292	IL (K) v ₁ -c ₁	1.184	0.243	IL (K) v ₁ -c ₁
1.771	0.298	IL (K) v ₁ -c ₁	1.205	0.222	IL (K) v ₁ -c ₂
1.867	0.190	IL (K) v ₁ -c ₁	1.205	-	-
1.964	0.377	IN-Mo (K) v ₂ -c ₁	1.275	0.152	IL (Γ - K, close to K) v ₁ -c ₁
-	-	-	1.290	0.169	IL (Γ - K, close to K) v ₁ -c ₂
1.973	0.368	IN-Mo (K) v ₂ -c ₁	1.462	/	IL (Γ - K, close to K) v ₁ -c ₂
2.043	0.359	IN-W (K) v ₁ -c ₄	1.496	0.204	IN-W (K) v ₁ -c ₄
2.079	0.323	IN-W (K) v ₁ -c ₄	1.565	0.175	IN-Mo (K) v ₂ -c ₁
MoS ₂ /WS ₂ AB			MoSe ₂ /WSe ₂ AB		
E [eV]	BE [eV]	Transition (K point)	E [eV]	BE [eV]	Transition (K point)
1.697	0.293	IL (K) v ₁ -c ₁	1.094	0.235	IL (K) v ₁ -c ₁
-	-	-	1.187	0.142	IL (Γ - K, close to K) v ₁ -c ₁
-	-	-	1.332	-	IL (Γ - K, close to K) v ₁ -c ₁
1.822	0.537	IL (K) v ₁ -c ₂	1.367	-	IL (Γ - K, close to K) v ₁ -c ₁
1.984	0.375	IN-Mo (K) v ₂ -c ₁	1.420	-	IL (M - K, close to K) v ₁ -c ₁
2.069	0.327	IN-W (K) v ₁ -c ₄	1.427	0.305	IN-W (K) v ₁ -c ₄
2.120	/	IL (Γ - K, close to K) v ₁ -c ₁	1.478	0.275	IN-Mo (K) v ₂ -c ₂
MoS ₂ /WS ₂ SP			MoSe ₂ /WSe ₂ AA		
E [eV]	BE [eV]	Transition (K point)	E [eV]	BE [eV]	Transition (K point)
1.383	0.290	IL (K) v ₁ -c ₁	1.198	0.252	IL (K) v ₁ -c ₁
-	-	-	1.223	0.278	IL (K) v ₁ -c ₂
1.481	0.192	IL (K) v ₁ -c ₁	1.285	0.168	IL (K) v ₁ -c ₁
1.684	/	IL (K) v ₁ -c ₂	1.435	0.349	IN-Mo (K) v ₂ -c ₁
1.693	0.379	IN-Mo (K) v ₂ -c ₁	1.433	0.298	IN-W (K) v ₁ -c ₄
-	-	-	1.554	/	IL (Γ - K, close to K) v ₁ -c ₁
1.753	0.367	IN-W (K) v ₁ -c ₃	1.587	0.164	IN-W (K) v ₁ -c ₄
MoS ₂ /WS ₂ AA			MoSe ₂ /WSe ₂ 21.8°		
E [eV]	BE [eV]	Transition (K point)	E [eV]	BE [eV]	Transition (K point)
1.515	0.283	IL (K) v ₁ -c ₁	1.305	0.314	IL (Γ and Γ - M, close to Γ) v ₁ -c ₁
-	-	-	1.332	0.287	IL (between Γ and Γ - M) v ₁ -c ₁
1.629	0.169	IL (K) v ₁ -c ₂	1.403	0.216	IL (Γ) v ₁ -c ₁
1.735	0.063	IL (Γ - K, close to K) v ₁ -c ₁	1.578	0.292	IN-W (K) v ₁ -c ₃
1.746	0.393	IN-Mo (K) v ₂ -c ₁	1.613	Mo: 0.308 W: 0.257	IN-Mo (K) v ₂ -c ₁
-	-	-	-	-	IN-W (K): v ₁ -c ₄
-	-	-	1.675	0.246	IN-Mo (K) v ₂ -c ₁
1.827	0.345	IN-W (K) v ₁ -c ₄	1.720	0.150	IN-W (Γ - K, close to K) v ₁ -c ₄

Table E5 In plane (IP) and out of plane (OOP) excitonic dipoles d (see also Fig. E3) for some of the interlayer excitons (IL) and intralayer excitons (IN-X) for all vdW HSs. We differentiate between dark excitons, with $d = 0$ (we set to zero anything smaller than 5×10^{-5}), “gray” with $5 \times 10^{-5} < d < 0.1$, and bright excitons with $d \geq 0.1$. The values are w.r.t. the most intense excitonic dipole which is set to 1. We highlight “gray” excitons in bold. Excitonic dipoles are normalized to 1 relative to the largest dipole in the system. A slash in the binding energy column indicates that the transition exceeds the electronic gap.

MoS ₂ /WS ₂ AA'			MoSe ₂ /WSe ₂ AA'		
E [eV]	IP	OOP	E [eV]	IP	OOP
1.765	2.55×10^{-4}	0.0	1.184	1.83×10^{-4}	0.0
1.964	0.0	0.162	1.275	0.0	1.07×10^{-2}
1.973	0.802	0.0	-	-	-
2.043	0.0	1.0	1.496	0.255	0.0
-	-	-	1.558	0.0	1.0
2.079	0.882	0.0	1.565	0.562	0.0
MoS ₂ /WS ₂ AB			MoSe ₂ /WSe ₂ AB		
1.697	1.68×10^{-3}	0.0	1.094	2.12×10^{-3}	0.0
-	-	-	1.187	0.0	.160
-	-	-	1.332	0.0	.248
1.822	0.0	.135	1.367	0.0	.331
1.984	0.76	0.0	1.420	5.82×10^{-5}	0.514
2.069	0.80	0.0	1.427	.416	0.0
2.122	0.0	1.81×10^{-3}	1.478	0.0	0.0
MoS ₂ /WS ₂ SP			MoSe ₂ /WSe ₂ AA		
1.383	3.68×10^{-4}	4.06×10^{-3}	1.198	5.78×10^{-3}	0.0
1.481	2.23×10^{-3}	4.49×10^{-2}	1.285	0.0	2.42×10^{-2}
1.684	1.67×10^{-4}	.13	1.435	8.5×10^{-2}	-
1.693	0.64	6.39×10^{-4}	1.453	0.96	0.0
1.753	0.0	1.0	1.587	.97	0.0
1.786	0.64	0.0	-	-	-
MoS ₂ /WS ₂ AA			MoSe ₂ /WSe ₂ 21.8°		
1.515	3.42×10^{-3}	0.	1.332	0.0	8.56×10^{-2}
1.629	0.0	1.00×10^{-2}	1.578	0.	1.00
1.735	0.0	1.26×10^{-3}	1.613	0.14	0.0
1.746	1.00	0.0	1.675	0.74	0.0
1.827	0.92	0.0	1.720	0.0	5.39×10^{-2}

Bibliography

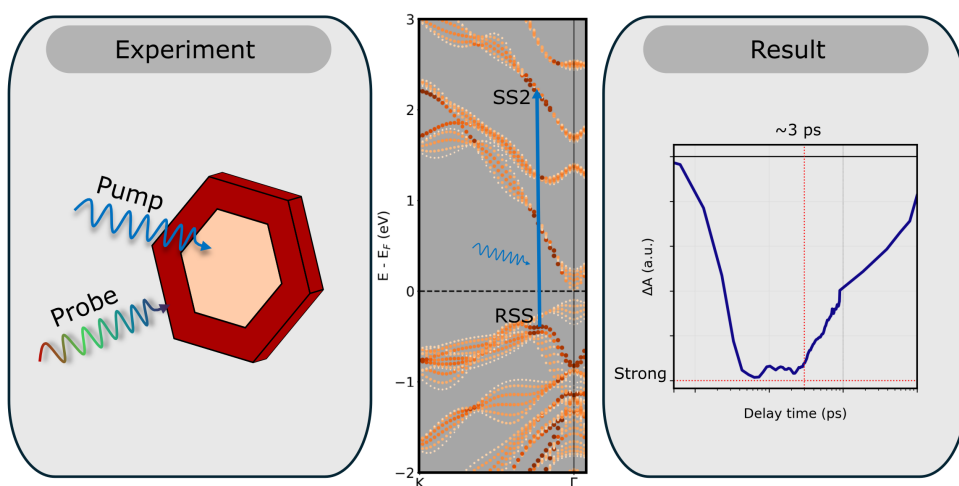
- 1 R. Reho, A. Botello-Méndez, D. Sangalli, M. Verstraete, and Z. Zanolli, *Physical Review B* **110**, 035118 (2024).
- 2 N. P. Wilson, W. Yao, J. Shan, and X. Xu, *Nature* **599**, 383 (2021).
- 3 K. S. Novoselov, D. Jiang, F. Schedin, T. Booth, V. Khotkevich, S. Morozov, and A. K. Geim, *Proceedings of the National Academy of Sciences* **102**, 10451 (2005).
- 4 A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, *Nano letters* **10**, 1271 (2010).
- 5 Y.-H. Lee, X.-Q. Zhang, W. Zhang, M.-T. Chang, C.-T. Lin, K.-D. Chang, Y.-C. Yu, J. T.-W. Wang, C.-S. Chang, L.-J. Li, and T.-W. Lin, *Advanced Materials* **24**, 2320 (2012), <https://onlinelibrary.wiley.com/doi/pdf/10.1002/adma.201104798>.
- 6 T. Sohier, P. M. de Melo, Z. Zanolli, and M. J. Verstraete, *2D Materials* **10**, 025006 (2023).
- 7 K. Tran, G. Moody, F. Wu, X. Lu, J. Choi, K. Kim, A. Rai, D. A. Sanchez, J. Quan, A. Singh, *et al.*, *Nature* **567**, 71 (2019).
- 8 W. Ma, Q. Zhang, L. Li, D. Geng, and W. Hu, *J. Mater. Chem. C* **11**, 15793 (2023).
- 9 W. Ma, Q. Zhang, L. Li, D. Geng, and W. Hu, *J. Mater. Chem. C* **11**, 15793 (2023).
- 10 R. Ribeiro-Palau, C. Zhang, K. Watanabe, T. Taniguchi, J. Hone, and C. R. Dean, *Science* **361**, 690 (2018).
- 11 G. Wang, A. Chernikov, M. M. Glazov, T. F. Heinz, X. Marie, T. Amand, and B. Urbaszek, *Reviews of Modern Physics* **90**, 021001 (2018).
- 12 Z. Ji, H. Hong, J. Zhang, Q. Zhang, W. Huang, T. Cao, R. Qiao, C. Liu, J. Liang, C. Jin, *et al.*, *ACS nano* **11**, 12020 (2017).
- 13 C. Trovatiello, F. Katsch, N. J. Borys, M. Selig, K. Yao, R. Borrego-Varillas, F. Scotognella, I. Kriegel, A. Yan, A. Zettl, *et al.*, *Nature communications* **11**, 5277 (2020).
- 14 J.-Y. Tsai, J. Pan, H. Lin, A. Bansil, and Q. Yan, *Nature communications* **13**, 492 (2022).
- 15 Y. Jiang, S. Chen, W. Zheng, B. Zheng, and A. Pan, *Light: Science & Applications* **10**, 72 (2021).
- 16 E. Torun, H. P. Miranda, A. Molina-Sánchez, and L. Wirtz, *Physical Review B* **97**, 245427 (2018).
- 17 R. Gillen and J. Maultzsch, *Physical Review B* **97**, 165306 (2018).

- 18** D. Sangalli, A. Ferretti, H. Miranda, C. Attaccalite, I. Marri, E. Cannuccia, P. Melo, M. Marsili, F. Paleari, A. Marrazzo, *et al.*, Journal of Physics: Condensed Matter **31**, 325902 (2019).
- 19** A. Marini, C. Hogan, M. Grüning, and D. Varsano, Computer Physics Communications **180**, 1392 (2009).
- 20** P. M. M. C. de Melo and A. Marini, Phys. Rev. B **93**, 155102 (2016).
- 21** P. Lechiffart, F. Paleari, D. Sangalli, and C. Attaccalite, Physical Review Materials **7**, 024006 (2023).
- 22** F. Paleari, H. P. Miranda, A. Molina-Sánchez, and L. Wirtz, Physical Review Letters **122**, 187401 (2019).
- 23** M. Palummo, M. Bernardi, and J. C. Grossman, Nano letters **15**, 2794 (2015).
- 24** H.-Y. Chen, M. Palummo, D. Sangalli, and M. Bernardi, Nano letters **18**, 3839 (2018).
- 25** P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, *et al.*, Journal of physics: Condensed matter **21**, 395502 (2009).
- 26** P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. B. Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, *et al.*, Journal of physics: Condensed matter **29**, 465901 (2017).
- 27** V. Barone, M. Casarin, D. Forrer, M. Pavone, M. Sambi, and A. Vittadini, Journal of computational chemistry **30**, 934 (2009).
- 28** L. Hedin, Physical Review **139**, A796 (1965).
- 29** B. Farid, R. Daling, D. Lenstra, and W. van Haeringen, Physical Review B **38**, 7530 (1988).
- 30** A. Guandalini, P. D’Amico, A. Ferretti, and D. Varsano, npj Computational Materials **9**, 44 (2023).
- 31** G. Onida, L. Reining, and A. Rubio, Reviews of modern physics **74**, 601 (2002).
- 32** D. Sangalli, J. Berger, C. Attaccalite, M. Grüning, and P. Romaniello, Physical Review B **95**, 155203 (2017).
- 33** F. Libbi, P. M. M. de Melo, Z. Zanolli, M. J. Verstraete, and N. Marzari, Physical Review Letters **128**, 167401 (2022).
- 34** X. Hong, J. Kim, S.-F. Shi, Y. Zhang, C. Jin, Y. Sun, S. Tongay, J. Wu, Y. Zhang, and F. Wang, Nature nanotechnology **9**, 682 (2014).

- 35 H. Heo, J. H. Sung, S. Cha, B.-G. Jang, J.-Y. Kim, G. Jin, D. Lee, J.-H. Ahn, M.-J. Lee, J. H. Shim, *et al.*, Nature communications **6**, 7372 (2015).
- 36 H. Chen, X. Wen, J. Zhang, T. Wu, Y. Gong, X. Zhang, J. Yuan, C. Yi, J. Lou, P. M. Ajayan, *et al.*, Nature communications **7**, 12512 (2016).
- 37 L. L. Li, R. Gillen, M. Palummo, M. V. Milošević, and F. M. Peeters, Applied Physics Letters **123**, 033102 (2023).
- 38 M. van Setten, M. Giantomassi, E. Bousquet, M. Verstraete, D. Hamann, X. Gonze, and G.-M. Rignanese, Computer Physics Communications **226**, 39 (2018).
- 39 J. D. Head and M. C. Zerner, Chemical physics letters **122**, 264 (1985).
- 40 S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, The Journal of chemical physics **132** (2010), 10.1063/1.3382344.
- 41 J. P. Perdew, K. Burke, and M. Ernzerhof, Physical Review Letters **77**, 3865 (1996).
- 42 K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Physical Review Letters **105**, 136805 (2010).
- 43 M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, and H. Zhang, Nature chemistry **5**, 263 (2013).
- 44 Y. Zhang, T.-R. Chang, B. Zhou, Y.-T. Cui, H. Yan, Z. Liu, F. Schmitt, J. Lee, R. Moore, Y. Chen, *et al.*, Nature nanotechnology **9**, 111 (2014).
- 45 W. Zhao, Z. Ghorannevis, L. Chu, M. Toh, C. Kloc, P.-H. Tan, and G. Eda, ACS nano **7**, 791 (2013).
- 46 F. Lan, R. Yang, Y. Xu, S. Qian, S. Zhang, H. Cheng, and Y. Zhang, Nanomaterials **8**, 100 (2018).
- 47 A. T. Hanbicki, H.-J. Chuang, M. R. Rosenberger, C. S. Hellberg, S. V. Sivaram, K. M. McCreary, I. I. Mazin, and B. T. Jonker, ACS nano **12**, 4719 (2018).
- 48 J. Choi, M. Florian, A. Steinhoff, D. Erben, K. Tran, D. S. Kim, L. Sun, J. Quan, R. Claassen, S. Majumder, *et al.*, Physical Review Letters **126**, 047401 (2021).
- 49 D. Lagarde, L. Bouet, X. Marie, C. Zhu, B. Liu, T. Amand, P. Tan, and B. Urbaszek, Physical Review Letters **112**, 047401 (2014).
- 50 T. Korn, S. Heydrich, M. Hirmer, J. Schmutzler, and C. Schüller, Applied Physics Letters **99** (2011), 10.1063/1.3636402.
- 51 H. Shi, R. Yan, S. Bertolazzi, J. Brivio, B. Gao, A. Kis, D. Jena, H. G. Xing, and L. Huang, ACS nano **7**, 1072 (2013).

- 52** N. Peimyoo, J. Shang, C. Cong, X. Shen, X. Wu, E. K. Yeow, and T. Yu, *ACS nano* **7**, 10985 (2013).
- 53** M. Re Fiorentin, F. Risplendi, M. Palummo, and G. Cicero, *ACS Applied Nano Materials* **4**, 1985 (2021).
- 54** F. Volmer, M. Ersfeld, P. E. Faria Junior, L. Waldecker, B. Parashar, L. Rathmann, S. Dubey, I. Cojocariu, V. Feyer, K. Watanabe, *et al.*, *npj 2D Materials and Applications* **7**, 58 (2023).
- 55** B. Miller, A. Steinhoff, B. Pano, J. Klein, F. Jahnke, A. Holleitner, and U. Wurstbauer, *Nano letters* **17**, 5229 (2017).
- 56** M. Baranowski, A. Surrente, L. Klopotoski, J. M. Urban, N. Zhang, D. K. Maude, K. Wiwatowski, S. Mackowski, Y.-C. Kung, D. Dumcenco, *et al.*, *Nano letters* **17**, 6360 (2017).
- 57** J. Kiemle, F. Sigger, M. Lorke, B. Miller, K. Watanabe, T. Taniguchi, A. Holleitner, and U. Wurstbauer, *Physical Review B* **101**, 121404 (2020).
- 58** P. Rivera, J. R. Schaibley, A. M. Jones, J. S. Ross, S. Wu, G. Aivazian, P. Klement, K. Seyler, G. Clark, N. J. Ghimire, *et al.*, *Nature communications* **6**, 6242 (2015).
- 59** M. Rohlfing, P. Krüger, and J. Pollmann, *Physical Review B* **57**, 6485 (1998).
- 60** H. Yu, X. Cui, X. Xu, and W. Yao, *National Science Review* **2**, 57 (2015).
- 61** N. R. Wilson, P. V. Nguyen, K. Seyler, P. Rivera, A. J. Marsden, Z. P. Laker, G. C. Constantinescu, V. Kandyba, A. Barinov, N. D. Hine, *et al.*, *Science advances* **3**, e1601832 (2017).

Role of surface bands in the photogeneration, cooling, and recombination of charge carriers in two-dimensional Bi_2Se_3



Based on

J. Vliem, S. A. Cayan, **R. Reho**, A. R. Botello-Méndez, P. M. M. C. Melo, P. Geiregat, Z. Zanolli D. Vanmaekelbergh, "Role of surface bands in the photogeneration, cooling, and recombination of charge carriers in two-dimensional Bi_2Se_3 ", submitted and under review in ACS Nano (2025)

Abstract

Bi_2Se_3 , a layered three-dimensional topological insulator, exhibits intriguing changes in its band structure when its thickness is reduced below 7 quintuple layers. The reduction in thickness leads to the hybridization between surface states and the opening of a gap between these states. We combine Density Functional Theory calculations with pump-probe spectroscopy to explore how these hybridized states affect photogeneration, cooling, and recombination of charge carriers in two-dimensional Bi_2Se_3 nanoplatelets. Our calculations reveal that the hybridized surface states are crucial for understanding the optical transitions. By comparing the experimental absorption spectrum with the calculated absorptance in the near infrared-visible region, we identify key transitions within the two-dimensional Brillouin zone. We distinguish transitions involving the hybridized surface states from those involving the interior layers. We observe a significant delay in carrier recombination when surface state transitions are excited, which we attribute to carrier accumulation in the valleys of the Rashba-shaped surface-state valence band and in higher-lying surface states of the conduction band. These findings emphasize the important role of surface state bands in the optical behavior of Bi_2Se_3 and their potential for manipulating carrier dynamics in two-dimensional materials. This chapter is based on Vliem et al. This work is a combined theoretical and experimental work. JV performed the experiments and took the lead in writing the manuscript. RR conducted the first-principles simulations, contributed in the writing of the manuscript, and developed the necessary routines in the YAMBO and YAMBOPY codes.

1 Introduction

Bismuth selenide (Bi_2Se_3), a layered van der Waals material composed of quintuple layers (QLs, i.e. Se-Bi-Se-Bi-Se layers), has been the subject of intense research since bismuth chalcogenides were found to be among the best thermoelectric materials¹⁻⁴. More recently, Bi_2Se_3 has gained interest due to its topological properties: bulk Bi_2Se_3 is a well-known three-dimensional (3D) topological insulator in which the inverted gap of 200-300 meV hosts a helical Dirac-cone surface state characterized by spin-momentum locking⁵⁻⁷. Besides the electronic topology that depends on the band structure around the Fermi level, the physics of optical excitations involving bands considerably below and above the Fermi level is also of interest. As of yet, the optical transitions and the cooling and recombination kinetics of electrons and holes within these bands is not fully understood⁸⁻¹⁰. Recently, Kung *et al.* (2019)¹¹ demonstrated that the surface states of 3D Bi_2Se_3 play an important role in optical transitions in the visible region, resulting in circularly polarized emission at 2.3 eV. This emission was attributed to the recombination of chiral excitons, composed of electrons with zero effective mass and massive holes on the material's surface. However, when the thickness of 3D Bi_2Se_3 is reduced below 7 QLs, ARPES measurements have shown that the surface states involved in these transitions hybridize and become gapped^{6,12,13}. Existing reports have indicated that surface states may still significantly affect the (optical) properties of 2D Bi_2Se_3 ¹⁴⁻¹⁷, but the question of how the hybridized surface bands (versus interior bands) determine the optical properties of 2D Bi_2Se_3 in the near infrared-visible (NIR-VIS) has not been investigated systematically.

To study the optical properties of 2D Bi_2Se_3 , we combined Density Functional Theory (DFT) calculations and experiments using ultrafast pump-probe spectroscopy on colloidal nanoplatelets (NPLs) of around 6 QLs with lateral dimensions in the 200 nm. These free-standing crystals have a uniform and controlled thickness, and their lateral dimensions are large enough to classify them as genuinely two-dimensional¹³. From our calculations, we find that the gapped surface states become an integral part of the band structure by forming regions with a high surface contribution in the bands. By comparing the experimental absorbance with the theoretical absorbance, we identified the most important transitions in the 2D Brillouin zone and located them in the calculated band structure. Our analysis revealed three primary groups of transitions: on the line Γ -K close to Γ involving the gapped surface state bands, around Γ involving interior QLs, and others involving the interior QLs, but more broadly distributed over the Brillouin zone. Using ultrafast pump-probe spectroscopy, we studied the cooling and recombination kinetics in the 2D Brillouin zone. We observe delayed recombination whenever bands with a large surface state contribution are involved. Specifically, our results point to the accumulation of holes at the valleys of a Rashba-split Surface State (RSS) band and accumulation of electrons in higher lying surface states of the conduction bands, which explains the above optical band-gap photoluminescence observed in literature¹¹.

2 Theoretical methods

We determined the ground state properties of Bi₂Se₃ 6QL nanocrystals by solving the Kohn-Sham (KS) equations within the DFT formalism, using the Quantum Espresso (QE) code^{18,19}. Structural relaxation has been performed, including spin orbit coupling (SOC) and vdW corrections^{20,21}.

For neutral excitations, we utilized the Bethe-Salpeter Equation (BSE) for electron-hole interactions, exploiting the Ai-MBPT formalism implemented in the YAMBO code^{22,23} [Eq. (31)]. We employed the independent particle (IP) approximation, where optical transitions are calculated based on electronic dipoles in a single-particle framework, thus omitting many-body effects from the BSE kernel. The justification for this approach is supported by GW calculations on similar systems with varying numbers of QLs, recently published by our collaborators¹³ (for further details see Section 4). The dielectric function is computed by summing transitions between all conduction (c) and valence (v) bands at each **k**-points in the Brillouin Zone (BZ), according to the formula

$$\epsilon_{\alpha,\alpha}(\omega) = 1 + \frac{16\pi}{\Omega} \sum_{c,v} \sum_{\mathbf{k}} \frac{1}{\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}}} \frac{|\langle v\mathbf{k} | \mathbf{d}_{\alpha} | c\mathbf{k} \rangle|^2}{(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}})^2 - (\omega + i\gamma)^2} \quad (1)$$

where $\epsilon_{c\mathbf{k}/v\mathbf{k}}$ are single-particle band energies, Ω is the BZ volume, and γ is an adjustable broadening parameter.

The optical absorption spectra are computed from the imaginary part of the dielectric function ϵ [Eq. (1)]. We compute **k**-resolved absorption plots isolating the individual **k**-points contribution in the summation of Eq. (1) and integrating over a given energy range $[E_{min}, E_{max}]$.¹

We analyzed the nature of the electronic band structure by projecting each state onto individual atoms within each quintuple layer, identifying whether electronic states are localized on the surface (*surface states*) or in the interior (*interior states*).

3 Results and discussion

The computed and measured absorption spectra of Bi₂Se₃ suspensions and films, with the films measured at 295 K and 9 K, are shown in Fig. 3.1. The spectra cover the NIR-VIS region, well above the fundamental (inverted) gap. The absorbance of the film and dispersion are nearly indistinguishable, with the only noticeable difference being the Fabry-Pérot oscillations in the film. From 1 to 2.2 eV, the experimental absorption spectrum shows a strong increase in absorbance, which then gradually decreases up to 3.0 eV. This is qualitatively similar to the absorbance spectra reported for 3D Bi₂Se₃ crystals¹¹. The theoretical absorptance, shown in the same figure, was computed with DFT in the IP approximation Eq. (1). Because the NPLs are on average 6 QLs thick, the band structure and the strength of the optical transitions were

¹The implementation of the post-processing routines needed to reproduce the main theoretical results of this work are available in one of the author's (R.R.) forked repository of the YAMBO Python library²

calculated for infinite slabs of Bi_2Se_3 with a thickness of 6 QLs. All calculated transitions have been broadened by 10 meVs to account for both homogeneous and inhomogeneous broadening effects in the experimental absorbance, resulting in a good qualitative agreement with the experimental spectrum. We expect the inhomogeneous broadening to be largely due to variations in the thickness of the NPLs, which ranges from 5 to 7 QLs²⁴. Although the overall shape of our computed absorbance is in good agreement with the experimental absorbance, we observe two main discrepancies. First, we find a redshift of approximately 0.25 eV relative to the experimental spectrum. Such a shift is often observed between theory and experiment, as outlined in the Section 4, and we will correct for this in the remainder of our argumentation. Second, in the higher-energy region above 2.5 eV, the experimental absorbance is stronger than the calculated absorbance. The absorbance in this region has previously been attributed to excitations into higher-lying electronic bands that are not included in our simulation, which may account for the observed difference²⁴. Since our analysis focuses on transitions occurring between 1-3 eV, absolute agreement between theory and experiment in the higher energy region is not critical to our argumentation.

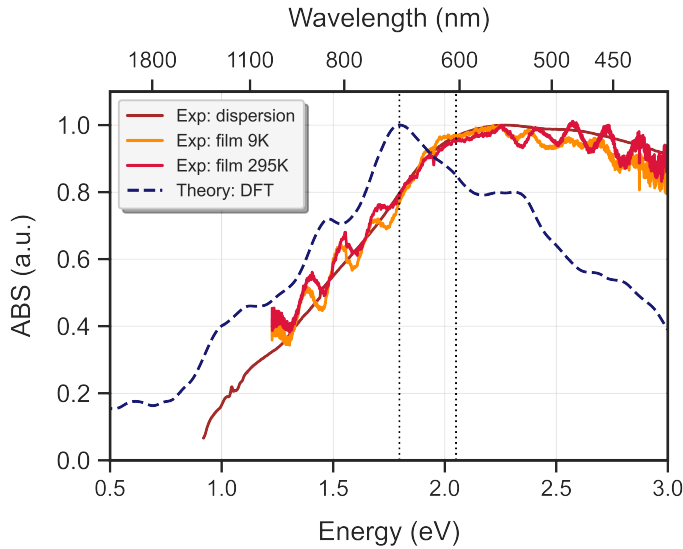


Figure 3.1 Comparison between the theoretical absorbance and experimental absorption spectra.

Absorption spectrum of Bi_2Se_3 NPLs in dispersion and drop-cast on films (measured at 295 K and 9 K), and the DFT absorbance for an infinite slab of 6 QLs. The dashed lines indicate the shift between the experimental and theoretical spectra of 0.25 eV.

The band structure of an infinite 2D Bi_2Se_3 crystal with a thickness of 6 QLs, is shown in Fig. 3.2.(A). The contribution of the outermost QLs (surface layers) to the states is represented with darker and thicker symbols, highlighting regions in the band structure characterized by

significant contributions from the surface QLs. We verified that the states in dark red are indeed located at the surface by visualizing the contribution to charge density (Fig. 3.3). Therefore, these regions in the band structure correspond to the dispersive surface states discussed in the literature, and we will refer to them as such^{11,25}. We followed the convention of Kung *et al.*¹¹ to label the surface state bands: we identified the RSS band and the empty first and second surface state bands (SS1 and SS2) forming part of the conduction band manifolds CB1 and CB3 respectively, similar to those found in bulk Bi₂Se₃ (Fig. 3.4). In the 2D case discussed here, the states from the surface and interior layers become mixed. Due to this mixing, there are several points of interest in the calculated band structure. We have indicated two points that will be useful for our later explanations: Z and Q. Z indicates the end of the RSS bands on the line Γ -K and Q is the charge transfer point in SS2, where further relaxation to the bottom of the CB3 involves charge transfer from surface to interior layers.

To understand the origin of the optical transitions underlying the absorption spectrum presented above, we presented regions of strong absorption in an optical (energy, momentum, absorbance) frame, directly related to the band structure. In this way, we created a unique mapping between optical transitions and their electronic states origin (transitions from valence to conduction bands), with the final goal of distinguishing surface from bulk transitions via the weighting factor of the interior orbitals. Knowledge of the initial band regions in which electrons/holes are generated is also important for a deeper understanding of the electron-hole cooling dynamics (see below). An example of such a map is shown in Fig. 3.2.(B). A coordinate system that shows how to interpret such $\mathbf{k}$ -resolved absorbance maps is shown for clarity: an energy range is chosen, after which the transitions that fall within this range are projected onto the Brillouin zone. For example, in this case the false-color plot shows the absorbance strength integrated over the entire energy window 0.5-3.0 eV. The color scale indicates the strength of the transitions (i.e. integrated absorbance) in arbitrary units. From the projected absorbance map, we find that the strongest transitions occur at Γ and on the line Γ -K. We note that when transitions starting from $E = 0$ are included, the integrated value at Γ is so large that it occludes the other transitions (Fig. E4).

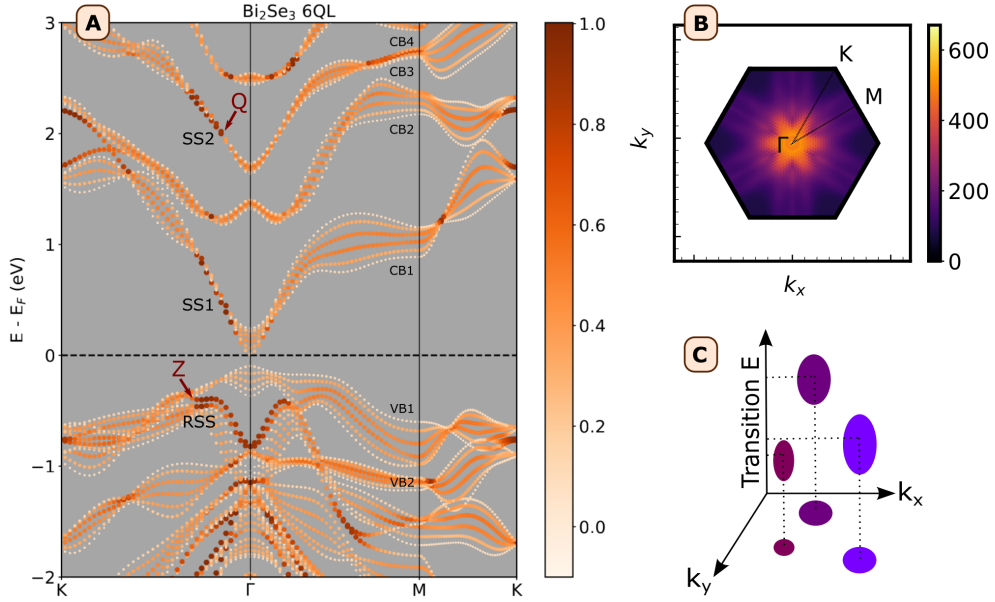


Figure 3.2 Band structure and k -resolved absorptance map of 6 QL Bi_2Se_3 .

A) Electronic band structure for 6 QL Bi_2Se_3 , with surface layer contributions projected onto the band structure. The color scale indicates the surface layers contribution (%). The conduction and valence band manifolds have been numbered for clarity and the surface state bands RSS, SS1, and SS2, are indicated. Z indicates the end of the RSS bands on the line Γ -K and Q is the charge transfer point at the bottom of SS2. B) k -resolved map showing the integrated absorptance (color scale, arbitrary units) between $E = 0.5$ – 3.0 eV, projected onto the ($E=0$, k_x , k_y) plane (2D Brillouin zone). C) Diagram showing how the k -resolved absorptance plots are constructed by projecting the transitions onto the Brillouin zone.

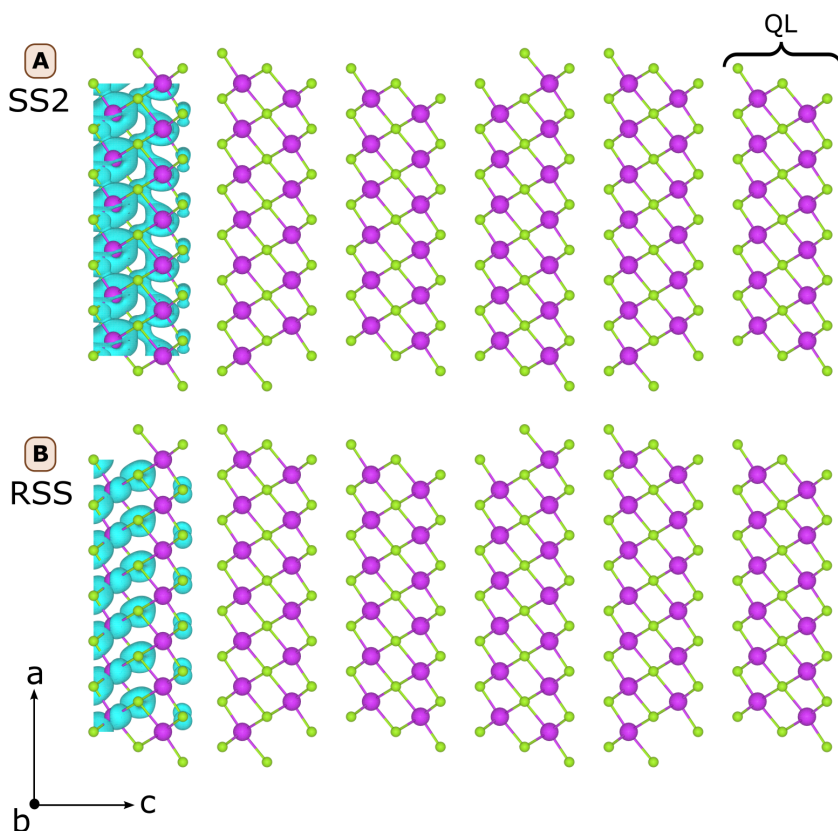


Figure 3.3 Visualization of the contribution to the charge density of a surface state in the atomic structure of 6 QL Bi_2Se_3 . Contribution of the SS2 (A) and RSS (B) states to the charge density. This contribution is computed for a $\mathbf{k}$ -point along $\Gamma - K$ with high surface contribution. The figure shows only one of the two energy-degenerate surface states. The paired surface state is located on the rightmost layer. a , b and c are the unit cell vectors.

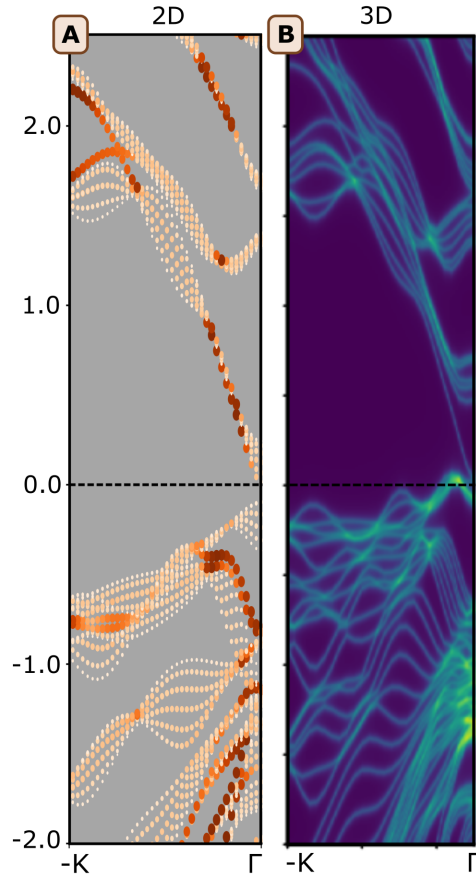


Figure 3.4 Comparison of the band structure of 2D and 3D Bi_2Se_3 .

Band structure of an infinite 6 QL Bi_2Se_3 slab calculated with DFT as described in the Computational details (A), and the 3D band structure reported by Kung *et al.* (B)¹¹. The band structures are very similar, except for the gapping of surface state bands around the Fermi energy and at 1.7 eV above the Fermi energy in the 2D case. The similarity between the band structures of 2D and 3D Bi_2Se_3 suggests nearly identical optical transitions in the high-energy range. This similarity is attributed to the layered structure, where the band structure is primarily determined by atomic interactions within a QL, with limited contributions from inter-QL interactions due to the separation by a van der Waals gap¹³.

For our subsequent analysis, we analyzed smaller energy windows (Fig. E5) to identify the location of specific strong transitions. The $\mathbf{k}$ -resolved absorptance maps integrated over selected energy ranges are shown in Figs. 3.5.(A-F). For each energy range, the strongest transitions occur at specific regions in the Brillouin zone. Based on their position, we found it instructive to group the transitions into three color categories as indicated in Fig. 3.5.(G): transitions at or close to Γ involving interior QLs (yellow), transitions on the Γ -K line involving the top of RSS (red), which we refer to as surface state transitions due to the larger contribution

of the surface layers, and transitions more broadly distributed over the Brillouin zone involving interior QLs (blue). We will use these colors to refer to groups of transitions in the remainder of this text. The color of the bars in Figs.3.5.(A-F) indicate to which group each transition belongs. For instance, in panel A ($E = 0.95 - 1.17$ eV), the strongest transitions occur at Γ (yellow group) and on the line Γ -K (red group). We show the positions of these transitions in the band diagram (see yellow and red arrows denoted A). Similarly, for panel D ($2.18 - 2.38$ eV) we can identify strong transitions half-way along the line Γ -K. These transitions belong to the blue group, as they originate from a position closer to K than the end of the RSS band [to the left of point Z in Fig. 3.2.(G)]. Since the transitions at this energy are more distributed across the Brillouin zone, arrow D in the band diagram represents only one possible position along the line Z-K. There are additional transitions around the path M-K, but considering their wide distribution in $\mathbf{k}$ -space, we do not show them in the band structure. Analogously, for panel E ($E = 2.63 - 2.73$ eV), we identified only the strongest transitions belonging to the yellow and red group in the band diagram. This procedure was repeated for the other strong transitions within the energy range of $E = 0.5 - 3.0$ eV, where we have primarily considered transitions from the top of VB1 (at Γ), the RSS band, or top of VB2 (at Γ). Notably, the transition in panel F on the line Γ -K can be positioned both at the top of RSS involving surface states (red group, right of Z), or just next to it left of Z, making it part of the blue group.

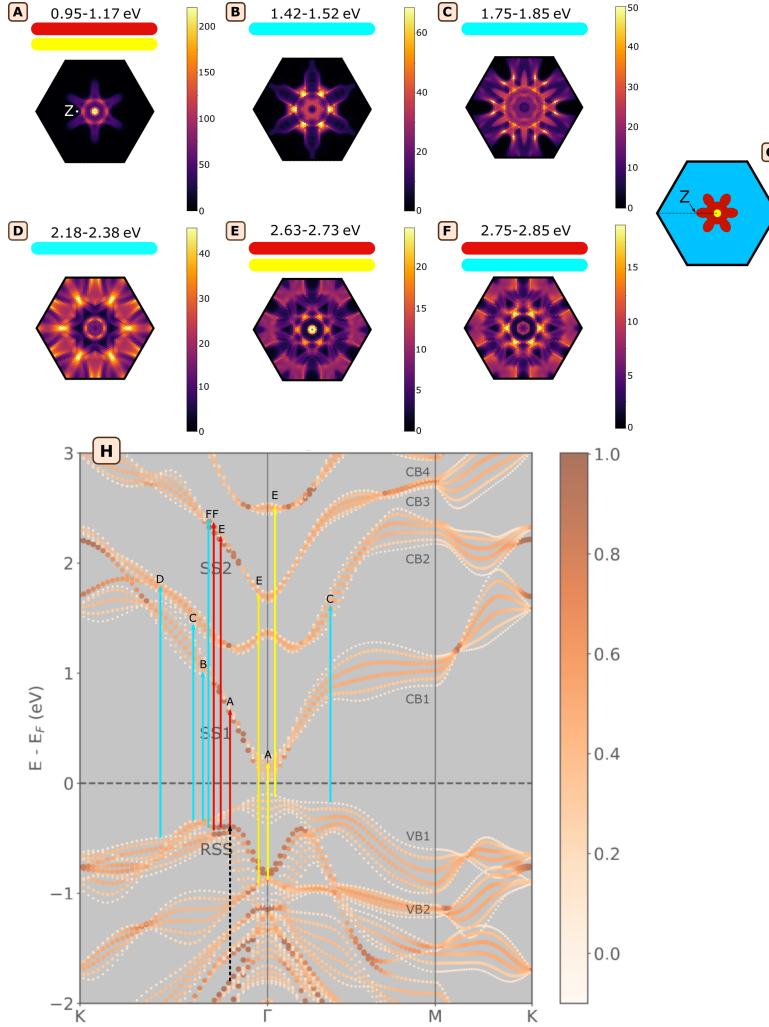


Figure 3.5 Identified transitions in the band structure of 6 QL Bi_2Se_3 .

A-F) $\mathbf{k}$ -resolved absorbance maps integrated over selected energy ranges (color scale: absorbance in a.u.). The colored bars underneath the energy range indicate transitions groups, as shown in G. G) Brillouin zone schematic with color-coded transitions: yellow (close to Γ), red (Γ -K involving RSS), and blue (interior QLS). Z indicates the end of the RSS bands along Γ -K, also shown in (A). H) Band structure for 6 QL Bi_2Se_3 with transitions A-F, colored by group (G). The dashed black arrow indicates a possible photo-induced absorption involving surface bands.

As shown in the band diagram, a significant part of the identified strong transitions involves the hybridized surface bands. To study how this affects the cooling and recombination dynamics in our 2D Bi_2Se_3 NPLs, we performed ultrafast transient absorption spectroscopy with a broad range of pump energies ranging from 1.18 to 3.6 eV to probe the higher-lying excitations (see Experimental Section 5). A 170 fs pump pulse was used to excite a drop-cast film of Bi_2Se_3

NPLs (Fig. A1), followed by broadband pulse to probe the sample after a time delay t . This gives the change in absorbance $\Delta A = A - A_0$, where A_0 is the absorbance of the sample without prior excitation by the pump.

Fig. 3.6.(A) presents a 2D map of the differential absorbance $\Delta A(\lambda, t)$ recorded at 15 K for excitation at 2.82 eV (440 nm). Panel B shows time-resolved traces extracted from this map. We used low-temperature data acquired on films to achieve the best-resolved signals, although measurements at room temperature and in dispersion yield similar results (Figs. E7 and E8). The 2D map in Fig. 3.6.(A) displays two different responses: a bleach signal ($\Delta A < 0$) at probe energies above 1.9 eV and a photo-induced absorption (PA, $\Delta A > 0$) at energies below 1.9 eV, in line with the literature¹⁵. These features are more easily distinguishable in panel B, which shows distinct bands around 2.0, 2.15, and 2.30 eV (bleach), and 1.8, 1.6, and 1.45 eV (PA). We can use our theoretical understanding to explain these observations. The supporting schematic in Fig. E9.(A) may be used for clarity.

First, an experimental excitation energy of 2.82 eV corresponds to a theoretical excitation of $(2.82-0.25)=2.57$ eV, which results in electrons generated in CB4 and CB3. These electrons may relax to the lower conduction bands, specifically to the valleys between Γ -K in CB2, thereby bleaching several strong transitions around Γ involving the interior layers, i.e. transitions A and E. Additionally, panel E in Fig. 3.5 shows that holes are generated at the top of RSS and in the interior layers at Γ (VB1 and VB2). The latter may cool to the valleys in VB1 and RSS, where they can bleach the blue and red groups of transitions. From our experiment, we find that the region of strong bleach, identified above as ranging from 2.0-2.3 eV, corresponds to a theoretical region of 1.75-2.05 eV. The $\mathbf{k}$ -resolved absorbance plots in Fig. 3.5 and E10 show that these energies correspond to transitions predominantly in the blue group [i.e. Figs 3.5.(C.D)]. This indicates that the accumulation of holes in the local maximum of VB1 bleaches the transitions C, D as indicated in Fig. 3.5.

The PA is more challenging to assign as these transitions are absent in the ground state (linear) absorption. For the holes generated at Γ (interior layers), we remark that there is nearly a continuum of states below VB1, enabling the photo-excitation of these holes roughly between 1 and 2 eV. Similarly, for the holes that are generated or accumulate in the RSS valley between Γ -K, several surface band photo-excitations are possible. We tentatively ascribe the broad PA centered around 1.8 eV to the photo-excitation around Γ , and the PA around 1.45-1.6 eV to the photo-excitation from RSS to the lower-lying surface states [dashed black arrow in Fig. 3.5.(H)]. In addition, we cannot entirely exclude the contribution of bandgap renormalization (BGR) to the photo-induced absorption signal. We observe that the PA signal roughly resembles the derivative of the linear absorption spectrum. Additionally, redshift-blueshift dynamics in the PA at longer delay times could be consistent with BGR effects (23,24). However, we also observe that the pump fluence is important here; as shown in Fig. 3.6.(B), the PA signal can be entirely suppressed to a bleach signal at high excitation fluences, which is inconsistent with an expected stronger BGR contribution at higher charge carrier densities. Concerning the bleach signal, we should remark that this bleach occurs in a photon energy region between 1.9

– 2.4 eV, while BGR results in a positive signal (PA) below 2.2 eV and a small negative signal (bleach) above 2.2 eV. The effect of BGR on the bleach can thus be neglected.

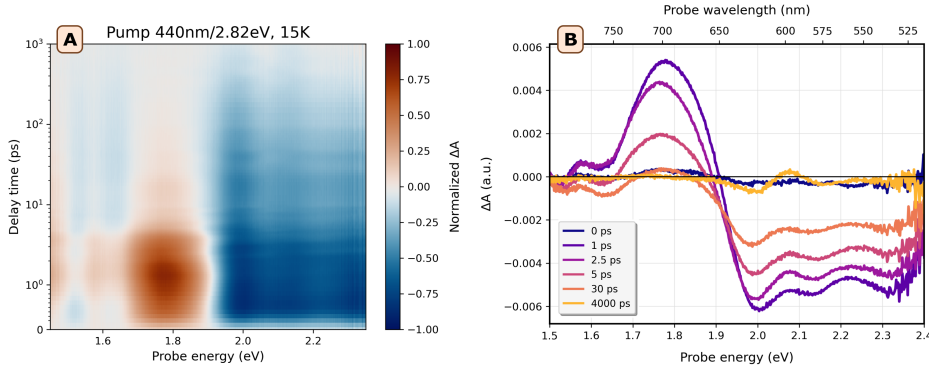


Figure 3.6 Time resolved pump(2.82 eV)-probe spectroscopy on a film of Bi_2Se_3 nanoplatelets.

A) Transient absorption map showing the normalized ΔA of a drop-cast Bi_2Se_3 NPL film at 15 K, after photoexcitation at 2.82 eV (440 nm). B) The transient bleach spectrum at various pump-probe delay times. A pump power of $426 \mu\text{W}$ was used, which translates to a fluence of 4.2×10^{13} photons/ cm^2 .

The strong optical transitions identified in our calculations align with the conclusions of Kung *et al.*¹¹ (among others^{14,16,26}), underscoring the significant contribution of surface states to the optical properties of Bi_2Se_3 . Specifically, Kung *et al.* observed a photoluminescence (PL) peak centered around 2.3 eV with preserved polarization when exciting a 3D Bi_2Se_3 crystal between 2.6 and 3.0 eV, alongside a non-polarized PL peak at 1.5 eV. The highest PL intensity of the polarized PL peak occurred at an excitation energy of 2.8 eV. As mentioned before, we find from the $\mathbf{k}$ -resolved absorptance and band diagram that RSS-SS2 transitions dominate between $E = 2.35\text{--}2.9$ eV, corresponding to an experimental excitation energy of $E = 2.60\text{--}3.15$ eV). This range closely resembles the range where polarization preserving PL was observed. Following excitation at these energies, carrier accumulation at the charge-transfer point Q [Fig. 3.2.(A)] may enhance radiative transitions back to the valleys of RSS or VB1 (2.3-2.4 eV, including the experimental shift), thereby accounting for the observed luminescence at 2.3 eV. Please note that the emission at 2.3 eV from a material with a bandgap of ~ 0.3 eV is highly remarkable in its own regard. The observed PL at 1.5 eV may result from electron relaxation to SS1, after which electrons and holes can recombine at the top of RSS. These findings highlight several distinct optical properties of layered Bi_2Se_3 compared to traditional semiconductors: (a) transitions involving the outer quintuple layers (surface state transitions) form an important contribution to the overall optical properties, (b) high-energy excitations do not necessarily decay to the primary band gap but can be emitted as high-energy photons, (c) electrons and holes may separate in momentum space by cooling in anomalously shaped bands, and (d) the bands have charge-transfer and saddle points where surface electrons accumulate, enhancing

charge-to-photon conversion.

In summary, our study demonstrates the significance of surface state band transitions in two-dimensional Bi₂Se₃. Through time-resolved pump-probe spectroscopy and **k**-resolved theoretical analysis, we identified important transitions from the RSS-SS2 band that play a key role in the recombination and bleach kinetics. The contribution to the absorbance of these surface states is comparable to that involving the interior layers. The distinct structure of the bands, characterized by valleys and charge transfer points, leads to charge carrier accumulation and delayed recombination in the 2.7-3.0 eV excitation range. Our findings align with previously reported chiral photoluminescence resulting from surface state transitions and they show the potential of surface state transitions for manipulating carrier dynamics in two-dimensional materials.

4 Computational details

All simulations have been performed employing the GGA-PBE²⁷ exchange correlation functional and fully relativistic pseudopotentials from PseudoDojo²⁸. We set plane wave kinetic energy cut-off to 140 Ry using a 12x12x1 **k**-point grid to compute the charge density. The transition energies and oscillator strength have been computed on a 48x48x1 **k**-point grid. The distance between periodic replicas is 20 Å. We included spin orbit coupling and vdW corrections^{20,21}. The system has been relaxed with the Broyden (BFGS²⁹) algorithm. Atomic forces and pressure were converged to within 10⁻⁶ Ry/Bohr, and the stress tensor components remained below 10⁻⁴ kbar.

We investigated the differences between the GW-BSE approach and IP methods for a 2L Bi₂Se₃. We observed a systematic energy shift of approximately ~ 100 meVs (Fig. E3) and a renormalization of the intensities. This can be explained as follows: the GW-BSE method accounts for correlations between electrons that are missing at the single-particle DFT level. Hence, the GW approximation often increases the band gap, improving the computed DFT gap. The BSE equation allows us to compute the excitonic energies, creating in-gap states due to the Coulomb interaction between electron and holes. Once the GW-BSE machinery is applied, the relative shift with respect to the IP approximation depends on these two effects. The GW approximation tends to blueshift the spectra, while the creation of exciton bound states usually results in a red-shift. In general, the net effect depends on the material and calculations will therefore always show a discrepancy with experiment. The GW-BSE approximation also shows a difference in intensity at lower energies compared to the IP approximation. For Bi₂Se₃ of 2QLs, there is an increase of the band gap and an emergence of new states below the DFT electronic gap. These in-gap states are exciton states with higher oscillator strength. Hence, the GW-BSE absorption spectra appear broader than the IP case. Since the absorption bands remain well-resolved regardless of whether the IP or GW-BSE method is used, our analysis which is based on the selected absorption bands remains valid. Hence, we use the

IP approximation, as performing GW-BSE calculations for a 6QL Bi₂Se₃ system would be computationally impractical

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Authorship statement

This chapter is based on a work by Vliem et al. submitted and reviewed on ACS Nano, to be published in (2025). Vliem conducted the experiments and took the lead in writing the manuscript. RR conducted the first-principles simulations and contributed to the writing of the manuscript relevant to the theoretical simulations. RR adapted this chapter to align with the scope and content of this thesis, highlighting the theoretical work. PG and SAC contributed to the experiments. ABM and ZZ contributed to the physical interpretation and provided feedback on the manuscript. DV, as the last author, secured funding for the project and assessed the correctness of the manuscript.

5 Appendices

A Nanoplatelets synthesis

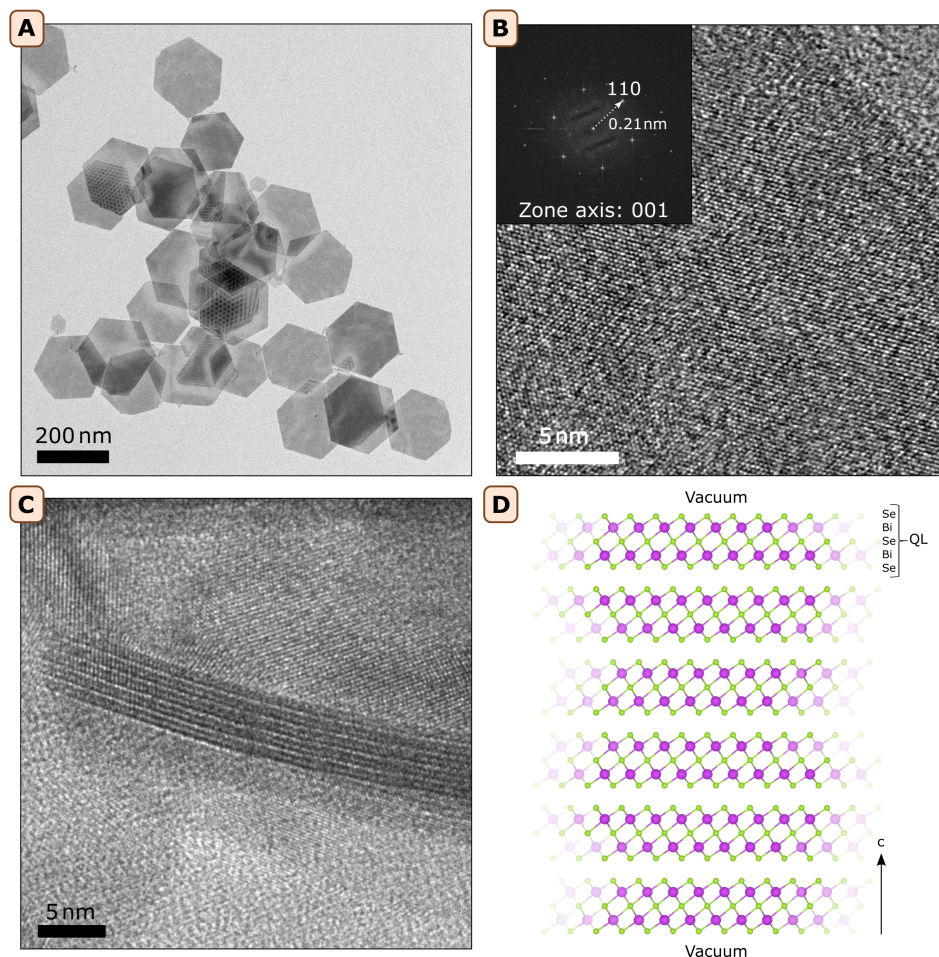


Figure A1 Synthesized Bi_2Se_3 NPLs.

A) TEM image of representative NPL sample. B) High resolution TEM image of a NPL edge, with a Fast Fourier Transform inset to show the crystallinity of the platelet. C) TEM image of a 5 QL NPL from the side. The Bi atoms can be recognized as darker lines in the layered structure D) Atomistic model of 6QLs Bi_2Se_3 employed in the theoretical calculations. The structure has infinite lateral dimensions and the stacking direction is along the c-axis.

We synthesized Bi_2Se_3 platelets with a lateral size of 180 ± 61 nm (TEM, 280 NPLs) and a thickness of, on average, 6 QLs (supporting information, Fig. E1). Fig. A1A shows a representative TEM image of the prepared hexagonal platelets. In Fig. A1.(B), a high

resolution TEM image of a nanoplatelet is shown with the corresponding Fast Fourier Transform (FFT), showing the crystallinity and orientation of the nanoplatelet. Fig. A1.(C) shows a nanoplatelet of 5 QLs imaged from the side, in which the bismuth atoms columns can be seen as darker lines. The optical measurements were conducted on dispersions in ethanol and drop-cast films of such NPLs.

B Chemicals

Na_2SeO_3 (99%, Aldrich), polyvinylpyrrolidone ($M_w = 10,000$, Aldrich), ethylene glycol (anhydrous, 99.8%, Aldrich), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.999%, Aldrich), ethanol (anhydrous 99.8%, VWR chemicals), acetone (anhydrous 99.8%, VWR chemicals), acetonitrile (anhydrous, 99.8%, Aldrich).

C Synthesis procedure

Bi_2Se_3 nanoplatelets (NPLs) were synthesized as previously described in Moes *et al.*¹³, except a growth time of two hours was used. In short, 0.05 g of sodium selenite, 0.22 g polyvinylpyrrolidone (PVP) and 9.5 mL ethylene glycol were mixed in a 50 mL roundbottom flask. Here, PVP functions as a surfactant and shape and size focusing agent.^{30–38} After degassing for 15 minutes at room temperature, the solution was heated to 50 °C to dissolve all sodium selenite. Upon reaching 50 °C the flask was put under N_2 and the mixture was heated to 190 °C. At 190 °C, a Bi precursor injection solution (0.2 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 1 mL ethylene glycol) was heated under N_2 on a 200 °C heating plate for 30 seconds after its color changed to turbid white. 0.5 mL of this Bi precursor was then injected into the selenium mixture. The NPLs were left to grow at 190 °C for 2 hours, after which the reaction mixture was cooled to room temperature using a water bath. The black product was transferred to a scintillation vial in a glovebox and washed by addition of a mixture acetonitrile and ethanol, followed by centrifugation. The resulting black precipitate was redispersed in 10 mL ethanol. The samples were stored in a glovebox under N_2 atmosphere.

D Sample characterization

TEM samples were prepared by drop-casting a diluted dispersion of NPLs on 200 mesh Formvar/carbon-coated Cu TEM grids. The samples were imaged using a Talos F200X (S)TEM operating at 200 keV.

AFM samples were prepared by diluting the NPL stock dispersion approximately 10x, sonicating this dilution for 10 minutes at room temperature, and subsequently drop-casting 20 μL of this dispersion onto a freshly cleaved mica surface. Measurements were carried out using a JPK Nanowizard II operating in intermittent-contact mode in ambient atmosphere. Bruker OTESPA-R4 (300 kHz, 26 N/m) SPM tips were used to acquire images with typical set-points of 0.6 V.

UV-VIS measurements were performed on a Perkin Elmer Lambda 950 UV-Vis-NIR spectrometer, using a quartz cuvette with a path-length of 1 cm. The samples were prepared by diluting a stock dispersion of NPLs in ethanol approximately 300 times.

E Transient absorption measurements

Samples were either measured as a dispersion or a film. For the dispersion measurements, a dispersion of Bi₂Se₃ NPLs in ethanol (anhydrous, handled in GB) was diluted to obtain a stock dilution of OD 0.3 around 2.1 eV. This concentration was chosen to obtain an optimal trade-off between having a good signal and not having a too strong absorption at the pump wavelength as to assure a uniform pumping of the sample. The sample was sealed under N₂ in a quartz cuvette of path-length 2 mm. During the measurements, the sample was stirred continuously to avoid charging or photo-degradation. Furthermore, after every few measurements the sample was refreshed from the stock dilution. For the measurements on films, the NPL stock dispersion was diluted 10x, after which 50 mL was dropcast onto a 1 mm thick sapphire (Al₂O₃) substrate of 12.7 mm in diameter, transparent from 150 nm up to 6 mm. The thin film was prepared to obtain enough probe light for a good signal-to-noise ratio. Although the thickness of the films differs locally, the UV-VIS absorbance maximum (OD) of each film was kept around 0.3. During measurements on films, the pump beam position on the sample was changed after a few measurements to reduce the degradation of the thin film. Fig. E2 shows photos taken of a film and a dispersed sample.

For measurements on dispersions, the samples were excited using 110 fs pump pulses at 400 nm through second-harmonic generation in α -BBO, or at other wavelengths created from the 800 nm fundamental (Spitfire Ace, Spectra Physics) through nonlinear conversion in an optical parametric amplifier (TOPAS, Light Conversion). The probe pulses were generated in a 4 mm thick Sapphire crystal using the 800 nm fundamental. The pulses were delayed relative to the pump using a delay stage with the maximum delay of 6 ns for TOPAS pumping and 3.3 ns for 400 nm pumping. The probe spectrum in our experiments covers the visible window from 480 to 750 nm.

For measurements on films, the samples were excited using 170 femtosecond pump pulses at 343, 375, 400, 440, 450, 515, 525 and 1050 nm, either through second and third harmonic generation in alpha-BBO (for 515 nm, and 343 nm respectively) of the 1030 nm fundamental coming from a Pharos PH2 (Light Conversion) or through an OPA (Orpheus-NEO). Probe pulses were generated in a 10 mm thick YAG or sapphire crystal using the 1030 nm fundamental. The pulses were delayed relative to the pump using a home-built spectrometer with a delay stage with a maximum delay of 6 ns. The probe spectrum in our experiments covers the spectral window from 520 nm up to 950 nm (YAG) and 440-800 nm (sapphire). For cryogenic temperature TA measurement, a cryostat CS204F-DMX-20 (Advanced Research Systems) was used to cool down to sample up to 9 K.

The beam area, approximated as an ellipse and obtained through a Thorlabs CCD beam profiler, is defined as $A_{beam} = \pi \times \sigma_x \sigma_y$ where σ_i is the standard deviation in the $i = x, y$

direction. The photon flux J_{ph} was calculated the beam area using the following formula:

$$J_{ph} = \frac{P_{pump}}{f_{pump} \times E_{ph}(eV) \times A_{beam} \times e} \quad (E1)$$

Where P_{pump} is the pump power, f_{pump} is the laser frequency divided by 2 to take into account the exposure time of the sample, E_{ph} is the pump energy and e is the elementary charge.

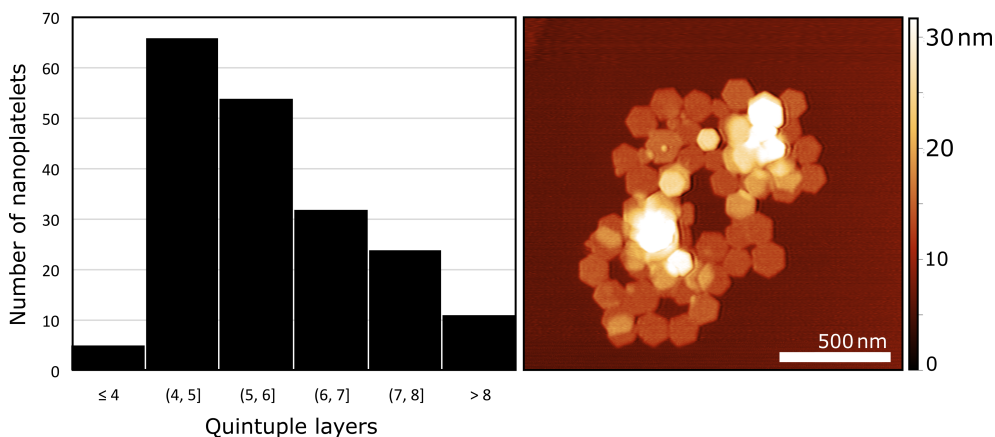


Figure E1 AFM on Bi_2Se_3 nanoplatelets.

Thickness distribution in quintuple layers, assuming an integer number of quintuple layers of 0.96 nm thick³⁹. The data was obtained by measuring 192 Bi_2Se_3 NPLs of 4 different batches used for TA experiments with atomic force microscopy (AFM). A representative AFM image is shown on the right. As the surfactant coverage of the NPLs is unknown, the effect of ligands on the measured thickness was excluded, which may result in an overestimated thickness. The average thickness is 6.2 ± 1.5 QLs.

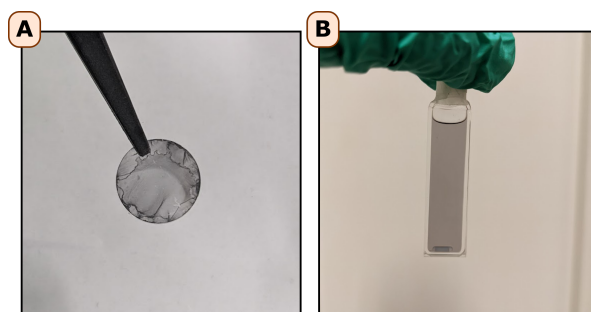


Figure E2 Representative samples used for pump-probe measurements.

Photo of A) a drop-cast film on a quartz substrate and B) a dispersion in ethanol of Bi_2Se_3 NPLs.

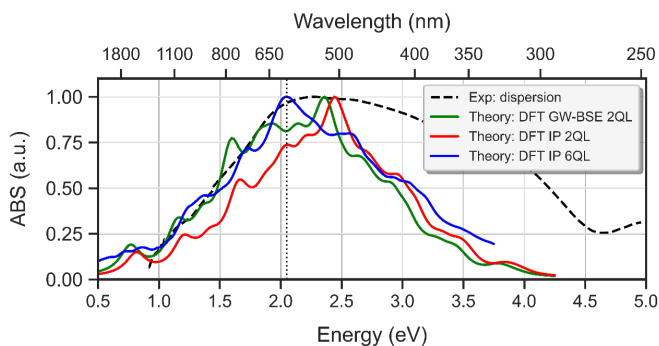


Figure E3 IP versus GW-BSE approach.

Absorbance spectra for an infinite Bi_2Se_3 slab of 2 QLs, computed with the GW-BSE approach (green) and the Independent Particle (IP) approximation (red). The blue spectrum was computed with the IP approximation for an infinite Bi_2Se_3 slab of 6 QLs. All theoretical spectra were blueshifted 0.25 eV to match the experimental absorbance (black dashed line).

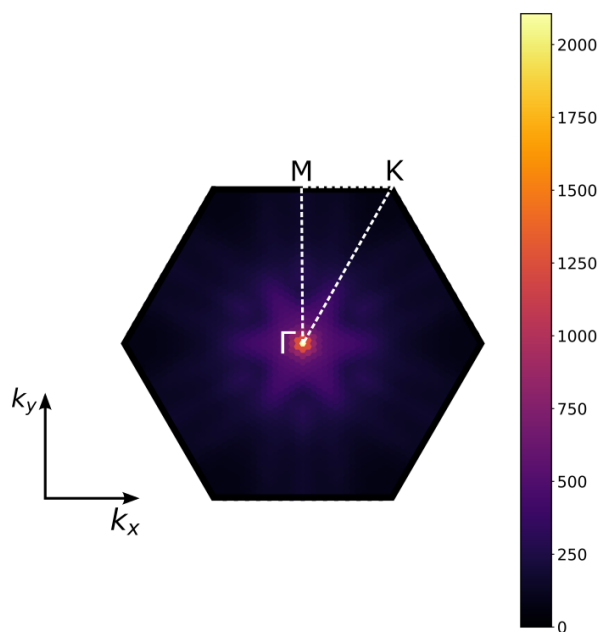


Figure E4 $\mathbf{k}$ -resolved absorbance map for $E=0.0-3.0$ eV.

$\mathbf{k}$ -resolved map showing the integrated absorbance (color scale, arbitrary units) between $E = 0.0-3.0$ eV, projected onto the ($E=0$, k_x , k_y) plane (2D Brillouin zone).

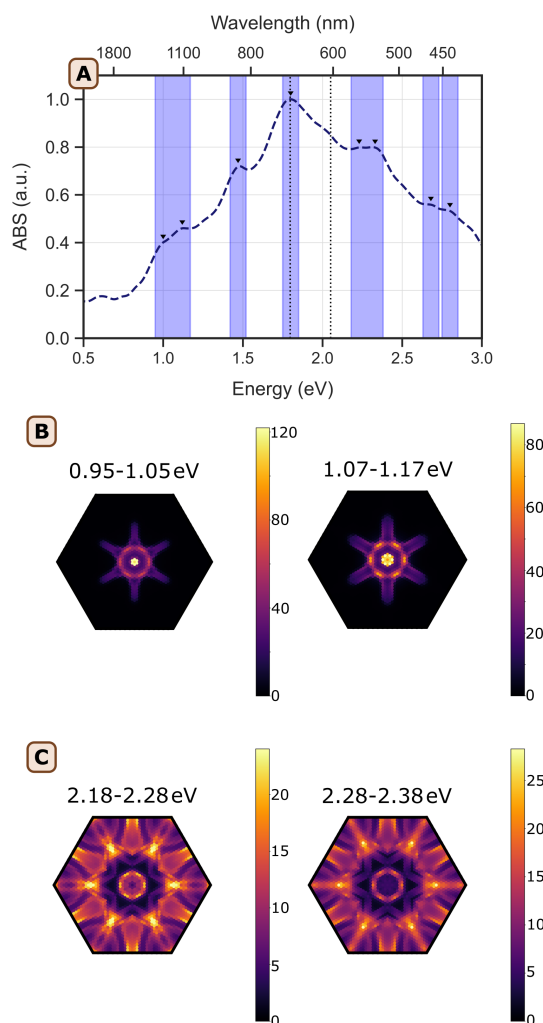


Figure E5 Integration ranges selected for k -resolved absorbance maps.

(A) computed absorbance for an infinite slab composed of 6 QLs. The black markers highlight specific transitions at 1, 1.12, 1.47, 1.8, 2.23, 2.33, 2.68, and 2.80 eV. The shaded blue regions indicate the energy ranges over which the k -resolved absorbance maps presented in Fig. 3.5 were integrated. Some consecutive transitions were grouped together due to the qualitative similarity of their k -resolved absorbance maps. These are the transitions centered around 1 and 1.12 eV, and 2.23 and 2.33 eV. Their k -resolved absorbance maps are shown in B) and C) respectively. The transitions at 2.68 and 2.80 eV were analyzed separately due to significant differences in the k -resolved absorbance near the Γ point.

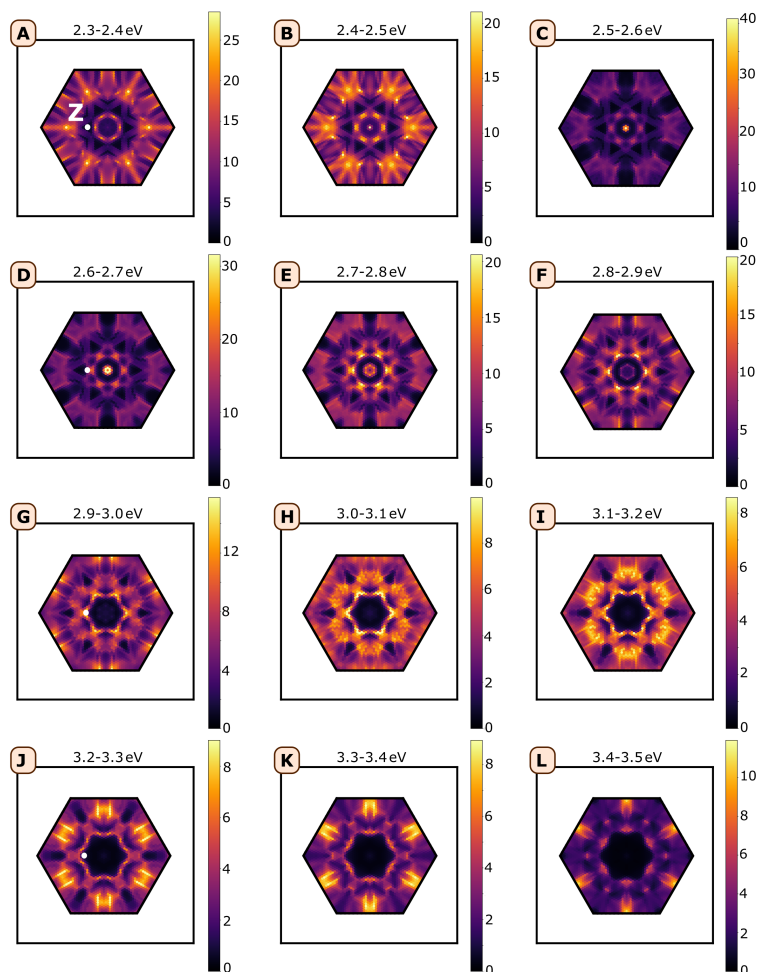


Figure E6 **k**-resolved absorbance maps integrated between 2.3-3.5 eV.

Maps of the absorbance between $E=2.3-3.5$ eV integrated in 0.1 eV intervals, projected onto the 2D Brillouin zone. The plots show where in the Brillouin zone the strongest transitions occur as indicated by the colour scale (integrated absorbance (a.u.)). As a visual aid, a Z point (i.e. the end of the RSS bands on the Γ -K line) is shown for the **k**-resolved plots in the first column.

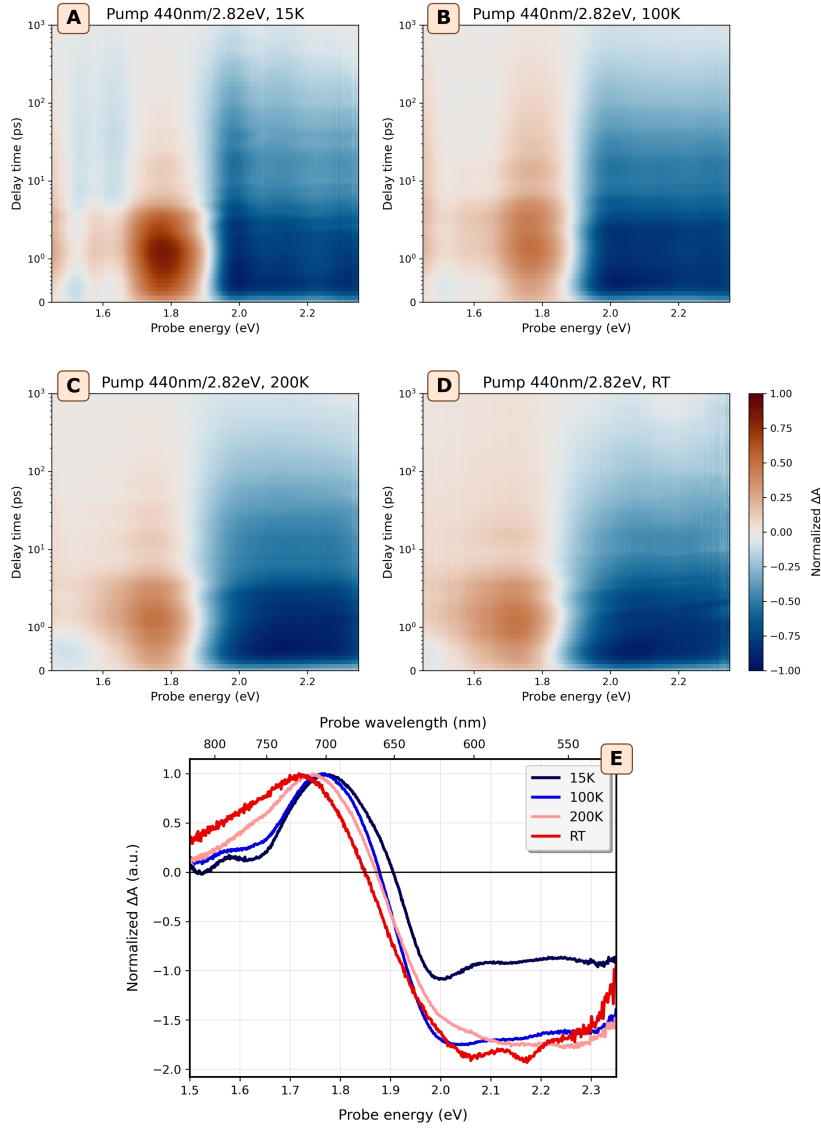


Figure E7 Pump(2.82 eV)-probe experiments at RT, 200, 100, and 15 K.

A-D) Transient absorption maps showing the normalized ΔA of a dropcast Bi_2Se_3 NPL film at 15 K - RT, after photo-excitation at 2.82 eV (440 nm). E) The transient bleach spectrum at 1.5 ps for RT, 200, 100, and 15 K. A pump power of approximately $450 \mu\text{W}$ was used for each measurement, which translates to a fluence of 4.5×10^{13} photons/ cm^2 .

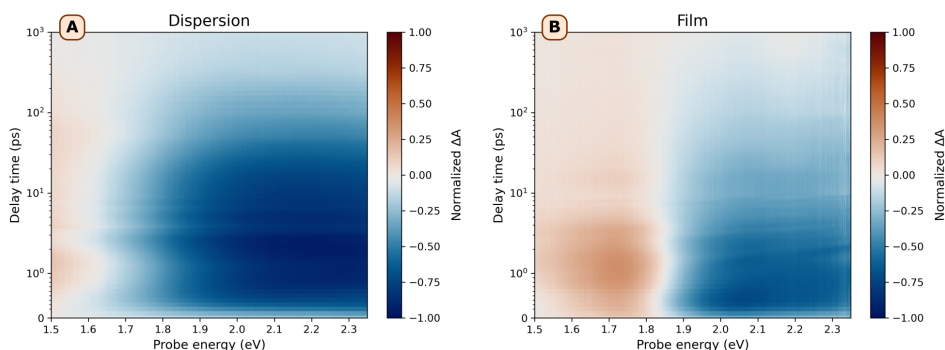


Figure E8 Pump(2.82 eV)-probe experiment on a film and dispersion of Bi_2Se_3 nanoplatelets. Transient absorption maps for dispersion (A) and film (B) showing the normalized ΔA . A pump wavelength of 2.82 eV (440 nm) was used, with a fluence of 5×10^{13} photons/cm². The measurements were performed at room temperature. Both film and dispersion exhibit a bleach at high probe energies followed by a PA signal at lower probe energies.

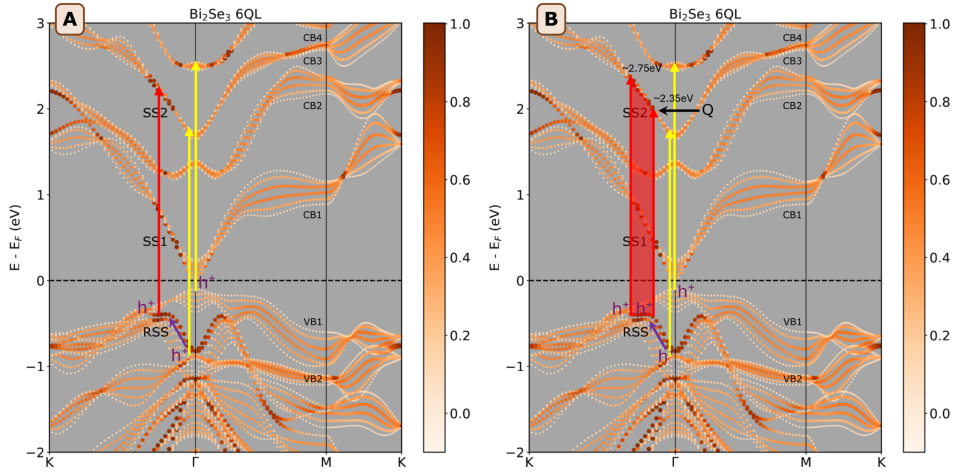


Figure E9 Band structure schemes illustrating transitions and movement of charge carriers.

A) Band diagram illustrating the transitions and movement of charge carriers upon experimental excitation at 2.82 eV. The colour of the arrows corresponds to the groups the transitions belong to (red = RSS transitions, yellow = transitions around Γ). h^+ indicates positions of holes, and purple arrows indicate the movement of holes along the bands. B) Band diagram illustrating the transitions and movement of charge carriers after experimental excitation between 2.7-3.0 eV. The shaded red region is used to indicate all transitions within that range are RSS $\rightarrow$ SS2 transitions. Q is the charge transfer point at which electrons would need to transfer to the interior layers in order to relax further to Γ .

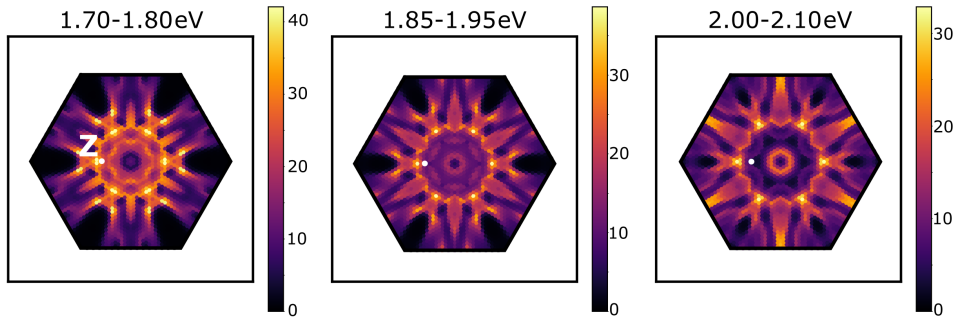


Figure E10 k-resolved absorptance maps integrated for strong experimental bleach bands.

Maps of the k-resolved absorptance for energy regions centered around 2.0, 2.15, and 2.30 eV (i.e. the theoretical energies that correspond to the strongest bleach observed experimentally at pump 2.82 eV). The integration range is given in the title. The maps show where in the Brillouin zone the strongest transitions occur as indicated by the colour scale (integrated absorptance (a.u.)). As a visual aid, a Z point (i.e. the end of the RSS bands on the Γ -K line) is shown in all plots.

Bibliography

- 1 L. Fu and C. L. Kane, *Physical Review B - Condensed Matter and Materials Physics* **76** (2007), 10.1103/PhysRevB.76.045302, arXiv:0611341 [cond-mat] .
- 2 I. T. Witting, T. C. Chasapis, F. Ricci, M. Peters, N. A. Heinz, G. Hautier, and G. J. Snyder, *Advanced Electronic Materials* **5**, 1800904 (2019).
- 3 G. S. Hegde and A. Prabhu, *Journal of Electronic Materials* **51**, 2014 (2022).
- 4 Y. Xu, Z. Gan, and S.-C. Zhang, *Physical Review Letters* **112**, 226801 (2014).
- 5 H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, *Nature Physics* (2009), 10.1038/NPHYS1270.
- 6 Y. Zhang, K. He, C. Z. Chang, C. L. Song, L. L. Wang, X. Chen, J. F. Jia, Z. Fang, X. Dai, W. Y. Shan, S. Q. Shen, Q. Niu, X. L. Qi, S. C. Zhang, X. C. Ma, and Q. K. Xue, *Nature Physics* **6**, 584 (2010).
- 7 F. Zhang, C. L. Kane, and E. J. Mele, *Physical Review B—Condensed Matter and Materials Physics* **86**, 081303 (2012).
- 8 G. Jnawali, S. Linser, I. A. Shojaei, S. Pournia, H. E. Jackson, L. M. Smith, R. F. Need, and S. D. Wilson, *Nano letters* **18**, 5875 (2018).
- 9 P. Sharma, R. Sharma, V. Awana, T. Narayanan, B. K. Gupta, N. Vashistha, L. Tyagi, and M. Kumar, *Journal of Alloys and Compounds* **886**, 161235 (2021).
- 10 A. Sinha, K. Mithun, and A. K. Sood, *ACS Photonics* **10**, 3944 (2023).
- 11 H. H. Kung, A. P. Goyal, D. L. Maslov, X. Wang, A. Lee, A. F. Kemper, S. W. Cheong, and G. Blumberg, *Proceedings of the National Academy of Sciences of the United States of America* **116**, 4006 (2019), arXiv:1903.01999 .
- 12 M. Neupane, A. Richardella, J. Sánchez-Barriga, S. Xu, N. Alidoust, I. Belopolski, C. Liu, G. Bian, D. Zhang, D. Marchenko, *et al.*, *Nature communications* **5**, 3841 (2014).
- 13 J. R. Moes, J. F. Vliem, P. M. de Melo, T. C. Wigmans, A. R. Botello-Méndez, R. G. Mendes, E. F. van Breuk, I. Swart, L. Maisel Licerán, H. T. Stoof, *et al.*, *Nano Letters* (2024).
- 14 Y. D. Glinka, S. Babakiray, T. A. Johnson, M. B. Holcomb, and D. Lederman, *Applied Physics Letters* **105** (2014).
- 15 Y. D. Glinka, J. Li, T. He, and X. W. Sun, *ACS Photonics* **8**, 1191 (2021).
- 16 Y. D. Glinka, T. He, and X. W. Sun, *Scientific Reports* **12**, 4722 (2022).

- 17** B. C. Park, T.-H. Kim, K. I. Sim, B. Kang, J. W. Kim, B. Cho, K.-H. Jeong, M.-H. Cho, and J. H. Kim, *Nature communications* **6**, 6552 (2015).
- 18** P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, *et al.*, *Journal of physics: Condensed matter* **21**, 395502 (2009).
- 19** P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. B. Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, *et al.*, *Journal of physics: Condensed matter* **29**, 465901 (2017).
- 20** V. Barone, M. Casarin, D. Forrer, M. Pavone, M. Sambi, and A. Vittadini, *Journal of computational chemistry* **30**, 934 (2009).
- 21** S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, *The Journal of chemical physics* **132** (2010).
- 22** D. Sangalli, A. Ferretti, H. Miranda, C. Attaccalite, I. Marri, E. Cannuccia, P. Melo, M. Marsili, F. Paleari, A. Marrazzo, *et al.*, *Journal of Physics: Condensed Matter* **31**, 325902 (2019).
- 23** A. Marini, C. Hogan, M. Grüning, and D. Varsano, *Computer Physics Communications* **180**, 1392 (2009).
- 24** M. Fang, Z. Wang, H. Gu, M. Tong, B. Song, X. Xie, T. Zhou, X. Chen, H. Jiang, T. Jiang, and S. Liu, *Applied Surface Science* **509**, 144822 (2020).
- 25** C. Jozwiak, J. A. Sobota, K. Gotlieb, A. F. Kemper, C. R. Rotundu, R. J. Birgeneau, Z. Hussain, D.-H. Lee, Z.-X. Shen, and A. Lanzara, *Nature communications* **7**, 13143 (2016).
- 26** Y. D. Glinka, S. Babakiray, T. A. Johnson, and D. Lederman, *Journal of Physics: Condensed Matter* **27**, 052203 (2015).
- 27** J. P. Perdew, K. Burke, and M. Ernzerhof, *Physical Review Letters* **77**, 3865 (1996).
- 28** M. J. Van Setten, M. Giantomassi, E. Bousquet, M. J. Verstraete, D. R. Hamann, X. Gonze, and G.-M. Rignanese, *Computer Physics Communications* **226**, 39 (2018).
- 29** J. D. Head and M. C. Zerner, *Chemical physics letters* **122**, 264 (1985).
- 30** S. Vinoth, T. Balaganapathi, B. KaniAmuthan, T. Arun, I. P. Muthuselvam, F.-C. Chou, and P. Thilakan, *Physica E: Low-dimensional Systems and Nanostructures* **92**, 17 (2017).
- 31** Y. Liang, W. Wang, B. Zeng, G. Zhang, Q. He, and J. Fu, *Materials chemistry and physics* **129**, 90 (2011).
- 32** Y. Hosokawa, K. Tomita, and M. Takashiri, *Scientific Reports* **9**, 10790 (2019).

- 33** L. Guo, A. Aglan, H. Quan, J. Sun, C. Tang, J. Song, G. Szulczewski, and H.-T. Wang, *Physical Chemistry Chemical Physics* **16**, 11297 (2014).
- 34** J. Buha and L. Manna, *Chemistry of Materials* **29**, 1419 (2017).
- 35** X. He, H. Zhang, W. Lin, R. Wei, J. Qiu, M. Zhang, and B. Hu, *Scientific reports* **5**, 15868 (2015).
- 36** G. Zhang, W. Wang, X. Lu, and X. Li, *Crystal Growth and Design* **9**, 145 (2009).
- 37** Z. Lin, Y. Chen, A. Yin, Q. He, X. Huang, Y. Xu, Y. Liu, X. Zhong, Y. Huang, and X. Duan, *Nano letters* **14**, 6547 (2014).
- 38** C. Bauer, R. Lesyuk, M. S. Khoshkhoo, C. Klinke, V. Lesnyak, and A. Eychmüller, *The Journal of Physical Chemistry C* **125**, 6442 (2021).
- 39** S. Yongfu, C. Hao, G. Shan, L. Qinghua, S. Zhihu, X. Chong, W. Changzheng, W. Shiqiang, and X. Yi, *J. Am. Chem. Soc.* **134**, 20294 (2012).

Summaries

English Summary

This thesis describes the theoretical and software developments carried out by the author to advance our understanding of the materials that surround us. Matter consist of vast collections of interacting particles (of the order of the Avogadro number $N_A = 6.022 \times 10^{23}$). The branch of physics that studies these interactions is known as many-body physics. The fundamental laws governing how a single particle interacts with its surroundings are well understood across different length scales, from macroscopic systems to the atomic level. However, when multiple particles interact, their collective behaviours become complex. At the atomic scale, the collective behaviours of particles is governed by quantum mechanics. As P.W Anderson stated: “More is different”, and I would add: “And difference is what makes it truly fascinating”.

Quantum mechanics governs matter at the atomic scale ($\sim 10^{-10}$ m) and is described by the Schrödinger equation. Surprisingly, interactions at these small scales manifest in macroscopic phenomena, such as superconductivity and light absorption/emission, with profound technological implications. As global energy demands increase, understanding and exploiting these quantum effects become crucial for developing more efficient materials for energy storage, conversion, and transmission. This challenge drives researchers to advance our ability to describe and predict material properties through physical theories. Today, computer simulations have advanced so much that they are not only capable of analyzing existing materials but also designing new ones, revolutionizing scientific research. Among various computational approaches, density functional theory (DFT) stands out as the most widely used ab initio method for accuracy and computationl feasibility.

In this manuscript, the author presents his work done during his PhD: (i) extend the capabilities of DFT theory to predict superconducting properties of materials, (ii) understand how the electronic and optical properties of two-dimensional materials change via stacking, straining and twisting.

What is density functional theory?

DFT is a widely used computational method in physics, chemistry, and materials science. It requires only the atomic species and positions as input and, based on fundamental quantum mechanical principles, accurately predicts a wide range of material properties. Metals, semiconductors, biological molecules and other systems falls directly within the capabilities of DFT. It provides an *exact* description of the ground state electron density of a many-body system. The DFT Hamiltonian constitute the starting point of more advanced theories. These advanced theories enable the study of excited systems (e.g., light-matter interactions) or other phases of matter, such as superconductivity.

Why studying superconductivity?

Superconductivity is a fascinating quantum phenomenon where electrons combine into pairs, known as *Cooper pairs*, allowing electrical current to flow without resistance. The two main properties of superconductors are: zero electrical resistance and the expel of magnetic fields (Meissner effect). Conventional superconductors find applications in energy transmission, magnetic levitation, and high-speed computing. However, they operate at very low temperature (below units of Kelvin). For real world applications, it would be ideal to achieve superconductivity at higher temperatures. Researchers are challenged to discover new materials with high superconducting critical temperature. Superconductivity in materials that display high critical temperature is usually driven by mechanism that are beyond the one explained by BCS theory and goes by the name of unconventional superconductivity.

This thesis presents the SIESTA-BdG method, an approach for computing both conventional and unconventional superconductivity from first principles. It builds on the Density Functional Theory (DFT) framework, starting with the electronic structure described by the Kohn-Sham system. A mean-field approximation is then introduced, leading to the emergence of a superconducting pairing potential. The electronic Hamiltonian is solved self-consistently within the Bogoliubov-de Gennes (BdG) formalism to capture superconducting properties. At first we validated our code with conventional superconductors and then we moved to more complex systems such as heterostructures.

Superconductivity play a key role in quantum computing. A special class of system known as topological superconductors hosts exotic particles called *Majorana zero mode* (MZMs). Unlike ordinary quantum states, MZMs are protected by the material's topological properties, making them robust against impurities and/or defects. This robustness makes them ideal candidates for quantum computation: if achieved, they could perform better than conventional qubits as decoherence effects do not affect them. Engineering devices that host MZMs has been, in the last decades, a major challenge. One proposed class of devices are semiconductor-superconductor nanowires or planar Josephson junctions. The functionality of these devices strongly depends on interfacial effects between the two constituent material. Therefore, we focussed our efforts on studying the interfacial properties of a PbTe/Pb heterostructure. PbTe has been suggested to offer robustness against charge impurities and Pb possess a relatively

high superconducting gap, making PbTe/Pb a promising candidate. We demonstrated that proximity induced superconductivity is possible and discuss some potential bottlenecks related to the emergence of MZMs in such systems. Lastly, we applied the SIESTA-BdG method to study superconductivity on a high temperature superconductor: monolayer FeSe on SrTiO₃ (STO) substrate.

What can you do with two-dimensional materials?

Two-dimensional (2D) materials, such as graphene and transition metal dichalcogenides (TMDs), exhibit unique electronic and optical properties, making them highly promising for applications in electronics, optoelectronics, sensors, and energy storage. By leveraging density functional theory (DFT), we can study and optimize these materials for specific technological advancements.

TMDs are lightweight and exfoliable, with layers held together by weak van der Waals forces, allowing for easy stacking. In this thesis, we investigate how stacking configurations, strain, and interlayer distance influence their optical properties. Specifically, we focus on the absorption and emission spectra of MoS₂/WS₂ and MoSe₂/WSe₂ heterostructures. Our findings demonstrate that these optical properties can be tuned through structural modifications, providing deeper insight into the nature of excitons in these materials.

How does it look like to perform DFT simulations?

In practice, DFT simulations are typically performed on large High-Performance Computing (HPC) facilities due to their substantial computational cost. Researchers typically employ their preferred DFT codes to run simulations, which can require thousands to millions of core hours, depending on system complexity and accuracy requirements. HPC centers operate on a shared resource mode, where researchers gain access through national or international allocation programs. Competing jobs are submitted to a queueing system, managed by system administrators, which schedules computations based on priority, resource requests, and availability. Efficient use of these resources is essential, making optimization of code performance, parallelization, and storage management a crucial part of a DFT researcher's work. Given the need for memory efficiency and parallelization, core computational tasks are typically handled using compiled languages such as Fortran (widely used in academia) and C. A good DFT researcher must not only understand the tools they use but also plan simulations strategically, manage computational time effectively, and, when necessary, develop or modify code to enhance performance or add functionalities.

Once a simulation is completed (ideally yielding meaningful results), the next step is post-processing the generated data. This phase is usually carried out using high-level programming languages like Python, which facilitate data analysis and visualization. Discussing and interpreting results with colleagues (other theoreticians or experimentalists), is the most engaging part of the research. At this stage, technical details become less important, allowing

the researcher to reach a broader perspective on the project and focus on interpreting natural occurring phenomena and underlying physical/chemical mechanism .

Finally, the last stage of a project involves disseminating findings through conferences, presentation, and outreach activities, contributing to the advancement of knowledge within the scientific community and beyond.

Chapter descriptions

Chapter 2 : This chapter introduces many-body physics and Density Functional Theory (DFT), covering its foundational principles, limitations, and extensions like GW and Bethe-Salpeter equations. It also presents an original introduction to superconductivity, discussing the Bogoliubov-de Gennes formalism and unconventional superconductors.

Chapter 3 : We integrate the Bogoliubov-de Gennes equations with DFT into the open-source SIESTA code, creating the SIESTA-BdG method. Its accuracy is demonstrated on conventional and unconventional superconductors.

Chapter 4 : Using SIESTA-BdG, we predict proximity-induced superconductivity in PbTe/Pb heterostructures and assess their potential for hosting Majorana Zero Modes (MZMs).

Chapter 5 : We employ the SIESTA-BdG method to investigate monolayer FeSe, both in its freestanding form and when placed on a SrTiO₃ (STO) substrate. Our results reveal the crucial role of the substrate in altering the superconducting properties of FeSe. We propose that FeSe-based heterostructures, especially those incorporating substrates with high electron affinity, can be engineered to enhance Cooper pair formation, potentially opening new avenues for high-temperature superconductivity.

Chapter 6 : 2D materials offer tunable properties through composition, stacking, straining, and twisting. Using Many-Body Perturbation Theory (MBPT), we analyze the excitonic response of MoSe₂/WS₂ and MoSe₂/WSe₂ heterostructures under these influences.

Chapter 7 : Bi₂Se₃ is a key material among topological insulators. Combining theory (DFT) and experiment (pump-probe spectroscopy), we explore how hybridized surface states shape its optical and electronic properties in the finite-size, few-layers limit.

Samenvatting in het Nederlands

Deze thesis beschrijft de theoretische analyse en softwareontwikkelingen die de auteur heeft uitgevoerd om onze kennis over de materialen om ons heen te vergroten. Materie bestaat uit enorme verzamelingen van interacterende deeltjes (orde van grootte van het Avogadro-getal $N_A = 6.022 \times 10^{23}$). De tak van de natuurkunde die deze interacties bestudeert, staat bekend als "many-body physics". De fundamentele wetten die bepalen hoe een enkel

deeltje interacteert met zijn omgeving zijn goed begrepen op verschillende lengteschalen, van macroscopische systemen tot het atomaire niveau. Echter, wanneer meerdere deeltjes met elkaar in wisselwerking treden, worden hun collectieve gedragingen complex. Op atomaire schaal wordt het collectieve gedrag van deeltjes bepaald door de kwantummechanica. Zoals P.W. Anderson zei: "More is different", en daar zou ik aan toe willen voegen: "and different is what makes it truly fascinating".

Kwantummechanica omvat de beschrijving van materie op de atomaire schaal ($\sim 10^{-10}$ m) en wordt beschreven door de Schrödinger-vergelijking. Verrassend genoeg manifesteren interacties op deze kleine schaal zich in macroscopische fenomenen, zoals supergeleiding en lichtabsorptie/-emissie, met vergaande technologische implicaties. Naarmate de wereldwijde energiebehoefte toeneemt, wordt het begrijpen en benutten van deze kwantumeffecten cruciaal voor de ontwikkeling van efficiëntere materialen voor energieopslag, -omzetting en -transmissie. Deze uitdaging motiveert onderzoekers om natuurkundige theorieën verder te ontwikkelen, met als doel onze capaciteit om materiaaleigenschappen te beschrijven en te voorspellen te vergroten. Tegenwoordig zijn computersimulaties zo geavanceerd dat ze niet alleen bestaande materialen kunnen analyseren, maar ook nieuwe kunnen ontwerpen, wat een revolutie teweegbrengt in wetenschappelijk onderzoek. Onder de verschillende computationele methoden is de dichtheidsfunctionaaltheorie (DFT) de meest gebruikte ab initio-methode.

In dit proefschrift beschrijft de auteur het onderzoek dat hij tijdens zijn promotietraject heeft verricht. Het doel hiervan is tweeledig: (i) de mogelijkheden van DFT uitbreiden om supergeleidende eigenschappen van materialen te voorspellen, en (ii) inzicht krijgen in hoe elektronische en optische eigenschappen van tweedimensionale materialen veranderen door stapeling, rotatie en vervorming.

Wat is de dichtheidsfunctionaaltheorie?

DFT is een veelgebruikte computationele methode in de natuurkunde, scheikunde en materiaalkunde. Het vereist enkel de atomaire samenstelling en posities als invoer en voorspelt op basis van fundamentele kwantummechanische principes nauwkeurig een breed scala aan materiaaleigenschappen. Metalen, halfgeleiders, biologische moleculen en andere systemen vallen direct binnen de mogelijkheden van DFT. Het biedt een *exacte* beschrijving van de elektronendichtheid in de grondtoestand van een many-body-systeem. De DFT-Hamiltoniaan vormt het startpunt voor meer geavanceerde theorieën, die het mogelijk maken aangeslagen systemen te bestuderen (bijvoorbeeld licht-materie-interacties) of andere fasen van materie, zoals supergeleiding.

Waarom bestudeert men supergeleiding?

Supergeleiding is een fascinerend kwantumfenomeen waarbij elektronen zich koppelen tot paren, bekend als *Cooper-paren*, waardoor elektrische stroom zonder weerstand vloeit. De twee belangrijkste eigenschappen van supergeleiders zijn: geen elektrische weerstand en het verdrijven van magnetische velden (Meissner-effect). Conventionele supergeleiders worden

toegepast in energieoverdracht, magnetische levitatie en hogesnelheidscomputing. Ze functioneren echter bij zeer lage temperaturen (onder enkele Kelvin). Voor praktische toepassingen zou supergeleiding bij hogere temperaturen ideaal zijn. Onderzoekers worden uitgedaagd om nieuwe materialen met een hoge kritische temperatuur te ontdekken. Supergeleiding in materialen met een hoge kritische temperatuur wordt vaak gedreven door mechanismen die verder gaan dan de BCS-theorie en staat bekend als onconventionele supergeleiding.

Dit proefschrift introduceert de SIESTA-BdG-methode, een benadering om zowel conventionele als onconventionele supergeleiding vanuit eerste principes te berekenen. Deze methode is gebaseerd op de dichtheidsfunctionaaltheorie (DFT), waarbij de elektronische structuur wordt beschreven door het Kohn-Sham-systeem. Een mean-field-benadering wordt vervolgens geïntroduceerd, wat leidt tot het ontstaan van een supergeleidende paarpotentiaal. De elektronische Hamiltoniaan wordt zelfconsistent opgelost binnen de Bogoliubov-de Gennes (BdG)-formalismen om supergeleidende eigenschappen te karakteriseren. Eerst valideerden we onze code met conventionele supergeleiders en daarna breidden we de studie uit naar complexere systemen zoals heterostructuren.

Supergeleiding speelt ook een cruciale rol in kwantumcomputing. Een speciale klasse van systemen, bekend als topologische supergeleiders, herbergt exotische deeltjes genaamd *Majorana zero modes* (MZMs). In tegenstelling tot gewone kwantumtoestanden worden MZMs beschermd door de topologische eigenschappen van het materiaal, waardoor ze robuust zijn tegen onzuiverheden en defecten. Deze robuustheid maakt ze ideale kandidaten voor kwantumcomputers, omdat ze minder gevoelig zijn voor decoherentie-effecten dan conventionele qubits. Het ontwerpen van apparaten die MZMs bevatten, is al decennialang een grote uitdaging. Een voorgestelde klasse van apparaten bestaat uit halfgeleider-supergeleider nanodraden of vlakke Josephson-juncties. De functionaliteit van deze apparaten hangt sterk af van de effecten van de raakvlakken tussen de twee samengestelde materialen. Wij hebben ons daarom gericht op het bestuderen van de grensvlak karakteristieken van een PbTe/Pb-heterostructuur. Er is gesuggereerd dat PbTe robuustheid biedt tegen ladingsonzuiverheden, en Pb heeft een relatief grote supergeleidingskloof, waardoor PbTe/Pb een veelbelovende kandidaat is. We hebben aangetoond dat nabijheidsgeïnduceerde supergeleiding mogelijk is, en we hebben enkele potentiële knelpunten besproken met betrekking tot het ontstaan van MZMs in dergelijke systemen. Tot slot hebben we de SIESTA-BdG-methode toegepast om supergeleiding te bestuderen in een hogetemperatuursupergeleider: een monolaag FeSe op een SrTiO₃-substraat.

Wat kun je doen met tweedimensionale materialen?

Tweedimensionale (2D) materialen, zoals grafeen en overgangsmetaaldichalcogeniden (TMD's), vertonen unieke elektronische en optische eigenschappen, waardoor ze veelbelovend zijn voor toepassingen in elektronica, opto-elektronica, sensoren en energieopslag. Met behulp van DFT kunnen we deze materialen bestuderen en optimaliseren voor specifieke technologische vooruitgang.

TMD's zijn lichtgewicht en exfolieerbaar, met lagen die door zwakke van der Waals-krachten bij elkaar worden gehouden, waardoor ze gemakkelijk gestapeld kunnen worden. In dit proefschrift onderzoeken we hoe stapelconfiguraties, rek en interlaagafstand hun optische eigenschappen beïnvloeden. Specifiek richten we ons op de absorptie- en emissiespectra van MoS_2/WS_2 en $\text{MoSe}_2/\text{WSe}_2$ heterostructuren. Onze bevindingen tonen aan dat deze optische eigenschappen kunnen worden afgestemd door structurele aanpassingen, wat een dieper inzicht geeft in de aard van excitonen in deze materialen.

Hoe ziet een DFT-simulatie eruit?

In de praktijk worden DFT-simulaties doorgaans uitgevoerd op grote High-Performance Computing (HPC)-faciliteiten vanwege hun aanzienlijke rekenkosten. Onderzoekers gebruiken hun favoriete DFT-software om simulaties uit te voeren, die duizenden tot miljoenen processorkernen kunnen vereisen, afhankelijk van de systeemcomplexiteit en nauwkeurigheidseisen.

HPC-centra werken met gedeelde resources, waarbij onderzoekers toegang krijgen via nationale of internationale allocatieprogramma's. Jobs worden ingediend in een wachtrijstelsel, beheerd door systeembeheerders, die berekeningen plannen op basis van prioriteit, resource-aanvragen en beschikbaarheid. Efficiënt gebruik van deze resources is essentieel, waardoor optimalisatie van codeprestaties, parallelisatie en opslagbeheer een cruciaal aspect van DFT-onderzoek is. Gezien de noodzaak van geheugenefficiëntie en parallelisatie worden de zwaarste berekeningen doorgaans uitgevoerd in gecompileerde programmeertalen zoals Fortran (veelgebruikt in de academische wereld) en C. Een goede DFT-onderzoeker moet niet alleen de gebruikte tools begrijpen, maar ook simulaties strategisch plannen, rekentijd efficiënt beheren en, waar nodig, code ontwikkelen of aanpassen om de prestaties te verbeteren of extra functionaliteit toe te voegen.

Wanneer een simulatie is afgerond (en idealiter zinvolle resultaten oplevert), volgt de fase van post-processing van de gegenereerde data. Deze stap wordt meestal uitgevoerd met behulp van hogere programmeertalen zoals Python, die het analyseren en visualiseren van gegevens vergemakkelijken. Het bespreken en interpreteren van de resultaten met collega's – theoretici of experimenteel werkenden, vormt vaak het meest boeiende onderdeel van het onderzoek. In deze fase worden technische details minder dominant, waardoor de onderzoeker een breder perspectief op het project krijgt en zich kan richten op het interpreteren van natuurverschijnselen en onderliggende fysische of chemische mechanismen.

Tot slot omvat de laatste fase van een project het verspreiden van de bevindingen via conferenties, presentaties en outreachactiviteiten. Op die manier wordt bijgedragen aan de vooruitgang van kennis binnen de wetenschappelijke gemeenschap en daarbuiten.

Hoofdstukbeschrijvingen

Hoofdstuk 2 : Dit hoofdstuk introduceert many-bodyfysica en Density Functional Theory (DFT), waarbij de fundamentele principes, beperkingen en uitbreidingen zoals de GW- en Bethe-

Salpeter-equaties worden behandeld. Ook bevat het een originele inleiding tot supergeleiding, met bespreking van het Bogoliubov-de Gennes-formalisme en onconventionele supergeleiders.

Hoofdstuk 3 : We integreren de Bogoliubov-de Gennes-vergelijkingen met DFT in de open-source SIESTA-code, waarmee we de SIESTA-BdG-methode ontwikkelen. De nauwkeurigheid ervan wordt aangetoond voor zowel conventionele als onconventionele supergeleiders.

Hoofdstuk 4 : Met behulp van SIESTA-BdG voorspellen we nabijheidsgeïnduceerde supergeleiding in PbTe/Pb-heterostructuren en evalueren we hun potentieel voor het herbergen van Majorana Zero Modes (MZMs).

Hoofdstuk 5 : We gebruiken de SIESTA-BdG-methode om monolaag FeSe te onderzoeken, zowel vrijstaand als op een SrTiO₃-substraat (STO). Onze resultaten tonen aan dat het substraat een cruciale rol speelt in het beïnvloeden van de supergeleidende eigenschappen van FeSe. We stellen dat FeSe-gebaseerde heterostructuren, in het bijzonder met substraten met een hoge elektronenaffiniteit, ontworpen kunnen worden om de vorming van Cooperparen te bevorderen, wat mogelijk nieuwe wegen opent richting hogetemperatuursupergeleiding.

Hoofdstuk 6 : Tweedimensionale materialen bieden instelbare eigenschappen via samenstelling, stapeling, vervorming en draaiing. Met behulp van Many-Body Perturbation Theory (MBPT) analyseren we de excitonrespons van MoSe₂/WS₂- en MoSe₂/WSe₂-heterostructuren onder invloed van deze factoren.

Hoofdstuk 7 : Bi₂Se₃ is een sleutelmateriaal binnen de topologische isolatoren. Door theorie (DFT) te combineren met experimenten (pomp-probe spectroscopie) onderzoeken we hoe gehybridiseerde oppervlaktetoestanden de optische en elektronische eigenschappen beïnvloeden in het grensgeval van enkele lagen.

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Scientific résumé

1 Publications

1. **R. Reho**^{*}, N. Wittemeier^{*}, A. H. Kole, P. Ordejón, Z. Zanolli, “Density functional Bogoliubov-de Gennes theory for superconductors implemented in the SIESTA code”, *Phys. Rev. B* **110**, 134505 (2024). Chapter 3.
2. **R. Reho**, A. R. Botello-Méndez, Z. Zanolli, “Proximity induced superconductivity in PbTe/Pb via first principles”, arXiv:2412.01749 (2024), under review in *Phys. Rev. B*. Chapter 4
3. **R. Reho**, N. Wittemeier, A. H. Kole, A. R. Botello-Méndez, Z. Zanolli, “The crucial role of substrate in FeSe/STO: new insights to interface-driven superconductivity from first-principles”, arXiv:2503.15025 (2025). Chapter 5.
4. **R. Reho**, A. Botello Méndez, M. Verstraete, Z. Zanolli “Excitonic response in transition metal dichalcogenide heterostructures from first-principles: impact of stacking, twisting, and interlayer distance”, *Phys. Rev. B* **110** (2024).
Selected as PRB Editors’ suggestions. Chapter 6
5. J. Vliem, S. A. Cayan, **R. Reho**, A. R. Botello-Méndez, P. M. M. C. Melo, P. Geiregat, Z. Zanolli, D. Vanmaekelbergh, “Role of surface bands in the photogeneration, cooling, and recombination of charge carriers in two-dimensional Bi₂Se₃”, submitted and under review in *ACS Nano* (2025). Chapter 7.
6. **R. Reho**, M. H. D. Guimarães and Zeila Zanolli, “Magnetic and optical frontiers in 2D semiconductors”, *Roadmap on Quantum Magnetic Materials, 2D Materials*, IOP Publishing Ltd (2025).

^{*} Both authors contributed equally

2 Presentations

2.1 *Invited Talks*

1. **R. Reho**, N. Wittemeier, A.H. Kole, Pablo Ordejón and Z. Zanolli “DFT for superconductors: theory and implementation in the SIESTA code”, Physics Seminars, Limpertsberg, Luxembourg, LXM, 26/02/2025.

2.2 *Invited seminars*

1. **R. Reho**, N. Wittemeier, A.H. Kole, Pablo Ordejón and Z. Zanolli “DFT for Superconductors: theory and implementation in the SIESTA code”, Debye Lunch Lecture, Utrecht University, Utrecht NL, 11/12/2024.
2. **R. Reho**, A. R. Botello-Méndez, M. J. Verstraete, Z. Zanolli “Optical properties of TMDs van der Waals heterostructures”, KNCV-CTC-Seminars, University of Twente, 20/09/2023.
3. **R. Reho**, A. R. Botello-Méndez, D. Sangalli, M.J. Verstraete, Z. Zanolli “Real-time photoluminescence from first-principles: Application to Van der Waals heterostructure”, ETSF workshop, Amsterdam, NL, 17/05/2023.
4. **R. Reho**, A. R. Botello-Méndez, D. Sangalli, M. J. Verstraete, Z. Zanolli “Controlling light-matter interaction in TMD heterostructures”, NWO Chains, Veldhoven NL, 3-4/12/2024.
5. **R. Reho**, N. Wittemeier, A.H. Kole, Pablo Ordejón and Z. Zanolli “DFT for Superconductors: theory and implementation in the SIESTA code”, ETSF Webinar, Online, 22/11/2024.

2.3 *Contributed oral presentations*

1. **R. Reho**, A. R. Botello-Méndez, Z. Zanolli “Proximity induced superconductivity in PbTe/Pb via first principles”, QuMaT yearly meeting, Enschede NL, 11-12/11/2024.
2. **R. Reho**, N. Wittemeier, A. H. Kole, P. Ordejón, Z. Zanolli “DFT for Superconductors: theory and implementation in the SIESTA code”, ETSF Electron-phonon collaboration team workshop, Louvain-la-Neuve BE, 23-25/09/2024.
3. **R. Reho**, A. R. Botello-Méndez, D. Sangalli, M. J. Verstraete, Z. Zanolli “Excitonic response in TMD heterostructures from first-principles: impact of stacking, twisting and interlayer distance”, CECAM workshop 'Frontiers in many-body excited-state dynamics from first principles', Lausanne, CH 15-17/07/2024.
4. **R. Reho**, A.R. Botello-Méndez, D. Sangalli, M. J. Verstraete, Z. Zanolli “Excitonic responses in MoS₂/WS₂ and MoSe₂/WSe₂ heterostructures from first-principles: impact

of stacking order and interlayer distance”, 27th ETSF workshop on Electronic Excitations “Shining light on matter through interdisciplinary theoretical approaches”, Marseille FR, 03-07/06/2024.

5. **R. Reho**, Z. Zanolli “Optical properties of van der Waals TMD heterostructures from first-principles”, DPG Spring Meetings, Berlin, Germany, 22-26/03/2024.
6. **R. Reho**, N. Wittemeier, A. H. Kole, P. Ordejón, Z. Zanolli “Density Functional Theory for Superconductors: theory and implementation in the SIESTA code”, NWO Physics, Veldhoven, NL, 23-24/01/2024.
7. **R. Reho**, P. M. M. C. de Melo, A. R. Botello-Méndez, A. Botello Méndez, M. J. Verstraete, D. Vanmaekelbergh, and Z. Zanolli “Identification of high-energy excitations in two-dimensional topological Bi_2Se_3 nanoplatelets”, QuMat meeting, Nijmegen, Netherlands, 22-25/10/2023.
8. **R. Reho**, A. Botello Méndez, M. J. Verstraete, Z. Zanolli “Absorption and emission in Van der Waals heterostructures from first-principles”, Colloquium HOWDI, Porquerolles, 8-12/05/2023.
9. **R. Reho**, A. Kole, N. Wittemeier, Z. Zanolli, “First-Principles Topological Superconductivity”, QuMat kick-off meeting, Utrecht, Netherlands, 26/10/2022.
10. **R. Reho**, P. Melo, M. Verstraete, H. Stoof, Z. Zanolli “Trions and biexcitons from first principles, questions, and future work”, Informal ETSF workshop ETSFCoimbra2021, Physics Department, University of Coimbra, Portugal, 13-15/12/2021.
11. **R. Reho**, P. Melo, M. J. Verstraete, Z. Zanolli “Quasi-equilibrium states in heterobilayers of transition metal dichalcogenides”, ETSF Young Researcher Meeting ETSF YRM2021, Cagliari, Italy, 06-10/09/2021.

2.4 Poster presentations

1. S. T. Bos, **R. Reho**, A. R. Botello-Méndez, Z. Zanolli “Shining light on matter through interdisciplinary theoretical approaches”, Marseille FR, 03-07/06/2024.
2. **R. Reho**, P. M. M. C. de Melo, M. J. Verstraete, Z. Zanolli, “Ab initio calculations on the band structure of TMDs”, 25th Workshop on Electronic Excitations, Leuven, BELG, 13/06/2022-17/06/2022.
3. **R. Reho** et al. “Pressure-induced Phase Transitions in Fe_4N ”, 20th International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods ICTP2021, The Abdus Salam International Centre for Theoretical Physics, Trieste, IT, 23/02/2021-25/02/2021.

3 Outreach

1. Press release: “New study highlights potential of 2D materials in advanced light-based technologies”, Utrecht University News, 09/07/2024.
2. Represented the ‘Quantum Materials Teams by Design’ team of Utrecht University at an industry-facing fair. TEKNOLOGY, NWO Innovation Festival 2022, Dutch festival of technology, science and innovation, Utrecht, NL ‘Quantum Materials by Design’, R. Reho, N. Wittemeier, A.H. Kole, Z. Zanolli, Utrecht, NL, 31/05/2022.
3. Personal webpage: <https://rreho.github.io/>

Curriculum Vitae

Riccardo Reho was born in Gallipoli, Italy. He developed a strong passion for mathematics and science from an early age. In high school, he won a national chemistry competition on green science, reinforcing his interest in research. He pursued theoretical physics in Bologna, focusing on General Relativity for both his bachelor's (with R. Balbinot) and master's theses (with F. Bastianelli). During his master's, he conducted research at the Max Planck Institute for Gravitational Physics.

Reho later transitioned to condensed matter theory, starting a PhD at Utrecht University, under the supervision of Z. Zanolli. He specialized in theoretical spectroscopy and superconductivity, publishing key works in both fields. His contribution in these fields involved theory validation and computational implementation, collaborating with experimental researchers and securing computational resources from European super computing facilities.

His PhD work included developing optimized code for large-scale materials simulations and initiating a spectroscopy simulation package. He has presented his research at over 15 international conferences and remains active in the Yambo and ETSF communities, contributing to open-source scientific software and mentoring researchers.

