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BACHELOR THESIS

Ab Initio Investigation of the CDW Phase Transition in TiSe₂

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Zusammenfassung

Ladungsdichtewellen (CDW) in niederdimensionalen Materialien bieten ein faszinierendes System zur Untersuchung des Zusammenspiels von elektronischen Wechselwirkungen, Gitterverzerrungen und Quanteneffekten. In dieser Arbeit wird der CDW-Phasenübergang in monolagigem TiSe₂ auf Grundlage von ab initio Methoden untersucht.

Die Effekte elektronischer Temperatur werden über Fermi–Dirac-Smearing modelliert, wodurch eine temperaturabhängige Analyse phononischer Instabilitäten ermöglicht wird. Die Phononenspektren zeigen ein charakteristisches mode-softening, das mit der CDW in Verbindung steht, und erlauben so die Bestimmung einer kritischen Übergangstemperatur. Die entsprechenden periodischen Gitterverzerrungen dienen als Grundlage zur Konstruktion von Potentialflächen, deren Temperaturabhängigkeit eine unabhängige Abschätzung der Phasenübergangstemperatur erlaubt.

Zur Untersuchung quantennuklearer Effekte wird die atomare Bewegung im Rahmen eines quantenmechanischen einteilchen-Modells innerhalb des durch die CDW definierten Konfigurationsraums beschrieben. Die Analyse der resultierenden Wellenfunktion liefert Einblicke in die quantenmechanische Delokalisierung und die Möglichkeit einer quantenstabilisierten CDW-Phase. Dieser Zugang unterstreicht die Relevanz quantennuklearer Effekte im Bereich des Phasenübergangs und deren Einfluss auf die Stabilisierung oder Unterdrückung von Gitterinstabilitäten in zweidimensionalen Materialien.

Abstract

Charge density wave (CDW) phases in low-dimensional materials offer a compelling framework for studying the interplay between electronic correlations, lattice distortions, and quantum effects. This work investigates the CDW phase transition in monolayer TiSe₂ based on first-principles methods.

Electronic temperature effects are modeled via Fermi–Dirac smearing, enabling an analysis of temperature-dependent phonon instabilities. Phonon spectra reveal the softening of specific modes associated with the CDW, allowing the determination of a critical transition temperature. The corresponding periodic lattice distortions are used to construct potential energy surfaces, from which the disappearance of the energy barrier at higher temperatures provides an independent estimate of the phase transition.

To explore quantum nuclear effects, atomic motion is treated within a single-particle quantum framework in the configuration space associated with the CDW. Analysis of the resulting wavefunction provides insight into quantum delocalization and the possibility of a quantumstabilized CDW phase. This approach highlights the relevance of quantum nuclear effects near the phase boundary and their role in stabilizing or suppressing lattice instabilities in two-dimensional materials.

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List of Abbreviations

DFT Density functional theory
DFPT Density functional perturbation theory
BOA Born–Oppenheimer approximation
CDW Charge density wave
PLD Periodic lattice distortion
BZ Brillouin Zone
TMDC Transition metal dichalcogenide
HS High symmetry
BVK Born–von-Kármán
PES Potential energy surface
BFGS Broyden–Fletcher–Goldfarb–Shanno
QNE Quantum nuclear effects

Chapter 1

Introduction

Charge density wave (CDW) phases are an intriguing class of electronic orders in condensed matter systems, characterized by periodic modulations of the electron density. These phases exhibit a complex interplay between electronic correlations, lattice distortions, and quantum effects, making them a powerful platform for exploring fundamental physical phenomena. The study of CDW in low-dimensional materials, particularly in monolayers, has attracted significant attention due to their potential application in future electronic devices. One such material is TiSe₂, a Transition metal dichalcogenide (TMDC), which has long been known for its CDW phase transition at low temperatures. Understanding the underlying mechanisms of this transition is crucial for both fundamental physics and potential applications in quantum technologies.

This thesis investigates the CDW phase transition in monolayer TiSe₂ through first-principles calculations, employing Density functional theory (DFT), Density functional perturbation theory (DFPT), and numerical methods to provide a comprehensive understanding of the material's behavior near the phase transition. The study focuses on the coupling between the electronic subsystem and the lattice degrees of freedom, which are central to the formation and suppression of the CDW phase. To introduce a physically meaningful temperature, the thermal occupations are broadened using Fermi–Dirac smearing, allowing for the simulation of temperature-dependent changes in the Phonon spectrum and electronic structure. By analyzing the phonon spectrum, electronic structure, and Potential energy surface (PES), this work aims to provide quantitative estimates of the phase transition temperature.

An essential aspect of this study is the exploration of Quantum nuclear effects (QNE), which are treated within the framework of a single-particle Schrödinger equation solved for the configuration space underlying the PES. The goal is to evaluate the role of QNE in stabilizing or suppressing the CDW phase. The methodology is inspired by similar techniques employed in the study of quantum paraelectrics [1]. The use of mass-weighted coordinates in this study avoids arbitrary choices of phonon mass and displacement amplitudes, enabling a physically grounded treatment of nuclear quantum motion. The combined analysis of DFPT,

PES topology, and quantum delocalization provides a comprehensive framework for understanding the role of quantum fluctuations in CDW phase transitions.

In summary, this thesis establishes a thorough first-principles analysis of the CDW phase transition in $TiSe_2$ and highlights the complex role of QNE. By combining phonon, electronic, and quantum mechanical approaches, it contributes to a deeper understanding of the CDW phenomenon in low-dimensional materials and paves the way for future studies in this exciting field.

Chapter 2

Theory and Methods

In the following, we adopt the Hartree atomic unit system, as is common in solid-state physics, to ensure consistency and clarity in all calculations. Within this unit system, the constants and expressions commonly given in SI units transform as follows:

$$\hbar = e = 4\pi\epsilon_0 = m_e = 1 \tag{2.1}$$

2.1 Density Functional Theorie

Similar to how newtons second law predicts the behavior and response of macroscopic objects to some initial conditions the Schrödinger equation describes any quantum-mechanical system and how it evolves. In solid state physics these systems are periodic structures (lattices) of a finite number of nuclei and electrons. To correctly describe such a system the Equation must include the correlation terms of the different constituents and is often reffered to as the many body schrödiger equation. Solving this equation analytically or numerically for larger systems is practically impossible.

Hence, the approach of DFT is employed. This chapter provides a basic derivation of the method, following the detailed exposition presented in Materials Modelling using Density Functional Theory by Giustino [2].

2.1.1 Many Body Schrödinger Equation

Solids consists of a finite number of nuclei and electrons. The state of such a quantummechanical system is described by the wavefunction Ψ_i , which accounts for all degrees of freedom within the system, including, in general, the positions and spin of each electron and nucleon. The wavefunction Ψ_i and its corresponding eigenvalue E_i , denoted by the index *i*, are solutions to the eigenvalue problem known as the Many-Body Schrödinger Equation.

$$\hat{H}\Psi_i = E_i\Psi_i \tag{2.2}$$

 \hat{H} represents the many-body Hamiltonian, the operator that governs the system's dynamics by incorporating the initial parameters, including the kinetic energy terms and the potential interactions arising from the charges of electrons and nuclei.

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{ee} + \hat{V}_{nn} + \hat{V}_{en}$$
(2.3)

• \hat{T} : Kinetic energy operator for electrons

$$\hat{T}_e = -\sum_{i=1}^{n} \frac{\nabla_i^2}{2} \tag{2.4}$$

• \hat{T}_n : Kinetic energy operator for nuclei

$$\hat{T}_n = -\sum_{I=1}^{N} \frac{\nabla_I^2}{2M_I} \tag{2.5}$$

• \hat{V}_{ee} : Operator for Electron-electron interactions

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\vec{r_i} - \vec{r_j}|}$$
(2.6)

• \hat{V}_{nn} : Operator for Nucleus-nucleus interactions

$$\hat{V}_{nn} = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|}$$
(2.7)

• \hat{V}_{en} : Operator for Electron-nucleus interactions

$$\hat{V}_{en} = -\sum_{i,I} \frac{Z_I}{|\vec{r}_i - \vec{R}_J|}$$
(2.8)

Where *i* and *j* represent indices for electrons, while *I* and *J* denote indices for nuclei, running over all electrons and nuclei in the system, respectively. The position vectors $\vec{r_i}$ and $\vec{R_I}$ correspond to the coordinates of the *i*th electron and the *I*th nucleus. M_I represents the mass of the *I*th nucleus, and Z_I denotes its charge, which corresponds to the number of protons in atomic units. The summations extend over all particles in the system, with the conditions

 $i \neq j$ and $I \neq J$ ensuring that self-interactions are excluded from the potential energy terms. Using the Hartree atomic unit system the external parameters required to solve the time independent Schrödinger equation are reduced to only the atomic Masses M_I and charges Z_I [2].

2.1.2 Born-Oppenheimer Approximation

Solving the many-body Schrödinger equation requires accounting for $3(N_e + N_n)$ degrees of freedom, where N_E and N_I represent the number of electrons and nuclei, respectively. To make this equation computationally feasible, it is necessary to introduce approximations. The first major simplification being the Born–Oppenheimer approximation (BOA) separating the electronic and nuclear degrees of freedom effectively decoupling their motion. Within this approximation the many-body wave function can be written as a product of an electronic and a nuclear wave function [3]:

$$\Psi(r,R) = \sum_{h} \psi_h(r;R)\phi_h(R).$$
(2.9)

Since nuclei are much heavier than electrons $(M_I \gg m_e)$, they move much more slowly. Consequently, electrons can instantaneously adjust to the positions R of the nuclei, allowing us to treat nuclear coordinates as fixed parameters when solving the electronic Schrödinger equation.

$$\hat{H}_e \psi_h(r; R) = E_h(R)\psi_h(r; R), \qquad (2.10)$$

where the electronic Hamiltonian is given by:

$$\hat{H}_e = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en}.$$
(2.11)

Accordingly the nuclear Schrödinger Equation is of the form:

$$\hat{H}_n \Omega_{hk}(R) = E_{hk}(R) \Omega_{hk}(R) \tag{2.12}$$

with the nuclear Hamiltonian:

$$\hat{H}_n = \hat{T}_n + \hat{V}_{nn} + E_h(R)$$
(2.13)

The BOA significantly reduces computational complexity by allowing the electronic structure problem to be solved independently for fixed nuclear positions thus reducing the systems degrees of freedom to $3N_e$.

2.1.3 Hohenberg-Kohn-Theorem

Despite the simplification achieved by the BOA, the computational cost of solving the manyelectron Schrödinger equation still increases exponentially with the number of electrons. In the 1960s, Hohenberg and Kohn developed a method with means to reduce this cost to a linear factor scaling [4]. The main insight of this Theorem is that ground state properties like the ground state wavefunction ψ_0 and energy E_0 of a system of electrons are entirely determined by the electron density n_0 .

The electron density and the electron density operator for an N_e -electron system are defined as:

$$n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle \tag{2.14}$$

$$\hat{n}(\mathbf{r}) = \sum_{i}^{N_e} \delta(\mathbf{r} - \hat{\mathbf{r}}_i), \qquad (2.15)$$

where $\hat{\mathbf{r}}_i$ are the particle position operators. Using this definition the external potential created by the nuclei can be expressed as:

$$\langle \psi | \hat{V}_{en} | \psi \rangle = \int n(\mathbf{r}) V_{en}(\mathbf{r}; R) \, d\mathbf{r}$$
 (2.16)

$$E_{h} = \langle \psi_{h} | \hat{H}_{e} | \psi_{h} \rangle = \langle \psi_{h} | \hat{T}_{e} + \hat{V}_{ee} | \psi_{h} \rangle + \int n(\mathbf{r}) V_{en}(\mathbf{r}; R) \, d\mathbf{r}$$
(2.17)

In this form it becomes obvious that the Energy is a functional of the many electron Schrödinger equation $E_h = \mathcal{F}[\psi_h(\mathbf{r}_1, \dots, \mathbf{r}_N)].$

Hohenberg-Kohn 1

The first part of the Hohenberg-Kohn theorem uniquely connects the ground-state electron density n_0 and the external potential \hat{V}_{en} . This unintuitive conclusion can easily be achieved by reductio ad absurdum.

Assume the ground-state density n_0 can be obtained by two different potentials V_{en}^I and V_{en}^{II} . If ψ_0^I and ψ_0^{II} are the corresponding ground states, we find:

$$\langle \psi_0^I | \hat{H}_e^I | \psi_0^I \rangle = E_0^I < \langle \psi_h^{II} | \hat{H}_e^I | \psi_h^{II} \rangle$$
(2.18a)

$$\langle \psi_0^{II} | \hat{H}_e^{II} | \psi_0^{II} \rangle = E_0^{II} < \langle \psi_0^I | \hat{H}_e^{II} | \psi_0^I \rangle$$
(2.18b)

By subtraction and equation (2.17), we obtain:

$$E_0^I - E_0^{II} < \int n(\mathbf{r}) \left[V_{en}^I(\mathbf{r}; R) - V_{en}^{II}(\mathbf{r}; R) \right] d\mathbf{r}$$
(2.19a)

$$E_0^{II} - E_0^I < \int n(\mathbf{r}) \left[V_{en}^{II}(\mathbf{r}; R) - V_{en}^I(\mathbf{r}; R) \right] d\mathbf{r}$$
(2.19b)

Adding (2.19a) and (2.19b), we obtain 0 < 0, a contradiction. This concludes the proof that no two different potentials V_{en} can yield the same ground-state electron density or, in other words, that the ground state density uniquely specifies the external potential V_{en} . As a result, any quantity that can be written as a functional of the ground-state wavefunction can instead be expressed as a functional of the electron density.

Hohenberg-Kohn 2

So far, we know that for a given $v(\mathbf{r})$, the ground-state density $n_0(\mathbf{r})$ uniquely determines the external potential and thus the Hamiltonian and wavefunction. However, it does not tell us how to obtain this ground-state density $n_0(\mathbf{r})$. The second part of the Theorem often referred to as the Hohenberg-Kohn variational principal of density functional theory states that the true ground state density is the one that minimizes the total energy. According to the first half of the Theorem this energy can be expressed as a functional of the ground state density:

$$E[n] = F[n] + \int V_{en}(\mathbf{r})n(\mathbf{r}) \, d\mathbf{r}$$
(2.20)

where F[n] is a universal functional incorporating kinetic and interaction energies:

$$F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T}_e + \hat{V}_{ee} | \Psi \rangle$$
(2.21)

Since F[n] is defined as a minimum over all wavefunctions yielding n, it follows that for any trial density $n' \neq n_0$,

$$F[n_0] \le F[n'] \tag{2.22}$$

The energy due to the external potential is determined simply by the electron density. Euqation 2.22 thus implies:

$$E[n_0] \le E[n'], \quad \forall n. \tag{2.23}$$

This constrained search formalism based on the proof by Hohenberg-Kohn and Percus-Levy-Lieb establishes that $n_0(\mathbf{r})$ minimizes the total Energy E[n] [5].

2.1.4 Kohn-Sham Equations

Despite the elegance of the Hohenberg-Kohn theorem, the exact form of the universal functional F[n] remains unknown due to the missing explicit expressions for the kinetic energy term \hat{T}_e and the exchange-correlation effects in \hat{V}_{ee} . To address this challenge, Kohn and Sham [6] introduced an auxiliary system of non-interacting electrons that reproduces the exact ground-state density of the interacting system.

The total energy functional can be written as:

$$E[n] = F[n] + \int V_{en}(\mathbf{r})n(\mathbf{r}) \, d\mathbf{r}, \qquad (2.24)$$

where V_{en} represents the external potential due to the nuclei. The functional F[n] is further decomposed as:

$$F[n] = E_{T_e}^n + E_{V_{ee}}^n, (2.25)$$

where $E_{T_e}^n$ is the exact kinetic energy and $E_{V_{ee}}^n$ accounts for electron-electron interactions. In the Kohn-Sham formalism, this is rewritten in terms of an auxiliary system:

$$F[n] = E_{T_{aux}}^n + E_H[n] + E_{XC}[n].$$
(2.26)

In this context the term $E_{T_{aux}}^n$ refers to the kinetic energy of the non-interacting auxiliary system. $E_H[n]$ is the Hartree energy, which represents the classical Coulomb interaction of the electron density. Finally, $E_{XC}[n]$ is the exchange-correlation energy, which accounts for the remaining many-body effects present in the interacting system. By expressing these terms explicitly the total Energy functional is given by:

$$E[n] = -\sum_{i} \int \phi_{i}^{*}(\mathbf{r}) \frac{\nabla^{2}}{2} \phi_{i}(\mathbf{r}) \, d\mathbf{r} + \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' + E_{XC}[n] + \int n(\mathbf{r})V_{en}(\mathbf{r}) \, d\mathbf{r}.$$
(2.27)

According to the Hohenberg-Kohn 2.1.3 variational principle, the total energy is minimized by the ground-state density:

$$\frac{\delta E}{\delta \phi_i^*} \bigg|_{n_0} = \frac{\delta E}{\delta n} \frac{\delta n}{\delta \phi_i^*} \bigg|_{n_0} = \frac{\delta E}{\delta n} \phi_i \bigg|_{n_0} = 0.$$
(2.28)

The othonormality constraint $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ is enfroced using the method of Lagrange multipliers:

$$L = E - \sum_{ij} \lambda_{ij} \left[\langle \phi_i | \phi_j \rangle - \delta_{ij} \right].$$
(2.29)

$$0 \stackrel{!}{=} \frac{\delta L}{\delta \phi_i^*} = \frac{\delta E}{\delta \phi_i^*} - \sum_j \lambda_{ij} |\phi_j\rangle.$$
(2.30)

$$\frac{\delta E}{\delta \phi_i^*} = \sum_j \lambda_{ij} |\phi_j\rangle.$$
(2.31)

Using the definition of the functional derivative while obeying the chain rule:

$$\frac{\delta E}{\delta \phi_i^*} = \left[-\frac{\nabla}{2} + \int d\mathbf{r}' \, \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{XC}[n]}{\delta n(\mathbf{r})} + V_{en}(\mathbf{r}) \right] \, |\phi_i(\mathbf{r})\rangle = \sum_j \lambda_{ij} \, |\phi_j\rangle. \tag{2.32}$$

To diagonalize the matrix λ_{ij} , we introduce a set of orthonormal wavefunctions φ_i and arrive at the Kohn-Sham equation:

$$\hat{H}_{KS}\,\varphi_i(\mathbf{r}) = \varepsilon_i\,\varphi_i(\mathbf{r})$$
(2.33)

With the Kohn-Sham Hamiltonian and Kohn-Sham potential:

$$\hat{H}_{KS} = -\frac{\nabla}{2} + V_{KS} \tag{2.34}$$

$$V_{KS} = V_{en}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}, [n])$$
(2.35)

where $V_H(\mathbf{r})$ is the Hartree potential and $V_{XC}(\mathbf{r}, [n])$ is the exchange-correlation potential. Their explicit expressions follow from Equation 2.32:

$$V_H(\mathbf{r}) = \int d\mathbf{r}' \, \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},\tag{2.36}$$

$$V_{XC}(\mathbf{r}, [n]) = \frac{\delta E_{XC}[n]}{\delta n(\mathbf{r})}.$$
(2.37)

The wavefunction of the auxiliary system is given by a single Slater determinant composed of the Kohn-Sham orbitals:

$$\Psi_{KS} = \frac{1}{\sqrt{N!}} \det |\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)...\varphi_N(\mathbf{r}_N)|$$
(2.38)

where the orbitals φ_i satisfy the Kohn-Sham equations. This construction ensures that the total electron density n(r) is obtained by summing over the squared moduli of the orbitals, thereby preserving the correct ground-state density:

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$$
(2.39)

Equations 2.33-2.39 form a set of self-consistent equations, which must be solved iteratively until convergence is reached [6]. However, since the exact form of $V_{XC}(\mathbf{r}, [n])$ is unknown, it is typically approximated using density functional approximations, such as the local density approximation (LDA) or generalized gradient approximation (GGA).

2.2 Density-Functional Perturbation Theory

DFPT is a powerful formalism that extends ground-state DFT to compute the linear response of a system to small perturbations, such as atomic displacements. In the context of phonon calculations, DFPT enables the evaluation of vibrational properties without the need for finite displacements or large supercells [7].

By considering a small perturbation parameter λ the external potential modifies as $V_{en} \rightarrow V_{en}^{(0)} + \lambda V_{en}^{(1)}$. The Kohn–Sham orbitals φ_i , eigenvalues ε_i , and electron density n are then expanded in powers of λ .

$$\varphi_i = \varphi_i^{(0)} + \lambda \varphi_i^{(1)} + \mathcal{O}(\lambda^2), \quad \varepsilon_i = \varepsilon_i^{(0)} + \lambda \varepsilon_i^{(1)} + \mathcal{O}(\lambda^2),$$
$$n(\mathbf{r}) = n^{(0)}(\mathbf{r}) + \lambda n^{(1)}(\mathbf{r}) + \mathcal{O}(\lambda^2).$$

Substituting into the Kohn–Sham equations and keeping only linear terms in λ , we obtain the linearized Kohn–Sham equation for the first-order correction to the orbitals $\varphi_i^{(1)}$ [8]:

$$\left(\hat{H}^{(0)} - \varepsilon_i^{(0)}\right)\varphi_i^{(1)} = -\left(V_{KS}^{(1)} - \varepsilon_i^{(1)}\right)\varphi_i^{(0)}.$$

Here, the perturbation to the Kohn-Sham potential $V_{KS}^{(1)}$ contains contributions from the first-order changes in the external potential, Hartree potential, and exchange-correlation potential.

These in turn depend on the first-order variation in the electron density:

$$n^{(1)}(\mathbf{r}) = 2\sum_{i} \operatorname{Re}\left[\varphi_{i}^{(0)*}(\mathbf{r})\varphi_{i}^{(1)}(\mathbf{r})\right]$$

Solving the linearized Kohn–Sham equations self-consistently provides access to the firstorder density response $n^{(1)}$, from which the variation of the total energy due to atomic displacements can be determined. The second-order derivative of the total energy defines the interatomic force constants, which describe the local curvature of the potential energy surface [8]:

$$C^{IJ}_{\alpha\beta} = \frac{\partial^2 E}{\partial u^I_{\alpha} \,\partial u^J_{\beta}},$$

where u_{α}^{I} denotes the displacement of atom I in Cartesian direction α .

In periodic crystals, atomic displacements are treated as collective perturbations with welldefined crystal momentum **q**. The corresponding dynamical matrix in reciprocal space is given by the mass-weighted Fourier transform of the real-space force constants:

$$D_{\alpha\beta}^{IJ}(\mathbf{q}) = \frac{1}{\sqrt{M_I M_J}} \sum_{\mathbf{R}} C_{\alpha\beta}^{IJ}(\mathbf{R}) \, e^{i\mathbf{q}\cdot\mathbf{R}},$$

where \mathbf{R} runs over lattice vectors connecting periodic images of atoms I and J [9].

Alternatively, within the DFPT formalism, the dynamical matrix can be computed directly in reciprocal space via the second derivative of the total energy with respect to q-modulated atomic displacements:

$$D_{\alpha\beta}^{IJ}(\mathbf{q}) = \frac{1}{\sqrt{M_I M_J}} \frac{\partial^2 E}{\partial u_{\alpha}^I(\mathbf{q}) \, \partial u_{\beta}^J(-\mathbf{q})},$$

where $u_{\alpha}^{I}(\mathbf{q})$ is the displacement of atom I in direction α with wavevector \mathbf{q} .

Diagonalizing the dynamical matrix yields the phonon frequencies $\omega_{\nu}(\mathbf{q})$ and eigenvectors $e_{I\alpha}^{\nu}(\mathbf{q})$ according to the eigenvalue equation:

$$\sum_{J\beta} D^{IJ}_{\alpha\beta}(\mathbf{q}) e^{\nu}_{J\beta}(\mathbf{q}) = \omega^2_{\nu}(\mathbf{q}) e^{\nu}_{I\alpha}(\mathbf{q}).$$

2.3 Bloch's Theorem and Electronic Structure

So far we managed to reduce the complexity by isolating the electronic system and paving the way for it to be expressed in terms of the ground state density. But for a macroscopic crystal the number of electrons and nuclei is in rough estimation of the magnitude of the Avogadro

number (~ 10^{23}) causing calculations to remain impractical. Since the Avogadro number out-ways the number of different nuclei the lattice and therefore the electronic structure crystallizes in a periodic pattern. It is this periodicity that allows for the drastic reduction of complexity and computation load by exploiting its translational symmetry using the Bloch's Theorem.

In terms of the previously derived Kohn-Sham potential this periodicity will manifest itself in the potentials invariance under shifts by the lattice vector \mathbf{R} :

$$V_{KS}(\mathbf{r}) = V_{KS}(\mathbf{r} + \mathbf{R}). \tag{2.40}$$

According to Bloch's theorem, the eigenfunctions solving these single-particle Schrödinger equations involving a potential with periodic properties such as 2.40 are given by Bloch wavefunctions of the form [10]:

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N_p}} u_{n,\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}},$$
(2.41)

where *n* denotes the band index, **k** the momentum within the first Brillouin Zone (BZ), N_p the number of unit cells, and $u_{n,\mathbf{k}}(\mathbf{r})$ a function with the same periodic symmetry as the crystal lattice. Due to this periodicity, it is sufficient to study the most compact primitive cell of the lattice and the corresponding first BZ, using Born–von-Kármán (BVK) boundary conditions. These allow the treatment of an extended periodic system by constructing a BVK supercell out of multiple unit cells (see Figure 3.7), with the reciprocal volume of the system given by $\Omega = N_p \Omega_p$. Since periodic functions can be represented as Fourier series, the eigenfunction for a given band *n* and wavevector **k** is written as:

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N_p\Omega_p}} \sum_{\mathbf{G}} c_{n,\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

where G are reciprocal lattice vectors and $c_{n,\mathbf{k}}(\mathbf{G})$ are plane-wave coefficients. Note that this eigenfunction is specific to a given band n and momentum \mathbf{k} . In computations, these states $\psi_{n,\mathbf{k}}(\mathbf{r})$ are evaluated at a finite number of \mathbf{k} -points, yielding a discrete set of eigenstates. Physical properties of the periodic lattice, are averaged over the sum of \mathbf{k} divided by the number of \mathbf{k} -points. In the limit of an infinitely dense \mathbf{k} -point grid, the eigenvalues $\varepsilon_{n,\mathbf{k}}$ form continuous energy bands. The Kohn-Sham equation in reciprocal space becomes:

$$\sum_{\mathbf{G}'} \left[\frac{|\mathbf{k} + \mathbf{G}|^2}{2} \delta_{\mathbf{G},\mathbf{G}'} + V_{KS}[n](\mathbf{G} - \mathbf{G}') \right] c_{n,\mathbf{k}}(\mathbf{G}') = \varepsilon_{n,\mathbf{k}} c_{n,\mathbf{k}}(\mathbf{G})$$

For practical computations, a kinetic energy cutoff is introduced to truncate the plane-wave expansion. Only reciprocal lattice vectors G satisfying the condition

$$\frac{|\mathbf{k} + \mathbf{G}|^2}{2} \le E_{\text{cut}}$$

are included. This limits the number of plane waves, reducing computational cost. Both the kinetic energy cutoff and the density of the k-point grid require careful consideration to ensure a well-converged and accurate description of the electronic structure.

2.4 Electronic Temperature - Fermi-Dirac smearing

In electronic structure calculations especially for systems with partially filled bands, achieving convergence with respect to k-point sampling can be challenging due to the sharp discontinuity of the occupation function at zero temperature. This issue is particularly pronounced in metallic systems, where the Fermi surface introduces numerical instabilities.

To address this, a finite electronic temperature is introduced via the Fermi–Dirac distribution, which smooths the occupation of electronic states:

$$f_{n\mathbf{k}} = \frac{1}{e^{(\varepsilon_{n\mathbf{k}}-\mu)/k_BT} + 1}$$

Here, $f_{n\mathbf{k}}$ denotes the occupation of the electronic state with band index n and wavevector \mathbf{k} , $\varepsilon_{n\mathbf{k}}$ is the Kohn–Sham eigenvalue, μ is the chemical potential, k_B is the Boltzmann constant, and T is the electronic temperature. This technique is commonly referred to as Fermi-Dirac smearing, and it allows for improved numerical stability and better convergence behavior [11, 12].

Beyond numerical benefits, thermal occupations are physically meaningful when studying finite-temperature effects such as phase transitions. This finite-temperature formulation allows for the simulation of systems under thermal excitation by smearing the electronic occupations. It provides a way to explore how structural and electronic properties evolve with temperature. In particular, it enables the study of temperature-driven phase transitions, changes in band structure, or the stabilization of thermodynamically favorable phases that would not appear at zero temperature. By varying the electronic temperature, one can track the evolution of the system's potential energy landscape, offering insights into thermal stability and the mechanisms driving phase changes.

2.5 Charge Density Wave

A CDW is a collective electronic phenomenon observed in certain low-dimensional materials. The CDW represents a spontaneous modulation of the electron density in a periodic crystal structure. This phenomenon arises due to the interplay of electron-phonon interactions and Fermi surface nesting, leading to a spontaneous breaking of translational symmetry [13, 14]. The Peierls instability offers a fundamental explanation for the formation of these waves in one-dimensional systems, while excitonic effects can influence or even drive the development of CDWs in certain materials [15].

Peierls Instability

The concept of the CDW is intricately linked to the Peierls instability, a mechanism that explains the formation of a CDW in one-dimensional systems. This instability is caused by the coupling between the electronic states and the lattice phonons, which are responsible for the periodic distortion of the lattice structure.

In a one-dimensional electron system with half-filled bands, the Fermi surface can be perfectly nested, making the system particularly susceptible to perturbations. When electrons couple to lattice vibrations (phonons), this interaction induces a periodic lattice distortion (Periodic lattice distortion (PLD)) with a wavevector of $2 k_F$, where k_F is the Fermi wavevector. This means that the periodicity of the distortion corresponds to twice the Fermi wavelength. The resulting modulation opens a gap at the Fermi level, reducing the electronic energy and stabilizing the distorted phase. This marks a phase transition from a hightemperature metallic phase to a low-temperature semiconducting or insulating phase [16]. Figure 2.1 illustrates this process, showing the periodic charge modulation, the associated lattice distortion, and the formation of a band gap at the Fermi level.

Phonons, representing the quantized lattice vibrations, mediate this instability by allowing the electronic system to lower its energy through coupling with specific vibrational modes. The resulting periodic modulation in both the electronic charge density and the atomic positions characterizes the CDW/PLD state. This electron-phonon interaction is central to the Peierls mechanism and is responsible for the energetic favorability and formation of a low temperature phase.



FIGURE 2.1: Peierls mechanism leading to PLD/CDW phase [17].

Excitonic Insulator

In certain low-dimensional materials, charge density wave (CDW) formation is not exclusively governed by electron–phonon interactions, as described by the Peierls instability. Instead, it may also originate from electron–electron correlations. A key mechanism in this context involves the formation of bound electron–hole pairs, known as excitons. When the exciton binding energy exceeds the electronic band gap or the overlap between conduction and valence bands, a phase transition into an excitonic insulator state can occur [18].

This scenario is particularly relevant for materials with small indirect band gaps or semimetallic band structures, such as $TiSe_2$. In these systems, excitonic condensation can lead to a spontaneous modulation of the charge density, resulting in a charge modulated ground state. Both experimental and theoretical studies suggest that the CDW in $TiSe_2$ involves a cooperative effect between lattice distortions and excitonic correlations [19, 20].

This interplay complicates the interpretation of the CDW origin, since both electron–phonon and electron–electron interactions contribute to the stabilization of the ordered phase. The relative importance of these interactions can be tuned by external parameters such as temperature, doping, or pressure, which may induce transitions between a metallic state, a Peierlstype CDW, and an excitonic insulator [21].

2.6 Transition Metal Dichalcogenides

TMDCs form a class of layered materials with the chemical composition MX_2 , where M represents a transition metal and X denotes a chalcogen [22]. TMDCs exhibit strong inplane covalent bonding within each layer and weak van der Waals interactions between layers. These anisotropic bonding characteristics reflect in the exfoliation into atomically thin sheets [23].

The vibrational properties such as intralayer and interlayer modes, are key indicators of structural integrity and stacking order. TMDCs exhibit diverse electronic properties, spanning metallic, semiconducting, and superconducting phases. Their structural polymorphism includes the 1T (trigonal) and 2H (hexagonal) phases, influencing their electronic and optical properties [24].

These materials also exhibit strong many-body interactions, including excitonic effects and electron-phonon coupling, which influence their optical and transport properties and can drive collective phenomena such as CDWs [15, 25].

The tunability of TMDC properties through external stimuli such as strain, electric fields, temperature and intercalation enables their use in next-generation electronic, sensing, and energy storage applications [26].

Chapter 3

CDW phase transition in TiSe₂

3.1 Crystal Structure of Titanium diselenide

Titanium diselenide (TiSe₂) belongs to the family of TMDCs and consists of one titanium atom (group 4) and two selenium atoms (group 16). Under normal conditions TiSe₂ crystallizes in a 1T-phase corresponding to a hexagonal layer of Ti atoms that is embedded between two hexagonal layers of Se atoms. In this configuration it adopts a trigonal structure belonging to the $P\bar{3}m1$ space group, where titanium atoms are octahedrally coordinated by selenium atoms (Figure 3.1). Adjacent (Se-Ti-Se) monolayers are bound by weak van der Waals interactions, allowing exfoliation into atomically thin sheets, down to a single monolayer, through mechanical or chemical methods.



FIGURE 3.1: Monolayer TiSe₂ from different angles. [27]

The experimental lattice parameters of TiSe₂ are a = b = 3.540 (3.538) Å in-plane and c = 6.008 Å out-of-plane for bulk (monolayer), with $\alpha = \beta = 90^{\circ}$ and $\gamma = 120^{\circ}$ [28, 29]. It is important to note that the out-of-plane lattice parameter c is not well-defined for monolayers, as their intrinsic nature involves a two-dimensional structure without periodicity in the vertical direction. It is therefore a reasonable approach to assume that the unit cell extents infinitely far in the out of plane direction. This results in a 2D hexagonal BZ characterized by distinct high-symmetry points (Γ , M and K) 3.2.



FIGURE 3.2: Two dimensional hexagonal BZ.

At approximately 200 K (230 K) TiSe₂ undergoes a CDW-phase transition, characterized by a PLD accompanied by a commensurate $2 \times 2 \times 2$ (2×2) superlattice modulation in bulk and monolayer respectively [30]. This transition has been attributed to a combination of electron-phonon interactions and excitonic correlations, leading to partial gap opening at the Fermi level [15]. This work specifically investigates the CDW-phase transition in the monolayer structure.

3.2 Computational Details

The computational framework employed in this work is the open-source materials modeling suite Quantum ESPRESSO (v.7.0). DFT calculations were performed using the selfconsistent plane-wave pseudopotential method (**PWscf**). The exchange–correlation functional was treated within the Generalized Gradient Approximation (GGA), using fully relativistic ultrasoft PBEsol pseudopotentials [31]. Spin–orbit coupling was included in all calculations to account for the relativistic effects arising from the heavier elements in TiSe₂. For phonon calculations, DFPT, based on the linear-response formalism, was employed through the **PHonon** package of Quantum ESPRESSO [7]. Based on preliminary convergence tests, the plane-wave kinetic energy cutoff was set to 80 Ry, and a $18 \times 18 \times 1$ Monkhorst–Pack grid was used for Brillouin zone sampling. Phonon calculations were performed on a $6 \times 6 \times 1$ grid of **q**-points.

3.3 Preliminary Analysis

Ensuring the accuracy of first-principles calculations requires a careful evaluation of numerical stability with respect to computational parameters. Before proceeding with a detailed investigation, an initial analysis is conducted to determine the optimal settings for studying the electronic and vibrational properties of $TiSe_2$ monolayer. This process focuses on achieving convergence in total energy, stress, and forces, ensuring a well-defined and stable ground-state configuration of the system.

3.3.1 Convergence Tests

In Section 2.3, the plane wave kinetic energy cutoff was introduced as the parameter that truncates the number of **G**-vectors used to expand the Kohn–Sham orbitals and charge density. This value was systematically converged to ensure an optimal balance between computational efficiency and total energy accuracy. As a result, a cutoff energy of 80 Ry was chosen for all subsequent calculations.

Another critical parameter is the **k**-point mesh used to sample the first BZ. Quantum ESPRESSO employs the Monkhorst–Pack scheme [32] to construct a uniform grid in reciprocal space. For a monolayer material, a two-dimensional **k**-point grid is sufficient due to the negligible interaction in the out-of-plane direction, which is effectively decoupled by introducing a vacuum layer. This results in an out-of-plane reciprocal lattice vector approaching zero. The total energy was converged with respect to the number of reducible **k**-points, leading to the choice of an $18 \times 18 \times 1$ mesh. Due to the hexagonal symmetry of the crystal, symmetry operations reduce the number of unique **k**-points sampled in practice.

A summary of the converged parameters used in all calculation is provided in Table 3.1. Detailed convergence plots are provided in Appendix A.1.

Ecut	80 Ry
Reducible k-point mesh	$18 \times 18 \times 1$
Pseudo potential	Fully relativistic, ultrasoft
XC-functional	PBEsol [33]

TABLE 3.1: Converged parameters used in further calculations.

As previously discussed, the out-of-plane lattice parameter c is not well-defined for monolayer materials. To model the two-dimensional nature of the system, a vacuum region is introduced between adjacent layers, effectively decoupling their interaction. The size of this vacuum was determined by converging the total energy with respect to the out-of-plane lattice parameter. Based on this analysis, a value of c = 15 Å was selected, ensuring negligible interlayer interaction. After fixing the out-of-plane lattice parameter, the remaining structural parameters were determined through a full relaxation of the system. This includes the in-plane lattice constant *a* as well as the atomic positions within the unit cell. The relaxation was carried out by minimizing both the atomic forces and the stress tensor using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [34]. The resulting lattice parameters and relaxed atomic positions are summarized in Table 3.2.

Lattic	Atomic Positions (crystal)				
DFT	Experiment [29]	Ti	0.0	0.0	0.50
a = 3.462	a = 3.538	Se	$0.\overline{6}$	$0.\overline{3}$	0.??
c = 15	c = (undefined)	Se	$0.\overline{3}$	$0.\overline{6}$	0.??

TABLE 3.2: *Ab-initio* crystal structure parameters of TiSe₂ monolayer. The atomic positions are given in units of the crystal lattice vectors.

3.3.2 Revealing the CDW Phase Instability

This section presents the band structure and phonon dispersion of the $TiSe_2$ monolayer in a single unit cell in the High symmetry (HS) phase. The band structure provides insights into the conduction properties, while the phonon dispersion indicates a dynamical instability, suggesting a tendency toward symmetry breaking. This broken symmetry arises from the PLD associated with the CDW.

Band structure

The band structure of a single unit cell of TiSe₂ monolayer, calculated along the highsymmetry path (Γ -M-K- Γ , see 3.2), is shown in 3.3b. At the M point, the Ti 3d band lies just below the Fermi energy, while at the Γ point, the Se 4p band rises slightly above it. Consistent with previous PBE-based studies, these features result in an indirect band gap of approximately -0.45 eV giving TiSe₂ a semimetallic nature. A comparison between calculations using the PBE and HSE06 functionals reveals significant differences at both the Mand Γ points, highlighting the impact of exchange-correlation treatment on the electronic structure. The indirect band gap of about 92 meV calculated using the HSE06 functional is in better aggreement with ARPES measurements 3.3d showing a bandgap of 98 meV [30, 35].



FIGURE 3.3: a:Se 4p and Ti 3d bands bandgap between Γ and M [36].
b: Calculated band structure along (Γ,M,K,Γ) using PBEsol.
c: Comparison of PBE and HSE06 calculations [35].
d: ARPES measurement at Γ and M (room temperature) [30]

Phonon Dispersion

The breaking of symmetry is indicated by instabilities that arise due to perturbations. The phonon dispersion provides insight into the nature of these instabilities. At a given wave vector \mathbf{q} , the phonon modes are obtained by diagonalizing the dynamical matrix $D(\mathbf{q})$, which yields the eigenfrequencies $\omega_{\mathbf{q}\nu}$ and the corresponding polarization vectors (eigenvectors) $\mathbf{e}_{\mathbf{q}\nu}^{\kappa}$, where ν is the mode index and κ labels the atom in the unit cell. For modes with $\omega_{\mathbf{q}\nu}^2 < 0$, the corresponding imaginary frequencies reflect structural instabilities. Calculated along the same high-symmetry path as the band structure, the phonon dispersion is shown in 3.4. The electronic temperature, introduced via Fermi-Dirac smearing, was set to 1 meV. A prominent Kohn anomaly at the *M*-point, with a frequency of $\omega = -94$, cm⁻¹ (indicating an

imaginary mode) with A_{1g} symmetry, suggests a significant instability, pointing to the onset of a phase transition (see section2.2).

In addition to the expected instability associated with the CDW instability at M-point, an additional soft mode is observed near Γ . Similar spurious instabilities have been reported in the phonon dispersions of low-dimensional materials and are often attributed to broken rotational or translational invariance in the interatomic force constants. These issues may arise due to incomplete basis sets, residual stresses, or insufficient convergence in first-principles calculations. As such, the presence of this mode is likely a numerical artifact and does not impact the conclusions drawn regarding the phase transition [37].



FIGURE 3.4: Phonon dispersion at 1 meV electron temperature

3.4 CDW-phase transition in DFPT

Section 3.3.2 presented the phonon dispersion of the HS structure at low electronic temperature (1 meV), revealing a pronounced instability at the M-point in the form of a Kohn anomaly. This behavior suggests the presence of a competing low-temperature phase. In this section, the temperature dependence of the instability is analyzed to explore the associated phase transition. As the electronic temperature increases, the soft mode at the M-point gradually hardens, eventually acquiring a positive real frequency, thereby stabilizing the HS structure. Figure 3.5 shows the phonon dispersion for different electronic temperatures.



FIGURE 3.5: Temperature-dependent phonon dispersion curves, illustrating the evolution of the soft mode (colored) at the *M*-point.

Since the instability is localized at the M-point, it is sufficient to track the phonon frequency at this point via single q-point calculations. Figure 3.6 shows the evolution of the M-point frequency as a function of electronic temperature. The zero-crossing of the frequency marks the critical temperature at which the phase transition takes place, occurring at approximately **63 meV**.



FIGURE 3.6: Temperature-induced softening of the A_{1u} mode at the *M*-point..

3.5 Condensation of the low temperature phase

The identification of a soft phonon mode with imaginary frequency at the M-point in the phonon dispersion indicates a structural instability. To investigate the corresponding PLD, the atomic displacement pattern associated with this unstable mode must be extracted from the phonon eigenvectors.

3.5.1 Periodic lattice distortion

To map the phonon eigenvector onto real-space atomic displacements, a BVK supercell (see Figure 3.7) commensurate with the modulation wave vector \mathbf{q} is constructed. In this case, $\mathbf{q} = M$ lies at the Brillouin zone boundary, requiring a supercell with lattice vectors that are integer multiples of the primitive cell to accommodate the modulation periodicity and thus a 2×2 BVK supercell is constructed. The distorted structure representing the PLD is then built by displacing each atom in the supercell according to its contribution from the eigenvector of the soft mode. This static displacement pattern reflects the structural manifestation of the CDW phase.



FIGURE 3.7: Schematic illustration of the BVK supercell and of the notation adopted to denote the nuclear displacements from equilibrium[38]

The coordinate of an displaced atom in this Supercell is then given by the position operator $\tau_{\kappa p} = \mathbf{R}_p + \tau_{\kappa} + \Delta \hat{\tau}_{\kappa p}$, where \mathbf{R}_p is a crystal lattice vector, τ_{κ} is the equilibrium coordinate of the κ th nucleus in the unit cell. The displacement $\Delta \hat{\tau}_{\kappa p}$ of the κ th nucleus in the *p*th unit cell is given by:

$$\Delta \hat{\boldsymbol{\tau}}_{\kappa p} = (N_p M_\kappa)^{-1/2} \sum_{\mathbf{q}\nu} e^{i\mathbf{q}\cdot\mathbf{R}_p} \mathbf{e}^{\kappa}_{\mathbf{q}\nu} \hat{U}_{\mathbf{q}\nu}$$
(3.1)

Here, N_p is the number of unit cells in the BVK supercell and M_{κ} is the mass of the κ th nucleus. The operator $\hat{U}_{q\nu}$ has units of length times $\sqrt{\text{mass}}$, and characterizes the coherent displacement amplitude of the lattice along the normal mode (\mathbf{q}, ν) .

Due to the threefold rotational symmetry of the hexagonal lattice, there are three symmetryequivalent M-points in the Brillouin zone, corresponding to distinct wavevectors \mathbf{q}_1 , \mathbf{q}_2 , and \mathbf{q}_3 (see Fig. 3.3a). These wavevectors are related by crystal symmetry operations, and as a result, the phonon dispersion must yield identical frequencies ω at each of them. By diagonalizing the dynamical matrix at \mathbf{q}_1 , \mathbf{q}_2 , and \mathbf{q}_3 , we obtain the corresponding (degenerate) phonon frequencies and their eigenvectors: $\mathbf{e}_{\mathbf{q}_1\nu}^{\kappa}$, $\mathbf{e}_{\mathbf{q}_2\nu}^{\kappa}$, and $\mathbf{e}_{\mathbf{q}_3\nu}^{\kappa}$ (compare 2.2). Figure 3.8 shows the resulting PLD patterns computed using Equation 3.1, illustrating the effect of including one, two, or all three symmetry-equivalent modes.



FIGURE 3.8: Illustration of PLDs for including one, two and all three modes.

3.5.2 Potential energy Surface

For each point in the configuration space defined by the triplet $(U_{\mathbf{q}_1}, U_{\mathbf{q}_2}, U_{\mathbf{q}_3})$, the corresponding total Energy value is obtained from a DFT-calculation for the associated atomic configuration. Together the configuration space and total Energy values form the PES. For a single mode, the PES takes the form of a one-dimensional double-well potential, as shown in Figure 3.9c. When two modes are involved, it extends to a two-dimensional "Mexican hat" potential, exhibiting four equivalent global minima (see Figure 3.9b). In this case, the one-mode PESs correspond to cuts through the two-dimensional surface along $U_{\mathbf{q}_2} = 0$ or $U_{\mathbf{q}_1} = 0$, respectively. Likewise, the two-mode PES can be viewed as a slice of the full three-mode subspace surface at $U_{\mathbf{q}_3} = 0$ as visualized by the red plain in 3.9a. The global minimum corresponds to the energetically most favorable configuration and is interpreted as the equilibrium structure in the classical limit.



FIGURE 3.9: Visualization of the full 3D PES and a 2D slice at $U_3 = 0$ and the three 1D slices corresponding to the configuration pathways given by the PLDs visualized in Figure 3.8. The color bar reflects the rescaling to a maximum of 1 for better visualization.

3.6 CDW-phase transition in DFT

In Section 3.5.2, the concept of the PES was introduced. The PLD associated with the global minima of the PES corresponds to the equilibrium atomic configuration in the low-temperature phase. By evaluating the PES at various temperatures, it becomes possible to identify the transition temperature at which the global minimum shifts to that of the HS, or high-temperature, phase.

Since this procedure only requires knowledge of the global minima and the HS structure, it is not necessary to compute the entire PES at this stage. The method employed involves displacing the atoms slightly from their equilibrium HS positions along specific phonon mode directions, as described in Section 3.5.1, thereby inducing the lower-symmetry distortions illustrated in Figure 3.8. A subsequent structural relaxation is performed, during which the atomic positions are optimized by following the force and stress vectors until convergence is reached. The relaxed configuration obtained in this manner corresponds to a local or global minimum of the PES. By comparing its total energy with that of the HS structure at the same electronic temperatures, the transition temperature can be estimated.

It is worth noting that initiating the relaxation from a displacement along a single mode or a pair of modes leads to a minimum corresponding to a double-well or a Mexican-hat type potential, respectively. Since the BFGS algorithm follows the gradient of the energy landscape, it naturally drives the system toward the nearest energy minimum, thereby revealing the symmetry-breaking pathway associated with the underlying phonon instability.

Figure 3.10a shows the total energy of the HS phase and of the equilibrium structures corresponding to PLDs involving one, two, and three phonon modes, plotted as a function of the electronic temperature. The energy difference between a given PLD phase and the HS structure plotted in 3.10b directly reflects the depth of the associated PES minimum (compare Figure 3.9c). The temperature at which the PES depth vanishes indicates the onset of symmetry breaking associated with the phase transition and is found to be approximately **65 meV**.



FIGURE 3.10: Total energy of Equilibrium structure for displacements along no HS, one (1M), two (2M) and all three modes (3M) **a** and the corresponding PES-depth **b**.

3.7 High and low temperature phase

Up to this point, the electronic transition temperature has been determined using both the DFPT approach (Section 3.4) and the DFT-based PES analysis (Section 3.6), yielding values of 63 meV and 65 meV, respectively. Additionally, equilibrium atomic configurations have been obtained for a range of electronic temperatures, spanning from below the phase transition ($T < T_{CDW}$) to above it ($T > T_{CDW}$). The following analysis focuses on the vibrational and electronic characteristics of the corresponding high- and low-temperature phases. To make the properties comparable calculations for both the HS and CDW phase were performed in a 2×2 BVK supercell. Due to the supercell formation the *M*-point of the primitive unit cell folds onto the zone center Γ of the supercell as visualized in Figure 3.11. The phonon dispersion relations in this chapter were calculated and generously provided by Christoph Emeis.



FIGURE 3.11: Zone folding due to 2×2 supercell formation [39].

3.7.1 Vibrational Properties

For $T > T_{CDW}$, the equilibrium structure corresponds to the HS atomic configuration. As discussed in Section 3.4, the A_{1u} mode at the *M*-point of the primitive unit cell is real under these conditions, indicating dynamical stability. Calculations in the 2×2 BVK supercell confirm this behavior. Unfortunately the corresponding phonon dispersion (see Appendix A.2) exhibits stronger numerical instabilities at Γ . To avoid artificially altering the spectrum, the acoustic sum rule was not enforced. Despite these instabilities, the A_{1u} mode remains real in the supercell, consistent with the behavior observed in the primitive cell.

In contrast, for $T < T_{CDW}$, the supercell calculation reveals that the A_{1u} mode at the Γ point becomes imaginary, signaling the onset of the dynamical instability. This is again consistent with the behavior seen in Section 3.3.2. The corresponding phonon dispersion is also provided in Appendix A.2.

For the phonon dispersion of the PLD/CDW phase at $T < T_{CDW}$, shown in Figure 3.12, the A_{1u} mode remains real, indicating that this distorted structure represents a dynamically stable phase below the transition temperature. In this case, the numerical instabilities were less pronounced, allowing for the application of the acoustic sum rule without introducing nonphysical distortions into the phonon spectrum.



FIGURE 3.12: Phonon dispersion of the PLD/CDW phase at $T < T_{CDW}$. This calculation was performed and kindly provided by Christoph Emeis.

3.7.2 Electronic Properties

The electronic properties of monolayer TiSe_2 are strongly affected by the CDW phase transition. In the high-temperature phase ($T > T_{\text{CDW}}$), the material is expected to exhibit semimetallic behavior due to a slight overlap between the Se 4p valence band at Γ and the Ti 3d conduction band at M (compare 3.3). Upon entering the CDW phase, a bandgap opens at the Fermi level, marking a transition towards a semiconducting or even insulating state.

Figure 3.13 displays the band structure of the (HS) phase in the 2×2 supercell. Due to Brillouin zone folding, the *M*-point of the primitive cell is mapped onto the Γ -point of the supercell (see 3.11). In this representation, the Se 4*p* and Ti 3*d* orbitals appear at Γ , showing a band overlap of approximately 0.6 eV.



FIGURE 3.13: Band structure of the HS phase in the 2×2 supercell.

The band structure of the distorted CDW phase is shown in Figure 3.14. A small negative indirect bandgap on the order of a few meV is observed. While the gap is not yet fully open, a clear trend toward gap formation is evident, indicating the onset of semiconducting behavior. The incomplete gap opening may be attributed to limitations of the exchange-correlation functional. As monolayer $TiSe_2$ is considered a candidate for an excitonic insulator, a larger bandgap may be expected when many electron interactions are properly included.



FIGURE 3.14: Band structure of the PLD/CDW phase in the 2×2 supercell.

3.8 CDW-phase transition with Quantum nuclear effects

One of the main goals of this thesis is to investigate the influence of QNE on the phase transition. The standard DFT and DFPT formalisms introduced in Chapter 2 do not account for the quantum nature of the nuclei that make up the lattice. One way to incorporate their quantum nature introduced by Esswein and Spaldin [1] is based on solving the Schrödinger equation exlicitly for the nuclear configuration space using the PES calculated with DFT. This is achieved by mapping the multi-nuclei and three dimensional tunneling problem onto a single-particle, one-dimensional one.

At this point, the approach taken in this thesis deviates from that of Esswein and Spaldin. In their work, the PES was approximated using a fourth-order polynomial to construct a onedimensional double-well potential along a generalized symmetry-breaking coordinate. This reduced potential represents the transition pathway to the lowest-energy (polarized) state and is particularly useful when the distorted phase involves multiple unstable modes, rendering the full configuration space unmanageably high-dimensional. However, this method inherently limits the description to a single reaction coordinate, offering no information about the surrounding potential landscape. Such an approach neglects alternative configurations that the abstract multi-particle quantum object could, in principle, explore. In contrast, the PLDs underlying the CDW in this system involve only three soft phonon modes at the M points, yielding a three-dimensional subspace that is still tractable and thus allows for an explicit treatment of the potential landscape. It is also worth noting that Esswein and Spaldins approach to construct the double-well potential from the PES depth and halfwidth strongly relies on the accuracy of the imaginary (negative) phonon modes. Given the steep slope of the frequency versus electronic temperature for the A_{1u} mode at M near the transition temperature (see Figure 3.5), the applicability of Esswein and Spaldin's method for accurately calculating the PES in this regime may be limited.

This work employs a direct numerical evaluation of the full three-dimensional, manually calculated PES, introduced in Section 3.5.2, enabling a comprehensive study of the wave-function behavior, including quantum delocalization effects beyond the single-coordinate description. The shape and localization of the resulting wavefunction provide insight into the quantum mechanical behavior of the system across different regimes.

3.8.1 Mass-weighted single-particle Schrödinger Equation

In order to describe the quantum dynamics of lattice distortions within the PES, it is essential to formulate the Schrödinger equation using mass-weighted coordinates. This is necessary because phonon eigenmodes do not have a well-defined physical mass. By transforming to mass-weighted coordinates, the kinetic energy operator assumes a standard form, and the phonon displacements U_{q_i} acquire consistent physical units. This allows for a meaningful and tractable quantum mechanical treatment of the collective lattice degrees of freedom.

The time-independent Schrödinger equation for a system with coordinates $\mathbf{x} = (x_1, x_2, \dots, x_i)$ and corresponding individual masses m_j is given by:

$$\left[-\sum_{j=1}^{i} \frac{1}{2m_j} \frac{\partial^2}{\partial x_j^2} + \tilde{V}(\mathbf{x})\right] \tilde{\psi}(\mathbf{x}) = E\tilde{\psi}(\mathbf{x})$$
(3.2)

Since neither the mass nor the displacement of a phonon is well defined the approach by Esswein and Spaldin combines the masses and displacements into mass-weighted coordinates $U_{\mathbf{q}_j} = \sqrt{m_j} x_j$, which are rigorously defined and avoid an arbitrary choice for the phonon mass and displacement. By applying the chain rule, the second derivative transforms as follows:

$$\frac{\partial^2}{\partial x_j^2} = m_j \frac{\partial^2}{\partial U_{\mathbf{q}_j}^2}$$

Substituting this into the original equation cancels out the mass terms, resulting in a simplified form of the Schrödinger equation:

$$\left[-\frac{1}{2}\sum_{j=1}^{i}\frac{\partial^{2}}{\partial U_{\mathbf{q}_{j}}^{2}}+V(\mathbf{U}_{\mathbf{q}})\right]\psi(\mathbf{U}_{\mathbf{q}})=E\psi(\mathbf{U}_{\mathbf{q}})$$
(3.3)

Here, $\mathbf{U}_{\mathbf{q}} = (U_{\mathbf{q}_1}, U_{\mathbf{q}_2}, \dots, U_{\mathbf{q}_i})$ defines a point in the mass-weighted configuration space, and $V(\mathbf{U}_{\mathbf{q}})$ represents the corresponding potential energy. This potential forms the PES, which was computed as outlined in Section 3.5.2. The mass-weighted Schrödinger equation was then solved numerically using a second-order central finite-difference method to approximate the second derivative, in combination with the sparse eigenvalue solver provided by the scipy Python package.

3.8.2 Light-driven CDW transition

The temperature introduced by Fermi–Dirac smearing, as described in Setion 2.4, pertains exclusively to the electronic subsystem. This approach is particularly relevant for modeling ultrafast pump–probe experiments, in which short laser pulses excite the electronic structure and rapidly raise the electronic temperature, while the lattice remains effectively at 0 K due to the ultrafast timescales involved [40]. In this idealized scenario, the ionic system remains in the lowest-energy eigenstate, the ground state.

To investigate the quantum mechanical evolution of the CDW with respect to the electronic temperature, the wavefunction corresponding to the ground state of the ionic subsystem is analyzed. The resulting probability density $|\psi_0|^2$ shown in Figure 3.15a reveals partial localization at the potential minima corresponding to the 3M configuration. However, the amplitude remains non-negligible around the HS configuration, reflecting quantum delocalization effects.

This indicates that even at electronic temperatures as low as 1 meV, the system is not fully localized in a single distorted configuration, but instead exhibits a fluctuating character across the PES. As the electronic temperature increases, the delocalization becomes progressively more pronounced. Figure 3.15b shows the probability density at an electronic temperature where the localization is almost vanished while 3.15c shows the probability density well above the transition point. The probability density at high temperature undoubtedly reflects the localization in the HS phase.













FIGURE 3.15: Evolution of the Ground state probability density normalized to the range [0, 1] to enhance visual clarity.

Due to the difficulty of visualizing full three-dimensional data, selected high-symmetry slices in higher temperature resolution are considered, corresponding to the PLD pathways introduced in Section 3.5.1 and illustrated in Figure 3.9a. These symmetry-restricted cuts of the full three-dimensional wavefunction allow for interpretation of how quantum fluctuations modulate the probability distribution along physically relevant PLD directions and how the underlying PES shape influences the localization behavior.

To determine the electronic transition temperature, defined here as the point where localization fully vanishes, the evolution of the probability density along these pathways is tracked and visualized in Figure 3.16. The color labels the temperature while the opacity indicates the different paths (lowest to highest). It is found that the peaks of the probability density become comparable to that at the HS point at approximately **35 meV**, suggesting a lower transition temperature than the $\approx 65 \text{ meV}$ predicted by the classical approaches using DFT/DFPT in Section 3.6 and 3.4. In this temperature regime the CDW phase, stable in the classical lattice picture, is melted by quantum fluctuations, manifesting the profound influence of QNEs on the phase transition.



FIGURE 3.16: Slices of the Wavefunction along the symmetry paths (Opacity) for different electronic temperatures (colour).

An additional question explored is whether the local maxima associated with symmetryequivalent 3M configurations become degenerate before their amplitudes equal that of the HS configuration, a condition that could be interpreted as a "*Quantum CDW*" phase. However, the analysis shows that these peaks merge at the same temperature where the HS configuration becomes dominant. Figure 3.17 shows the amplitude of the peaks (color) and the HS point (black). This implies that the partial localization due to the barrier between symmetry-equivalent distorted states vanishes concurrently with the collapse of the entire CDW phase.



FIGURE 3.17: Amplitude of the wavefunction peaks on the symmetry paths (color) and the HS point (black) versus electronic temperature.

3.8.3 Finite temperature considerations

In contrast to the nonequilibrium, light-driven scenario, the temperature-driven CDW phase transition involves raising both the electronic and lattice temperatures in equilibrium. In such a regime, the lattice temperature governs the thermal occupation of eigenstates through the Boltzmann distribution. As a result, the probability density reflects a mixed thermal ensemble rather than a pure quantum ground state [41].

To explore whether stronger localization can be recovered by considering contributions from low-lying excitations, a coherent superposition of the first four eigenstates is constructed. These include the ground state and the first three degenerate excited states. The resulting probability density from this linear combination shows markedly stronger localization than any individual eigenstate, reconstructing a sharply defined CDW state. This suggests that coherent quantum interference between eigenstates can reinforce localization in regimes where the ground state alone appears delocalized. Figure 3.18 shows the localization of the wavepocket in one of the global minima corresponding to the 3M configuration. The other coherent linear combinations of the first four eigenstates exhibits the same behavior.



FIGURE 3.18: Coherent superposition of the first four eigenstates exhibiting strong localization in one of the global minima. The amplitude is normalized to lie in range [0, 1] to enhance visual clarity.

However, it is important to note that such coherent sums do not reflect a thermal ensemble. In true thermal equilibrium, the state of the system would be governed by the density matrix with Boltzmann weights, and not by a coherent superposition. Nonetheless, the qualitative behavior observed in the coherent sum suggests that significant localization can persist in the low-energy sector even when the ground state appears delocalized. As determining the transition temperature in the context of a finite lattice temperature necessitates incorporating Boltzmann statistics at finite lattice temperature, this work does not attempt to quantify or characterize the transition any further.

Chapter 4

Conclusion and outlook

In this study, a first-principles approach was employed to characterize the CDW phase transition in a TiSe₂ monolayer. Through the use of DFT and DFPT, the CDW phase was successfully identified, with the symmetry breaking instability arising from the M points in the phonon dispersion. The transition temperature was determined by analyzing the mode softening at the M point, yielding a value of approximately **63 meV**, which marks the onset of the CDW transition.

Further investigation into the periodic lattice distortions, reconstructed from the phonon eigenvectors and modeled in a 2×2 BVK supercell, provided deeper insights into the nature of the transition and allowed the calculation of the PES. The depth of the PES was computed, and the transition temperature was determined to be **65 meV**, based on the vanishing potential depth.

The atomic CDW configurations associated with the minima of the PES at low temperatures were found to be the stable equilibrium structure, as evidenced by phonon dispersion calculations. The electronic properties also reflected the onset of the CDW phase, as indicated by the formation of a band gap, though the gap did not fully open at the Fermi energy. This suggests that more sophisticated exchange-correlation functionals might yield more accurate results.

The influence of QNE on the CDW wave was explored by solving the Schrödinger equation for a single particle-like quantum object within the previously calculated PES. The results revealed that the wavefunction partially localized in the global minima. The delocalization, however, persisted over the saddle points even at low temperatures, as low as 1 meV, suggesting a fluctuating behaviour across the PES. This seems to apply in the theoretical picture of a light-driven CDW phase transition, where the lattice temperature is assumed to be $T_{lat} =$ 0 K, and the system is confined to its ground state.

The transition temperature, at which the localization of the wavefunction vanishes, was found to be approximately **35 meV**. In the temperature range of **35–65 meV**, quantum fluctuations

appear to suppress the formation of a stable CDW, preventing the localization of the wavefunction in the minima of the PES. Notably, the degeneracy of symmetry-equivalent configurations does not result in a "*Quantum CDW*"-like state as the evolution of the wavefunction surface seems to favor the melting of localization in neither the direction of symmetry equivalent points nor the HS point.

While the present study did not explicitly consider finite lattice temperatures, the coherent superposition of the first four eigenstates, broadly simulating the effects of thermal occupation, was found to lead to a more pronounced localization of the wavefunction. Future studies that incorporate finite lattice temperatures using the Boltzmann distribution may provide further insights into the phase transition, particularly in relation to the effects of thermal fluctuations on the CDW.

Finally, incorporating the influence of QNE on the phase transition into DFPTcalculations, and utilizing more advanced exchange-correlation functionals, could offer more accurate predictions of the transition temperature. This approach may bring theoretical results closer to experimental measurements, helping to refine our understanding of the CDW phase in TiSe₂ and similar two-dimensional materials. This work thus provides a solid foundation for future investigations into the interplay between quantum effects, lattice dynamics, and electronic properties in low-dimensional systems.

Appendix



FIGURE A.1: Convergence studies.



a $T > T_{CDW}$



FIGURE A.2: Phonon dispersion of the HS phase in 2×2 supercell. Calculations performed and kindly provided by Christoph Emeis.

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