



Optical properties of semiconductors at finite temperatures from first principles

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In this thesis we develop a new first-principles method for the calculation of optical absorption spectra and band structures in semiconductors and insulators at finite temperatures. The theoretical framework of our methodology originates back to 1950s in two pivotal research papers by F. Williams and M. Lax. Here, we expand the scope of the pioneering works by Williams and Lax, and we present a new theory of phonon-assisted optical absorption and temperature-dependent band structures. We demonstrate that our technique is highly efficient and simple to the point that a single calculation is sufficient to capture temperature-dependent absorption coefficients including the effect of quantum zero-point motion. We report calculations of optical absorption spectra and of direct and indirect band gaps of Si, C, GaAs and MAPbI₃. We obtain good agreement with experiment and with previous calculations. The approach proposed in this thesis is highly versatile, and can straightforwardly be combined with improved descriptions of the dielectric function by including electron-hole effects via the Bethe-Salpeter and GW equations. In this thesis we also investigate the underlying mechanisms leading to the “inverse Varshni effect” in materials that belong to the family of metal halide perovskites. We show, using the example of MAPbI₃, that the vibrational modes with metal-halide-metal bending or rocking character are the major cause of the band gap opening with increasing temperature. To this aim we present an approach for elucidating the physics underpinning the changes of the band gap with vibrational motion. Our methodologies developed in this thesis are simple to implement in any electronic structure package as a post-processing step, having the potential to find broad applications in the *ab-initio* community. We anticipate that our work will open the way to predictive calculations, as well as will contribute to the better understanding of the optoelectronic properties of solids at finite temperatures.

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Chapter 1

Introduction

Condensed matter physics is ubiquitous in the technological applications. In fact, understanding of the electronic and optical properties of matter has led to the revolution of nanotechnology, optoelectronic devices, computer science, as well as to several developments in biophysics and materials science.

The understanding of new phenomena and concepts at the theoretical level stimulate important experimental discoveries and vice versa. For example, the joint effort between theorists and experimentalists in the area of solid state physics has allowed the accurate interpretation of optical spectra and electronic structures of semiconductors [1]. The implementation of the optical absorption theory [1, 2] in first principles calculations has been made possible through several attempts to gradually improve the agreement with experimental observations [3–7]. Thanks to this effort, nowadays, existing software packages are capable of performing successful numerical predictions on new compounds. However, it is still a great challenge to develop new methods for the calculation of the optical properties at *finite temperatures*.

Modern *ab-initio* calculations of the optical and the electronic properties of solids based on density-functional theory [8] and many-body perturbation theory [9] rely on one important approximation: the atomic nuclei are described as classical particles, completely immobile in their crystallographic positions. The use of this approximation to study electronic band structures and optical excitations has been central and

fundamental for the successful description of materials properties. Among many, these properties include the band gap, effective masses and quasiparticle corrections to the electron energies, as well as the dielectric function, dielectric permittivity and electron-hole corrections to optical absorption [1, 7, 10]. The three most important limitations of the clamped nuclei calculations are: the effect of thermal fluctuations on the optical properties of solids is ignored; the effect of quantum zero-point motion on the electron energies [11] is not included; phonon-assisted optical transitions [12] are absent. Owing to these three disadvantages, first principles calculations on the optical spectra are completely missing the temperature dependence of the absorption onset; a fact that is particularly evidenced in the case of indirect gap semiconductors. However, as the supercomputing power grows relentlessly and computational techniques become more widely adopted, the *ab-initio* community concentrates on the next steps towards implementing theoretical concepts for the calculation of optoelectronic properties including nuclear dynamics.

The underlying mechanism associated with the temperature dependence of the optoelectronic properties of solids is the *electron-phonon* coupling [13]. This phenomenon describes the interaction of the electrons with quantised lattice vibrations. Recent *ab-initio* implementations made it possible to study these interactions. In particular, the electron-phonon renormalisation of band structures was calculated from first principles in Refs. [14–19] using the theory of Allen and Heine [11]. The phonon-assisted optical transitions were investigated from first principles in Ref. [20] using the theory developed by Hall, Bardeen, and Blatt [12]. A review of the standard formalism and the of most recent literature of electron-phonon interactions can be found in Ref. [21].

In this thesis we aim to establish a new first-principles computational method for performing predictive calculations of the optical absorption spectra of semiconductors and insulators at finite temperature, including both zero-point fluctuations and phonon-assisted optical transitions. The theoretical foundations upon which our method is

based originate back to 1951 and 1952, when F. Williams [22] used an elegant approximation to calculate photoluminescence spectra of defects in potassium chloride, and M. Lax [23] developed the relevant theoretical framework. The central idea of the present work is to demonstrate the link between the Williams and Lax theory to the main effects associated with electron-phonon coupling in optical absorption: quantum zero-point motion and phonon-assisted transitions as described in the Allen-Heine and Hall-Bardeen-Blatt theories, respectively. This will further bridge the gap between predictive calculations and experimental measurements of the absorption coefficient at finite temperatures. Furthermore, *ab-initio* techniques require the development of efficient and simple computational strategies for their successful implementation. This is one of the most important challenges that we face in this thesis in order to make our methodology a robust tool for the calculation of optical spectra at finite temperatures.

In this thesis we also aim to elucidate the main mechanisms underlying the renormalisation of the band structure due to the vibrational motion of the nuclei. The idea behind this objective came up after a simple observation: "Although the band gap decreases with increasing temperature for the majority of semiconducting materials, in a few cases opens". Lead halide perovskites, among the most promising candidates for solar cell applications [24], belong to this class of semiconductors and constitute the main reason to investigate this observation. To this aim, in the present work, we analyse from first-principles the fundamental components of the two terms governing the band gap renormalisation with temperature. Those terms are the *Fan* (or self-energy) and *Debye-Waller* electron-phonon terms, developed and examined independently of each other in 1951 and 1955, respectively [25, 26].

Having clarified the general goals, let us turn to the organisation of this thesis. In Chapter 2 we present the theoretical framework behind *ab-initio techniques*, as well as the theories of phonon-assisted optical absorption and energy level renormalisation of the band structure at finite temperatures. In particular, in Sec 2.1 we introduce *density functional theory* and we focus on the most important approximations and methods

that are widely adopted in our first principles calculations. In Sec 2.2, we discuss the classical and quantum picture of the *harmonic approximation*, which is predominantly employed for incorporating electron-phonon interactions in our calculations. We close Chapter 2 with Sec. 2.3 by introducing the fundamental concepts of optical absorption in semiconductors, and then the theories of Allen-Heine, Hall-Bardeen-Blatt and Williams-Lax. For Chapters 3-5 we choose to present our results as follows: Firstly, we introduce the reader to our research by explaining its context and main motivations. Then we focus on our main results. These are followed by the computational setup used for our calculations and finally by a discussion on our major conclusions. The organisation of each chapter is presented in detail at the end of each introduction. Here we briefly outline the main topics: In Chapter 3 we demonstrate that the Williams-Lax theory can be employed successfully for the first-principles calculation of phonon-assisted optical spectra by using a stochastic approach. We demonstrate our method in Sec. 3.2 for the case of silicon. In Chapter 4 we develop an efficient and exact computational strategy for performing *one-shot* calculations of the optical spectra and band gaps at finite temperatures. To support the effectiveness of our methodology we report applications to silicon, diamond and gallium arsenide in Secs. 4.6 and 4.7. In Sec. 4.4 we also provide for the first time a rigorous mathematical proof to introduce the Williams-Lax theory as a *new theory* of optical absorption that describes on the same footing the Allen-Heine and Hall-Bardeen-Blatt theories. In Chapter 5 we investigate the origin of the band gap opening with increasing temperature in lead halide perovskites. In Sec. 5.2 we report calculations for the case of methylammonium lead iodide using our one-shot technique within the Williams-Lax theory. In Sec. 5.2.4 we perform an analysis of the Fan and Debye-Waller contributions to the band gap renormalisation. Finally, in Chapter 6 we summarise our key conclusions and in Chapter 7 we indicate avenues for future work. Lengthy formal derivations, additional technical details and supporting information are left to Appendices A-E.

Chapter 2

Literature Review

2.1 Density functional theory

2.1.1 Introduction

Density functional theory [8] (DFT) methods constitute an important component of materials research for describing the ground state properties of condensed matter systems. DFT has been proven to be very successful, not only in calculating electronic and structural properties of bulk and two dimensional materials, but also of complex extended systems, such as carbon nanotubes and proteins. The growing significance of DFT reflects the development of more accurate functionals and efficient algorithms, combined with the increasing performance of supercomputers.

In *ab-initio* methods, the properties of materials, determined by the electron and nuclei interactions, are calculated by solving the Schrödinger Equation (SE). However, for many-body systems the SE cannot be solved analytically and this made the use of numerical approaches indispensable. In 1964 and 1965, Hohenberg, Kohn and Sham [27, 28] developed the fundamental principles of DFT, a theory based on a function of three spatial coordinates, the electron density. The derived Kohn-Sham (KS) equations allow for an adequate description of an interacting particle system, in terms of a computationally manageable system of non-interacting particles, which

have the same electron density. Several sophisticated codes, such as *ABINIT* [29], *CASTEP* [30], *exciting* [31], *Quantum ESPRESSO* [32], and *VASP* [33] have been developed to solve KS equations. Finally, the combination of these codes with the progress of supercomputers allows many solid state physics and chemistry problems to be addressed by DFT.

2.1.2 Approximations in DFT

A difficult problem in *many-body* theory is the solution of the time-independent Schrödinger equation [34] of a system composed by a number of interacting nuclei and electrons:

$$\hat{H}\Phi(\mathbf{R}, \mathbf{r}) = E^T\Phi(\mathbf{R}, \mathbf{r}), \quad (2.1)$$

where $\Phi(\mathbf{R}, \mathbf{r})$ and E^T are the ground state full wavefunction and total energy of the system. The Hamiltonian describing the interactions in the system has the following form:

$$\begin{aligned} \hat{H} = & -\sum_{I=1}^M \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{2} \sum_{I=1}^M \sum_{J \neq I}^M \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \\ & + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{I=1}^M \sum_{i=1}^N \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|}, \end{aligned} \quad (2.2)$$

where M_I and Z_I are the nuclear masses and charges, respectively. m_e and e stand for the mass and charge of the electron, and ϵ_0 represents the permittivity of free space. For the rest of this thesis, the sets of M nuclear and N electronic coordinates are indicated collectively as $\mathbf{R}$ and $\mathbf{r}$, respectively. The first and second terms in the right hand side correspond to the kinetic energy operators of the nuclei and electrons. The third, fourth and last terms represent the potential energy arising from the nucleus-nucleus, electron-electron and nucleus-electron interactions.

The difficulty of solving Eq. (2.1) is reduced by introducing the *Born-Oppenheimer* [35] and *Classical nuclei* [34] approximations. According to the former, the atomic nu-

clei are assumed to be stationary if the nuclear masses are much larger than the electron mass. As a result, electronic wavefunctions follow the nuclear motion adiabatically and one can write the full wavefunction of the system as a product of the electronic part $\Psi(\mathbf{R}, \mathbf{r})$ and nuclear part $X(\mathbf{R})$, i.e.:

$$\Phi(\mathbf{R}, \mathbf{r}) = \Psi(\mathbf{R}, \mathbf{r})X(\mathbf{R}). \quad (2.3)$$

Within the Classical nuclei approximation, atomic nuclei are treated as classical particles, i.e. they are considered to be point-like. Using these two approximations, the first and third terms of the Hamiltonian are separated out and one can solve them classically. Consequently, the initial problem is simplified to the electronic SE for a system of N interacting electrons given by:

$$\hat{H}_e \Psi(\mathbf{R}, \mathbf{r}) = E(\mathbf{R})\Psi(\mathbf{R}, \mathbf{r}), \quad (2.4)$$

where $\hat{H}_e$ is the electronic adiabatic Hamiltonian composed of the three terms of Eq. (2.2) that involve electronic coordinates and $E(\mathbf{R})$ is the total adiabatic electronic energy. Despite this simplification, the electronic SE is still extremely complex and further approximations are essential for its solution.

The first approach for simplifying the electronic SE was reported by Hartree [36], in 1928. Hartree postulated that the full electron wavefunction $\Psi(\mathbf{R}, \mathbf{r})$ can be written as a product of *single-electron* wavefunctions $\psi_v(\mathbf{r})$, as follows:

$$\Psi(\mathbf{R}, \mathbf{r}) = \prod_{v=1}^N \psi_v(\mathbf{r}_v), \quad (2.5)$$

where for the sake of notation simplicity, we omit the dependence of the single-electron states on the positions of atomic nuclei $\mathbf{R}$. The above is known as the *Hartree Approximation* which reduces the N particle problem to a set of one-electron SE equations. However, the Hartree full wavefunction does not treat the electrons as distinguish-

able particles, because it is not an eigenfunction of the permutation operator. A step forward is to build an antisymmetric many electron wavefunction, known as *Slater determinant* [37], defined as:

$$\Psi(\mathbf{R}, \mathbf{r}) = SD\{\psi_v(\mathbf{r}_v, \sigma_v)\} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1, \sigma_1) & \psi_1(\mathbf{r}_2, \sigma_2) & \cdots & \psi_1(\mathbf{r}_N, \sigma_N) \\ \psi_2(\mathbf{r}_1, \sigma_1) & \psi_2(\mathbf{r}_2, \sigma_2) & \cdots & \psi_2(\mathbf{r}_N, \sigma_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\mathbf{r}_1, \sigma_1) & \psi_N(\mathbf{r}_2, \sigma_2) & \cdots & \psi_N(\mathbf{r}_N, \sigma_N) \end{vmatrix}, \quad (2.6)$$

where σ_v indicates the spin component of the electron in the state $\psi_v(\mathbf{r}_v)$. The wavefunction now satisfies the Pauli Exclusion Principle and changes sign upon exchange of electrons. This equation is one of the starting points of the *Hartree-Fock* approximation [38] and provides a reasonable description of some atomic systems [39]. Nevertheless, the major drawback of a Slater determinant calculation is that it lacks an accurate evaluation of electron correlations, leading to an overestimation of the exact solution of the Schrödinger equation [39].

2.1.3 The Hohenberg-Kohn Theorem

The initial idea of Density Functional Theory (DFT) is based on two pivotal theorems introduced by Hohenberg and Kohn [27]. Those are as follows:

Theorem 1: The external potential felt by electrons, $V_{\text{ext}}(\mathbf{r})$, is a unique functional of the electron density $n(\mathbf{r})$.

A straightforward consequence of *Theorem 1* is that $n(\mathbf{r})$ also uniquely determines the ground state wavefunction, Φ .

Theorem 2: The ground state density $n(\mathbf{r})$ is the one which *minimises* the ground state energy. Therefore, for a trial density $\tilde{n}(\mathbf{r})$, such that $\tilde{n}(\mathbf{r}) \geq 0$, and normalised to

N, we have for the ground state energy:

$$E^{(0)} = E_V[n] < E_V[\tilde{n}], \quad (2.7)$$

where E_V is the variational energy given by:

$$E_V[\tilde{n}] = F[\tilde{n}] + \int \tilde{n}(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r}. \quad (2.8)$$

Here $F[\tilde{n}]$ is the so-called *universal* functional that represents the electronic energy of the system, and is given by:

$$F[\tilde{n}] = \langle \Phi[\tilde{n}] | \hat{T} + \hat{V}_{ee} | \Phi[\tilde{n}] \rangle = T + V_{ee}, \quad (2.9)$$

where we introduce the symbolic notation $\hat{T}$ and $\hat{V}_{ee}$ for the kinetic energy and electron-electron interaction operators, respectively. $\Phi[\tilde{n}]$ indicates the trial ground state wavefunction for the external potential V_{ext} .

Proof of Theorem 2: Applying the variational principle to the electron density, we have for the expectation value of $\Phi[\tilde{n}]$:

$$\begin{aligned} \langle \Phi[\tilde{n}] | \hat{H} | \Phi[\tilde{n}] \rangle &= F[\tilde{n}] + \int \tilde{n}(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} \\ &= E_V[\tilde{n}] \geq E_V[n] = E^{(0)} = \langle \Phi | \hat{H} | \Phi \rangle. \end{aligned} \quad (2.10)$$

The above expression states that an electron density, $\tilde{n}(\mathbf{r})$, different than the ground state density, $n(\mathbf{r})$, will necessarily correspond to a higher energy of the system.

We emphasise that $F[n]$ depends only on the electron density and does not depend explicitly on the external potential $V_{\text{ext}}(\mathbf{r})$ [34]. As a result of this form, the knowledge of $F[n]$ reduces the N-particle problem to the determination of a function of three spatial coordinates, i.e. $n(\mathbf{r})$, which minimises the ground state energy.

2.1.4 The Kohn-Sham Equations

By separating the electron-electron interaction V_{ee} into the classical Coulomb interaction (E_H) and the exchange-correlation contribution (E_{xc}), the universal functional in Eq. (2.9) reads:

$$F[n] = T + E_H + E_{xc} . \quad (2.11)$$

Therefore, the main problem is reduced to find the expressions for the *unknown* forms of T and E_{xc} . The latter represents the non-classical contributions to the electron-electron interaction: the exchange energy and electronic correlation [28]. *Correlation effects*, which are enhanced at the quantum regime, decrease the probability of finding two electrons within immediate proximity. Moreover, for electrons with the same spin orientation, the *exchange interaction* further reduces this probability as a consequence of the Pauli exclusion principle. The unknown form of E_{xc} is treated by using approximate functionals, discussed below in Sec. 2.1.5.

Kohn and Sham [28] suggested to replace the true kinetic energy T of the interacting electrons with the kinetic energy (T_{KS}) of a hypothetical non-interacting system and leave the electron density, $n(\mathbf{r})$, unchanged. That is:

$$T_{KS} = \frac{-\hbar^2}{2m_e} \sum_v \langle \psi_v | \nabla^2 | \psi_v \rangle , \quad (2.12)$$

and

$$n(\mathbf{r}) = \sum_v |\psi_v(\mathbf{r})|^2 , \quad (2.13)$$

where the summation extends over the initially occupied states equal to N and $\psi_v(\mathbf{r})$ is the single-electron wavefunction, introduced in Eq. (2.5).

Using the new definition for the kinetic-energy in Eq. (2.12) and the *mean-field approximation* [40] for the Coulomb interaction term, then the universal functional

can be rewritten as:

$$F[n] = T_{\text{KS}}[n] + \frac{1}{2} \int \int \frac{e^2}{4\pi\epsilon_0} \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{\text{xc}}[n]. \quad (2.14)$$

It is important to note that T_{KS} is not equal to the true kinetic energy of the system T and therefore the exchange-correlation energy functional $E_{\text{xc}}[n]$, must be modified such that it includes the correlation part of T . Finally, by substituting Eq. (2.14) into Eq. (2.8), the energy Kohn-Sham functional reads:

$$E_{\text{KS}}[n] = T_{\text{KS}}[n] + \int n(\mathbf{r})V_{\text{ext}}(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \int \frac{e^2}{4\pi\epsilon_0} \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{\text{xc}}[n]. \quad (2.15)$$

Now each electron experiences an effective potential that accounts for all the interactions with the other electrons. Therefore, we can write for the one-electron Kohn-Sham equations [28]:

$$\left(\frac{-\hbar^2}{2m_e} \nabla^2 + V_{\text{KS}}[n(\mathbf{r})] \right) \psi_v(\mathbf{r}) = \varepsilon_v \psi_v(\mathbf{r}), \quad (2.16)$$

where ε_v is the energy of the corresponding KS state, ψ_v . The notation V_{KS} stands for the effective Kohn-Sham potential, which is given as the sum of three terms: the external potential (V_{ext}) indicating the electron - nuclei interaction, the Hartree potential (V_{H}) arising from the electrostatic repulsion of the electron cloud with density $n(\mathbf{r})$, and the exchange-correlation potential (V_{xc}), i.e.:

$$V_{\text{KS}}[n(\mathbf{r})] = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}[n(\mathbf{r})] + V_{\text{xc}}[n(\mathbf{r})]. \quad (2.17)$$

The Hartree and exchange-correlation potentials expressed as functional derivatives are given by:

$$V_{\text{H}}[n(\mathbf{r}), \mathbf{r}] = \frac{\delta E_{\text{H}}}{\delta n(\mathbf{r})} = \int \frac{e^2}{4\pi\epsilon_0} \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (2.18)$$

and

$$V_{\text{xc}}[n(\mathbf{r}), \mathbf{r}] = \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r})}. \quad (2.19)$$

In order to reach the expression for the Kohn-Sham equations in Eq. (2.16), we need to evaluate the functional derivative $\frac{\delta E_{\text{KS}}}{\delta n}$ at the ground-state density, and employ the method of Lagrange multipliers with the constraint that KS states are orthonormal. For a detailed derivation we refer the reader to Ref. [40]. It becomes apparent that the Kohn-Sham formulation presented here succeeds in transforming the many-electron problem into N single-electron problems each coupled via the effective potential V_{KS} .

Because of the functional dependence of the potential on $n(\mathbf{r})$, the KS equations form a set of non-linear equations. Typically, for solving such equations, an iterative procedure is used until self-consistency is obtained. This is depicted in Fig. 2.1.1. One provides an initial density to start the iteration and calculate V_{KS} . This potential is then fed into the KS equations, where ε_v and ψ_v are calculated. Finally, the derived eigenfunctions yield a new density and this procedure is repeated until the eigenfunctions and the associated energies remain same within a given threshold, i.e. up to the point self consistency has been obtained.

In specific cases, the external potential, $V_{\text{ext}}(\mathbf{r})$, is expressed in the form of the actual nucleus-electron interaction given by the last term of Eq. (2.2). However, in many applications, the inclusion of all nucleus-electron interactions makes the calculation computationally prohibitive, and therefore we have to resort to the pseudopotential approach [8], discussed in Sec. 2.1.8.

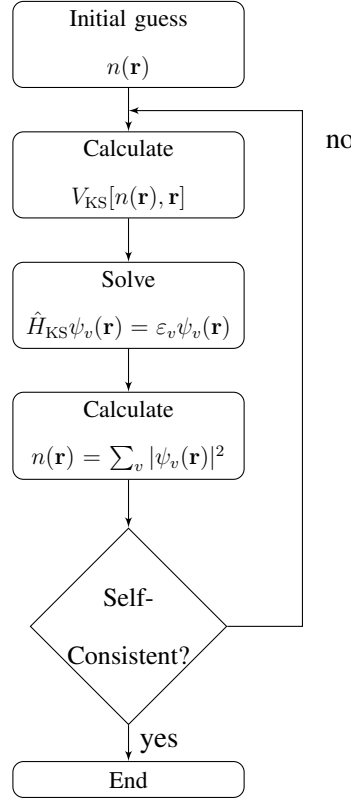


Figure 2.1.1: Self-consistent cycle illustrating a Kohn-Sham calculation.

2.1.5 Functional approximations for exchange and correlation

Depending on the nature of the system and its physical constraints, such as geometric structure or electron character, approximate functionals were developed to treat exchange-correlation effects. Some of the main approximations include: the Local Density Approximation (LDA) [28], the Generalised Gradient Approximation (GGA) [41], meta-GGA [42], hyper-GGA [43] and hybrid functionals, such as B3LYP (Becke, three-parameter, Lee-Yang-Parr) [44, 45] and PBE0 [46, 47]. Here, we present briefly the semi-local functionals LDA and GGA which are used for the purposes of this study. For a detailed review we refer the reader to Ref. [48].

Within LDA and for a spin-unpolarised system, the exchange correlation energy E_{xc} is equivalent to that of a homogeneous electron gas (HEG) of the same electron

density given by:

$$E_{xc}^{LDA} = \int n(\mathbf{r}) \varepsilon_{xc}^{HEG}(n) d\mathbf{r}, \quad (2.20)$$

where $\varepsilon_{xc}^{HEG}(n)$ is solely a function of the charge density and its accurate values can be obtained using Quantum Monte Carlo methods [49]. Despite the fact that LDA is the simplest approximation, it is considerably successful for many systems of interest. Nevertheless, there is a number of cases where LDA fails to reproduce accurate results [50].

The description of these cases can be improved by employing the Generalised Gradient Approximation. The reason is that in GGA we account for the fact that real systems have a spatial varying density, at variance with a homogeneous electron gas. Consequently, E_{xc} is written as a function not only of the electron density n , but also of the gradient of the density ∇n . This introduces semi-local exchange-correlation effects [41].

2.1.6 Periodic systems

A perfect crystal can be idealised as a set of atoms, infinitely repeated in all spatial dimensions. Obviously, one cannot assign positions to an infinite number of ions in a simulation. Due to this reason, electronic structure codes are based on the *supercell approach* [51], where we can simulate only the group of atoms that would regenerate the entire crystal when repeated periodically, and then impose periodic boundary conditions on the simulation box, known as *Born-Von Karman* boundary conditions.

This group of atoms is enclosed in a *simulation cell*. The choice of that cell depends on the symmetry of the system, so that its repetition would lead to the desired structure. Sometimes the smallest simulation cell, the primitive cell, is not the optimum choice and thus we might need to resort to a larger conventional cell, the *supercell*. The use of a supercell is useful, for example, when the symmetry of the system is lowered by impurities. In this thesis we use extensively the supercell approach to include in our calculations the effect of nuclear dynamics, described in Sec. 2.2.

2.1.7 Plane waves

One method for reducing the difficulty of solving the Kohn-Sham equations in real space is by using the plane wave approach [8]. In this method, the KS eigenstates are expanded into plane waves, which form a set of basis functions. This is useful for the calculation of the total charge density and energy of solids, since it takes into account the periodicity of the system, discussed in Sec. 2.1.6.

If we consider the discrete Fourier transform of the periodic function in Bloch's theorem, then the Kohn-Sham eigenfunctions take the form [28]:

$$\psi_{v\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_{v\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \quad (2.21)$$

where Ω is the volume of the system, $c_{v\mathbf{k}}(\mathbf{G})$ represents the expansion coefficients of the wavefunction in the basis of orthonormal plane waves $\frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$, v is the band index and $\mathbf{k}$, $\mathbf{G}$ are the wave and reciprocal lattice vectors, respectively. The summation in the above equation extends over the total number of plane waves N_{PW} . Substituting Eq. (2.21) into Eq. (2.13), the plane wave expansion of the electron density is given by:

$$n(\mathbf{r}) = \sum_v \int \frac{d\mathbf{k}}{\Omega_{\text{BZ}}} f(\varepsilon_{v\mathbf{k}}) n_{v\mathbf{k}}(\mathbf{r}), \quad (2.22)$$

where

$$n_{v\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{G}, \mathbf{G}'} c_{v\mathbf{k}}^*(\mathbf{G}') c_{v\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}}. \quad (2.23)$$

Here $f(\varepsilon_{v\mathbf{k}})$ stands for the Fermi occupation number of the state with energy $\varepsilon_{v\mathbf{k}}$ and the integration is over the $\mathbf{k}$ wavevectors inside the first Brillouin zone (BZ) of volume Ω_{BZ} .

The expression shown in Eq. (2.22) does not lead to the most efficient way of calculating the electron density $n(\mathbf{r})$ [8]. In particular, the construction of the charge density using Eq. (2.23) involves $\mathcal{O}(N_{\text{PW}}^2)$ operations. This computational effort can be significantly reduced, especially for large systems, by using a fast Fourier transform

(FFT) that allows the transformation of the electronic wavefunctions from reciprocal to real space in $N_R \log(N_R)$ operations, where N_R is the number of the FFT grid points. The use of the FFT technique is critical in modern DFT software packages based on plane waves leading to better performances in terms of computational speed. For an extended discussion on FFT and its applications in electronic structure codes, we refer the reader to Refs. [8, 52].

In practice, it is not possible to perform *ab-initio* calculations over an infinite number of vectors $\mathbf{k}$ and $\mathbf{G}$ and therefore we have to introduce two convergence parameters in order to truncate the summations in Eqs. (2.22) and (2.23). The problem of integrating over infinite $\mathbf{k}$ wavevectors in BZ is encountered by replacing the integral with a finite sum over a chosen $\mathbf{k}$ -point mesh [53]. For DFT calculations, several sampling schemes have been employed to approximate the BZ integration, but the most widely adopted is the one proposed by *Monkhorst* and *Pack* [54]. Similarly, we can truncate the summation over the Fourier components up to some kinetic energy cutoff defined by $E_{\text{cut}} \leq \frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}|^2$. This requires the systematic convergence of the final results, like the total energy of the system with respect to E_{cut} .

In the case of insulators or semiconductors at zero temperature, the summation in Eq. (2.22) includes all the states with energy below the Fermi level (ε_F) and therefore the occupation factors $f(\varepsilon_{v\mathbf{k}})$ can be written as a step function, i.e. [55]:

$$f(\varepsilon_{v\mathbf{k}}) = \theta(\varepsilon_F - \varepsilon_{v\mathbf{k}}). \quad (2.24)$$

For metallic systems, the discontinuous variation of the occupancies across the Fermi level leads to instabilities in self-consistent calculations [56]. Fractional occupation numbers can be introduced using the Fermi-Dirac or Gaussian distributions as filling factors [55]. These distributions smear the occupations of the states near the Fermi level with a fictitious electronic temperature, thereby improving the convergence with respect to the Brillouin zone sampling.

The plane wave approach is one of the simplest formalism to implement in elec-

tronic structure codes. Nevertheless, the treatment of the core wavefunctions or the rapid oscillations of valence wavefunctions inside the core region is considerably inefficient when represented by plane waves. In order to overcome this problem the *pseudopotential approximation* can be employed in conjunction with the plane wave basis formalism. This is discussed in the next section.

2.1.8 The Pseudopotential Approach

In the pseudopotential approach, the external potential is simplified by dividing the electrons into two categories: the core and valence electrons. Because of the strong localisation of the core electrons around the nucleus, these electrons do not participate into the chemical bonding of atoms [57]. Therefore, we can consider that the inner electrons form with the nucleus an ionic core, which interacts with the outer valence electrons. This assumption is used for replacing the effects arising from the core electrons and the nucleus by an effective pseudopotential.

One of the apparent benefits of the pseudopotential approach is that fewer Kohn-Sham wavefunctions are included in the calculations, because only the valence electrons are taken into account. Another advantage is that the computational cost of calculating the total energy of the system is significantly reduced, since the complex form of the external potential is replaced by the smoother shape of an effective potential produced by the screening of the nucleus from the core electrons.

In the literature there exist many methods for generating pseudopotentials (PPs) [8]. Among them, two popular pseudisation techniques are the norm-conserving PPs by Troullier and Martins [58] and ultra-soft PPs by Vanderbilt [59]. An alternative to the pseudopotential method is the projector augmented wave (PAW) approach [60], which combines the ideas of linearised augmented plane wave methods [61, 62] and the pseudopotential approach. Unlike the latter, in the PAW method the valence wave functions are transformed into smooth auxiliary functions which can be used to calculate the total energy of the system with the accuracy of all-electron calculations. For our calcula-

tions presented in this thesis, norm-conserving pseudopotentials are employed and are described briefly in the following.

A significant step forward in the theory of pseudopotentials took place in 1979 with the development of norm-conserving pseudopotentials (NCPPs) by Hamman *et al* [63]. The concept of norm-conservation, i.e. the norm of the pseudo wavefunctions matches the norm of the all-electron wavefunctions, simplifies the use of pseudopotentials, as well as makes them more transferable and accurate [8]. For constructing NCPPs, the pseudo wavefunction must satisfy the following conditions:

1. The radial part of the pseudo wavefunction is *nodeless* inside the core region.
2. Pseudo and all-electron wavefunctions agree beyond the core radius.
3. The charge enclosed inside the core region for the pseudo and all-electron wavefunctions must be equal (norm-conservation).
4. The first two derivatives of the pseudo wavefunction are required to be continuous at the core radius.

After employing the norm-conserving method, the resulting pseudopotential is different for each angular momentum. In order to deal with this and explicitly calculate the matrix elements of these “nonlocal” pseudopotentials [8], the spherical expansion of the plane waves is employed. Another important property of the NCPPs, mentioned above, is related to their good transferability, meaning that the pseudopotential for a specific element can be used in a variety of atomic environments [63].

2.2 Nuclear dynamics

2.2.1 Introduction

Nuclear dynamics plays an important role not only in the optical properties of solids, but also in determining resistivity of metals, superconductivity, thermal lattice expansion, Raman spectra and other physical properties [64]. In 1927, Born and Oppenheimer [35] introduced the idea to separate the nuclear from the electronic motion that led to a significant simplification to the problem of solving the Schrödinger equation, discussed in Sec. 2.1.2. Later in 1954, Born and Huang [65] developed the foundations for the theory of the lattice dynamics in solids, and since then the progress in the field has been remarkable. In the 1970s, two notable works published by Decicco *et al* and Pick *et al* [66, 67] revealed the connection between the electronic properties of materials to lattice vibrations.

In this part of Chapter 2, we introduce the theory of nuclear dynamics in the classical and quantum picture of the harmonic oscillator [see Secs. 2.2.2 and 2.2.3, respectively]. The expressions presented here are used extensively throughout this thesis. Supporting equations and definitions are left to Appendix A.

2.2.2 Harmonic approximation

In Sec. 2.1.2 we have seen that the electronic Schrödinger equation can be solved by partitioning the full Hamiltonian and wavefunction into a nuclear and an electronic adiabatic part [Eq. (2.4)]. In addition, we have dropped the nuclear index $\mathbf{R}$ assuming that all calculations refer to atoms at fixed coordinates. However, in real crystals, the nuclei vibrate around their crystallographic sites in response to thermal effects. In this section we explore the nuclear part of the Hamiltonian and we employ the harmonic approximation [68] for the description of lattice vibrations.

Taking together Eqs. (2.1), (2.2), (2.3), and (2.4), then the nuclear part of the total

Hamiltonian is given by:

$$\hat{H}_{eN} = - \sum_{I=1}^M \frac{\hbar^2}{2M_I} \nabla_I^2 + U_e(\mathbf{R}), \quad (2.25)$$

where $U_e(\mathbf{R})$ indicates the adiabatic potential-energy surface (PES), which we define here as [2, 65]:

$$U_e(\mathbf{R}) = E_e(\mathbf{R}) + \frac{1}{2} \sum_{I=1}^M \sum_{J \neq I}^M \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}. \quad (2.26)$$

$E_e(\mathbf{R})$ is the energy eigenvalue associated to the many-electron eigenstate $\Psi_e(\mathbf{R}, \mathbf{r})$ of the electronic adiabatic Hamiltonian [see Eq. (2.4)]. In the DFT framework, this quantity is equivalent to the total Kohn-Sham energy introduced in Eq. (2.15). We note that the subscript e is introduced to uniquely identify one excited electronic state of the system. For the electronic ground state we use the subscript 0. Recalling that the time scales of electronic and nuclear evolution are decoupled within the Born-Oppenheimer approximation, the quantity $U_e(\mathbf{R})$ essentially defines the potential energy landscape in which the nuclei move.

In this study, we are interested in the response of $U_0(\mathbf{R})$ around the equilibrium positions of the nuclei $\mathbf{R}^0$. For this reason we assume that the nuclear displacements $\mathbf{u}_I$ from the equilibrium positions are small compared to the lattice parameters of the crystal. The new coordinates of the nuclei are then defined as:

$$\mathbf{R}_I = \mathbf{R}_I^0 + \mathbf{u}_I. \quad (2.27)$$

We expand $U_0(\mathbf{R})$ in a Taylor series around the unperturbed coordinates and we keep terms up to the quadratic order to obtain [66]:

$$U_0(\mathbf{R}) = U_0(\mathbf{R}^0) + \sum_{l,I,\alpha} \frac{\partial U_0(\mathbf{R})}{\partial R_{lI\alpha}} u_{lI\alpha} + \frac{1}{2} \sum_{\substack{l,I,\alpha \\ l',J,\beta}} \frac{\partial^2 U_0(\mathbf{R})}{\partial R_{lI\alpha} \partial R_{l'J\beta}} u_{lI\alpha} u_{l'J\beta}, \quad (2.28)$$

where all derivatives are evaluated at the unperturbed positions of the nuclei. Here $u_{lI\alpha}$ stands for the displacement of the nucleus I in the unit cell l , along a Cartesian direction α . The summation runs over the total number of nuclear degrees of freedom which are equal to $3M$.

As a first approximation we resort to the classical nuclei approximation, introduced in Sec. 2.1.2, and we treat the dynamics of the nuclei using the Newton's equation of motion [40]. Hence, the forces acting on each atom are given by $F_{lI\alpha} = -\frac{\partial U_0(\mathbf{R})}{\partial R_{lI\alpha}}$. At the equilibrium configuration, the coefficients $\frac{\partial U_0(\mathbf{R})}{\partial R_{lI\alpha}}$ become zero and therefore the terms linear in $u_{lI\alpha}$ of Eq. (2.28) vanish. The remaining terms up to second order in atomic displacements constitute the harmonic approximation of the adiabatic potential-energy surface [2]; this approximation is valid when lifetime and anharmonic effects such as thermal expansion are negligible [67]. To make contact with the literature, we define the interatomic Born-Von Karman force constants as [66]:

$$C_{lI\alpha, l'J\beta} = \frac{\partial^2 U_0(\mathbf{R})}{\partial R_{lI\alpha} \partial R_{l'J\beta}} = -\frac{\partial F_{lI\alpha}}{\partial R_{l'J\beta}}. \quad (2.29)$$

The numerical evaluation of the force constants constitutes the starting point for calculating nuclear dynamics [40]. We now substitute Eqs. (2.29) and (A.1) into (2.28) to obtain for the harmonic adiabatic potential:

$$U_0(\mathbf{R}) = U_0(\mathbf{R}^0) + \frac{1}{2} \sum_{\substack{l,I,\alpha \\ l',J,\beta}} \sqrt{M_I M_J} D_{lI\alpha, l'J\beta} u_{lI\alpha} u_{l'J\beta}, \quad (2.30)$$

where $D_{lI\alpha, l'J\beta}$ represents the matrix elements of the dynamical matrix, defined by Eq. (A.1). In Appendix A, we show how the normal eigenmodes $\{e_{lJ\alpha}^\nu\}$ and eigenfrequencies $\{\omega_\nu\}$, related to the ground-state PES of the system, can be evaluated using the dynamical matrix.

The last term in Eq. (2.30) corresponds to the perturbation of the nuclear Hamiltonian in Eq. (2.25) and drives the harmonic nuclear motion. Using the normal mode representation in Eq. (A.2), then this perturbation takes the standard textbook form for

the potential energy of the vibrational Hamiltonian [40]:

$$\Delta H_N = \sum_{\nu} \frac{1}{2} M_P \omega_{\nu}^2 x_{\nu}^2. \quad (2.31)$$

Here the summation runs over the total number of degrees of freedom, M_P is a reference mass (usually equal to the proton mass) and x_{ν} represents the amplitude of the normal mode ν . For the derivation of this expression we combine Eqs. (A.1), (A.2), and (A.3) with the orthonormality relations of the eigenvectors [Eqs. (A.4a) and (A.4b)].

2.2.3 Schrödinger equation for the harmonic oscillator

Now we extend the notion of the harmonic oscillator to quantum mechanics by solving the Schrödinger equation of the nuclear system:

$$\hat{H}_{eN} X_{en}(x) = E_{en}^T X_{en}(x), \quad (2.32)$$

or equivalently:

$$\hat{H}'_N X_{en}(x) = E_{en} X_{en}(x), \quad (2.33)$$

where the nuclear wavefunction X_{en} is associated with the electronic state e and is expressed as a function of the normal coordinates $\{x_1, \dots, x_{3M}\}$, which we represent collectively as x . To indicate the solutions of the above equation we use the index n . In the second expression, we redefine the Hamiltonian as $\hat{H}'_N$, so that the vibrational eigenenergy is given by $E_{en} = (E_{en}^T - U_e^{\mathbf{R}^0})$, where E_{en}^T is the total Born-Oppenheimer energy of the system, analogous to E^T in Eq. (2.1).

Considering the ground-state PES ($U_0^{\mathbf{R}^0}$) in Eq. (2.33), the Hamiltonian that drives the harmonic motion of the nuclei is given by:

$$\hat{H}'_N = \sum_{\nu} \left(-\frac{\hbar^2}{2M_P} \frac{\partial^2}{\partial x_{\nu}^2} + \frac{1}{2} M_P \omega_{\nu}^2 x_{\nu}^2 \right). \quad (2.34)$$

To reach this expression we also use the linear transformation to normal mode coor-

ordinates for the kinetic energy operator. This Hamiltonian consists of non-interacting independent harmonic oscillators and therefore Eq. (2.33) can be solved by expressing the nuclear wavefunction into a product of wavefunctions, in complete analogy to Eq. (2.5) [69]:

$$X_{0n}(x) = \prod_{\nu}^{3M} \chi_{n_{\nu}}(x_{\nu}). \quad (2.35)$$

Here n_{ν} is used as an index to indicate the nuclear quantum state $\chi_{n_{\nu}}$. As a result, the problem of solving the nuclear SE simplifies to determine the solution of $3M$ single-mode equations:

$$\left(-\frac{\hbar^2}{2M_P} \frac{\partial^2}{\partial x_{\nu}^2} + \frac{1}{2} M_P \omega_{\nu}^2 x_{\nu}^2 \right) \chi_{n_{\nu}}(x_{\nu}) = E_{n_{\nu}} \chi_{n_{\nu}}(x_{\nu}). \quad (2.36)$$

The above second-order differential equation can be solved using standard textbook procedures. After solving Eq. (2.36), the single-mode eigenfunction is given by [69]:

$$\chi_{n_{\nu}}(x_{\nu}) = \frac{(2\pi l_{\nu}^2)^{-1/4}}{\sqrt{2^{n_{\nu}} n_{\nu}!}} \exp\left(-\frac{x_{\nu}^2}{4l_{\nu}^2}\right) H_{n_{\nu}}(x_{\nu}/\sqrt{2}l_{\nu}), \quad (2.37)$$

where we introduce the parameter $l_{\nu} = \sqrt{\frac{\hbar}{2M_P \omega_{\nu}}}$ and $H_{n_{\nu}}$ indicates a Hermite polynomial of degree n_{ν} . The set of the independent quantum harmonic oscillators $\{\chi_{n_{\nu}}\}$ forms a complete and orthonormal basis. The corresponding eigenvalues are obtained as:

$$E_{n_{\nu}} = \left(n_{\nu} + \frac{1}{2} \right) \hbar \omega_{\nu}. \quad (2.38)$$

The solution of Eq. (2.36) is such that n_{ν} is an integer $(0, 1, 2, \dots)$ and can be interpreted as the occupation number of each nuclear quantum state.

This is the quantum mechanical description of nuclear dynamics in the harmonic approximation. Essentially, we have added to the nuclear Hamiltonian a small perturbation arising from the change in the adiabatic ground-state PES and introduced $3M$ new generalised coordinates so that the Hamiltonian is diagonalised. Therefore, we have separated the collective oscillations of the lattice into $3M$ independent normal

modes whose energies are found to be quantised. The associated quanta are called *phonons* and from now on we will refer to the solutions of the dynamical matrix in Eq. (A.3) as phonon modes and phonon frequencies.

The phonon occupation n_ν of each vibrational mode is important to determine the joint electron-nuclear energy, given by:

$$E_{0n}^T = U_0^{\mathbf{R}^0} + \sum_{\nu} \left(n_\nu + \frac{1}{2} \right) \hbar \omega_\nu. \quad (2.39)$$

The lowest energy is obtained for $n_\nu = 0$ and the correction $\sum_{\nu} \frac{1}{2} \hbar \omega_\nu$ is referred to as zero-point energy [70]. Therefore, the evaluation of the phonon frequencies ω_ν from the diagonalisation of the dynamical matrix is sufficient to calculate the zero-point energy of a system. However, in semiconductors and insulators we are also interested in calculating the *zero-point renormalisation* of the Kohn-Sham electron states. For example the energy renormalisation of the states at the valence band top and conduction band bottom lead to the renormalisation of the optical band gap. This correction varies with temperature and amounts to an energy shift in the absorption edge of the optical spectra. In order to evaluate the effect of lattice vibrations on the electron states and optical spectra we need to incorporate *electron-phonon interactions* in *ab-initio* calculations. This is discussed in the next sections. In particular, in Secs. 2.3.3 and 2.3.4, we analyse the existing theories and implementations used for the calculation of phonon-assisted optical absorption and phonon-induced energy level renormalisation of the band structure.

2.3 Optical properties

2.3.1 Introduction

The knowledge of the theoretical framework behind the interaction of electromagnetic radiation with condensed matter is fundamental for our interpretation of the experimental results. In semiconductors, electrons can interact with photons of adequate energy and then make a transition from filled valence bands to unoccupied conduction bands. This simple but key physical mechanism underpins optical absorption and can provide a rich source of information on the optical, as well as on the electronic properties of semiconductors.

There is a wide range of experimental techniques that are employed for measuring the optical properties of solids [1]. One of the most versatile used is spectroscopic ellipsometry. In this technique the material of interest is illuminated with linearly polarised light. Then the complex reflectance is measured by analysing the reflected beam from the sample and finally the complex dielectric function $\epsilon(\omega)$ is obtained through Fresnel's formulae [71]. The data from the reflectance measurements can also serve for the extraction of the extinction and absorption coefficients. The knowledge of the latter provides useful information for the optimisation of optoelectronic devices and solar cells. In addition, the measured dielectric function is used to extract optical band gaps from the so-called Tauc plots [72] or to identify critical points in the band structure from lineshape analysis of second-derivative spectra [73–75]. These methods are discussed later in this thesis, in Sec. 4.5.

Photoemission techniques are used to probe the electronic structure of solids. Unlike reflectance measurements, photoluminescence measurements can yield *direct* information on the optical band gap of the material. A typical photoluminescence experiment is divided into three stages: Firstly, the semiconductor is illuminated with light and electrons interact with photons to complete a transition from the valence to the conduction band. Then, the photoexcited electron interacts with the holes left be-

hind via the Coulomb interaction forming electron-hole pairs. Finally, the electron recombines with the hole in the valence band and re-emits a photon whose energy is measured. The measured photoluminescence spectrum exhibits intense signals usually at energies equal to the optical band gap of the sample. A more advanced photoemission technique that yields information on the valence band structure of the material in reciprocal space is angle-resolved photoemission spectroscopy [76]. This method is the only technique available for probing the energy, momentum and spin of the electron and therefore mapping these quantities to the valence band dispersion of the solid [76].

In this thesis, we aim to develop a new technique to incorporate an important physical phenomenon in the calculation of the optoelectronic properties of semiconductors, thereby improving our interpretation of experimental results. This phenomenon is the coupling of the electrons with lattice vibrations at finite temperatures leading to indirect transitions and to energy level renormalisation of the band structure. In this part of Chapter 2 we set up the theoretical framework of our present study. In Sec. 2.3.2 we present the theory of direct optical absorption that leads to the calculation of the dielectric function in the absence of thermal effects and electron-hole interactions. In Sec. 2.3.3 we introduce the concept of electron-phonon interactions and the Hall-Bardeen-Blatt theory of indirect optical transitions. This is followed by Sec. 2.3.4 in which we present the Allen-Heine theory of temperature-dependent band structures. In Sec. 2.3.5 we define the “Varshni effect” and we list materials which exhibit the opposite behaviour. In Sec. 2.3.6 we describe additional corrections to the temperature dependence of the band structures coming from the thermal expansion of the lattice and Fröhlich polar coupling. In Sec. 2.3.7 we introduce the Williams-Lax theory as an alternative approach for calculating indirect optical absorption. Finally, in Sec. 2.3.8 we present a short summary of this part of Chapter 2 in order to make contact with the following chapters. Lengthy derivations and supporting equations are presented in Appendices B.1-B.6.

2.3.2 Direct optical absorption: Dielectric function

In this section we introduce the theoretical principles of optical absorption in the absence of lattice vibrations. The expression for the dielectric function is presented in the independent-particle picture and for a homogeneous and isotropic material. Here, we employ the approximation of linear response, and we neglect local field effects, as well as electron-hole interactions [2, 7]. We use these simplifications in order to describe the dielectric function in its simplest possible form, and thereby focus on the quantum nuclear effects in the subsequent sections.

We consider the unperturbed one-electron Hamiltonian [Eq. (2.16)] given by:

$$\hat{H} = \frac{\mathbf{p}^2}{2m_e} + V_{\text{KS}}(\mathbf{r}), \quad (2.40)$$

where m_e is the mass of the electron, $\mathbf{p}$ indicates the momentum operator ($-i\hbar\nabla$) and $V_{\text{KS}}(\mathbf{r})$ stands for the one-electron potential, introduced in Eq. (2.17). Now we examine the response of the system to a perturbation caused by a weak electromagnetic field of the form:

$$\Delta\hat{H} = \frac{e}{m_e c} \mathbf{A} \cdot \mathbf{p}, \quad (2.41)$$

where e and c stand for the electronic charge and the speed of light in vacuum, respectively. As shown in Appendix B.1, the last expression is obtained by considering the Coulomb gauge [71]. We also assume for the moment that the Kohn-Sham potential has only local components and remains invariant in the presence of the external field [77]. The vector potential $\mathbf{A}$ satisfying Maxwell's equations has the plane wave form:

$$\mathbf{A}(\mathbf{r}, t) = A_0 \hat{\mathbf{e}} \exp[i(\boldsymbol{\xi} \cdot \mathbf{r} - \omega t)] + \text{c.c.}, \quad (2.42)$$

where $\hat{\mathbf{e}}$ is the polarisation vector of the electric field perpendicular to the wavevector $\boldsymbol{\xi}$. The frequency and amplitude of the electromagnetic wave are represented by ω and A_0 , respectively, and c.c. stands for the complex conjugate of the previous term. By

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employing time-dependent perturbation theory and Fermi Golden Rule, expressed in Eq. (B.21), the total *absorption rate* is given by:

$$\Gamma(\boldsymbol{\xi}, \omega) = \frac{2\pi}{\hbar} \left(\frac{eA_0}{m_e c} \right)^2 \sum_{v,c} |\langle \psi_c | e^{i\boldsymbol{\xi} \cdot \mathbf{r}} \hat{\mathbf{e}} \cdot \mathbf{p} | \psi_v \rangle|^2 \delta(\varepsilon_c - \varepsilon_v - \hbar\omega), \quad (2.43)$$

where the bra-ket notation $\langle | \cdot | \rangle$ in the above equation represents an integration over the electronic coordinates $\mathbf{r}$. This expression describes the rate of an electron undergoing a transition from an occupied Kohn-Sham state $|\psi_v\rangle$ to an unoccupied state $|\psi_c\rangle$ after the absorption of a photon with energy $\hbar\omega$. The presence of the Dirac delta function ensures conservation of energy, so that the absorption process occurs if and only if the difference between the energy of the initial, ε_v , and final, ε_c , states is equal to the photon energy $\hbar\omega$.

Following the prescription in Appendix B.1, the imaginary part of the macroscopic dielectric function at a finite wavevector $\boldsymbol{\xi}$ is given by Eq. (B.6). In the long wavelength limit, i.e. $\boldsymbol{\xi} \rightarrow 0$, the imaginary part of the dielectric function can be calculated as:

$$\epsilon_2(\omega) = 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{v,c} |\hat{\mathbf{e}} \cdot \mathbf{p}_{cv}|^2 \delta(\varepsilon_c - \varepsilon_v - \hbar\omega), \quad (2.44)$$

where Ω indicates the volume of the system and the electric dipole matrix element is given $\mathbf{p}_{cv} = \langle \psi_c | \hat{\mathbf{p}} | \psi_v \rangle$. The last expression is known as the *Electric Dipole Approximation* [10] of the dielectric function and is obtained by retaining only the zeroth order term in the Taylor expansion of $e^{i\boldsymbol{\xi} \cdot \mathbf{r}}$. We stress here that for first principle calculations of the optical spectra is important to account for the extra contribution to the dielectric function coming from the nonlocal part of the KS potential [78]. The method used to incorporate this contribution in *ab-initio* calculations is presented in Appendix B.2.

In the case of periodic solids, it is convenient to employ the Bloch representation of the wavefunction ψ_c , given by:

$$\psi_c(\mathbf{r}) \rightarrow \psi_{c\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{c\mathbf{k}}(\mathbf{r}), \quad (2.45)$$

where $\mathbf{k}$ represents a wavevector in reciprocal space and $u_{c\mathbf{k}}$ is the periodic part of the wave function which is invariant under lattice translation. Now the expression of the imaginary part of the dielectric function takes the form [40]:

$$\epsilon_2(\omega) = 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{v,c} \int \frac{d^3 \mathbf{k}}{\Omega_{\text{BZ}}} |\hat{\mathbf{e}} \cdot \langle u_{c\mathbf{k}} | \mathbf{p} | u_{v\mathbf{k}} \rangle|^2 \delta(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}} - \hbar\omega), \quad (2.46)$$

where the integration with respect to $\mathbf{k}$ wavevector is over the Brillouin zone (BZ) of volume $\Omega_{\text{BZ}} = \frac{2\pi^3}{\Omega}$. In first-principle calculations, it is always convenient to replace the integral with a weighted sum over $\mathbf{k}$ wavevectors as: $\frac{\Omega}{2\pi^3} \int d^3 \mathbf{k} \rightarrow \sum_{\mathbf{k}} w_{\mathbf{k}}$. In this work, unless specified otherwise, we use Voronoi analysis [79] to assign the weights $w_{\mathbf{k}}$. A more detailed discussion about the Voronoi procedure is presented in Sec. 3.3.

We emphasise here that in the summation over the states in Eq. (2.46), only the pairs between wavefunctions with the same wavevector are involved. This arises from the relation $\mathbf{p}_{cv}(\mathbf{k}_c, \mathbf{k}_v) = \delta(\mathbf{k}_c, \mathbf{k}_v) \langle u_{c\mathbf{k}_c} | \mathbf{p} | u_{v\mathbf{k}_v} \rangle$ [40], where the delta function ensures vertical transitions only. This is a direct consequence of crystal momentum conservation. Within this theoretical framework, Eq. (2.46) predicts an optical absorption onset which is equal to the minimum energy difference $\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}}$. It becomes apparent from the above relation that the theory presented so far can only be used as an approximation to describe optical absorption at energies above the fundamental direct gap.

Figure 2.3.1 compares the optical spectra of silicon calculated (red line) using the expression for the dielectric function in Eq. (2.46) and the absorption coefficient in Eq. (B.9) with the experimental data (blue line) from Ref. [80]. Theory and experiment differ quantitatively and qualitatively below and above the direct gap of silicon at 3.3 eV indicated by the grey vertical line in Fig. 2.3.1. In contrast to the calculated absorption coefficient, the experimental spectrum displays absorption well below the fundamental direct gap. This is a characteristic of indirect gap materials, like silicon, whose valence band top and conduction band bottom states have different momenta. In order to account for the optical coupling between states with different momentum in

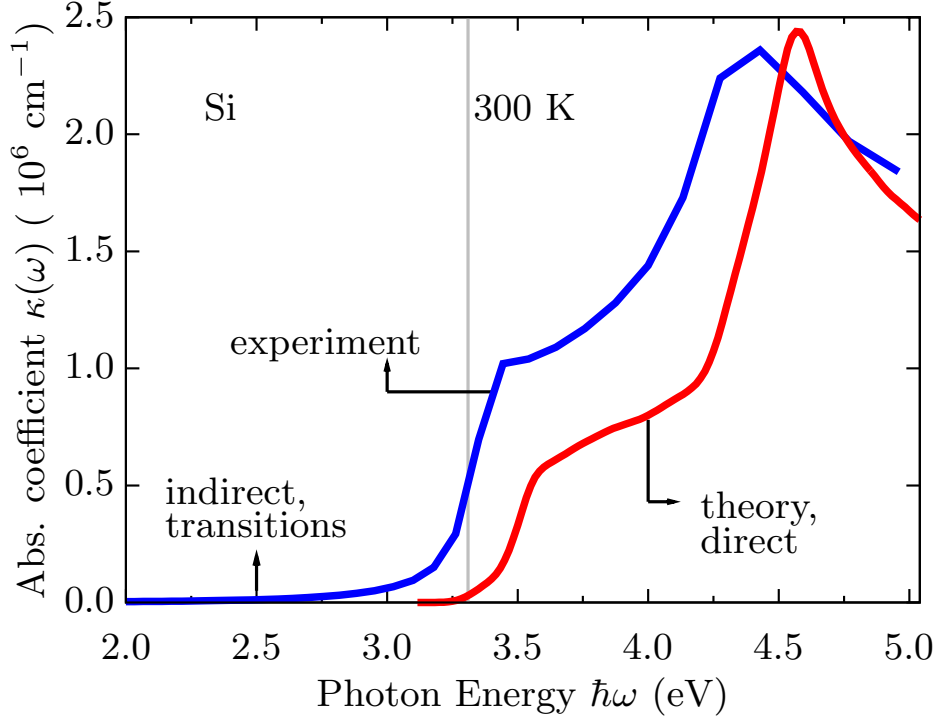


Figure 2.3.1: Absorption coefficient of Si calculated with the atoms clamped at their equilibrium positions (red line). The experimental data (blue line) measured at 300 K are from Ref. [80]. The thin vertical line (grey) indicates the direct band gap calculated with the nuclei in their equilibrium positions.

k -space another mechanism is needed. This mechanism is known as phonon-assisted optical absorption [2] and is directly related to the quantum nuclear motion at finite temperatures (even at 0 K). Including phonon-assisted transitions in DFT calculations is a challenging task and is the main topic of this thesis, discussed in the next section.

In the energy range 3.3 eV–4.0 eV (energies around the shoulder at 3.5 eV) the calculated absorption coefficient underestimates the experimental data. This discrepancy is attributed to excitonic effects [2] which are absent from our calculations. In fact, our calculations shown in Fig. 2.3.1 are performed within the one-electron approximation, where the electrons are assumed to move independently in the Kohn-Sham potential. Inclusion of many-body effects will alter this picture and the excited electron in the conduction band will interact with the hole left behind in the valence band through a Coulomb potential. The coupled electron-hole pair will form bound states, called *excitons*, which are characterised by excitations energies lower than the energy gap. The effect of the electron-hole interaction in silicon has been demonstrated from first

principle studies to redistribute the oscillator strengths from higher to lower photon energies and enhance the absorption in the energy range 3.3 eV–4.0 eV [7]. Given the high computational cost involved in calculating excitonic effects, a full calculation that combines electron-hole interaction and indirect optical absorption is a formidable task. Therefore, we decide to omit excitonic effects from our main results, presented later in this thesis, and include only indirect optical transitions. These transitions are analysed in the next section.

2.3.3 Indirect optical absorption: Hall-Bardeen-Blatt theory

So far we have dealt with direct vertical transitions, whose contributions are dominating the fundamental absorption edge of direct gap semiconductors, like GaAs, InP, CdTe, CdS and MAPbI₃. In indirect gap semiconductors, like Si, SiC, diamond, TiO₂, Ge and GaP, an electron is promoted from the top of the valence band to the bottom of the conduction band ($k_v \neq k_c$) with the assistance of a phonon. This mechanism is known as *indirect optical absorption* coming from *electron-phonon interactions* and is discussed in every introduction to solid state physics [2, 10, 81–83].

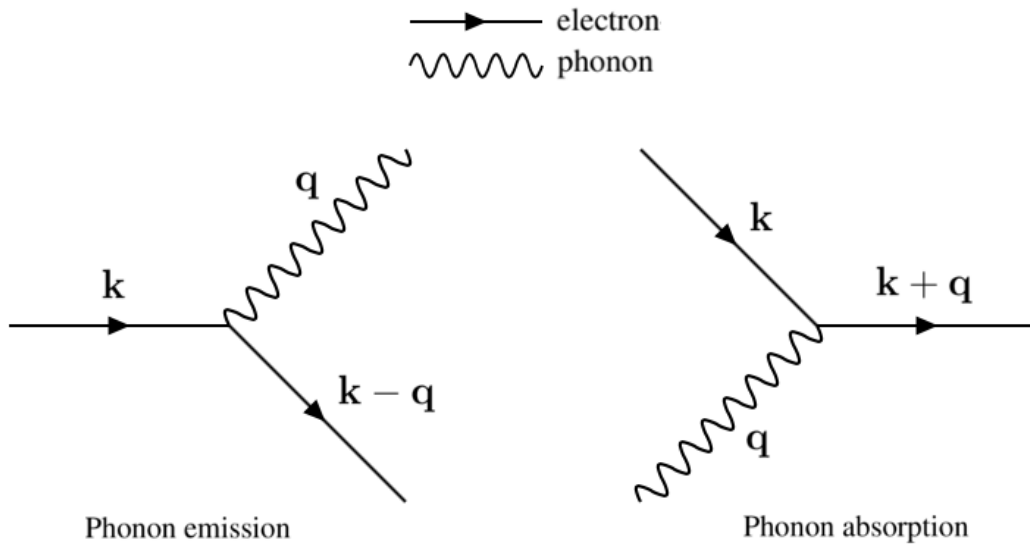


Figure 2.3.2: Diagrams showing electron-phonon interaction processes.

2.3. OPTICAL PROPERTIES

When a phonon of wavevector $\mathbf{q}$ and frequency $\omega_{\mathbf{q}}$ is involved in optical absorption, energy and momentum conservation are satisfied as follows:

$$\hbar\omega = \varepsilon_{c\mathbf{k}_c} - \varepsilon_{v\mathbf{k}_v} \pm \hbar\omega_{\mathbf{q}}, \quad (2.47)$$

and

$$\mathbf{k}_c - \mathbf{k}_v = \mp \mathbf{q}, \quad (2.48)$$

where $+$ corresponds to the emission and $-$ to the absorption of a phonon. These are the basic electron-phonon interaction processes illustrated in Fig. 2.3.2.

The concept of indirect optical absorption is shown schematically in Fig. 2.3.3. Along path (1), an electron at the valence band maximum absorbs a photon and makes a *virtual* transition to a state in the conduction band (blue arrow). The process is considered to be virtual because the transition conserves momentum but not energy. This is followed by a transition to the conduction band minimum, via phonon absorption or

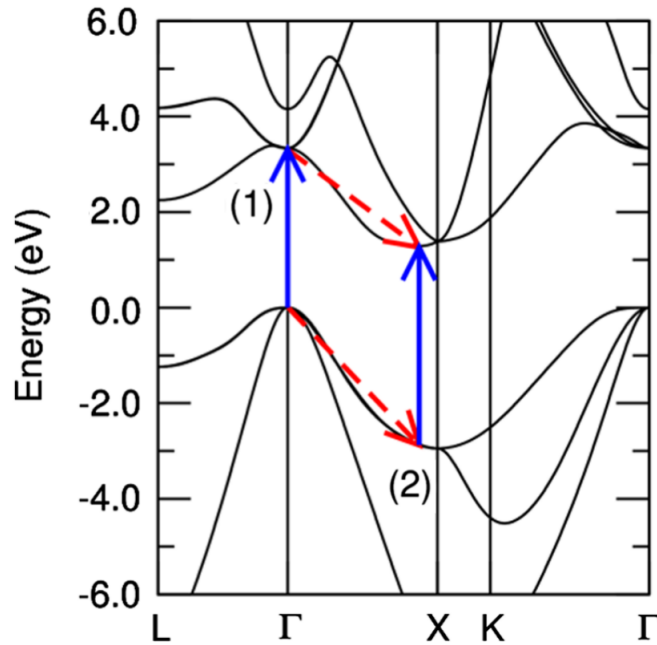


Figure 2.3.3: Band structure of silicon illustrating phonon-assisted processes. The arrows show two alternative paths that an electron can follow to complete an indirect transition. Blue arrows show the vertical transitions from the valence band to the conduction band after the electron couples to a photon. Red arrows indicate electron-phonon scattering events. Figure from Ref. [20].

emission (red arrow). The second path (2), involves a virtual transition between two states in the valence band via phonon absorption or emission (red arrow), and then a vertical transition via photon absorption, with the electron ending up at the bottom of the conduction band (blue arrow). One should note that there also exist processes involving more than one phonon, but the probability of such events is much smaller.

The theory of phonon-assisted (or indirect) optical transitions was developed by Hall, Bardeen, and Blatt (HBB) [12], and forms the basis for our current understanding of phonon-assisted optical processes. The premise of the conventional HBB theory is that electrons in solids experience a time-dependent potential which arises from the oscillatory motion of the atoms around their equilibrium positions. Following this premise, indirect electronic transitions are obtained within time-dependent perturbation theory to first order in the atomic displacements [2]. This amounts to considering optical transitions whereby the absorption of a photon is accompanied by the emission or absorption of one phonon, as shown in Fig. 2.3.3.

Within the HBB theory, indirect transitions are taken into account through second order time-dependent perturbation theory (see Appendix B.3). This is a consequence of the two processes involved (photon absorption + phonon emission or absorption). The interaction of the electrons with light is driven by a perturbation $\Delta\hat{H}^{(2)}$ of the form given by Eq. (2.41). To account for the electron-phonon interaction we consider a perturbation equal to the first order variation of the Hamiltonian in Eq. (2.40) with the atomic displacements given by:

$$\Delta\hat{H}^{(1)} = \sum_{\nu\mathbf{q}} \frac{\partial\hat{H}}{\partial x_{\nu\mathbf{q}}} x_{\nu\mathbf{q}}. \quad (2.49)$$

If we use the representation of the harmonic oscillator in second quantisation, given in Eq. (A.5), and perform some algebraic manipulations, we obtain the HBB expression for the imaginary part of the dielectric function at a finite temperature T

as [20, 84, 85]:

$$\begin{aligned} \epsilon_2(\omega, T) = & 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{v,c,\nu} \int \frac{d^3 \mathbf{k}}{\Omega_{\text{BZ}}} \int \frac{d^3 \mathbf{q}}{\Omega_{\text{BZ}}} \\ & \times \left[\left| M_1(\mathbf{k}, \mathbf{q}) + M_2^-(\mathbf{k}, \mathbf{q}) \right|^2 n_{\nu \mathbf{q}, T} \delta(\varepsilon_{c, \mathbf{k}+\mathbf{q}} - \varepsilon_{v, \mathbf{k}} - \hbar\omega - \hbar\omega_{\nu \mathbf{q}}) \right. \\ & \left. + \left| M_1(\mathbf{k}, \mathbf{q}) + M_2^+(\mathbf{k}, \mathbf{q}) \right|^2 (n_{\nu \mathbf{q}, T} + 1) \delta(\varepsilon_{c, \mathbf{k}+\mathbf{q}} - \varepsilon_{v, \mathbf{k}} - \hbar\omega + \hbar\omega_{\nu \mathbf{q}}) \right], \end{aligned} \quad (2.50)$$

where the generalised optical matrix elements M_1 and $M_2^\pm$ are defined as:

$$M_1 = \hat{\mathbf{e}} \cdot \sum_{\beta} \frac{\mathbf{p}_{u\beta}(\mathbf{k}) g_{\beta c \nu}(\mathbf{k}, \mathbf{q})}{\varepsilon_{\beta, \mathbf{k}} - \varepsilon_{v, \mathbf{k}} - \hbar\omega}, \quad (2.51a)$$

$$M_2^\pm = \hat{\mathbf{e}} \cdot \sum_{\beta} \frac{g_{u\beta \nu}(\mathbf{k}, \mathbf{q}) \mathbf{p}_{\beta c}(\mathbf{k} + \mathbf{q})}{\varepsilon_{\beta, \mathbf{k}+\mathbf{q}} - \varepsilon_{v, \mathbf{k}} \pm \hbar\omega_{\nu \mathbf{q}}}. \quad (2.51b)$$

The steps for the derivation of Eq. (2.50) are shown for completeness in Appendix B.4. Here $n_{\nu \mathbf{q}, T} = [\exp(\hbar\omega_{\nu \mathbf{q}}/k_B T) - 1]^{-1}$ is the Bose-Einstein occupation factor of the ν -th mode with wavevector $\mathbf{q}$ and frequency $\omega_{\nu \mathbf{q}}$. $g_{\beta c \nu}(\mathbf{k}, \mathbf{q})$ indicates the electron-phonon matrix elements accounting for the coupling between states $|\psi_{\beta, \mathbf{k}}\rangle$ and $|\psi_{c, \mathbf{k}+\mathbf{q}}\rangle$. The matrix elements M_1 and $M_2^\pm$ involve summations over all possible intermediate states $|\psi_{\beta, \mathbf{k}}\rangle$ and account for the calculation of the two paths shown in Fig. 2.3.3.

Despite the popularity of the HBB theory, only very recently was this formalism combined successfully with first-principles density-functional theory calculations [20] powered by Wannier interpolation [86, 87]. The work of Ref. [20] stands as one of the most sophisticated calculations of indirect optical absorption available today. The essential role of the HBB theory in describing phonon-assisted optical absorption in semiconductors can be understood from Fig. 2.3.4.

Figure 2.3.4(a) compares the calculated absorption coefficient of silicon (red line) in the *absence* of indirect transitions using the independent particle approximation [Eq. (2.46)] and the experimental data (blue discs) from Ref. [80]. At variance with Fig. 2.3.1, we use a logarithmic scale to focus on the energy range below the direct gap where optical transitions of low probability take place. As expected our optical

spectrum exhibits *no* absorption below the direct gap failing completely to describe the full spectrum in semiconductors with an indirect band gap. In the particular case of silicon, one of the most suitable materials for photovoltaic applications [89], the

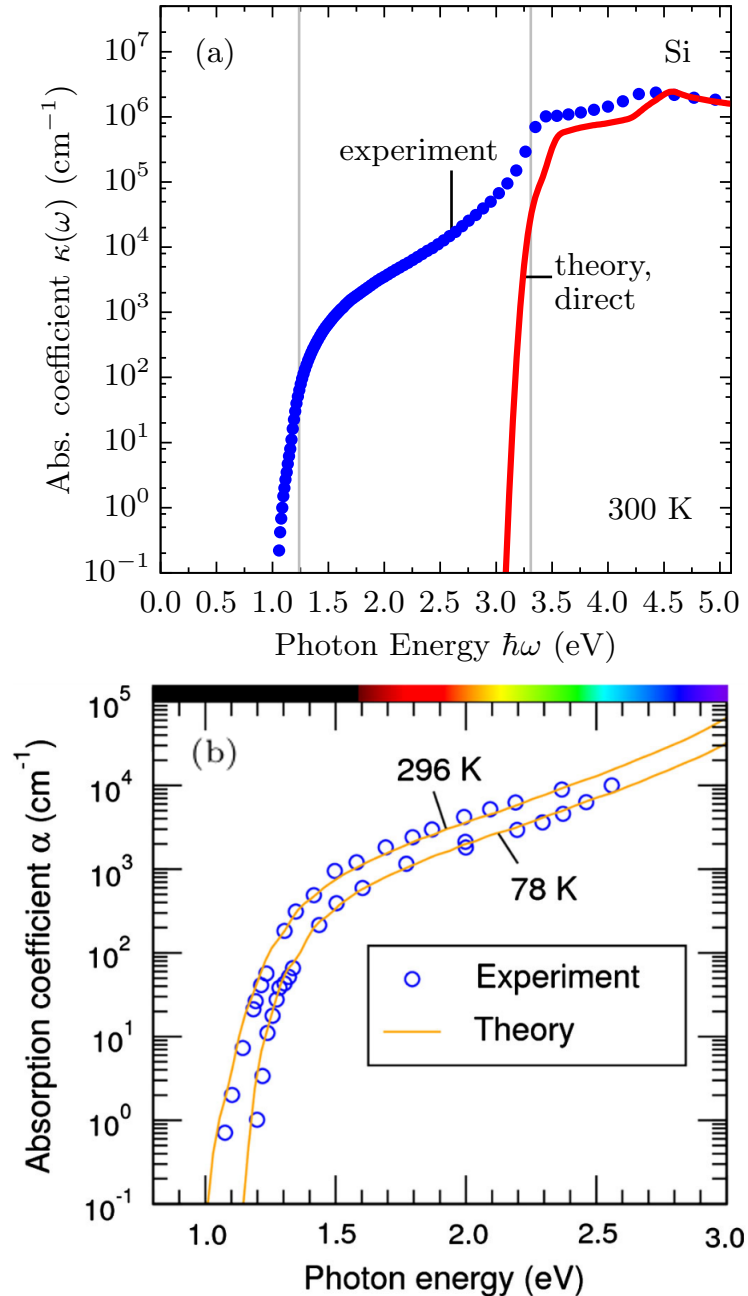


Figure 2.3.4: Absorption coefficient of silicon on a logarithmic scale. (a) Calculations with the atoms clamped at their equilibrium positions and experimental data [80] are shown as solid lines and discs, respectively. The thin vertical lines indicate the direct and indirect band gaps calculated with the nuclei in their equilibrium positions. (b) Calculations using the HBB theory and experimental data at 296 K and 78 K from Ref. [88] are shown as solid lines and circles, respectively. HBB spectra have been rigidly red shifted by 0.15-0.23 eV in order to match the absorption onset of the experimental curves. Figure from Ref. [20].

absence of phonon-assisted transitions leads to zero optical absorption in the visible region (i.e. energies < 3.3 eV).

Figure 2.3.4(b) shows the absorption coefficient of silicon calculated from first principles in Ref. [20] using the HBB theory [Eq. (2.50)] for temperatures 296 K and 78 K. Now the inclusion of electron-phonon interactions leads to indirect transitions and optical absorption at energies below the first direct gap. The agreement between the HBB theory with the experimental data from Ref. [88] is excellent. However, the calculations of Ref. [20] are not entirely parameter-free, since the agreement with experiment was achieved by empirically shifting the absorption onset at each temperature. This correction is unavoidable because the HBB theory does not take into account the temperature dependence of band structures. This can be readily understood from Eq. (2.50) where the Kohn-Sham electron energies inside the delta function correspond to eigenvalues of the unperturbed Hamiltonian. The temperature dependence is only taken into account through the phonon occupation factor $n_{\nu\mathbf{q}}(T)$. Hence, upon increasing temperature only the optical absorption intensity increases and the energy of the absorption onset remains unchanged.

A consistent theory for the calculation of temperature-dependent band structures was developed by Allen and Heine [11, 70], and is presented in Sec. 2.3.4. It becomes intuitively apparent that an HBB calculation on a temperature-dependent band-structure, at variance with the band structure presented in Fig. 2.3.3, will also reveal energy shifts on the optical spectra. However, it is reasonable to ask how the temperature dependence of the eigenenergies enters the HBB expression in Eq. (2.50) and how can be incorporated in first principle calculations. A full theory that combines energy-level renormalisation and phonon-assisted optical absorption at finite temperatures is not yet available. This is the main gap between literature and first-principle calculations that we are aiming to address in this thesis.

To this end, we should point out that in Fig. 2.3.4(b) transitions above the direct gap of silicon ($\hbar\omega > 3.3$ eV) are not shown. The reason is that the HBB theory neglects

direct optical absorption. One could naively assume that the combination of the expressions in Eqs. (2.46) and (2.50), would lead to the calculation of the complete spectrum including direct and indirect transitions. However, as we will explain in Chapter 4 a more complete treatment is required, bringing higher-order terms in the perturbation expansion, to calculate the full dielectric function. In Appendix B.3 we show that the transition probability up to second order [Eq. (B.27b)] includes cross-coupling terms that account for the mixing of first (direct) and second (indirect) order processes. Such terms do not contribute to the temperature dependence of the absorption coefficient within the HBB theory, since they do not survive upon the thermal average. As it will reveal later in Chapter 4, our approach within the Williams-Lax theory (see Sec. 2.3.7) contains interference terms between direct and indirect processes, coming from the temperature dependence of the energy levels.

2.3.4 Temperature dependent band structures: Allen-Heine theory

As we have seen in Sec. 2.3.3, the electron-phonon interaction plays a central role in the optical properties of solids. Despite their effect on phonon-assisted optical transitions, quantised vibrations disturb the ideal lattice of solids and the effective electrostatic potential felt by electrons changes. This change is accompanied by the energy level renormalisation of the ideal band structure. In fact, electron-phonon coupling is responsible for the temperature dependence and the quantum zero-point renormalisation of the critical point energies, leading to the temperature-dependent broadening of light absorption and emission lineshapes, as well as to the energy shift of the absorption onset.

Recently, it has become possible to study this effect using *ab-initio* calculations. The phonon-induced renormalisation of band gaps and band structures was investigated from first principles in Refs. [14–19, 90–97] starting from the theory of Allen and Heine (AH) [11]. In the following we present the basic principles and equations

of the AH theory.

In order to construct the theory of Allen and Heine, we employ the adiabatic and harmonic approximations, as well as time-independent perturbation theory. At variance with Sec. 2.3.3, here we adopt a Born-von Kármán (BvK) supercell approach and we consider that all phonon and electron states have zero wavevectors $\mathbf{k}$ and $\mathbf{q}$. This is done for simplifying the notation and be consistent with the supercell calculations presented in the subsequent chapters. With the atoms at the equilibrium configuration the Kohn-Sham eigenvalues are given by:

$$\varepsilon_c = \langle \psi_c | \hat{H} | \psi_c \rangle, \quad (2.52)$$

where $\hat{H}$ and ψ_c are the unperturbed Kohn-Sham Hamiltonian and eigenstates related through Eq. (2.16).

As a result of the motion of the nuclei at finite temperatures, different time snapshots of the system will find the nuclei in different configurations, specified by the set of normal coordinates $\{x_\nu\}$. Therefore for an instantaneous configuration of the atoms we indicate the Kohn-Sham energies using the superscript x . The expansion of ε_c^x to second order in normal-mode coordinates is given by:

$$\varepsilon_c^x = \varepsilon_c + \sum_\nu \frac{\partial \varepsilon_c^x}{\partial x_\nu} x_\nu + \frac{1}{2} \sum_{\mu\nu} \frac{\partial^2 \varepsilon_c^x}{\partial x_\mu \partial x_\nu} x_\mu x_\nu + \mathcal{O}(x^3), \quad (2.53)$$

where the derivatives are evaluated at the equilibrium geometry. For the derivative coefficients we differentiate Eq. (2.52) with respect to the normal modes and make use of the Hellmann-Feynman theorem [98, 99] to obtain:

$$\frac{\partial \varepsilon_c^x}{\partial x_\nu} = \langle \psi_c | \frac{\partial \hat{H}}{\partial x_\nu} | \psi_c \rangle, \quad (2.54)$$

and

$$\frac{\partial^2 \varepsilon_c^x}{\partial x_\mu \partial x_\nu} = \langle \psi_c | \frac{\partial^2 \hat{H}}{\partial x_\nu \partial x_\mu} | \psi_c \rangle + \frac{1}{2} \left[\left(\left\langle \frac{\partial \psi_c}{\partial x_\nu} \left| \frac{\partial \hat{H}}{\partial x_\mu} \right| \psi_c \right\rangle + \left\langle \frac{\partial \psi_c}{\partial x_\mu} \left| \frac{\partial \hat{H}}{\partial x_\nu} \right| \psi_c \right\rangle \right) + \text{c.c.} \right], \quad (2.55)$$

where c.c. denotes the complex conjugate of the previous term in parentheses. The derivation of Eq. (2.55) is laborious and is left to Appendix B.5.

If we use the linear perturbative expansion of the KS eigenstates as in Eq. (B.19) and some straightforward manipulations we obtain for the electron-phonon coupling coefficient:

$$\frac{\partial^2 \varepsilon_c^x}{\partial x_\mu \partial x_\nu} = \frac{2}{l_\mu l_\nu} \left[h_{c\mu\nu} + \sum_{\beta}' \frac{g_{c\beta\nu} g_{\beta c\mu}}{\varepsilon_c - \varepsilon_\beta} \right], \quad (2.56)$$

where the primed summation indicates that we skip the term such that $\beta = c$. l_ν is the zero-point amplitude of the mode ν , defined in Eq. (A.6). To make contact with the standard definitions used in AH theory we introduced the linear electron-phonon matrix elements:

$$g_{\beta c\nu} = l_\nu \langle \psi_\beta | \frac{\partial V_{\text{KS}}}{\partial x_\nu} | \psi_c \rangle. \quad (2.57)$$

and the “Debye-Waller” electron-phonon matrix element [11, 14, 21, 69]:

$$h_{c\mu\nu} = \frac{1}{2} l_\mu l_\nu \langle \psi_c | \frac{\partial^2 V_{\text{KS}}}{\partial x_\mu \partial x_\nu} | \psi_c \rangle. \quad (2.58)$$

Here $\partial V_{\text{KS}} / \partial x_\nu$ stands for the variation of the Kohn-Sham potential with respect to the normal mode coordinate x_ν .

We now account for the temperature dependence of the band structure based on a heuristic argument [69]. Assuming that electrons follow the nuclei motion adiabatically and employing the harmonic approximation, then the probability to find the atoms in a configuration x is given by $\prod_\nu |\chi_{n_\nu}|^2$, where χ_{n_ν} are the single nuclear wavefunctions, introduced in Eq. (2.37). If we consider our system to be in thermal equilibrium at a finite temperature T , then the occupation of the quantum nuclear states is determined by the Gibbs distribution law, and the temperature dependence of

the Kohn-Sham energy in Eq. (2.53) is obtained from [69]:

$$\langle \varepsilon_c^x \rangle_T = \frac{1}{Z} \sum_{n_\nu} e^{\frac{-E_{n_\nu}}{k_B T}} \langle \chi_{n_\nu} | \varepsilon_c^x | \chi_{n_\nu} \rangle, \quad (2.59)$$

where $Z = \sum_{n_\nu} e^{\frac{-E_{n_\nu}}{k_B T}}$ is the partition function and k_B is the Boltzmann constant. This operation represents effectively a thermal average, where the sum over the quantum states is weighted by the customary Boltzmann factor $e^{\frac{-E_{n_\nu}}{k_B T}}$. In order to evaluate the thermal average we consider the action of the ladder operators on $|\chi_{n_\nu}\rangle$, shown in Eq. (A.7). After some straightforward manipulations, the temperature dependence of the electron energy levels within the AH theory is given by:

$$\Delta \varepsilon_{c,T} = \sum_{\nu} \frac{1}{2} \frac{\partial^2 \varepsilon_c}{\partial x_\nu^2} \sigma_{\nu,T}^2, \quad (2.60)$$

where:

$$\sigma_{\nu,T}^2 = (2n_{\nu,T} + 1) l_\nu^2, \quad (2.61)$$

represents the mean square displacement of the nuclei along a phonon mode ν at temperature T . The total electron-phonon coupling coefficient $\frac{\partial^2 \varepsilon_c^x}{\partial x_\nu^2}$ is given by:

$$\frac{\partial^2 \varepsilon_c^x}{\partial x_\nu^2} = \frac{2}{l_\nu^2} \left[\sum_{\beta}' \frac{|g_{c\beta\nu}|^2}{\varepsilon_c - \varepsilon_\beta} + h_{c\nu\nu} \right], \quad (2.62)$$

where the first and second terms in the square brackets represent the self-energy and Debye-Waller corrections to the KS energy ε_c .

The Feynman diagram in Fig. 2.3.5 shows the two contributions to the renormalisation of the electron energy to second order in normal coordinates. The electron self-energy (SE) diagram is also known as the Fan diagram [25, 100]. It involves two open circles representing that the electron-one phonon interaction is considered twice. The Debye-Waller (DW) diagram represents the electron-two phonon interaction, where the phonon line has the same starting and ending points [11, 21, 26, 70, 86]. Both

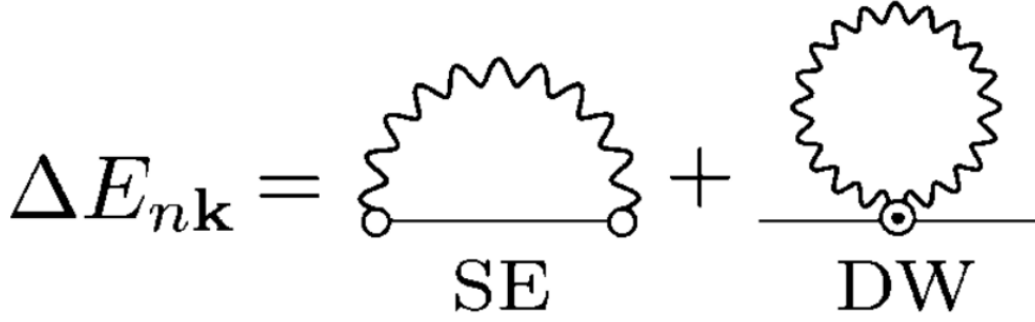


Figure 2.3.5: Feynman diagram showing the self-energy (or Fan) and Debye-Waller contributions to the energy level renormalisation. The wiggly and solid lines represents phonon and electron propagators, respectively. The open circles in the two diagrams represent the bare electron-phonon matrix element (SE) and the electron-two phonon matrix element (DW). Figure from Ref. [16].

terms can be derived from a diagrammatic analysis by considering only one-phonon processes [101]. The contribution of the self-energy term to the band gap renormalisation can be either positive or negative. This is reflected by the energy denominator of the first term appeared in Eq. (2.62) which can be of either sign. The Debye-Waller contribution [second term of Eq. (2.62)] to the energy correction of the gap is usually negative [102] leading to the decrease of the band gap energy. It is also possible that the two contributions have opposite sign leading to the partial cancellation of each other. In the following we use the example of silicon to analyse the SE and DW terms.

In Fig. 2.3.6 we show the zero-point Debye-Waller (green curve) and self-energy (red curve) contributions to the Eliashberg spectral function of the valence band maximum (a) and conduction band minimum (b) of silicon. The Eliashberg spectral function of a state with energy ε_c is defined as:

$$g^2 F_c(\omega, T) = \sum_{\nu} \frac{1}{2} \frac{\partial^2 \varepsilon_c}{\partial x_{\nu}^2} \sigma_{\nu, T}^2 \delta(\hbar\omega - \hbar\omega_{\nu}). \quad (2.63)$$

The above function represents the phonon density of states weighted by the electron-phonon renormalisation (self-energy + DW terms) calculated for each vibrational degree of freedom. The total of the two contributions (blue curve) shows that the two terms tend to cancel each other in the low energy part of the Eliashberg function. It

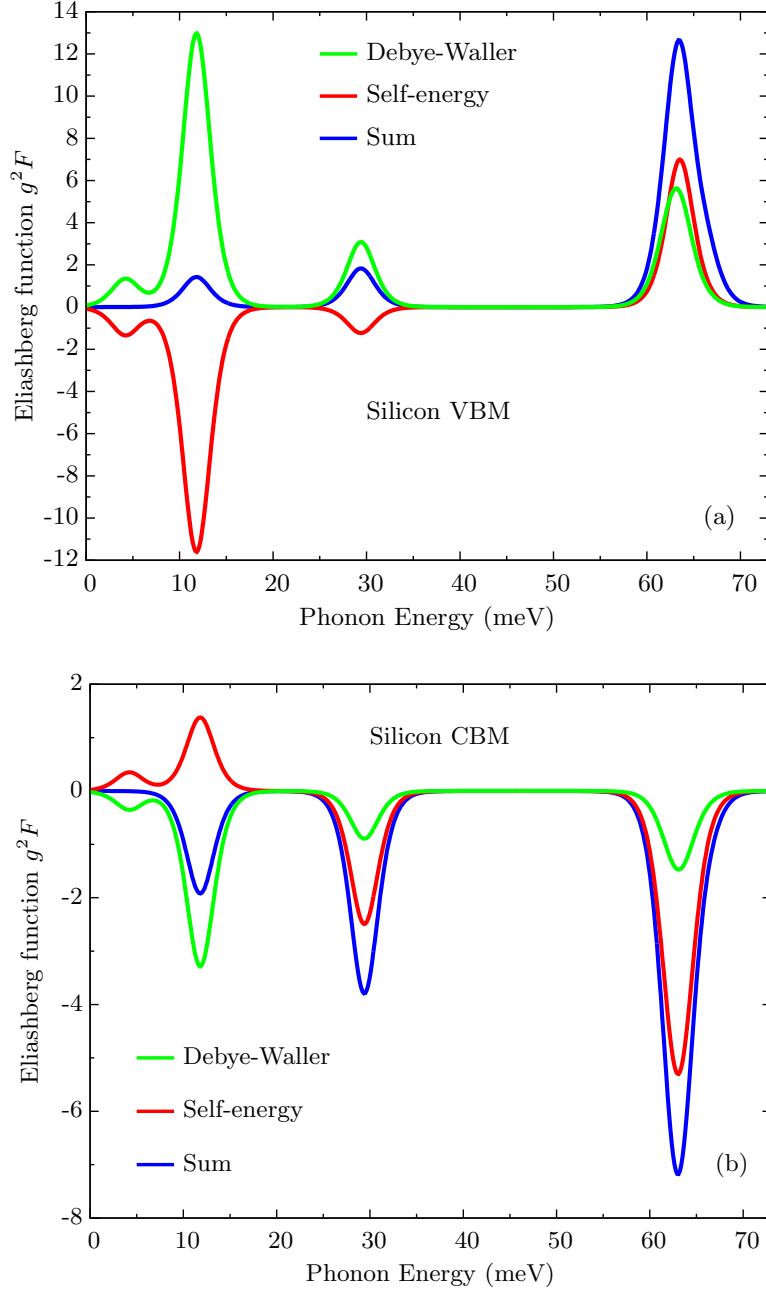


Figure 2.3.6: Debye-Waller (green) and self-energy or Fan (red) contributions to the Eliashberg spectral function calculated for the valence band maximum (a) and conduction band minimum (b) of silicon. The sum of the two contributions is represented by the blue line. Data from Ref. [103].

is also evident that the SE term changes sign with phonon energy for both the VBM and CBM. In contrast to the latter, the DW term calculated for the VBM/CBM remains positive/negative with phonon energy. The sum of the two terms shows that the zero-point corrections to the energy of the VBM and CBM are positive and negative, respectively, thereby closing the band gap. Given that the zero-point renormalisation

of the band gap is negative and $\sigma_{\nu,T}^2$ follows the Bose-Einstein distribution, then we can easily predict that the band gap will decrease with increasing temperature. This is indeed what has been calculated in Refs. [19, 93–96] using the AH theory and is the conventional picture observed in several semiconductors, known as “Varshni effect” [104], discussed in the next section. Some examples other than silicon include gallium arsenide [105], diamond [74], germanium [14], boron nitride [106, 107], and anatase TiO_2 [108].

2.3.5 Temperature dependence of the band gap: Varshni effect

The “Varshni effect” was named after Y. P. Varshni who studied the decrease of the band gap (E_g) with increasing temperature (T) observed in several semiconductors [104]. Varshni, using experimental data for Si, Ge, GaAs, InP and InAs, first

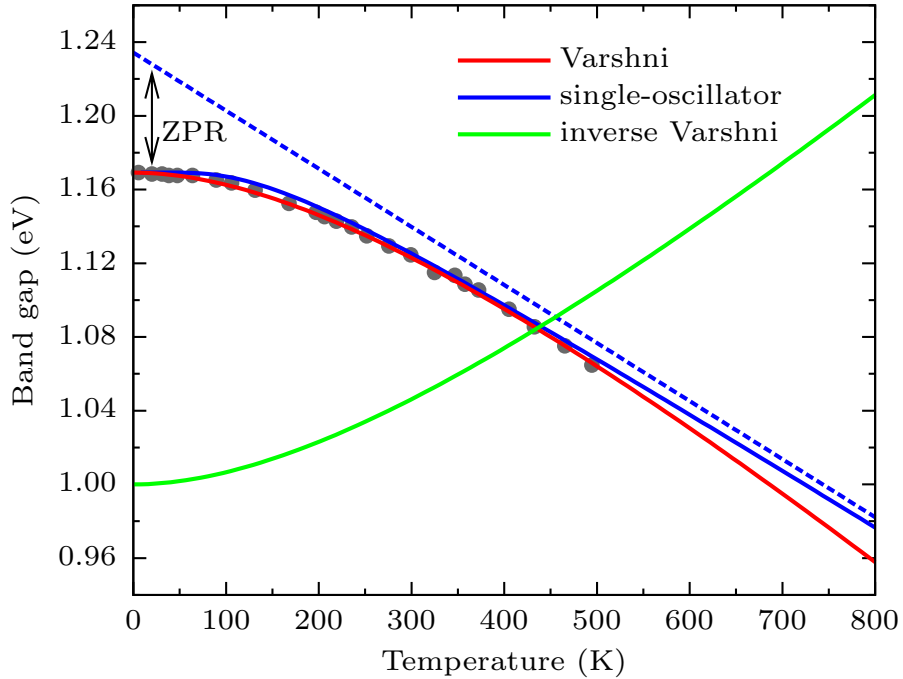


Figure 2.3.7: Temperature-dependent band gap of silicon. The solid red and blue lines are Varshni [Eq. (2.64)] and single-oscillator [Eq. (2.65)] fits to the experimental data from Ref. [109]. The dashed blue line is the high-temperature asymptote to the single-oscillator fit with slope $-2a_B/\Theta$ that intersects the vertical axis at E_B [see definitions in the main text]. The solid green line represents a hypothetical inverse Varshni behaviour using the fitting parameters α and β obtained from the fit with the solid red line, $E_g(0) = 1$ eV, and flip the sign of the second term in Eq. (2.64).

proposed the following *empirical* expression to examine this behaviour:

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta}, \quad (2.64)$$

where α and β are fitting parameters. At high temperatures ($T \gg 0$) the above relation depends linearly on T with gradient $-\alpha$, while for low temperatures ($T \rightarrow 0$) becomes quadratic in T . This is shown in Fig. 2.3.7 where the solid red line represents the fit of the Varshni relation to the temperature dependence of the band gap of silicon [109]. From the fit we obtain $\alpha = 4.6 \times 10^{-4} \text{ eV K}^{-1}$ and $\beta = 647 \text{ K}$. Here β is comparable to the Debye temperature of the solid [104]. We point out that the Varshni model incorrectly describes a T^2 dependence in the vicinity of $T = 0 \text{ K}$. In Ref. [110], it has been shown that in the low temperature limit, the band gap follows an asymptotic behaviour like T^4 . This is also discussed in Ref. [111].

An alternative *semi-empirical* expression to study the “Varshni effect” was suggested by L. Viña *et al* [112] who considered a single Einstein oscillator [113] to describe the temperature dependence of the band gap:

$$E_g(T) = E_B - a_B \left[1 + \frac{2}{\exp(\Theta/T) - 1} \right], \quad (2.65)$$

where E_B , a_B and Θ are fitting parameters representing the bare gap [113], the zero-point renormalisation (ZPR), and the effective temperature of the phonons, respectively. We note that the band gap at 0 K is related to the fitting parameters by $E_g(0) = E_B - a_B$. The particular choice of the expression in Eq. (2.65) is readily related to the dependence of the band gap on $\sigma_{\nu,T}^2 = (2n_{\nu,T} + 1) l_\nu^2$ and therefore on the Bose-Einstein occupation factors $n_{\nu,T}$. The single-oscillator fit to the experimental data of silicon [solid blue line in Fig. 2.3.7] yields $\Theta = 413 \text{ K}$, $a_B = 65 \text{ meV}$ and $E_B = 1.23 \text{ eV}$. Improved models for the extraction of the zero-point renormalisation (a_B) of semiconductors from the experimental data are proposed in Refs. [111, 113–115].

In Fig. 2.3.7 we also plot a hypothetical inverse Varshni behaviour (solid green

line) based on the fitting parameters found for silicon and changing the sign of α in Eq. (2.64). In contrast to the conventional picture found in several semiconductors, some others are known to exhibit a *band gap opening* with increasing temperature, which we call here the “*inverse Varshni effect*”. Examples of such materials include black phosphorus [116], copper chloride [117], lead telluride [118], indium nitride [119], rutile TiO₂ [120], and some perovskites [116, 121, 122].

The physical mechanisms driving the origin of the band gap opening with increasing temperature in metal-halide perovskites is poorly understood. A possible explanation to this behaviour can be found by determining the self-energy and Debye-Waller terms in these semiconductors, or by examining effects beyond the harmonic approximation, discussed in the next section. In this thesis we aim to elucidate the thermal effects that underpin the inverse Varshni behaviour in the orthorhombic and tetragonal phases of MAPbI₃ using a general approach. This is presented in Chapter 5.

2.3.6 Thermal expansion of the lattice and Fröhlich polar coupling

The vibrational motion of the nuclei is one of the main physical phenomena leading to the renormalisation of the energy levels at finite temperatures. The crucial assumption we use for the description of the vibrational motion is the harmonic approximation, which makes the *ab-initio* calculation of electron-phonon interactions a simplified task. The reason is that the harmonic phonon modes and energies remain constant with temperature and do not interact with other phonons. However, in many systems anharmonic effects play an important role in describing properly the thermodynamic properties [123, 124]. These systems are characterised by weak bonding interactions and nuclei oscillations of relatively large amplitudes, exceeding the range in which the assumption of a harmonic potential is valid. Therefore, the crystals undergo thermal expansion and phonon-phonon scattering processes leading to the temperature dependence of the vibrational degrees of freedom. This renormalisation of the normal modes causes an extra contribution to the temperature dependence of the band gap. In this the-

sis we take into account anharmonicity only in the case of lattice thermal expansion. This is done by calculating phonon frequencies within the quasi-harmonic approximation [64].

In the case of polar materials we need to consider the band gap correction arising from the Fröhlich electron-phonon coupling [25, 97, 125, 126]. The reason is that the displacement of the atoms along the longitudinal optical (LO) modes induces macroscopic electric fields which scatter the electrons leading to an extra renormalisation of the Kohn-Sham states. These electric fields are generated by the opposite movement of the atoms having different charge. In order to account for the polar coupling (electrons with LO phonons) in our results, we combine independent first principles calculations and the analytic expression [25, 97]:

$$\Delta\varepsilon_{c,T}^{\text{Fr}} = -\frac{\alpha\hbar\omega_{\text{LO}}}{\pi} \left\{ 2 \tan^{-1}(q_{\text{F}}a_{\text{LO}})[n_{\nu,T} + 1] + \ln \left| \frac{q_{\text{F}} - a_{\text{LO}}^{-1}}{q_{\text{F}} + a_{\text{LO}}^{-1}} \right| n_{\nu,T} \right\}. \quad (2.66)$$

For the derivation of this extra contribution to the renormalisation of the energy levels, one needs to employ second-order perturbation theory, the Fröhlich electron-phonon vertex given by [9, 127]:

$$g^{\text{Fr}}(q) = i \frac{\hbar\omega_{\text{LO}}}{q} \left(\frac{4\pi\alpha\alpha_{\text{LO}}}{\Omega} \right)^{1/2}, \quad (2.67)$$

and integrate over phonon wavevectors q up to a cutoff radius q_{F} . For a detailed derivation we refer the reader to Refs. [97, 127]. Here, the strength of the polar coupling is characterised by the dimensionless polaron constant $\alpha = \frac{e^2}{4\pi\epsilon_0} \frac{1}{\hbar} \left(\frac{1}{\kappa_{\infty}} - \frac{1}{\kappa_0} \right) \left(\frac{m^*}{2\hbar\omega_{\text{LO}}} \right)^{1/2}$ [9], where m^* is the effective mass of the carrier, ω_{LO} is the frequency of the LO phonon, and κ_{∞} , κ_0 are the high-frequency dielectric constant and static permittivity, respectively. The distance a_{LO} is defined as $\sqrt{\hbar/2m^*\omega_{\text{LO}}}$, similarly to the zero-point amplitude given in Eq. (A.6). The radius of integration q_{F} is used as a truncation parameter to avoid double counting of the Fröhlich contribution in a supercell calculation. For our calculations we take q_{F} equal to the radius of the Debye

sphere, i.e. the sphere whose volume is equal to the Brillouin zone of the system. We note that in the limit of $q_F \rightarrow \infty$ and at $T = 0$ K, Eq. (2.66) reduces correctly to the standard textbook formula $\Delta\varepsilon_{c,T}^{\text{Fr}} = -\alpha\hbar\omega_{\text{LO}}$ [9, 127, 128].

The difficulty of calculating the influence of the polar coupling on the band structure from first principles comes from the divergence of the Fröhlich electron-phonon matrix element in Eq. (2.67) for phonons with long wavelengths (i.e $q \rightarrow 0$). This means that a very fine and expensive q-grid is required to determine accurately the the Fröhlich electron-phonon matrix elements. This problem has been resolved in Refs. [125, 126] by accounting for the *generalised* Fröhlich vertex [see Eq. (4) in Ref. [125]] in conjunction with the Wannier-Fourier interpolation technique [86, 87]. Given the complexity and computational cost involved in calculating the correct Fröhlich vertex from first principles, we decide to use Eq. (2.66) to evaluate $\Delta\varepsilon_{c,T}^{\text{Fr}}$. This expression is expected to have similar accuracy to a correct *ab initio* treatment, since the *ab initio* electron-phonon matrix elements are found to be in good agreement with the Fröhlich model for small q [85].

2.3.7 Indirect optical absorption with nuclear dynamics: Williams-Lax theory

We have already introduced the concept of indirect transitions in Sec. 2.3.3. We have also discussed the limitations of the HBB theory and the need of a new theory to combine phonon-assisted optical absorption and the temperature dependence of the band structure. Here, we present a semiclassical approach to optical absorption, as originally proposed by Williams and Lax [22, 23].

In his short paper on 1951 [22], Williams proposed that an accurate evaluation of the optical spectra involves summing over the optical matrix elements between all the initial and final quantum vibrational levels. In order to simplify his computations, Williams made the reasonable assumption that the final states for transition, which have large quantum numbers, can be treated classically by the Bohr correspondence

principle. One year later, Lax [23] set up the mathematical framework of Williams' idea making a connection between the Franck-Condon principle and optical absorption in crystals. Recently, Patrick and Giustino [69], based on Williams and Lax foundations, proposed a unified theory of optical absorption for molecules and solids that incorporates energy-level renormalisation and phonon-assisted optical absorption.

Williams-Lax (WL) theory was successfully employed to calculate the photophysics of diamondoids [129] and cold lithium clusters [130] using stochastic methods. However, a systematic assessment of this quasiclassical approach to the optical absorption of solids is not available in the literature. In this thesis, we aim to present first principle calculations on the optical spectra of direct and indirect gap semiconductors within the framework of the WL theory.

At variance with the HBB point of view, in the WL approach electrons and phonons are described on the same footing, and optical excitations correspond to transitions between Born-Oppenheimer product states of electrons and quantum nuclei [22, 23]. The quantised final vibrational states are then replaced by a classical continuum, leading to an expression for the optical absorption which only involves the quantum nuclear wavefunction of the initial state [23]. This replacement can be justified using the adiabatic approximation. The temperature dependence is then obtained as a canonical average over the initial states of the system. Here, we present the main steps for the derivation of the WL expression for optical absorption. Lengthy derivations are attached to Appendix B.6. For an extended analysis we refer the reader to Ref. [69].

We consider electronic transitions between the initial and final Born-Huang states [65] $\Psi_\alpha(x, \mathbf{r})X_{\alpha n}(x)$ and $\Psi_\beta(x, \mathbf{r})X_{\beta m}(x)$, where x indicates the set of normal coordinates defined in Eq. (2.33). Employing the Fermi Golden Rule (Appendix B.3), we obtain for the transition rate:

$$\Gamma_{\alpha n \rightarrow \beta}(\omega) = \sum_m \frac{2\pi}{\hbar} |\langle X_{\alpha n} | P_{\alpha\beta}^x | X_{\beta m} \rangle|^2 \delta(E_{\beta m}^T - E_{\alpha n}^T - \hbar\omega), \quad (2.68)$$

where $P_{\alpha\beta}^x$ is the transition matrix element between the electronic states and the sum-

mation runs over the final vibrational states. To keep contact with the literature, we refer to this quantity as the Herzberg-Teller rate [131], because the optical matrix elements depend on the nuclear coordinates. The Herzberg-Teller rate is the starting point of the Williams-Lax theory [23].

It is apparent that for an extended system (solids), the number of possible transitions between all initial and final vibrational states scales combinatorially, making the calculation of the total Herzberg-Teller rate a formidable task. For this reason Williams and Lax introduce a classical approximation and replace the joint electron-nuclear energies $E_{\beta m}^T$ and $E_{\alpha n}^T$ by the corresponding adiabatic potential energy surfaces U_{β}^x and U_{α}^x , defined in Eq. (2.26). Using this approximation and the closure relation $\sum_m |X_{\beta m}\rangle \langle X_{\beta m}| = \mathbb{1}$, we can write for the transition rate [69]:

$$\Gamma_{\alpha n \rightarrow \beta}^{(\text{SC})}(\omega) = \frac{2\pi}{\hbar} \langle X_{\alpha n} | |P_{\alpha\beta}^x|^2 \delta(E_{\beta}^x - E_{\alpha}^x - \hbar\omega) | X_{\alpha n} \rangle, \quad (2.69)$$

where we have used that $U_{\beta}^x - U_{\alpha}^x = E_{\beta}^x - E_{\alpha}^x$. This classical approximation can be justified by assuming that the final states for transition have large quantum numbers [23], and thus, according to the Bohr correspondence principle, those can be treated as approximately classical continuous variables. That is, for large occupation numbers the probability density $P_{n_{\nu}}(x_{\nu}) = |\chi_{n_{\nu}}(x_{\nu})|^2$, where $\chi_{n_{\nu}}(x_{\nu})$ is given by Eq. (2.37), concentrates around the energy of the adiabatic PES. This can be understood schematically in Fig. 2.3.8, where the amplitude of the probability density decreases as the quantum number increases. Similarly, when many initial vibrational states are involved in the transitions, one can use the mean-value approximation and replace the joint electron-nuclear energy of the initial state with its classical counterpart. The rigorous justification of this classical approximation consists of neglecting the matrix elements that involve the kinetic energy operator. The proof of this is attached as Appendix B.6.

The temperature dependence of Eq. (2.69) is obtained by setting the initial electronic state to the ground state and performing a thermal average over the initial nuclear states of the system. By exploiting the harmonic approximation as well as the property

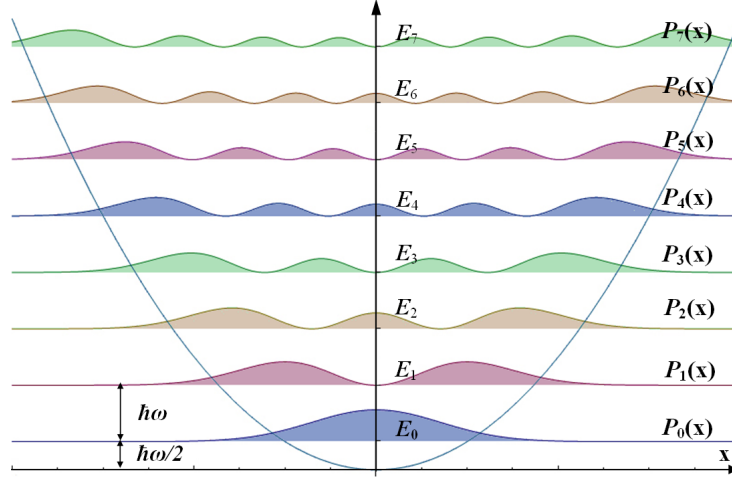


Figure 2.3.8: Energy quanta and probability distributions for the quantum harmonic oscillator. Figure extracted from Ref. [132].

of Hermite functions and Mehler’s formula [Eq. (B.43)] we obtain the semiclassical Franck-Condon [23] expression for the transition rate:

$$\Gamma_{0 \rightarrow \beta}^{(\text{SC})}(\omega; T) = \prod_{\nu} \int dx_{\nu} \frac{\exp(-x_{\nu}^2 / 2\sigma_{\nu, T}^2)}{\sqrt{2\pi}\sigma_{\nu, T}} |P_{0\beta}^x|^2 \delta(E_{\beta}^x - E_0^x - \hbar\omega). \quad (2.70)$$

For completeness we also include the derivation of the above equation in Appendix B.6. This expression is referred to as *semiclassical* because, although the transition energy is replaced by a classical continuum, the probability to find the system in the initial configuration x is described using quantum mechanics. In the harmonic approximation, this probability is simply given by a product of Gaussian functions, each of width $\sigma_{\nu, T}^2$.

Now it is natural to ask whether we can link the transitions between the adiabatic potential energy surfaces [Eq. (2.70)] to the transition rate between single electronic states [Eq. (2.43)] and thereby to DFT calculations. In the DFT language, the adiabatic PES is equivalent to the total Kohn-Sham energy E_{KS} given by Eq. (2.15). The ground state Kohn-Sham PES E_0^x corresponds to the case where the electrons occupy the lowest energy states (valence states) with the nuclei clamped in a configuration x . The excited Kohn-Sham PES E_{β}^x corresponds to the case where an electron makes a

transition from a valence state $|\psi_v^x\rangle$ to a conduction state $|\psi_c^x\rangle$, after its interaction with a photon. Therefore, in view of Eq. (2.70), we can replace E_0^x/E_β^x with $\varepsilon_v^x/\varepsilon_c^x$ and the $P_{0\beta}^x$ with the optical matrix element p_{uc}^x that couples the two states. A more rigorous argument to this replacement emerges by relating the total KS energy to the total energy of the band structure. This is done by adding and subtracting to Eq. (2.15) the term $\int d\mathbf{r} [\frac{1}{2}V_H(\mathbf{r}) + V_{xc}(\mathbf{r})]n(\mathbf{r})$ to obtain for the ground state PES [40]:

$$E_0^x = \sum_v^{occ} \varepsilon_v^x - \left[E_H^x + \int d\mathbf{r} V_{xc}^x(\mathbf{r})n^x(\mathbf{r}) - E_{xc}^x \right]. \quad (2.71)$$

If we excite an electron to a state higher in energy, then we can safely write $E_\beta^x - E_0^x = \lim_{N \rightarrow \infty} \varepsilon_c^x - \varepsilon_v^x$. This is justified for an extended system because the changes in the electron density, and hence in E_H^x , V_{xc}^x and E_{xc}^x , after the excitation will be negligible, as the number of electrons N is very large.

Using the above reasoning, Eq. (2.70), and the procedure in Appendix B.1, the imaginary part of the dielectric function at a finite temperature is obtained as:

$$\epsilon_2^{SC}(\omega; T) = \prod_\nu \int dx_\nu \frac{\exp(-x_\nu^2/2\sigma_{\nu,T}^2)}{\sqrt{2\pi\sigma_{\nu,T}^2}} \epsilon_2^x(\omega), \quad (2.72)$$

where, similarly to Eq. (2.44), the dielectric function evaluated with the nuclei frozen in configuration x is given by:

$$\epsilon_2^x(\omega) = 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{v,c} |p_{cv}^x|^2 \delta(\varepsilon_c^x - \varepsilon_v^x - \hbar\omega). \quad (2.73)$$

Here the polarisation vector $\hat{\mathbf{e}}$ has been dropped, by considering the isotropic average of the optical matrix elements over the photon polarisation directions. An intuitive interpretation of the Williams-Lax dielectric function in Eq. (2.72) is that in the adiabatic approximation the electronic and nuclear timescales are decoupled, and the measured absorption spectrum can be described as an ensemble average over instantaneous absorption spectra at fixed nuclear coordinates. Following this notion, the optical spec-

tra of diamondoids [129] and cold lithium clusters [130] were calculated using up to 10,000 and 100,000 configurations, respectively.

We expect that the sampling over many configurations will lead effectively to the sampling of the variations in the Kohn-Sham potential. In view of the form of the electron-phonon coupling coefficients in Eqs. (2.57) and (2.58), we expect that these changes in the Kohn-Sham potential will eventually cause the renormalisation of the band structure, as immediately derives from Eq. (2.60). We stress that at variance with the HBB and AH theories, in the Williams-Lax theory the dependence of the optical matrix elements and energy levels on the nuclear coordinates is included up to all orders. Therefore, we anticipate that calculations of optical spectra using Eq. (2.72) will capture single as well as multi-phonon processes.

As it has been mentioned before, in this thesis we aim to elucidate the applicability of the Williams-Lax theory in calculating optical spectra and band structure renormalisation in the case of solids. We also anticipate to develop a computational strategy for the efficient sampling of the configurational space. That is to calculate as few as possible configurations that would lead to the precise evaluation of the Williams-Lax expression. These and several physical aspects are presented in the next chapters, where our main results are discussed.

2.3.8 Summary

In Secs. 2.3.3 and 2.3.4, we have presented the HBB and AH theories for indirect optical absorption and energy level renormalisation of the band structure at finite temperatures. The latter effect is absent from *ab-initio* calculations of phonon-assisted optical spectra, highlighted in Sec. 2.3.3. In Sec. 2.3.7 we have presented a new formalism of the dielectric function, based on the WL theory, that can practically lead to the calculation of temperature-dependent optical spectra including energy level renormalisation. This will be demonstrated in Chapters 3 and 4 using a stochastic and a deterministic approach, respectively, for the *ab-initio* evaluation of the WL dielectric

function [Eq. (2.72)] for Si, C and GaAs. We have also seen in Sec. 2.3.4 that the AH correction to the band structure depends on the sum of two terms, the Debye-Waller and self-energy (or Fan) terms, whose signs and magnitudes can possibly lead to intriguing phenomena like the “inverse Varshni effect”, introduced in Sec. 2.3.5. However, the physical picture that determines the sign and magnitude of these two corrections has not been yet understood. In Chapter 5, we attempt to clarify this picture using the example of MAPbI₃. In Sec. 2.3.6, we have also discussed that despite the Debye-Waller and Fan contributions, in some cases we need to account for the extra renormalisation coming from the thermal lattice expansion, as well as from the Fröhlich polar coupling [Eq. (2.66)]. In Chapters 4 and 5 we present the influence of these corrections on the band gap of GaAs and MAPbI₃.

Chapter 3

Stochastic approach

3.1 Introduction

In this Chapter, we present a first-principles theory of phonon-assisted optical absorption in semiconductors and insulators which incorporates the temperature dependence of the electronic structure. In the first part, we concentrate the discussion on our main results as well as the physics involved. We show that the Hall-Bardeen-Blatt theory of indirect optical absorption and the Allen-Heine theory of temperature-dependent band structures can be derived from the Williams-Lax formalism by retaining only one-phonon processes. We demonstrate this method by calculating the optical absorption coefficient of silicon using an importance sampling Monte Carlo scheme, and we obtain temperature-dependent lineshapes and band gaps in good agreement with experiment. We also perform systematic convergence tests to assess the performance of our approach with respect to the size of the system and the number of configurations. In the second part of this Chapter we present all the computational details behind our calculations and technique. The technique developed here opens the way to predictive calculations of the optical properties of solids at finite temperature. The present study has been published in the journal of Physical Review Letters [[133](#)].

3.2 Results and discussion

3.2.1 Optical spectra of silicon at finite temperature

In insulators and semiconductors exhibiting indirect band gaps, the optical transitions near the fundamental edge require the absorption or emission of phonons in order to fulfil the crystal momentum selection rule. This mechanism and its formalism, developed by Hall, Bardeen, and Blatt (HBB), is discussed in Sec. 2.3.3. Even though this theory is well understood, it was not long ago that its first *ab-initio* implementation appeared in the literature [20]. Although the work of Ref. [20] reveals remarkable agreement for the indirect absorption spectra of silicon with experimental data, it does not come without drawbacks, since an empirical temperature-dependent correction is unavoidable to match the experimental absorption onsets. This is because the HBB theory does not take into account the temperature dependence of band structures.

In Sec. 2.3.4, we discussed the consistent theory of Allen and Heine (AH) [11, 70] for the temperature renormalisation of the energy levels. In recent years this approach was successfully demonstrated and improved within the framework of first-principles density-functional theory calculations [15, 16, 18, 92]. Given these recent advances it is natural to ask whether the HBB theory of indirect absorption and the AH theory of temperature-dependent band structures could be combined in a more general formalism, in view of fully predictive calculations of phonon-assisted optical processes at finite temperature.

In this section we show that the quasiclassical approach developed by Williams [22] and Lax [23] (WL) provides a unified framework for calculating optical absorption spectra of semiconductors, including indirect optical absorption and phonon-induced renormalisation on the same footing. Indeed we prove that the WL formalism for the dielectric function leads to the HBB and AH theories by neglecting electron-phonon interaction beyond first order. In order to demonstrate the power of the WL theory we employ a stochastic importance sampling Monte Carlo method [129] to calculate

from first principles the phonon-assisted optical absorption spectrum of silicon at several temperatures. At variance with the work of Ref. [20] no adjustable parameters are applied to our spectra. Our calculations for different temperatures exhibit very good agreement with experimental absorption coefficients. Using the Tauc's method we extracted temperature-dependent band gaps and we also find good agreement with experiment. Finally, we show that our calculations include correctly both direct and indirect transitions revealing optical absorption for a wide photon energy range.

The imaginary part of the WL temperature-dependent dielectric function is calculated using Eqs. (2.72) and (2.73). For simplicity we calculate the dielectric function within the independent-particle approximation, although the present formalism is general and can be used with any description of optical transitions at fixed nuclei. The importance sampling Monte Carlo integration technique in a BvK supercell is used to generate the nuclear configurations x . The temperature dependence of the atomic positions is determined by the width $\sigma_{\nu,T}^2$ of the Gaussian functions in Eq. (2.72). More information regarding this technique is given in Sec. 3.3.

In Fig. 3.2.1 we compare the optical absorption coefficient of silicon calculated from first principles with the experimental spectrum, both at 300 K. The absorption coefficient was obtained using Eq. (B.9). The spectrum calculated with the nuclei fixed in their equilibrium positions [dashed blue line in Fig. 3.2.1] exhibits an onset around 3.3 eV, corresponding to the direct $\Gamma'_{25v} \rightarrow \Gamma_{15c}$ transition in silicon. Here Γ indicates the states at centre of the Brillouin zone and the subscript stands for the irreducible representations of the cubic point group. The indirect absorption in the energy range 1.1–3.3 eV evidenced in experiments [80] is completely absent in this calculation. At variance with this result, our WL spectrum correctly captures phonon-assisted transitions [solid blue line in Fig. 3.2.1], and exhibits very good agreement with experiment without any adjustable parameters. Because we do not account for excitonic effects, the strength of the E'_0 and E_1 transitions [73] is underestimated in our calculations, as can be seen at energies around 3.3 eV in Fig. 3.2.1 [7]. The agreement

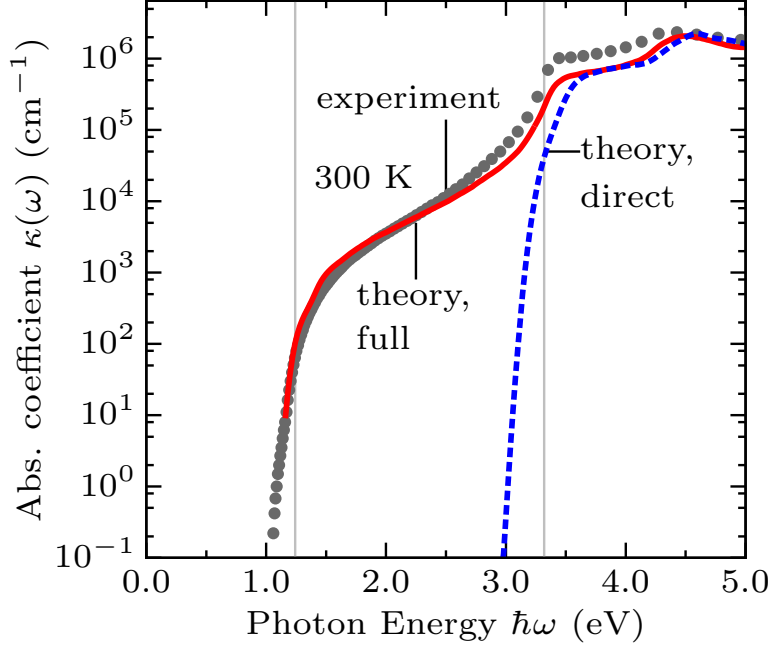


Figure 3.2.1: The absorption coefficient of bulk silicon at 300 K: calculation with the atoms clamped at their equilibrium positions (blue dashed line), calculation using the WL method [Eq. (2.72), blue solid line], and experimental data from Ref. [80] (grey filled discs). The thin vertical lines indicate the direct and indirect band gaps with nuclei in their equilibrium positions.

between theory and experiment in Fig. 3.2.1 remarkably extends over five orders of magnitude.

In order to elucidate the ability of the WL theory to predict correctly phonon-assisted optical transitions we employ time-independent perturbation theory (Appendix B.3) to describe the dependence of the optical matrix elements on the atomic positions. To first order in the atomic displacements we have:

$$p_{cv}^x = p_{cv} + p_{cv}^{(1)}, \quad (3.1a)$$

$$p_{cv}^{(1)} = \sum'_{\beta\nu} \left[\frac{p_{c\beta} g_{\beta\nu\nu}}{\varepsilon_v - \varepsilon_\beta} + \frac{g_{c\beta\nu} p_{\beta v}}{\varepsilon_c - \varepsilon_\beta} \right] \frac{x_\nu}{l_\nu}, \quad (3.1b)$$

where $g_{\beta\nu\nu}$ is the electron-phonon matrix element associated with the Kohn-Sham potential [Eq. (2.57)], and the primed summation denotes that the terms $\beta = c, v$ are skipped. To obtain the expression in Eq. (3.1b), we take the derivative of the linear expansion of the one-electron state in Eq. (B.19) with respect to x_ν and substitute for

$p_{cv}^{(1)} = \sum_{\nu} \frac{\partial p_{cv}}{\partial x_{\nu}} x_{\nu}$. The spectral range of indirect absorption corresponds to photon energies ($\hbar\omega$) less than the first direct band gap of silicon with energy $E_g^d = 3.3$ eV. Therefore, in the range $\hbar\omega \ll E_g^d$ direct transitions are not involved in optical absorption, and from Eq. (3.1) we can set $p_{cv} = 0$. By retaining only one-phonon processes, i.e. the term $p_{cv}^{(1)}$, and neglect the dependence of the electron energies on the nuclear coordinates, then Eqs. (2.72), (2.73) and (3.1b) yield:

$$\begin{aligned} \epsilon_2^{\text{HBB}}(\omega; T) &= 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{c\nu\nu'} \left| \sum_{\beta} \frac{p_{c\beta} g_{\beta\nu\nu'}}{\varepsilon_{\beta} - \varepsilon_{\nu}} + \frac{g_{c\beta\nu} p_{\beta\nu}}{\varepsilon_{\beta} - \varepsilon_{\nu} - \hbar\omega} \right|^2 \\ &\times \delta(\varepsilon_c - \varepsilon_{\nu} - \hbar\omega) (2n_{\nu,T} + 1), \end{aligned} \quad (3.2)$$

where we used the Gaussian integral of the form $\int dx \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}} x^2 = \sigma^2$ to carry out the integration. This expression is essentially the same as given by the conventional HBB theory of phonon-assisted optical absorption [Eq. (2.50)], and employed in the first-principles calculations of Ref. [20]. The only difference is that the HBB theory contains phonon energies $\pm\hbar\omega_{\nu}$ in the denominators and the Dirac delta functions, corresponding to phonon emission and absorption processes, respectively. In the WL theory these terms are neglected because we are in the adiabatic limit $\hbar\omega_{\nu} \ll \varepsilon_c - \varepsilon_{\nu}$. We note here that the same expression in Eq. (3.2) can be derived from time-dependent perturbation theory by considering a static phonon field. This amounts to neglecting the time dependence of the normal coordinates in Eq. (B.29).

In Fig. 3.2.2 we show that our present result agrees well with the indirect absorption spectrum of silicon calculated using the conventional HBB theory in Ref. [20].

At this point, we discuss the effect of the interference terms between direct and indirect transitions on the optical spectra, when we neglect the temperature dependence of the energy levels. We combine Eqs. (2.73) and (3.1a) to write an approximation to the dielectric function:

$$\epsilon_2^{(1)}(\omega) = 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{v,c} \left[|p_{cv}|^2 + p_{cv} p_{cv}^{(1)*} + p_{cv}^* p_{cv}^{(1)} + |p_{cv}^{(1)}|^2 \right] \delta(\varepsilon_c - \varepsilon_v - \hbar\omega). \quad (3.3)$$

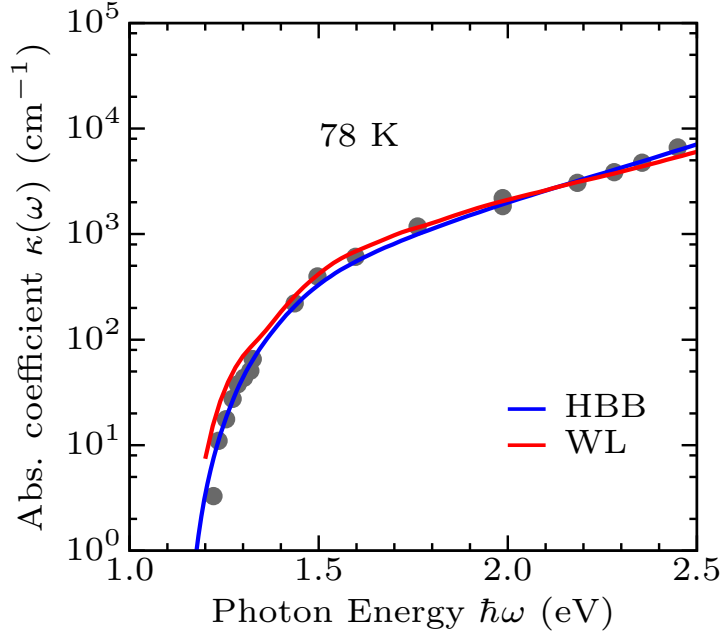


Figure 3.2.2: Comparison between the optical absorption spectrum of silicon calculated in the WL approach (red solid line), the spectrum calculated in Ref. [20] using the HBB theory (blue solid line), and the experimental data from Ref. [88] (grey filled discs). All spectra are for $T = 78$ K. The contributions to the optical matrix elements arising from the nonlocal components (see Appendix B.2) of the pseudopotential were not included in Ref. [20]. For consistency in this figure we calculated spectra *without* such contributions.

Here we obtain two cross-coupling terms, $p_{cv}p_{cv}^{(1)*}$ and $p_{cv}^*p_{cv}^{(1)}$, representing the mixing of direct and indirect optical transitions. These terms are analogous to those derived for the transition probability [see Eq. (B.27b)] starting from time-dependent perturbation theory. As in the case for the HBB theory, these terms will not contribute to optical absorption [Appendix B.4], since they are linear to normal coordinates and thereby do not survive the integration in Eq. (2.72). This is a direct consequence of neglecting the temperature dependence of the band structure as for the HBB theory. As we will discuss later in Sec. 4.4.3, interference terms of direct and indirect processes contribute to the full WL dielectric function.

Finally, in Fig. 3.2.3 we compare our calculated temperature dependence of the indirect optical absorption lineshape of silicon with experiment. We focus on the energy range 1.1–2.3 eV where the effect of excitonic spectral weight transfer on the dielectric function is negligible. Our calculations are in good agreement with experiment. In particular, the theoretical spectra capture both the smooth increase of the absorption

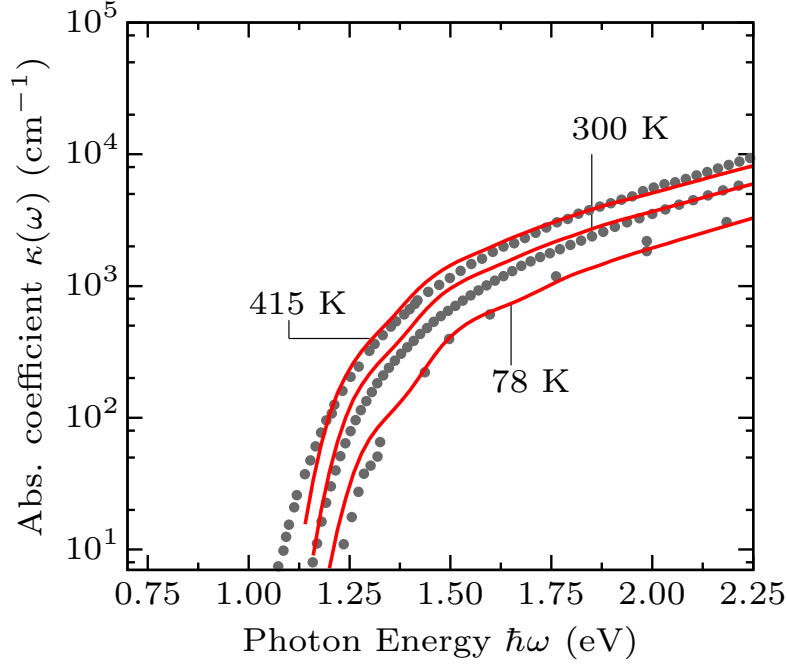


Figure 3.2.3: Temperature dependence of the absorption coefficient of silicon: WL theory (solid lines) and experimental data for 78 K [88], 300 K [80], and 415 K [134] (grey discs). The calculated spectra were broadened using Gaussians of width 30 meV, and truncated at the smallest excitation energy in order to avoid artefacts.

coefficient with temperature, and the concurrent redshift of the absorption onset. We emphasise that the observed redshift arises naturally in our calculations, in contrast with the HBB theory where this effect needs to be included empirically [20]. We stress that the slight loss of intensity near the indirect edge at the highest temperature [spectrum at 415 K in Fig. 3.2.3] results from the incomplete sampling of multi-phonon processes in our stochastic approach.

3.2.2 Temperature-dependent shift of the absorption onset

We have seen in the previous section that in order to make contact with the conventional HBB theory we need to neglect the temperature dependence of the electronic energy levels. However, to understand the complete effect of electron-phonon coupling in the WL approach we note that temperature enters the formalism in two ways: firstly in the Bose-Einstein factors $(2n_{\nu,T} + 1)$ in Eq. (3.2), as in the HBB theory. This term mainly modifies the absorption intensity. Secondly temperature enters in the electron-

phonon renormalisation of the band structure, leading to a temperature-dependent shift of the absorption onset. The latter contribution can be analysed by rewriting the energies inside the Dirac delta functions in Eq. (2.73) using time-independent perturbation theory. The result accurate to second order in the atomic displacements reads:

$$\varepsilon_c^x = \varepsilon_c + \sum_{\nu} g_{c\nu} \frac{x_{\nu}}{l_{\nu}} + \sum_{\mu\nu} \left[\sum'_{\beta} \frac{g_{c\beta\mu} g_{\beta c\nu}}{\varepsilon_c - \varepsilon_{\beta}} + h_{c\mu\nu} \right] \frac{x_{\mu} x_{\nu}}{l_{\mu} l_{\nu}}, \quad (3.4)$$

where we combine Eqs. (2.53)–(2.58). If we evaluate the thermal average of ε_c^x in Eq. (3.4) following the same prescription as in Eq. (2.59), we obtain (up to third order in the displacements):

$$\varepsilon_c^{\text{AH}}(T) = \varepsilon_c + \sum_{\nu} \left[\sum'_{\beta} \frac{|g_{c\beta\nu}|^2}{\varepsilon_c - \varepsilon_{\beta}} + h_{c\nu\nu} \right] (2n_{\nu,T} + 1). \quad (3.5)$$

In the first term inside the square brackets we recognise the Fan (or self-energy) electron-phonon renormalisation; the second term is the Debye-Waller renormalisation; both introduced in Sec. 2.3.4 and Fig. 2.3.5. Equation (3.5) represents precisely the AH theory of temperature-dependent band structures, discussed in Sec. 2.3.4, and explains the temperature shift of the indirect absorption lineshapes in Fig. 3.2.3.

From the calculated optical absorption spectra we can extract the temperature dependence of the indirect and direct band gaps of silicon, following the standard *experimental* procedure and using Tauc plots [72]. In fact, within the HBB theory, the absorption coefficient near the indirect edge goes like $\omega^{-1}(\hbar\omega - E_g \pm \hbar\omega_{\nu})^2$ [2, 10], therefore the indirect gap E_g is straightforwardly extracted from a linear fit to $\omega^{1/2}\kappa(\omega)^{1/2}$. As expected Fig. 3.2.4(a) shows that our calculated spectra follow a straight line when plotted as $\omega^{1/2}\kappa(\omega)^{1/2}$. The intercept of this line with the photon energy axis yields the indirect band gaps for each temperature, and the results are shown in Fig. 3.2.4(b) for two fitting ranges, 0–1.5 eV and 0–2 eV. Single-oscillator fits to our data using Eq. (2.65), and following Ref. [73], give a zero-point renormalisation of $a_B = 60$ –72 meV and an effective temperature $\Theta = 368$ –494 K for the two ranges consid-

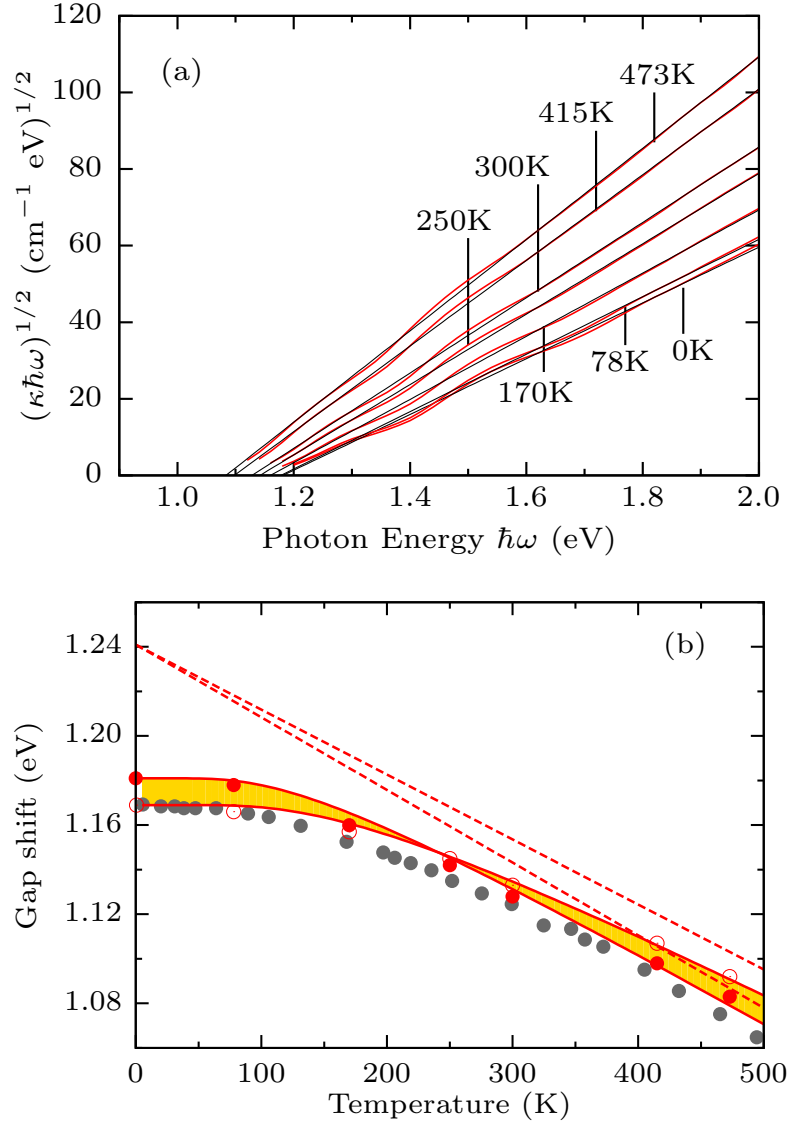


Figure 3.2.4: (a) Extraction of the temperature-dependent indirect band gap of silicon using lineshape analysis. The calculated $[\omega\kappa(\omega)]^{1/2}$ at each temperature are shown as red lines, and the corresponding linear fits as thin black lines. The intercepts of the straight lines with the horizontal axis give the band gaps. The linear fits were determined in the energy range 0–2 eV. (b) Temperature-dependent indirect band gap of silicon: the band gaps extracted from the lineshape analysis in (a) using linear fits in the ranges 0–2 eV and 0–1.5 eV are shown as red filled discs and open circles, respectively. Grey filled discs are experimental data from Ref. [109]. The solid lines are single-oscillator fits [Eq. (2.65)] to the calculated data, and the dashed lines are the corresponding high-temperature asymptotes. Fig. C.1.1 shows the sensitivity of the band gaps to the fitting range. The shading is a guide to the eye and can be taken as the uncertainty of the theoretical band gaps.

ered. These values are in good agreement with the experimental data 62 meV and 395 K [102], respectively, and those obtained in Sec. 2.3.5 by fitting the experimental data from Ref. [109] ($a_B = 65\text{meV}$ and $\Theta = 413\text{ K}$). We note here that our value for

the zero-point renormalisation carries some uncertainty due to the smearing applied on the spectra. A more precise methodology for determining the effect of zero-point motion on the band gap is presented in the next Chapter and Sec. 4.7.5.

In Appendix C and Fig. C.1.2 we show that the WL spectrum can also be used to extract the temperature dependence of the *direct* band gap of silicon using standard lineshape analysis of second-derivative spectra. Also in this case we obtain good agreement with experiment. Overall the agreement between theory and experiment in Figs. 3.2.1, 3.2.3, 3.2.4, and C.1.2 provides strong support to the validity of the WL theory for first-principles calculations of phonon-assisted optical absorption spectra.

3.3 Methods and computational setup

3.3.1 Computational details

Density functional theory calculations were performed by using the local density approximation, as parametrised by Perdew and Zunger [49, 135]. The interaction of valence electrons with the nucleus was taken into account by using norm-conserving pseudo potentials [136], available from Quantum ESPRESSO databases [32]. Kohn-Sham wavefunctions were expanded in a plane wave basis with a kinetic energy cutoff of 40 Ry. The optimised lattice parameter was found to be 5.40 Å.

We obtained vibrational frequencies and eigenmodes via the frozen-phonon method [137, 138]. This method involves self-consistent calculations in a supercell, in which the atoms are displaced from their equilibrium positions one by one. The changes in the forces are calculated to evaluate the interatomic force constant matrix elements as in Eq. (2.29). The dynamical matrix elements and consequently the vibrational frequencies and eigenmodes are obtained using Eqs. (A.1) and (A.3), respectively. For a converged calculation of the phonon density of states we need to use a large supercell size (see below). This leads to high computational costs, especially if we have to displace all the nuclei in the supercell and then calculate the forces. In order to minimise

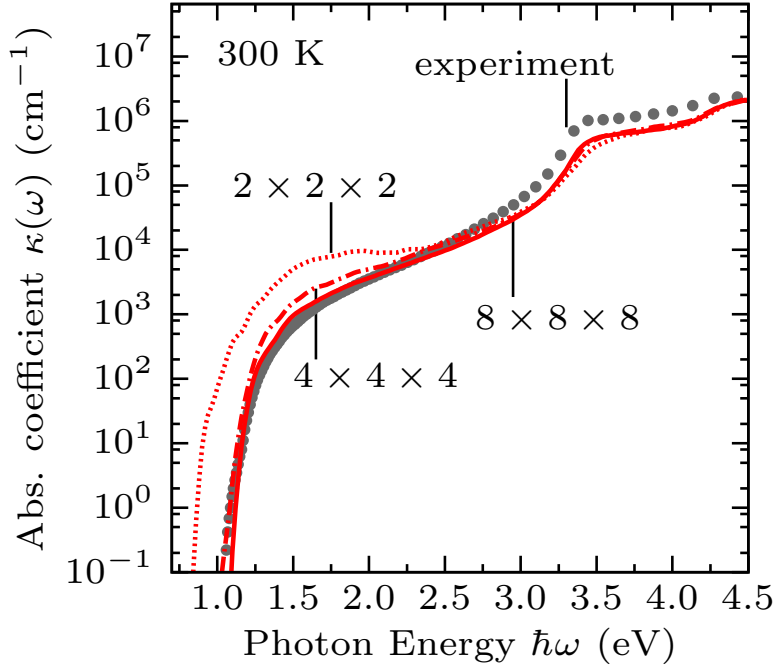


Figure 3.3.1: Numerical convergence of the calculated absorption coefficient of silicon with respect to the size of the BVK supercell (red lines), compared with the experimental data from Ref. [80] (grey filled discs). Dotted, dash-dotted, and solid lines refer to $2 \times 2 \times 2$, $4 \times 4 \times 4$, and $8 \times 8 \times 8$ BVK supercells, respectively. Larger supercells are expected to further improve the agreement between our calculations and experiment at a very fine scale. The calculations for $2 \times 2 \times 2$, $4 \times 4 \times 4$, and $8 \times 8 \times 8$ supercells were performed using 50, 20 and 5 atomic configurations, respectively.

the computational effort, we take into account the translational symmetry of the crystal and we displace only the atoms of one unit cell. The accuracy of the calculations is refined by taking averages between the interatomic force constant matrix elements that are related through the symmetry operations of the crystal's space group [139].

In Fig. 3.3.1 we show the convergence of the absorption spectrum with respect to the supercell size. Increasing the supercell size corresponds to accommodating phonons of larger wavelengths. The increase from $2 \times 2 \times 2$ (dotted line) to $4 \times 4 \times 4$ (dash-dotted) leads to conspicuous changes of the calculated absorption coefficient in the energy range 1–2.5 eV. The spectrum calculated for the $8 \times 8 \times 8$ (solid line) BVK supercell improves the agreement with experiment and exhibits small refinements compared to the $4 \times 4 \times 4$ case. To this end we note that the number of atomic configurations needed to obtain numerical convergence of the optical spectra is reduced with the size of the simulation cell.

The results presented in Figs. 3.2.1, 3.2.2, 3.2.3 and 3.2.4 were obtained using $8 \times 8 \times 8$ BvK supercells. We found that 5–8 atomic configurations are enough to converge the spectra at high/low temperature, respectively. Details about the sampling procedure of the configurations are presented in Sec. 3.3.3. We sampled the Brillouin zone of the supercell using 30 random points with weights determined by a Voronoi analysis [79]. In particular, for each point i of the grid, we assign weights equal to the volume including the set of points that are closer to i than any other grid point. The convergence test with respect to the Brillouin zone sampling is shown in Fig. C.1.4(a). For all calculated spectra we used a Gaussian broadening of 30 meV; in Fig. C.1.4(b) we show that even when using a broadening of only 1 meV the spectra remain essentially unaltered. Finally, in order to examine the effect of the lattice expansion on the absorption onset of our spectra, we calculated the variation of the band gap due to the thermal expansion of the lattice [140]. Figure C.1.5 shows that the change in the band gap is smaller than 5 meV up to 500 K, and can be neglected.

The optical matrix elements including the nonlocal components of the pseudopotential [77] were evaluated using Yambo [103]. A brief discussion about the extra contribution to the dielectric function arising from the nonlocal part of the pseudopotential is presented in Appendix B.2. Calculations with and without the nonlocal components of the pseudopotential are compared in Fig. C.1.3 of Appendix C. The WL optical spectra are obtained by first evaluating the dielectric function for each Cartesian direction, and then performing the isotropic average over the photon polarisations.

3.3.2 Violation of the f -sum rule

In order to address the band gap problem of DFT calculations [141] we used a scissor correction $\Delta = 0.75$ eV in *all* calculations, close to the value of Ref. [142] evaluated within the GW approximation [143, 144]. The GW approach corresponds to the lowest expansion of the electron self-energy [143], representing the one-particle Green's function (G) and the screened Coulomb interaction (W). The self energy con-

tains the many-body effects of exchange and correlation among electrons, and is calculated within the GW approximation to obtain the quasiparticle band structure [145]. In Ref. [145], it has been shown that a scissor operation on the band structure of silicon is a good approximation to the corresponding GW corrections.

The nonlocality of the scissor operator was taken into account in the oscillator strengths [77] via the renormalisation factors $(\varepsilon_c - \varepsilon_v)/(\varepsilon_c - \varepsilon_v + \Delta)$, thereby ensuring that the f -sum rule be correctly fulfilled. This operation is justified as follows.

If we neglect the nonlocal part of the Kohn-Sham potential we can show that the first moment of the spectrum is given by [146]:

$$\int_{-\infty}^{\infty} \omega \epsilon_2(\omega) d\omega = \frac{\pi}{2} \omega_p^2, \quad (3.6)$$

where this relation is known as the f -sum rule of the imaginary part of the dielectric function. Here ω_p stands for the plasma frequency [2]. If we combine Eqs. (2.44), (3.6), and replace ω with the expression in the delta function, then we obtain:

$$2 \frac{4\pi^2 e^2}{m_e^2 \Omega} \sum_{v,c} \frac{|p_{cv}|^2}{(\varepsilon_c - \varepsilon_v)^2} (\varepsilon_c - \varepsilon_v) = \frac{\pi}{2} \omega_p^2 \quad (3.7)$$

A rigid shift of the spectra amounts to replacing the energy of the conduction band ε_c in the delta function of Eq. (2.44) by $\varepsilon_c + \Delta$. This operation violates the f -sum rule, as it is straight forward to show that [6]:

$$\int_{-\infty}^{\infty} \omega \epsilon_2^{\text{rs}}(\omega) d\omega = 2 \frac{4\pi^2 e^2}{m_e^2 \Omega} \sum_{v,c} \frac{|p_{cv}|^2}{(\varepsilon_c - \varepsilon_v)^2} (\varepsilon_c - \varepsilon_v + \Delta) > \frac{\pi}{2} \omega_p^2 \quad (3.8)$$

where ϵ_2^{rs} stands for the rigidly shifted spectrum. By direct comparison with Eq. (3.9), it is immediate to understand that the rigid shift of the dielectric function leads to the *overestimation* of the f -sum rule. To treat this artefact, we multiply the square modulus

of the optical matrix elements $|p_{cv}|^2$ by the normalising factor:

$$f_{cv} = \frac{\varepsilon_c - \varepsilon_v}{\varepsilon_c - \varepsilon_v + \Delta}. \quad (3.9)$$

We should point out here, that f_{cv} is not a unique choice to treat this overestimation. For example, we can simply multiply the rigidly shifted spectrum by a constant equal to the ratio of the integrals in Eqs. (3.6) and (3.8). In the case of a single transition, that constant becomes identical to our initial choice in Eq. (3.9).

We also note that in the presence of nonlocal potentials, violations to the f -sum rule in Eq. (3.6) are to be expected. This derives immediately from the extra contribution to the optical matrix elements, shown in Eq. (B.14). Given that the effect of the nonlocal components leads to a small modification of the oscillator strengths, shown in Fig. C.1.3, we decided to neglect such contribution from the present analysis. The treatment of the violation of the f -sum rule in the case of nonlocal potentials warrants separate investigation [147].

In Fig. 3.3.2 we compare the absorption coefficients calculated without and with the scissor correction using the normalising factor, introduced above. It is seen that the correction yields *essentially* a rigid blue-shift of the entire spectrum, and does not introduce any artefacts. We can rationalise this observation as follows. The scissor correction modifies the imaginary part of the dielectric function in two ways: firstly by rigidly shifting the transition energies, and secondly by renormalising the oscillator strengths. This latter aspect is important since the scissor operator is a projection over the unoccupied bands, and its nonlocality (i.e. does not commute with the position operator) needs to be taken into account in order to obtain the correct dipole matrix element [77]. Let us indicate the dielectric function *without* scissor $\epsilon(\omega)$, and that *with* scissor as $\epsilon^s(\omega)$. Following the discussion above, in the independent-particle approximation the imaginary parts are related as follows: $\epsilon_2^s(\omega) = (1 + \Delta/\hbar\omega)\epsilon_2(\omega - \Delta/\hbar)$. Using the above relation we find that the absorption coefficients with/without scissor are related as follows: $\kappa^s(\omega) = [n(\omega - \Delta/\hbar)/n^s(\omega)]\kappa(\omega - \Delta/\hbar)$, where we have used

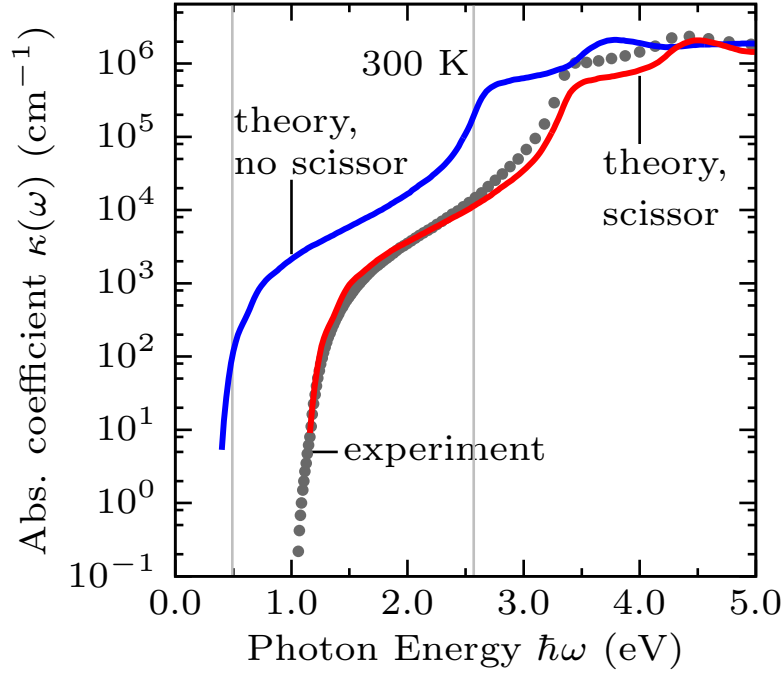


Figure 3.3.2: Calculated absorption coefficient of bulk silicon at 300 K with (red solid line) and without (blue solid line) the scissor operator. The experimental data are from Ref. [80] (grey filled discs). The thin vertical lines indicate the indirect and direct band gaps (without scissor), with nuclei in their equilibrium positions. The scissor operation yields *essentially* a rigid blue-shift of the calculated spectrum.

Eq. (B.8). In the present case, the ratio of the refractive indices with/without scissor is found to be approximately equal to unity in the photon energy range of interest (0.91–1.01 for energies up to 4.5 eV). This reflects the fact that below the direct gap the refractive index is dominated by the real part of the dielectric function, and that there is no sharp structure in $\epsilon_2(\omega)$ below the direct gap. As a result the absorption spectrum in the presence of scissor correction appears simply as a blue-shifted version of the unmodified spectrum, shown in Fig. 3.3.2.

3.3.3 Sampling procedure

In order to calculate the WL dielectric function [Eq. (2.72)], we averaged over the atomic configurations using the method of *Importance Sampling Monte Carlo* integration [129]. The estimator [148] of $\epsilon_2(\omega; T)$ in Eq. (2.72) was obtained using configurations generated from a random set of normal coordinates $\{x_\nu\}$, as determined from

the quantile function of the Gaussian distribution, $x_\nu = (2\sigma_{\nu,T}^2)^{1/2}\text{erf}^{-1}(2t - 1)$ [149]. In order to approximate the quantile function, the Beasley-Springer-Moro [150, 151] algorithm was used. The t values (one for each normal coordinate, $0 < t < 1$) were generated via Sobol low-discrepancy sequences [152] by skipping the first 1000 steps. This choice is justified by statistical arguments which are presented below.

The Monte Carlo estimator of the dielectric function in Eq. (2.72) is given by:

$$\tilde{\epsilon}_2(\omega; T) = \frac{1}{S} \sum_{s=1}^S \epsilon_2(\omega; x_T^s), \quad (3.10)$$

where x_T^s is the set of the normal mode coordinates distributed according to the importance function $\Pi_\nu^d G[x_\nu^s; \sigma_{\nu,T}]$ and S stands for the total number of the generated nuclear configurations. $G[u; \sigma]$ is a normalised Gaussian of width σ in the variable u and d indicates the dimensionality of the configurational space equal to the number of normal modes ($d = 3M$). The importance function represents a multivariate normal distribution, with the variables x_ν^s being independent to each other. A special characteristic of x_T^s is that the summation of the dimensionless phonon displacements, defined as $q^s = \sum_\nu (x_\nu^s / \sigma_{\nu,T})^2$, follows a χ^2 distribution with d degrees of freedom [153]. For large systems, the Central limit theorem states that the χ^2 distribution can be approximated by a normal distribution with mean d and variance $2d$ [154].

In Fig. 3.3.3 we show that indeed, the distribution of q^s for a million configurations, generated for a $4 \times 4 \times 4$ BvK supercell of the silicon unit cell, follows a normal distribution. For large systems ($d > 100$) we expect that the majority of the atomic configurations will have $q^s \simeq d$. This can be used as a useful measure to exclude any spurious configurations that may arise during the sampling procedure. We found that the first 10 configurations obtained from the sobol generator give q^s values that are not as evenly distributed as the rest ones, since they lie on the tails of the distribution shown in Fig. 3.3.3. As a precaution we decided to skip the first 1000 atomic configurations generated from the Sobol sequences. This choice avoids the extra computational cost needed to compensate for the artefacts that arise from any spurious configurations. As

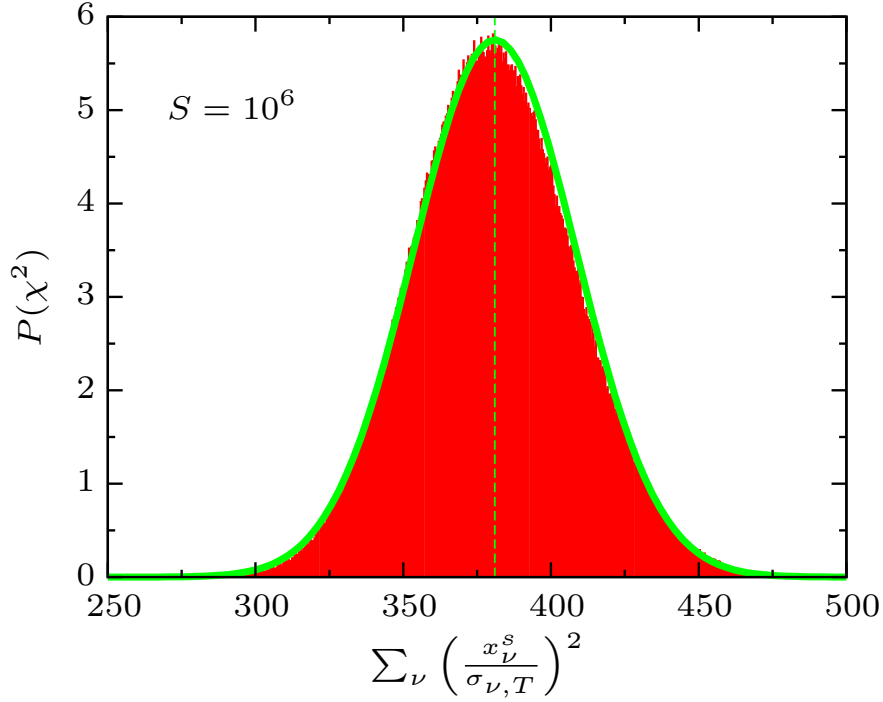


Figure 3.3.3: Distribution (red bars) of the summation of the dimensionless phonon displacements for a million configurations. The configurations were generated for a $4 \times 4 \times 4$ supercell of the silicon unit cell following the procedure described in the main text. The green curve represents a Gaussian function of the form: $\frac{1}{\sqrt{2\pi\nu}} \exp \left[-\frac{(x-\mu)^2}{2\nu} \right]$, where μ and ν stand for the mean and variance, which we take equal to d and $2d$, respectively. The green dashed line indicates the position of the mean of the Gaussian function, which we take equal to the number of phonon modes in the system ($d = 381$).

a sanity check we performed calculations on $4 \times 4 \times 4$ BvK supercells by skipping 0, 100 and 1000 configurations. We find that the Monte Carlo estimator of the dielectric function reaches convergence for 80, 25 and 20 configurations, respectively. The procedure of skipping some of the first points in the sobol sequences is also recommended in the documentation of statistical computational platforms [155]. To this end, we note that q^s can be used as a measure for *stratified* Monte Carlo integration [148] which is known to outperform [156], in some cases, the *crude* Monte Carlo estimator in Eq. (3.10).

3.4 Conclusions

In conclusion we have demonstrated a new theory of phonon-assisted optical absorption in solids, based on the Williams-Lax quasiclassical approximation, introduced in Sec. 2.3.7. This theory incorporates for the first time the quantum zero-point renormalisation of the electronic structure, and enables calculations of temperature-dependent optical spectra over a broad spectral range. At variance with the results of Ref. [20], our optical spectra encompass both indirect and direct transitions, demonstrating that our technique has the potential to be applied on a wide range of materials. Our present method depends on supercell calculations that can be computationally prohibitive if the sampling procedure requires a large set of nuclear configurations. Here, we observe that by increasing the supercell size less and less configurations are used to obtain convergence of the optical properties. This admits that our sampling approach requires further investigation to understand why it is more efficient as the supercell size increases. Although the present approach depends on supercell calculations and lacks the elegance of the standard phonon calculations using density-functional perturbation theory [64], it comes with important advantages: (i) at variance with HBB, the electron-phonon interaction is included to all orders, (ii) the method can be used with higher-level theories, such as hybrid functionals [157, 158], and the GW/Bethe-Salpeter method [159]. Finally, we stress that our stochastic approach can be implemented on top of any electronic structure package, because the only input information required is the phonon frequencies and eigenvectors. As we will address in Chapter 4, the present work can open the way to systematic calculations of optical spectra of semiconductors and insulators at finite temperature.

Chapter 4

One-shot calculation of optical spectra

4.1 Introduction

In Chapter 3, we presented a new theory for the *ab-initio* calculation of temperature-dependent optical spectra and band gaps in semiconductors and insulators. The zero-point renormalisation and the temperature dependence were included in our calculations by sampling the nuclear wavefunctions using a stochastic approach. Here, we show that the stochastic sampling can be replaced by fully deterministic supercell calculations based on a single optimal set of the atomic positions. In particular, we demonstrate that a single supercell calculation is enough to encompass quantum nuclear effects in both direct-gap and indirect-gap semiconductors. In order to demonstrate this methodology we calculate from first principles the phonon-assisted optical spectra and the renormalisation of critical point energies in three tetrahedral semiconductors: silicon, diamond and gallium arsenide. We obtain good agreement with experiment and with previous calculations. In this chapter we also establish the *formal* connection between the Williams-Lax theory of optical absorption [Sec. 2.3.7] and the theories of indirect absorption by Hall, Bardeen, and Blatt, [Sec. 2.3.3] and of temperature-dependent band structures by Allen and Heine [Sec. 2.3.4]. The present study has been published in the journal of Physical Review B [160].

The organisation of this Chapter is as follows: In Sec. 4.2 we present the motiva-

tion for developing the one-shot method. This is followed by three sections describing the theory underpinning our approach. In particular, in Sec. 4.3 we present how our choice of the optimal atomic configuration can lead to accurate one-shot calculations. That is, we prove that our optimal configuration yields the exact WL dielectric function in the limit of a very large supercell. In Sec. 4.4 we demonstrate the *formal* link between the WL theory of temperature-dependent optical spectra, the AH theory of temperature-dependent band structures, and the HBB theory of indirect optical absorption. In Sec. 4.5 we show how experimental procedures can be used to extract the band gap using WL optical spectra. In the second part of this chapter we present our results. In Sec. 4.6 we outline the ‘one-shot’ procedure for evaluating the WL expression in Eq. (2.72) using a single atomic configuration. In order to emphasise on the simplicity and effectiveness of the formalism we show our main results for the optical absorption spectra of silicon, diamond, and gallium arsenide. We also extend the concepts of Sec. 4.3 by showing that it is possible to deterministically select further atomic configurations in order to control and systematically reduce the error resulting from the configurational averaging. In Sec. 4.7 we present our calculations of temperature-dependent band gaps for silicon, diamond, and gallium arsenide. Section 4.8 reports all computational details of the calculations presented in this Chapter. In Sec. 4.9 we summarise our key findings. Lengthy formal derivations and further technical details are left to Appendices D.1-D.5.

4.2 From stochastic to deterministic: Motivation

In this section we present the *key observation* that will lead us to the development of an efficient deterministic approach for the calculation of the Williams-Lax dielectric function using a single configuration of the nuclei.

The two main disadvantages of the WL method are: (i) the calculations require the use of supercells in order to accommodate phonon wavevectors within the first Brillouin zone. (ii) The evaluation of expectation values over the nuclear wavefunc-

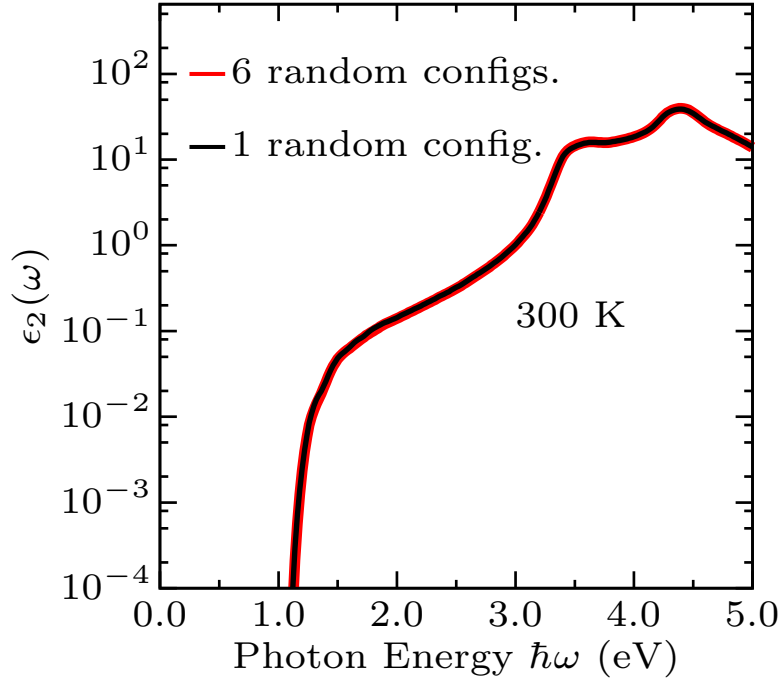


Figure 4.2.1: Sensitivity of the calculated imaginary part of the WL dielectric function of silicon to the number of nuclear configurations used for evaluating the Monte Carlo estimator. The thin black line and the thick red line correspond to averages over 1 and 6 random configurations, respectively. These calculations refer to $8 \times 8 \times 8$ BVK supercells and 300 K.

tions requires calculations for many nuclear configurations. In Ref. [129] and our study in Chapter 3, the latter issue was addressed by using a stochastic approach based on importance-sampling Monte Carlo integration. In fact, we found that 5–8 atomic configurations of $8 \times 8 \times 8$ BVK supercells are sufficient to obtain convergence of the Monte Carlo estimator of the dielectric function [Eq. (3.10)], and that the total number of configurations needed is reduced upon increasing the size of the simulation cell.

Surprisingly, Fig. 4.2.1 shows that even using one random atomic configuration (thin black line), the spectrum is in good agreement with the converged one calculated for 6 random atomic configurations (thick red line). We confirm that the spectra calculated for each of the 6 random atomic configurations reproduce similar agreement. This shows that the stochastic approach employed in Chapter 3 is remarkably efficient in sampling the vibrational phase space, to the point that the WL dielectric function can be calculated using a *single configuration* of the nuclei.

Motivated by this unexpected observation, we decide to investigate in more detail

in order to provide an explanation for the efficiency of our stochastic approach, and if possible to determine the conditions under a *single set* of nuclear coordinates can lead to the accurate evaluation of temperature-dependent optical properties. This is one of the main challenges of our study, which we encounter in the next section.

4.3 Formal justification for the optimum configuration

In this section we provide the rationale for the choice of a single atomic configuration to calculate the WL dielectric function [Eq. (2.72)]. We start from a heuristic argument, and then we provide a formal justification in Secs. 4.3.1 and 4.3.2.

In the WL theory the imaginary part of the dielectric function of a solid at the temperature T is given by:

$$\epsilon_2(\omega; T) = Z^{-1} \sum_n \exp(-E_{0n}/k_B T) \langle \epsilon_2^x(\omega) \rangle_n. \quad (4.1)$$

This expression can be obtained following the same procedure as for Eq. (B.41) and constitutes an alternative to the Williams-Lax dielectric function, before employing the harmonic approximation. Each expectation value $\langle \dots \rangle_n$ is taken with respect to the quantum nuclear state with energy E_{0n} , evaluated in the Born-Oppenheimer approximation. After exploiting the harmonic approximation, Eq. (4.1) leads to Eq. (2.72) which we rewrite here for convenience:

$$\epsilon_2^{\text{SC}}(\omega; T) = \prod_{\nu} \int dx_{\nu} \frac{\exp(-x_{\nu}^2/2\sigma_{\nu,T}^2)}{\sqrt{2\pi\sigma_{\nu,T}^2}} \epsilon_2^x(\omega). \quad (4.2)$$

The configurational average appearing in Eq. (4.2) was evaluated in Chapter 3 (see Sec. 3.3.3), using the importance-sampling Monte Carlo integration technique [129]. More specifically, the Monte Carlo estimator of the integral [Eq. (3.10)] was evaluated by averaging over a set of atomic configurations in a Born-von Kármán supercell. Each configuration in the set was generated according to the importance function

$\exp(-x_\nu^2/2\sigma_{\nu,T}^2)/\sqrt{2\pi}\sigma_{\nu,T}$. In Chapter 3 it was remarked that, in the case of the optical spectrum of silicon, < 10 random samples were sufficient in order to converge the integral in Eq. (4.2). Furthermore, in Sec. 4.2, we have shown that calculations performed using a *single* sample are in remarkable agreement with fully-converged calculations [see Fig. 4.2.1]. Based on these observations, we proceed to explain why the stochastic evaluation of Eq. (4.2) requires less samples as the size of the supercell increases.

4.3.1 Heuristic approach

According to Eq. (4.2), the WL dielectric function can be interpreted as the average of $\epsilon_2^x(\omega)$ over $3M$ standard normal random variables $x_\nu/\sigma_{\nu,T}$ [see Eq. (3.10)]. Let us consider the sum of the squares of these variables, $q^2 = \sum_\nu (x_\nu/\sigma_{\nu,T})^2$, as in Fig. 3.3.3. The random variable q^2 follows by construction the χ^2 distribution [153]. Owing to the central limit theorem, the χ^2 distribution tends to a normal distribution for $M \rightarrow \infty$. More specifically, we have already seen that in the limit of large M the variable $(q^2 - 3M)/(6M)^{1/2}$ follows a standard normal distribution. As a result, as M increases, the variable q^2 becomes strongly peaked at M , with a standard deviation $(6M)^{1/2}$ [154]. As a sanity check, in Sec. 3.3.3, we verified these limits numerically by generating one million random atomic configurations for a $4 \times 4 \times 4$ supercell of diamond [see Fig. 3.3.3]. Based on these considerations, we infer that for a large number of atoms M the integration in Eq. (4.2) is dominated by atomic configurations such that $\sum_\nu (x_\nu/\sigma_{\nu,T})^2 = 3M$. This same conclusion can alternatively be reached by rewriting the integral in Eq. (4.2) as the product of an integral over the ‘radial’ variable q , and an integral over a generalised ‘angular’ variable which runs over the $(3M-1)$ -dimensional sphere of radius q .

In the absence of information about the electron-phonon coupling constants of each vibrational mode, we must assume that all modes are equally important in the evaluation of the integral in Eq. (4.2). Therefore the most representative sets of coordinates

for evaluating the integral in Eq. (4.2) are those satisfying the condition $x_\nu/\sigma_{\nu,T} = \pm 1$ with $\nu = 1, \dots, 3M$. This is precisely what we observed in the importance-sampling Monte Carlo calculations reported in Fig. (3.3.3). A similar conclusion was reached in Ref. [96], where the concept of “thermal lines” was introduced. Here, we do not follow up on the idea of thermal lines since, as we prove below, there exists *one* atomic configuration which yields the exact temperature-dependent dielectric function in the limit of large M . If we were to choose a single configuration to evaluate the integral in Eq. (4.2), in absence of information about the electron-phonon couplings the least-biased choice would correspond to taking random signs for each normal coordinate. This reasoning formed the *heuristic* basis for the choice of the single atomic configuration, discussed in the following section.

4.3.2 Formal proof

We now proceed to demonstrate that, indeed, there exist an optimal configuration for evaluating Eq. (4.2) which will be employed for the one-shot calculation of temperature-dependent optical spectra. To this aim we perform a Taylor expansion of $\epsilon_2^x(\omega)$ in the variables x_ν , and then evaluate each individual integral $\int dx_\nu$ in Eq. (4.2) analytically. The result is:

$$\epsilon_2(\omega; T) = \epsilon_2(\omega) + \frac{1}{2} \sum_{\nu} \frac{\partial^2 \epsilon_2^x(\omega)}{\partial x_\nu^2} \sigma_{\nu,T}^2 + \mathcal{O}(\sigma^4). \quad (4.3)$$

In this expression $\epsilon_2(\omega)$ denotes the dielectric function evaluated for nuclei clamped in their equilibrium positions, and the term $\mathcal{O}(\sigma^4)$ is a short-hand notation to indicate all terms of the kind $\sigma_{\nu,T}^4$ and higher powers.

We now consider the dielectric function calculated with the nuclei fixed in the positions specified by the following set of nuclear coordinates:

$$x^{1C} = \{+\sigma_{1,T}, -\sigma_{2,T}, \dots, +\sigma_{3M-1,T}, -\sigma_{3M,T}\}, \quad (4.4)$$

where the vibrational modes are sorted in ascending order with respect to their frequencies, and, in the first instance, we assume that M is even. We denote this function by $\epsilon_2^{1C}(\omega; T)$, with “1C” standing for “one configuration”. Another Taylor expansion in the normal mode coordinates yields:

$$\begin{aligned}
 \epsilon_2^{1C}(\omega; T) = & \epsilon_2(\omega) + \sum_{\nu} (-1)^{\nu-1} \frac{\partial \epsilon_2^x(\omega)}{\partial x_{\nu}} \sigma_{\nu, T} \\
 & + \frac{1}{2} \sum_{\nu \mu} (-1)^{\nu+\mu-2} \frac{\partial^2 \epsilon_2^x(\omega)}{\partial x_{\nu} \partial x_{\mu}} \sigma_{\nu, T} \sigma_{\mu, T} \\
 & + \frac{1}{6} \sum_{\nu \mu l} (-1)^{\nu+\mu+l-3} \frac{\partial^3 \epsilon_2^x(\omega)}{\partial x_{\nu} \partial x_{\mu} \partial x_l} \sigma_{\nu, T} \sigma_{\mu, T} \sigma_{l, T} \\
 & + \mathcal{O}(\sigma^4).
 \end{aligned} \tag{4.5}$$

By comparing Eqs. (4.3) and (4.5) we see that $\epsilon_2^{1C}(\omega; T)$ and $\epsilon_2(\omega; T)$ do coincide up to $\mathcal{O}(\sigma^4)$ if the following conditions hold: (i) the summations on the first and third lines of Eq. (4.5) vanish; (ii) all terms $\nu \neq \mu$ in the second line of the same equation vanish.

In general the conditions (i) and (ii) do not hold, therefore calculations of $\epsilon_2^{1C}(\omega; T)$ and $\epsilon_2(\omega; T)$ will yield very different results. However, these conditions are fulfilled in the limit $M \rightarrow \infty$ because of the choice of the signs that appear in Eq. (4.4), as we show in the following. To this aim let us consider the summation on the first line of Eq. (4.5). We focus on two successive terms in the sum, ν and $\nu + 1$. Assuming a vibrational density of states (vDOS) which is nonvanishing up to the highest vibrational frequency, when $M \rightarrow \infty$, then $\omega_{\nu+1} - \omega_{\nu} \rightarrow 0$, therefore these modes are effectively degenerate, and hence must exhibit the same electron-phonon coupling coefficients. Under these conditions we can write:

$$\begin{aligned}
 & (-1)^{\nu-1} \frac{\partial \epsilon_2^x(\omega)}{\partial x_{\nu}} \sigma_{\nu, T} + (-1)^{\nu+1-1} \frac{\partial \epsilon_2^x(\omega)}{\partial x_{\nu+1}} \sigma_{\nu+1, T} \\
 & \simeq \frac{\partial \epsilon_2^x(\omega)}{\partial x_{\nu}} \sigma_{\nu, T} (-1)^{\nu-1} [1 + (-1)] = 0.
 \end{aligned} \tag{4.6}$$

4.3. FORMAL JUSTIFICATION FOR THE OPTIMUM CONFIGURATION

The same reasoning can be used for every pair of vibrational modes $(\nu, \nu + 1)$ that appear in the first line of Eq. (4.5). In the case where M is even, then the sum in the first line reduces to zero. If M is odd, only one mode survives, but its contribution is negligibly small for $M \rightarrow \infty$. Let us now consider that the vDOS exhibits discontinuities. In this case, the above reasoning remains valid by considering separately the phonon frequency ranges where the vDOS is nonzero. This completes the proof that the sum in the first line of Eq. (4.5) vanishes in the limit of a large system.

In view of the third line of Eq. (4.5), the summation can be analysed along the same lines, after noticing that we can rearrange as follows:

$$\sum_{\nu} \left[\frac{1}{6} \sum_{\mu l} (-1)^{\mu+l-3} \frac{\partial^3 \epsilon_2^x(\omega)}{\partial x_{\nu} x_{\mu} x_{\lambda}} \sigma_{\nu,T} \sigma_{\mu,T} \sigma_{l,T} \right] (-1)^{\nu}. \quad (4.7)$$

Also in this case we can consider any pair of successive eigenmodes ν and $\nu + 1$ and repeat the reasoning made above for the first line of Eq. (4.5). The result is that for $M \rightarrow \infty$ the entire sum must vanish.

We now consider the second line of Eq. (4.5). The sum of the terms with $\nu \neq \mu$ must vanish as we approach the limit of a large number of vibrational degrees of freedom, $3M$. In fact, the second derivatives $\partial^2 \epsilon_2^x(\omega) / \partial x_{\mu} \partial x_{\nu}$ and $\partial^2 \epsilon_2^x(\omega) / \partial x_{\mu} \partial x_{\nu+1}$ enter the expression with different signs, and hence their contribution vanishes for $M \rightarrow \infty$. On the other hand, when $\nu = \mu$, two successive terms contribute with the same sign, yielding $2 \frac{1}{2} \partial^2 \epsilon_2^x(\omega) / \partial x_{\nu}^2$. These contributions lead seamlessly to the second term on the r.h.s. of the exact expansion of the WL dielectric function, shown in Eq. (4.3).

If we combine together Eqs. (4.3)-(4.7) and the above discussion, we demonstrate that our single-configuration dielectric function, $\epsilon_2^{1C}(\omega; T)$, and the exact WL dielectric function, $\epsilon_2(\omega; T)$, do coincide to $\mathcal{O}(\sigma^4)$ for $M \rightarrow \infty$. We emphasise that the same reasoning can be generalised to all orders in $\sigma_{\nu,T}$, and hence the following general statement holds true:

In the limit of a large supercell the dielectric function evaluated with the nuclei clamped in the configuration determined by Eq. (4.4) approaches the WL dielectric function in Eq. (4.2).

In mathematical notation we can write:

$$\lim_{M \rightarrow \infty} \epsilon_2^{1C}(\omega; T) = \epsilon_2(\omega; T). \quad (4.8)$$

This result forms the basis for the methodology presented in this Chapter. The accurate procedure of calculating optical spectra using the optimal configuration proposed in Eq. (4.4) and convergence tests for Si, C, and GaAs are reported in Sec. 4.6.1.

4.4 Link between the Williams-Lax, Allen-Heine, and Hall-Bardeen-Blatt theories

In this section we present a rigorous proof for the relation between the Williams-Lax (WL) [22, 23], the Hall, Bardeen, and Blatt (HBB) [12], and the Allen-Heine theory [11]. In Sec. 3.2.2 we have shown that the AH theory of temperature-dependent band structures can alternatively be derived from the WL theory by neglecting the optical matrix elements. Using a separate approach we have also shown that the adiabatic limit of the HBB theory of indirect optical absorption can be derived from the WL theory by retaining only one-phonon processes and neglecting the dependence of the electronic energy levels on the atomic positions. Here, we present a more rigorous derivation that leads naturally the WL dielectric function [Eq. (2.72)] to an expression of optical absorption that contains both the HBB, and the AH theory. This constitutes one of the *most important* findings of this thesis and will be analysed in the following.

In the first part of this section we refer to some of the main equations encountered in the previous chapters so that we keep the discussion compact. In the rest, we only

4.4. LINK BETWEEN THE WILLIAMS-LAX, ALLEN-HEINE, AND HALL-BARDEEN-BLATT THEORIES

present our main results, leaving the mathematical details to Appendices D.1 and D.2.

As discussed in Sec. 2.3.3, the HBB theory describes indirect optical absorption by means of time-dependent perturbation theory, and the final expression [see Eq. (2.50)] involves the momentum matrix elements evaluated for the nuclei clamped in their equilibrium positions, p_{cv} , and the linear electron-phonon matrix elements, $g_{c\beta\nu}$, given by Eq. (2.57). In order to make these quantities explicit in Eq. (2.73), we expand the momentum matrix elements p_{cv}^x to first order in the atomic displacements, as in Eq. (3.1), and the energies ε_c^x to second order in the displacements, as in Eq. (3.4). For convenience, we rewrite these expressions here:

$$p_{cv}^x = p_{cv} + \sum_{\nu\beta}' \left[\frac{p_{c\beta} g_{\beta\nu\nu}}{\varepsilon_\nu - \varepsilon_\beta} + \frac{g_{c\beta\nu} p_{\beta\nu}}{\varepsilon_c - \varepsilon_\beta} \right] \frac{x_\nu}{l_\nu} + \mathcal{O}(x^2), \quad (4.9)$$

and

$$\varepsilon_c^x = \varepsilon_c + \sum_{\nu} g_{cc\nu} \frac{x_\nu}{l_\nu} + \sum_{\mu\nu\beta}' \left[\frac{g_{c\beta\mu} g_{\beta c\nu}}{\varepsilon_c - \varepsilon_\beta} + h_{c\mu\nu} \right] \frac{x_\mu x_\nu}{l_\mu l_\nu} + \mathcal{O}(x^3), \quad (4.10)$$

with $h_{c\mu\nu}$ being the Debye-Waller electron-phonon matrix element given by Eq. (2.58).

To make contact with the AH theory of temperature-dependent band structures and with the HBB theory of indirect absorption, we analyse separately the cases of (i) direct gaps and (ii) indirect gaps.

4.4.1 Direct gaps

Let us consider that the energy gap is direct. The optical matrix elements p_{cv}^x in Eq. (4.9) are dominated by direct transitions and therefore the term p_{cv} . In fact, if we denote by g the characteristic electron-phonon matrix element and by E_g the minimum gap, and we note that $x_\nu/l_\nu \sim 1$, then the terms in the square brackets are $\sim (g/E_g)p_{cv}$, and therefore can be neglected when compared to p_{cv} . This approximation is implicitly used in *all* calculations of optical absorption spectra which do not include phonon-

assisted processes [15]. By using this approximation in Eqs. (2.73) and (4.2) we obtain:

$$\epsilon_2(\omega; T) = 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{cv} |p_{cv}|^2 \Pi_\nu \int dx_\nu \frac{\exp(-x_\nu^2 / 2\sigma_{\nu,T}^2)}{\sqrt{2\pi}\sigma_{\nu,T}} \delta(\varepsilon_{cv} + \Delta\varepsilon_{cv}^x - \hbar\omega), \quad (4.11)$$

where we have defined $\varepsilon_{cv}^x = \varepsilon_c^x - \varepsilon_v^x$, $\varepsilon_{cv} = \varepsilon_c - \varepsilon_v$, and $\Delta\varepsilon_{cv}^x = \varepsilon_{cv}^x - \varepsilon_{cv}$. Equation (4.11) can be rewritten using the Taylor expansion of the Dirac delta distribution in powers of $\Delta\varepsilon_{cv}^x$. The derivation is laborious and is left to Appendix D.1. The final result is:

$$\epsilon_2(\omega; T) = 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{cv} |p_{cv}|^2 \frac{1}{\sqrt{2\pi}\Gamma_{cv}} \exp \left[-\frac{(\varepsilon_{c,T}^{\text{AH}} - \varepsilon_{v,T}^{\text{AH}} - \hbar\omega)^2}{2\Gamma_{cv}^2} \right] + \mathcal{O}(\sigma^4). \quad (4.12)$$

In this expression, $\varepsilon_{m,T}^{\text{AH}}$ denotes the temperature-dependent electron energy in the Allen-Heine theory [11], given by Eq. (3.5). The quantity Γ_{cv} in Eq. (4.12) is the width of the optical transition, and is defined as follows:

$$\Gamma_{cv}^2 = \sum_\nu |g_{cc\nu} - g_{vv\nu}|^2 (2n_{\nu,T} + 1). \quad (4.13)$$

Equation (4.12) shows that, in the case of direct absorption processes, the WL theory yields a dielectric function which exhibits normalised peaks at the temperature-dependent excitation energies $\varepsilon_{cv,T}^{\text{AH}}$. In addition, when we compare Eq. (4.12) to Eq. (2.44), i.e. the dielectric function evaluated for the equilibrium case, we can conclude that the temperature-dependent optical spectra of a direct gap material can be approximated with a rigid shift of the spectrum evaluated with atoms at their relaxed positions. This can be readily realised from our calculated optical spectra of GaAs, discussed later in Sec. 4.6.1.

We also note that the width of the optical transitions Γ_{cv} is similar to but does *not* coincide with the electron-phonon linewidth obtained in time-dependent perturbation

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theory, compare for example with Eq. (170) of Ref. [21]. In fact, within the WL theory, Γ_{cv} scales as $\sqrt{n_{\nu,T}}$, while in full perturbation theory, Γ_{cv} scales as $n_{\nu,T}$. This subtle difference is a direct consequence of the semiclassical approximation upon which the Williams-Lax theory is based.

To the best of our knowledge the connection derived here between the Williams-Lax theory and the Allen-Heine theory, as described by Eqs. (4.12) and (3.5), is a novel finding. In particular, the present analysis demonstrates that, to lowest order in perturbation theory, the WL theory of optical spectra yields the adiabatic version of the AH theory of temperature-dependent band structures.

4.4.2 Indirect gaps

In the case of indirect semiconductors, owing to the momentum selection rule [see Eq. (2.48)], optical transitions between the band edges are forbidden in the absence of phonons [10]. Hence, the optical matrix elements at equilibrium do not contribute to optical absorption, and we can set $p_{cv} = 0$ in Eq. (4.9). This observation is valid only for transitions below the fundamental direct gap and represents the starting point of the classic HBB theory of indirect optical processes [12]. In this case Eq. (4.2) becomes:

$$\begin{aligned} \epsilon_2(\omega; T) = & 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{cv} \prod_{\nu} \int dx_{\nu} \frac{\exp(-x_{\nu}^2/2\sigma_{\nu,T}^2)}{\sqrt{2\pi}\sigma_{\nu,T}} \\ & \times \left| \sum'_{\mu\beta} \left[\frac{p_{c\beta} g_{\beta v \mu}}{\varepsilon_v - \varepsilon_{\beta}} + \frac{g_{c\beta \mu} p_{\beta v}}{\varepsilon_c - \varepsilon_{\beta}} \right] \frac{x_{\mu}}{l_{\mu}} \right|^2 \delta(\varepsilon_{cv} + \Delta\varepsilon_{cv}^x - \hbar\omega) + \mathcal{O}(\sigma^4). \end{aligned} \quad (4.14)$$

We stress that in this expression we keep only the terms in Eq. (4.9) which are linear in the normal coordinates. This choice corresponds to considering only *one-phonon* processes, as it is done in the HBB theory. While multi-phonon processes are automatically included in the WL theory, in the following we do not analyse them explicitly.

As in the case of direct gaps, we perform a Taylor expansion of the Dirac delta

appearing in Eq. (4.14) in powers of $\Delta\varepsilon_{cv}^x$ to arrive at the following expression:

$$\begin{aligned} \epsilon_2(\omega; T) = & 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{cv\nu} \left| \sum_{\beta} \left[\frac{p_{c\beta} g_{\beta\nu\nu}}{\varepsilon_v - \varepsilon_{\beta}} + \frac{g_{c\beta\nu} p_{\beta\nu}}{\varepsilon_c - \varepsilon_{\beta}} \right] \right|^2 \\ & \times \frac{1}{\sqrt{2\pi}\Gamma_{cv}} \exp \left[-\frac{(\varepsilon_{c,T}^{\text{AH}} - \varepsilon_{v,T}^{\text{AH}} - \hbar\omega)^2}{2\Gamma_{cv}^2} \right] (2n_{\nu,T} + 1) + \mathcal{O}(\sigma^6). \end{aligned} \quad (4.15)$$

The derivation of the above result is lengthy, and is reported for completeness in Appendix D.2.

Equation (4.15) shows that the WL theory correctly describes indirect optical absorption. In fact, if we neglect the broadening Γ_{cv} and the temperature dependence of the electronic energy levels, we obtain the HBB expression given by Eq. (3.2). The only difference between this last expression and the original HBB theory is that here the Dirac delta function does not contain the phonon energy. Physically this corresponds to stating that the WL theory provides the *adiabatic* limit of the HBB theory of indirect absorption.

To the best of our knowledge, this is the first derivation of the precise formal connection between the WL theory of indirect absorption, as expressed by Eq. (4.15), and the theories of Hall, Bardeen, and Blatt and of Allen and Heine, as given by Eqs. (3.2) and (3.5).

We re-emphasise that the adiabatic HBB theory does *not* incorporate the temperature dependence of the band structure, as it can be seen from Eq. (3.2). Instead, the WL theory includes band structure renormalisation by default, as can be seen from Eq. (4.15). This point is very important in view of performing predictive calculations at finite temperature.

From Eq. (4.15) we can also see that for generalising the HBB theory such that it includes temperature-dependent band structures, one needs to account for the temperature dependence only in the energies in the Dirac deltas of Eq. (3.2), corresponding to *real* transitions, and not in the energies that appear in the energy denominators, corresponding to *virtual* transitions.

4.4.3 Cross-coupling terms

In this section we show that the WL theory includes contributions to the dielectric function coming from the interference between direct and indirect transitions.

As we have discussed at the end of Sec. 2.3.3 and Appendix B.4, mixing of direct and indirect transitions do not contribute to the HBB theory of indirect optical absorption. We have also seen in Sec. 3.2.1 that when we treat separately phonon-assisted transitions and the dependence of the energy levels on nuclear coordinates, the cross-coupling terms between direct, p_{cv} , and indirect, $p_{cv}^{(1)}$, optical absorption do not survive the thermal average. Hence, these terms do not participate to the temperature dependence of the dielectric function [see Eq. (3.3)]. We stress that in both cases mentioned above the temperature dependence of the band structure is neglected.

In Secs. 4.4.1 and 4.4.2 we treated the nuclear dependence of the energy levels and optical matrix elements on the same footing. However, we distinguished between the cases of direct and indirect transitions. Let us now consider both terms in the expansion of the optical matrix elements without neglecting the dependence of the energy levels on the atomic positions. We take together Eqs. (2.73) and (3.1a) to obtain:

$$\epsilon_2^{(1)}(\omega, x) = 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{v,c} \left[|p_{cv}|^2 + p_{cv} p_{cv}^{(1)*} + p_{cv}^* p_{cv}^{(1)} + |p_{cv}^{(1)}|^2 \right] \delta(\epsilon_c^x - \epsilon_v^x - \hbar\omega), \quad (4.16)$$

where the matrix elements $p_{cv}^{(1)}$ depend on the nuclear coordinates, as shown in Eq. (3.1b).

We have seen that the first and fourth terms in the square brackets lead to Eqs. (4.12) and (4.15), respectively. If we follow the same prescription as in Appendices D.1 and D.2, and retain terms up to second order, then the contribution from the cross-coupling terms (cct) to the temperature-dependent dielectric function is given by:

$$\begin{aligned} \epsilon_2^{\text{cct}1}(\omega; T) &= 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{cv} 2 p_{cv} \frac{\delta(\epsilon_c - \epsilon_v - \hbar\omega)}{(\epsilon_c - \epsilon_v - \hbar\omega)} \\ &\times \sum_{\nu} \left[\sum_{\beta} \left[\frac{p_{c\beta} g_{\beta v \nu}}{\epsilon_v - \epsilon_{\beta}} + \frac{g_{c\beta \nu} p_{\beta v}}{\epsilon_c - \epsilon_{\beta}} \right] \right] [g_{cc\nu} - g_{vv\nu}] (2n_{\nu, T} + 1) + \mathcal{O}(\sigma^4). \end{aligned} \quad (4.17)$$

To reach this expression we also used the definition of the derivative of the delta function $\delta'(x) = -\delta(x)/x$ [161]. We emphasise that this term survives the thermal average because of the *linear* dependence of the energy levels on the atomic positions.

The cross-coupling term appearing in Eq. (4.17) is not the only one that contributes to optical absorption and scales as $n_{\nu,T}$. This is immediate verified by including the next term, $p_{cv}^{(2)} = \frac{1}{2} \sum_{\nu\mu} \frac{\partial^2 p_{cv}}{\partial x_\nu \partial x_\mu} x_\nu x_\mu$, in the expansion of the optical matrix elements, p_{cu}^x . If we substitute this higher-order expansion into Eq. (2.73), expand the square modulus, retain the zeroth-order in the expansion of the Dirac delta function [Eq. (D.4)] and perform the thermal average, then we obtain another cross-coupling term proportional to $n_{\nu,T}$. The result is:

$$\epsilon_2^{\text{cct2}}(\omega; T) = 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{cv\nu} p_{cv} \frac{\partial^2 p_{cv}}{\partial x_\nu^2} (2n_{\nu,T} + 1) \delta(\varepsilon_c - \varepsilon_v - \hbar\omega), \quad (4.18)$$

where l_ν^2 is absorbed in $\frac{\partial^2 p_{cv}}{\partial x_\nu^2}$. The explicit form of $\frac{\partial^2 p_{cv}}{\partial x_\nu^2}$ in terms of optical matrix elements and electron-phonon coupling coefficients is not derived here. Simply put, the above expression shows another second-order contribution to optical absorption that corresponds to the mixing of direct transitions and *electron-two phonon* coupling. One could evaluate the above expression using finite-difference formulas to obtain $\frac{\partial^2 p_{cv}}{\partial x_\nu^2}$ for each degree of freedom. An analogous expression to the one appearing in Eq. (4.18) can be obtained from time-dependent perturbation theory by expanding the transition probability in Eq. (B.27) up to the *third order*.

We note that although the contributions from the cross coupling terms $\epsilon_2^{\text{cct1}}(\omega; T)$ and $\epsilon_2^{\text{cct2}}(\omega; T)$ are included inherently in our WL calculations of the optical spectra, we do not evaluate them explicitly in this thesis.

4.5 Band gap from Williams-Lax optical spectra

In the previous section we proved that the temperature-dependent optical spectra in the WL theory are characterised by an absorption onset at the temperature-dependent

band gap determined by the AH theory. This is shown in Eqs. (4.12) and (4.15). The result suggests that we can extract the temperature dependence of the band gap directly from calculations of the dielectric function or the absorption coefficient, following the standard experimental procedure.

In Sec. 4.5.1 we present the basic relations underpinning the use of Tauc plots in the Williams-Lax theory. This is followed by Sec. 4.5.2, where we present how information on the joint-density of states can be used to determine the zero-point renormalisation of the band gap.

4.5.1 Tauc plots

Considering Eqs. (4.12) and (4.15) and the *parabolic approximation* of the band edges in solids [2], the following Tauc relations [72] can be obtained after a few simple manipulations [10]:

$$\text{direct:} \quad [\omega^2 \varepsilon_2(\omega; T)]^2 = \text{const} \times (\hbar\omega - E_{g,T}), \quad (4.19)$$

$$\text{indirect:} \quad [\omega^2 \varepsilon_2(\omega; T)]^{\frac{1}{2}} = \text{const} \times (\hbar\omega - E_{g,T}). \quad (4.20)$$

Here $E_{g,T}$ represents the *temperature-dependent* band gap, and these expressions are correct under the assumption that the optical matrix elements remain nearly constant with energy. This assumption is usually valid for energies near the absorption edge [10]. Equations (4.19) and (4.20) reflect the joint-density of states of semiconductors $J(\omega)$ (see Sec. 4.5.2), and constitute the basis for the Tauc method which is commonly used in experiments in order to extract band gaps from optical spectra [72]. These expressions are used as follows: after the calculation of $\varepsilon_2(\omega; T)$, one plots $(\omega^2 \varepsilon_2)^2$ for direct-gap materials, or $(\omega^2 \varepsilon_2)^{1/2}$ for indirect-gap materials as a function of photon energy. The resulting curve should be linear in the vicinity of the absorption onset, and the intercept with the energy axis yields the value of $E_{g,T}$.

We note that in the case of indirect-gap semiconductors we cannot use Eq. (4.19)

to determine the first *direct* gap. Nevertheless, we can still obtain the value of the gap by analysing second-derivative spectra of the real part of the dielectric function, $\partial^2 \varepsilon_1(\omega; T)/\partial \omega^2$. See for example Fig. C.1.2 in Appendix C. These spectra are characterised by maxima or minima, which can be used to identify the energy of the critical points in the band structure. According to Refs. [73–75], this is precisely the technique employed in experiments in order to measure direct band gaps. In Secs. 4.7.1–4.7.3, we use the techniques just described to identify the band gaps of Si, C, and GaAs.

4.5.2 Joint-density of states

We now consider the joint-density of states (JDOS), defined as the convolution between the density of states of valence and conduction bands [10]:

$$J(\omega) = \sum_{cv} \delta(\varepsilon_{cv} - \hbar\omega). \quad (4.21)$$

Within an energy range where band extrema are parabolic, it can be shown that $J(\omega) = \text{const} \times (\hbar\omega - E_g)^2$ [2]. This relation holds both for direct-gap and indirect-gap semiconductors. Within the WL theory, the above relation can be shown to remain essentially unchanged:

$$J(\omega; T) = \sum_{cv} \delta(\varepsilon_{cv,T}^{\text{AH}} - \hbar\omega) + \mathcal{O}(\sigma^4). \quad (4.22)$$

The only difference is that now the Allen-Heine temperature dependence of the energy levels enters the Dirac delta function. This result can be derived by following the same prescription used to obtain Eq. (D.8). Therefore, also in this case we have $J(\omega; T) = \text{const} \times (\hbar\omega - E_{g,T})^2$. Using Eqs. (4.21) and (4.22), we can determine the zero-point renormalisation of the band gap as the horizontal offset between the curves $J(\omega)^{1/2}$ and $J(\omega; T = 0)^{1/2}$.

4.6 Results: Optical spectra

In this section we outline the procedure for calculating temperature-dependent optical spectra using one-shot frozen-phonon calculations. For clarity we also anticipate our main results on silicon, diamond, and gallium arsenide, leaving all computational details to Sec. 4.8. In addition, we introduce a new strategy for improving numerical convergence using deterministic configurational averaging. Finally we verify the validity of Eq. (4.15) by comparing optical spectra calculated within the WL and HBB theories.

4.6.1 One-shot method and main results: Si, C, and GaAs

In Sec. 4.3 we have provided the formal proof that, in the limit of a large simulation cell, only one nuclear configuration is enough for evaluating Eq. (4.2). This atomic configuration is determined by the set of nuclear coordinates appearing in Eq. (4.4). In the remainder of this section we outline the calculation procedure, and we focus on our main results.

In order to calculate the optical absorption spectrum (including energy level renormalisation) at finite temperature using a *one-shot* frozen-phonon calculation, we proceed as follows:

1. We consider a $m \times m \times m$ supercell of the primitive unit cell. We determine the interatomic force constants (IFCs) [21] by means of density-functional perturbation theory calculations in the *primitive* unit cell, using a $m \times m \times m$ Brillouin zone grid [32, 64].
2. We use translational invariance of the crystal to fill the square IFCs matrix [Eq. (2.29)] of size $3M \times 3M$, where M is the total number of atoms in the supercell.
3. By diagonalising the dynamical matrix obtained from the matrix of force constants, we determine the vibrational eigenmodes $e_{\kappa\alpha,\nu}$ and eigenfrequencies Ω_ν

(κ and α indicate the atom and the Cartesian direction, respectively).

4. For a given temperature T , we generate *one* distorted atomic configuration, based on Eq. (4.4), by displacing the atoms from equilibrium by an amount:

$$\Delta\tau_{\kappa\alpha} = (M_p/M_\kappa)^{\frac{1}{2}} \sum_{\nu} (-1)^{\nu-1} e_{\kappa\alpha,\nu} \sigma_{\nu,T}. \quad (4.23)$$

In this expression M_κ is the mass of the κ -th nucleus, and the sum runs over all normal modes. The vibrational modes are assumed to be sorted in ascending order with respect to their frequencies. In order to ensure the same gauge for each degree of freedom, the sign of each eigenvector is chosen so as to have the first non-zero element positive. The choice of signs shown in Eq. (4.23) was explained in Sec. 4.3.

5. We calculate the dielectric function using the atomic configuration specified by Eq. (4.23). The result will be the temperature-dependent dielectric function at the temperature T .
6. We check for convergence by repeating all previous steps using increasingly larger supercells.

Figure 4.6.1 compares the optical absorption coefficients at room temperature of Si, C, and GaAs calculated using the procedure just described (red solid lines) with experiment [80, 162–165] (grey discs). For completeness we also present the optical spectra evaluated with the atoms at their equilibrium positions (blue solid line). The DFT/LDA calculations were performed on $8 \times 8 \times 8$ supercells, using a scissor correction, following Sec. 3.3.2. All information about the computational details is provided in Sec. 4.8, as well as in the captions of each figure. Our results for Si in Fig. 4.6.1(a), obtained using the optimal configuration, are in perfect agreement with those reported in Fig. 3.2.1 using importance-sampling Monte Carlo integration. In Fig. 4.6.1(a) we see that the absorption coefficient calculated with the nuclei at their equilibrium posi-

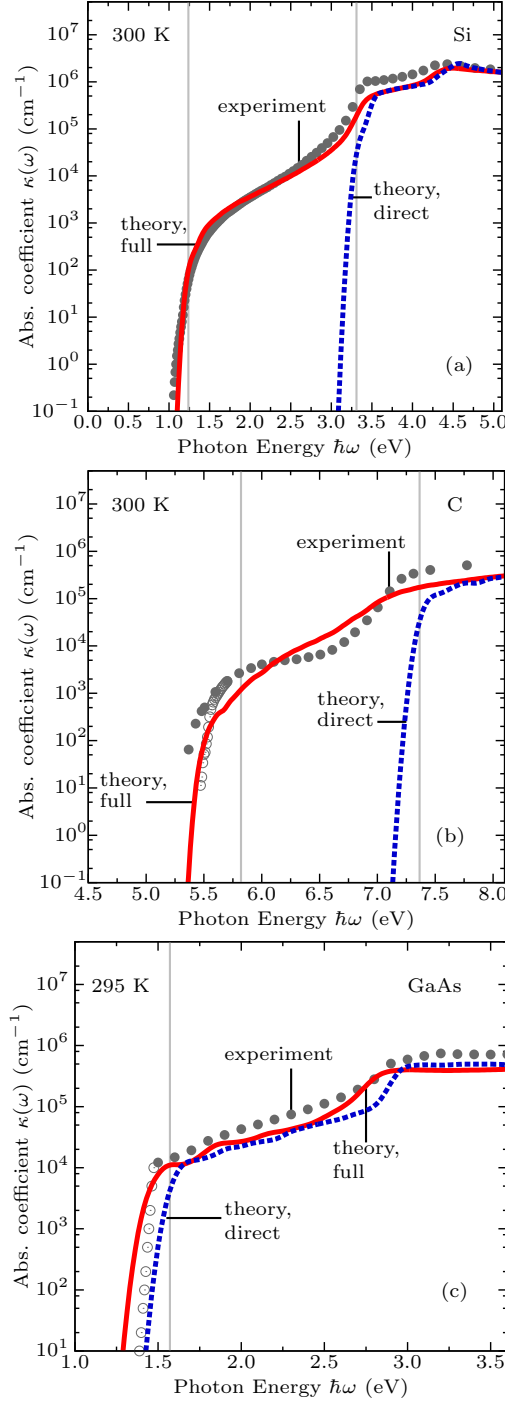


Figure 4.6.1: Absorption coefficient of (a) Si, (b) C, and (c) GaAs at room temperature. Calculations with the atoms at their equilibrium positions are shown as blue dashed lines. WL calculations using the optimal configuration specified by Eq. (4.23) are represented by red solid lines. The experimental data for Si are from Ref. [80] (grey discs), those for C are from Refs. [162] (grey discs) and [163] (grey circles). Experimental data for GaAs are from Refs. [164] (grey discs) and [165] (grey circles). The thin vertical lines indicate the direct and indirect band gaps calculated for nuclei in their equilibrium positions. The calculations were performed using $8 \times 8 \times 8$ supercells, using a Gaussian broadening of 30 meV for Si and C, and of 50 meV for GaAs.

tions exhibits optical transitions only above the fundamental direct gap, as expected. At variance with these calculations, our one-shot calculation based on the WL theory correctly captures indirect optical absorption. In particular, this calculation is in good agreement with experiment throughout a wide range of photon energies [80, 162]. This agreement extends over several orders of magnitude. However, we should point out that our adiabatic theory does not capture the fine structure close to the absorption edge. There, the non-adiabatic HBB theory exhibits two different slopes representing phonon emission and absorption processes [20, 166]. Near the onset for direct transitions at 3.3 eV, our calculation underestimates the experimental data. As discussed in Sec. 2.3.2, this underestimation is expected because we are not including electron-hole interactions [7].

Figure 4.6.1(b) shows the WL calculation for diamond. Here our technique correctly includes optical transitions in the range below the direct gap. However, the deviations between theory and experiment are more pronounced than in the case of Si. This residual discrepancy is attributed to the inability of DFT/LDA to accurately describe the band structure of diamond. At variance with silicon, in diamond a scissor correction is not sufficient to mimic GW corrections [142]. In fact, the quasiparticle corrections to the X_{1c} , L_{1c} , and L_{3c} states of Si are in the narrow energy range between 0.66 and 0.75 eV; while those for diamond span a wider range, between 1.47 and 2.04 eV [142]. Therefore, a significant redistribution of the spectral weights is expected, precisely in the indirect range shown in Fig. 4.6.1(b). Also in the case of C the absorption intensity of the E_1 peak around 7.3 eV is underestimated because of the absence of excitonic effects in our calculations [7]. In Fig. 4.6.1(b) we are presenting two sets of experimental data [162, 163]. These data reveal different intensities close to the absorption onset (at energies < 5.7 eV). According to Ref. [162], the intensity of the optical spectra for photon energies below 6.5 eV is not to be fully trusted. Our calculated absorption coefficient is in better agreement with the experimental data from Ref. [163], exhibiting a sharper absorption edge. This comparison suggests that our

technique presented here might prove useful for checking the reliability of challenging experiments, particularly close to the weak absorption edge. Similarly to Fig. 4.6.1(a), the fine structure features [163] near the absorption onset are not captured in our calculation.

Figure 4.6.1(c) compares the WL optical spectra at 295 K for GaAs with the measured values from Ref. [164, 165]. Here, we clearly demonstrate that our methodology correctly describes the optical spectrum of a semiconductor exhibiting direct band gap. Now, the shape of the absorption coefficient is not altered, as expected, but the spectrum is almost redshifted due to the zero-point renormalisation of the band structure. This confirms the validity of the expression derived for the WL dielectric function for direct gap materials in Eq. (4.12). In addition, the calculated absorption coefficient underestimates the experimental data. This is partially due to the absence of excitonic interactions from our calculations [167], but most importantly it is due to the underestimation of the effective masses of GaAs in DFT/LDA. In fact, according to theory of optical transitions in direct-gap semiconductors [2], the absorption coefficient is proportional to $(m^*)^{3/4}$, where m^* represents the average isotropic effective mass. Because DFT calculations underestimate the effective masses of GaAs by up to a factor of 2, we expect the absorption coefficient to be smaller by up to a factor of $2^{3/4} \sim 2$ when compared to experimental values. This estimate is in line with our results in Fig. 4.6.1(c). We point out that this problem does not appear in Fig. 4.6.1(a), since the DFT/LDA effective masses of silicon are in remarkable agreement with measured values [40].

We now comment on the numerical convergence and computational effort of our calculations. In Fig. 4.6.2 we show the imaginary part of the WL dielectric function at 0 K of the three tetrahedral semiconductors employing the procedure described above. To obtain convergence we run calculations upon increasing the size of the simulation cell, from $2 \times 2 \times 2$ to $8 \times 8 \times 8$. It becomes apparent that large supercells are required to achieve converged results. The increase of the supercell size has the following

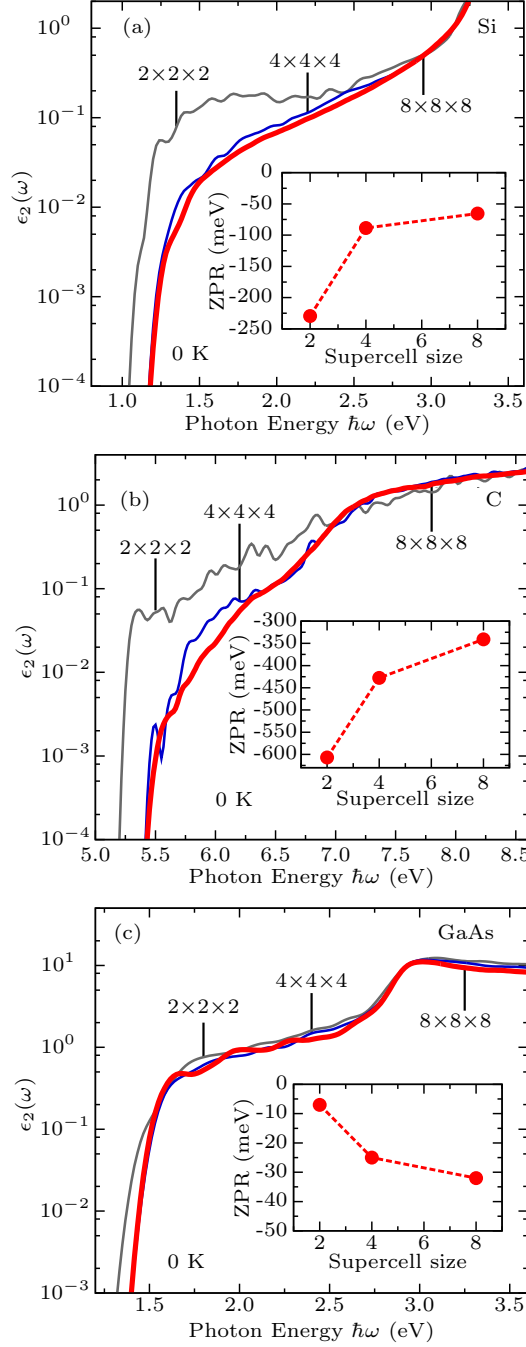


Figure 4.6.2: Convergence of the imaginary part of the dielectric function calculated within the WL theory as a function of supercell size: (a) Si, (b) C, and (c) GaAs. Calculations using $2 \times 2 \times 2$, $4 \times 4 \times 4$, and $8 \times 8 \times 8$ supercells are indicated by solid grey, solid blue and solid thick red lines, respectively. Each spectrum was evaluated using the optimum configuration specified by Eq. (4.23). For sampling the electronic Brillouin zone of $2 \times 2 \times 2$, $4 \times 4 \times 4$, and $8 \times 8 \times 8$ supercells of Si and C, we used 1920, 240, and 30 $\mathbf{k}$ -points, respectively. For GaAs we used a finer sampling of 6400, 800 and 100 $\mathbf{k}$ -points. For our calculations of the dielectric function in Eq. (2.73) we replaced the Dirac delta function with a Gaussian of width 30 meV for Si and C, and of 50 meV for GaAs. The insets report the zero-point renormalisation obtained using the Tauc method.

two effects: (i) better sampling of the electron-phonon interactions in the equivalent Brillouin zone, and (ii) the limit where Eq. (4.8) becomes valid is approached. In the insets of Fig. 4.6.2 we also show the band gap variation with the supercell size of Si, C, and GaAs. These values were extracted from the WL dielectric function using the standard Tauc plots [72], and are in good agreement with previous work. Details will be discussed in Sec. 4.7. Based on this figure we see that, for both direct- and indirect-gap semiconductors, our method correctly captures the zero-point corrections to the band gap. To this end, we stress that our calculations were performed using a single atomic configuration in each case. To the best of our knowledge this is the first time that calculations of temperature-dependent band gaps using a single atomic configuration have been reported.

In view of Figs. 4.6.1 and 4.6.2 it becomes clear that, despite the inherent deficiencies of the DFT/LDA calculations, with the new method we propose here, we are able to compute optical properties in both direct and indirect semiconductors at finite temperatures. It is seen that, for these tetrahedral semiconductors, converged results are obtained for $8 \times 8 \times 8$ supercells. We stress that in Fig. 4.6.2, $\epsilon_2^{1C}(\omega; T)$ is presented in logarithmic scale. In a linear scale the changes between optical spectra referring to $4 \times 4 \times 4$ and $8 \times 8 \times 8$ calculations would be barely discernible. Calculations using $8 \times 8 \times 8$ supercells are obviously computationally expensive. However, one should keep in mind that each line in this figure corresponds to a *single* calculation of the dielectric function at fixed-atoms, and hence this method enables the incorporation of temperature without the need of configurational sampling.

4.6.2 Improvements using configurational averaging: Si

There might be systems for which calculations in large supercells are prohibitively expensive, and the limit in Eq. (4.8) is practically beyond reach. In this case, we can extend the technique presented in Sec. 4.3 to calculations using more than one atomic configuration. In this section, we introduce a new strategy for constructing a hierarchy

of nuclear configurations in order to achieve systematic improvement of the evaluation of Eq. (4.2), using a *fixed* supercell size.

We restart our discussion in Sec. 4.3.2 by considering nuclear configurations determined by the normal coordinates $x_\nu = s_\nu \sigma_{\nu,T}$, where s_ν can be either 1 or -1 . We take the Taylor expansion as in Eq. (4.5) to obtain:

$$\begin{aligned} \epsilon_2^S(\omega; T) = & \epsilon_2(\omega) + \sum_{\nu} s_{\nu} \frac{\partial \epsilon_2^x(\omega)}{\partial x_{\nu}} \sigma_{\nu,T} + \frac{1}{2} \sum_{\nu\mu} s_{\nu} s_{\mu} \frac{\partial^2 \epsilon_2^x(\omega)}{\partial x_{\nu} \partial x_{\mu}} \sigma_{\nu,T} \sigma_{\mu,T} \\ & + \frac{1}{6} \sum_{\nu\mu l} s_{\nu} s_{\mu} s_l \frac{\partial^3 \epsilon_2^x(\omega)}{\partial x_{\nu} \partial x_{\mu} \partial x_l} \sigma_{\nu,T} \sigma_{\mu,T} \sigma_{l,T} + \mathcal{O}(\sigma^4). \end{aligned}$$

Here the superscript S represents the entire set of $3M$ signs, $S = (s_1, \dots, s_{3M})$. With this notation, the choice given by Eq. (4.4) is equivalent to setting $S = \{+ - + - + - \dots\}$.

In the language of Monte Carlo sampling, the atomic configurations that correspond to S and $-S$ are called an *antithetic pair* [148]. We can readily see that the WL dielectric function obtained using both S and $-S$ leads to the cancellation of the odd powers of $\sigma_{\nu,T}$. In fact from Eq. (4.24) we get:

$$\frac{1}{2} [\epsilon_2^S(\omega; T) + \epsilon_2^{-S}(\omega; T)] = \epsilon_2(\omega) + \frac{1}{2} \sum_{\nu\mu} s_{\nu} s_{\mu} \frac{\partial^2 \epsilon_2^x(\omega)}{\partial x_{\nu} \partial x_{\mu}} \sigma_{\nu,T} \sigma_{\mu,T} + \mathcal{O}(\sigma^4). \quad (4.24)$$

This expression is already close to the expansion in Eq. (4.3), without taking into account the size of the supercell. In order to get closer to the exact expansion in Eq. (4.3), we have to further eliminate the terms $\nu \neq \mu$ in the sum that appears in Eq. (4.24). This can be achieved in a *systematic* way by introducing another configuration S' defined as:

$$\begin{aligned} S &= \{ \quad + \quad - \quad + \quad - \quad \bigg| \quad + \quad - \quad + \quad - \quad \}, \\ S' &= \{ \quad + \quad - \quad + \quad - \quad \bigg| \quad - \quad + \quad - \quad + \quad \}, \end{aligned} \quad (4.25)$$

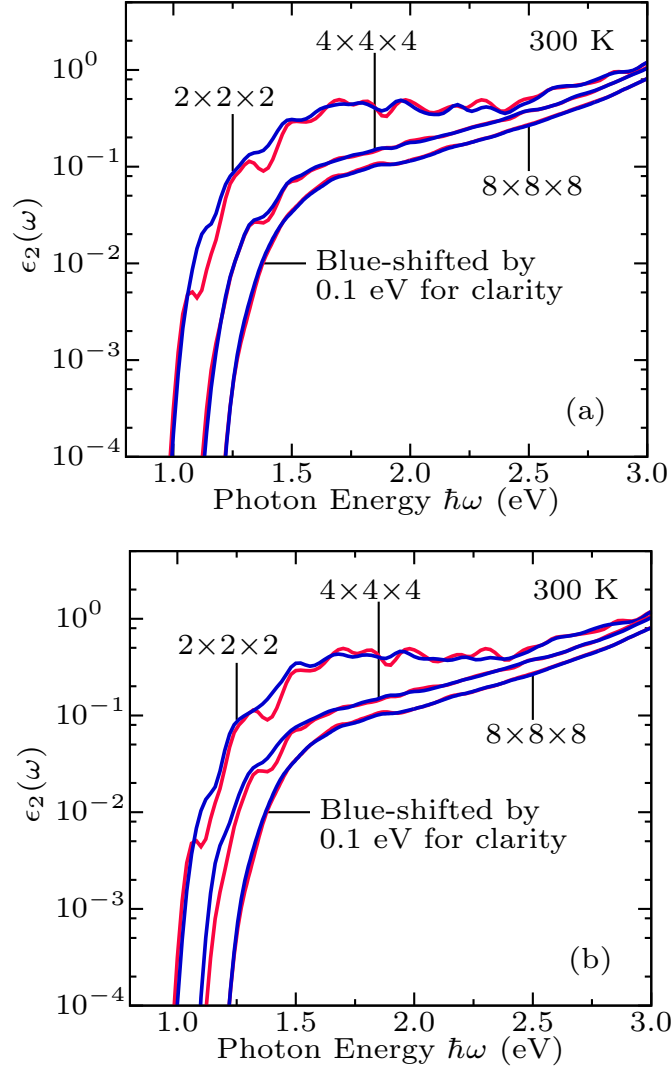


Figure 4.6.3: Improvement using multiple nuclear configurations for the calculations of the WL optical spectra of silicon. (a) Comparison between computations performed using the optimal configuration given by Eq. (4.4) (red solid lines), and its combination with its antithetic pair given by Eq. (4.24) (blue solid line). The spectra at 300 K refer to increasing supercell sizes, as indicated on the plot. (b) Comparison between runs performed using the optimal configuration as in (a) (red solid lines), and those for 4 configurations, given by Eqs. (4.23), (4.24), and (4.25). For the spectra referring to the $8 \times 8 \times 8$ supercell, we have applied a *rigid blue-shift* of 0.1 eV. This shift is necessary to avoid the overlap with those obtained for a $4 \times 4 \times 4$ supercell.

where for clarity we show the simple case of 8 degrees of freedom. In practice S' is simply generated by changing all the signs of the second-half of the vector S . It is easy to verify that the WL dielectric function evaluated by averaging over the 4 nuclear configurations given by S , $-S$, S' , and $-S'$ retains only half of the terms $\mu \neq \nu$ that are shown in Eq. (4.24). Since each atomic configuration satisfies the relation in Eq. (4.8),

it is immediate to see that the calculation involving the 4 atomic configurations will get closer to the precise WL spectrum faster upon increasing the size of the supercell.

This methodology can also be iterated by dividing each subset in Eq. (4.25) in two, and change the sign of two out of four of the resulting subsets. At each individual iteration, the total number of nuclear configurations doubles, while the total number of the remaining cross terms $\mu \neq \nu$ in Eq. (4.24) halves. For example, we can see that, by using 4, 16, and 64 nuclear configurations specified in this way, we can eliminate 50%, 87.5%, and 96.875% of the cross terms, respectively. These conclusions are justified in Appendix D.3. We stress that the choices of the signs made here and in Eq. (4.25) are not unique. An alternative approach is also presented in Appendix D.3.

In Fig. 4.6.3(a) we show the improvement achieved by employing the configurations specified by Eq. (4.24) for the calculation of the WL dielectric function of silicon at 300 K. In Fig. 4.6.3(b) we repeat the runs, but now using 4 distinct configurations, based on Eqs. (4.24), and (4.25). Here we conclude that as the number of nuclear configurations increases, the spurious fluctuations in the spectra suppresses. This effect is more important for the smallest supercell. We note that, in Fig. 4.6.3, the spectra corresponding to the $8 \times 8 \times 8$ supercell are *rigidly blue-shifted* to facilitate comparison. Without this shift of 0.1 eV the curves overlap with those obtained using a $4 \times 4 \times 4$ supercell.

In view of Fig. 4.6.3, it is immediate to verify that irrespective of the level of configurational averaging, small supercells may not be adequate to precisely calculate the WL dielectric function. This is explained from the fact that the correct calculation of an indirect absorption edge, requires a supercell that accommodates phonons which connect the band extrema.

4.6.3 Comparison between calculations using the Williams-Lax theory and Hall-Bardeen-Blatt theory: Si and C

Here we demonstrate the advantage of the WL theory over the HBB theory to capture correctly quantum zero-point renormalisation and temperature dependence of the

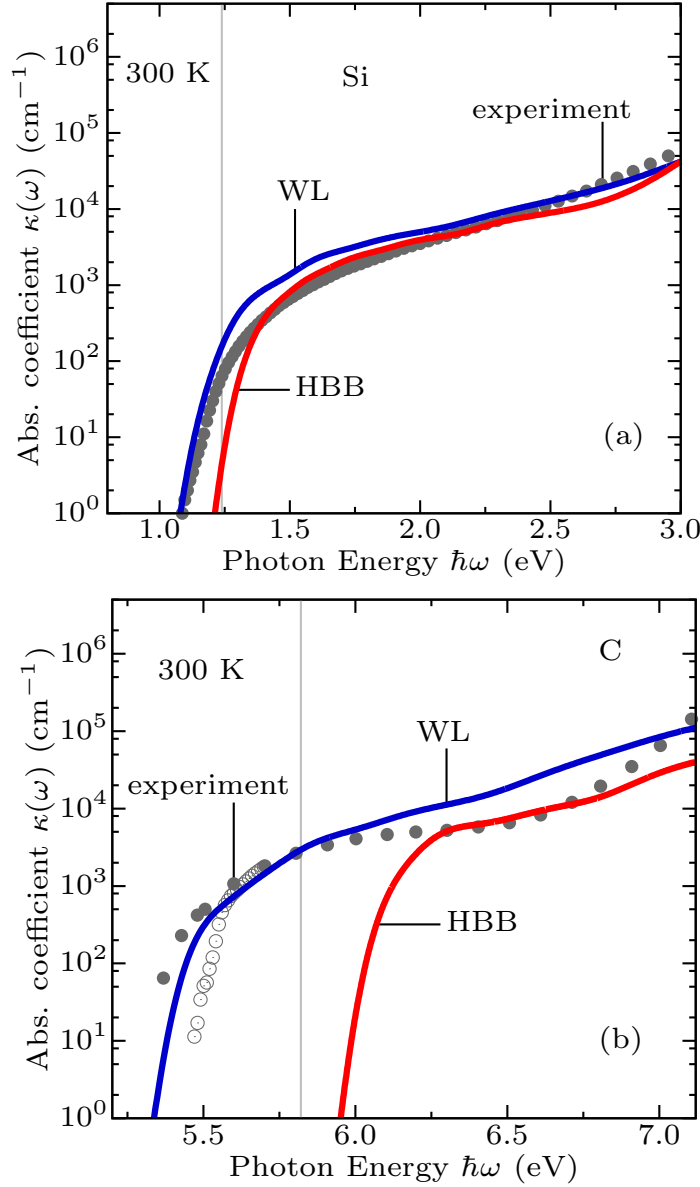


Figure 4.6.4: Comparison between our calculated absorption coefficient at 300 K using the HBB theory (solid red line) or the WL theory (solid blue line) of Si (a) and C (b) and the corresponding experimental data from Refs. [80] [discs in (a)], [162] [discs in (b)], and [163] [circles in (b)]. In both cases the calculations refer to $4 \times 4 \times 4$ supercells. Here we sample the electronic Brillouin zone with 65 random $\mathbf{k}$ -points (i.e. > 4000 points in the Brillouin zone of the crystalline unit cell), and we use a Gaussian broadening of 50 meV. The band gaps determined with the atoms clamped at the equilibrium geometries are shown by the thin vertical lines.

band structure, discussed in Secs. 4.4.1 and 4.4.2. In Fig. 4.6.4, we present phonon-assisted absorption spectra of silicon and diamond calculated for both: the HBB and the WL theory. For the HBB calculations we employed the adiabatic approximation and we recast Eq. (3.2) in the following equivalent form:

$$\epsilon_2^{\text{HBB}}(\omega; T) = \frac{1}{2} \sum_{\nu} \frac{\partial^2 \epsilon_2(\omega; x)}{\partial x_{\nu}^2} \sigma_{\nu, T}^2. \quad (4.26)$$

The equivalence between this expression and Eq. (3.2) is readily understood by substituting Eq. (3.1a) into Eq. (2.73), and then taking the second derivative with respect to x_{ν} with all quantities evaluated at equilibrium. For the calculation of the electron-phonon coupling coefficients for each vibrational mode we employed finite-difference formulas. That is, we performed $2(3M - 3)$ frozen-phonon calculations, where $3M$ is total number of phonon modes. For the cases shown in Fig. 4.6.4 we used $4 \times 4 \times 4$ supercells. This is equivalent to 762 calculations on supercells with 128 atoms. We should point out that the WL calculation on the optimal configuration requires instead only one calculation.

In Fig. 4.6.4(a) we compare the calculated absorption coefficient of Si within the WL theory (blue line) and the HBB theory (red line) with the experiment [80] (grey dots). All data refer to $T = 300$ K. Here we conclude that the HBB and WL spectra are in close agreement. However, the HBB optical spectra exhibit an absorption onset that coincides with the indirect band gap of silicon calculated at equilibrium, as expected from Eq. (3.2). On the other hand, the WL spectrum is *red-shifted* by ~ 0.1 eV. As expected from Eq. (4.15), this value corresponds to the zero-point renormalisation and the additional temperature shift of the gap at $T = 300$ K. Owing to this, the WL absorption coefficient is in better agreement with experiment. We emphasise again that the curves in Fig. 4.6.4 do not include any empirical parameters.

The effect of capturing correctly the renormalisation of the band structure becomes more prominent in the case of C. This is shown in Fig. 4.6.4(b). Here the HBB calculation is above from the absorption edge by an amount ~ 0.5 eV. Instead, the WL

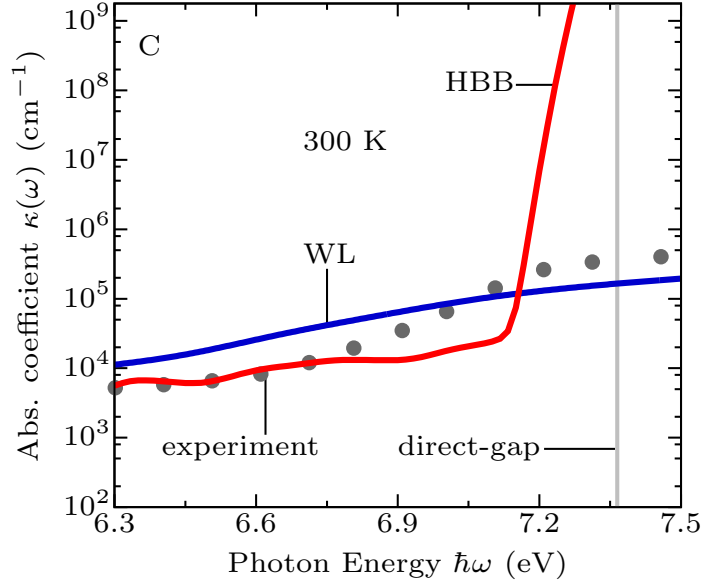


Figure 4.6.5: Comparison between our calculated absorption coefficient at 300 K using the HBB theory (solid red line) or the WL theory (solid blue line) of C and the corresponding experimental data from [162] [discs in (b)]. The calculations refer to $4 \times 4 \times 4$ supercells. The electronic Brillouin zone was sampled using 65 random $\mathbf{k}$ -points. A Gaussian smearing of 50 meV was applied to all calculated spectra. The direct band gap determined with the atoms fixed at the equilibrium geometries is shown by the vertical grey line.

spectrum exhibits an onset in close agreement with experiment. The difference between the calculation of the adiabatic HBB spectrum and experiment is assigned to the large phonon-induced renormalisation of the band gap of diamond [16, 18, 92]. We emphasise again that the adiabatic HBB theory also misses the small redshift corresponding to phonon-absorption processes [20].

To this end, in Fig. 4.6.5 we also compare the absorption coefficient of C calculated within the WL (blue line) and HBB (red line) theories for photon energies around the direct gap energy (vertical grey line). Here, we can see that our WL spectrum exhibits a smooth variation from the indirect to direct transitions regime. In contrast to the WL spectrum, the spectrum calculated using the HBB theory tends to infinity as it approaches the direct gap energy. This can be understood in view of Eq. (3.2), where as the direct gap energy is approached, the photon energy $\hbar\omega$ in the energy denominators becomes very close to the transition energy and a divergence appears. This problem is eliminated in the WL calculation which incorporates all second-order and higher-order terms in the perturbation series of the imaginary part of dielectric function [in contrast

to Eq. (4.26) for HBB]. We should point out that the correct treatment of the second-order term in the expansion for the WL dielectric function will reveal not only the term $\epsilon_2^{\text{HBB}}(\omega; T)$ in Eq. (4.26), but as well as the contributions from the cross-coupling terms $\epsilon_2^{\text{cct1}}(\omega; T)$ and $\epsilon_2^{\text{cct2}}(\omega; T)$ appearing in Eqs. (4.17) and (4.18), respectively.

We stress that the WL theory does not come without drawbacks. As mentioned before, unlike the conventional HBB theory, it does not capture the fine features associated to phonon emission and absorption processes close to the absorption edge [see Eq. (2.50)]. This fact reflects the WL semiclassical approximation, where the quantisation of the initial and final vibrational states is replaced by a classical continuum [23].

4.7 Results: Band gap renormalisation

In this section we extract the phonon-induced renormalisation of the indirect and direct band gaps of Si, C, and GaAs using the Tauc method and line shape analysis of second-derivative spectra, both described in Sec. 4.5.1. The assumption of using Tauc plots is that the optical matrix elements remain nearly constant with energy in the vicinity of the absorption onset. We can justify this by comparing the optical spectra of Si and C with the corresponding joint-density of states in Fig. D.4.1 of Appendix D.4.

4.7.1 Indirect semiconductors: Si

In Fig. 4.7.1(a) we present the Tauc plots obtained for silicon using the WL spectra in the temperature range 0–473 K. As expected from Eq. (4.19), we obtain a linear behaviour over a photon energy range of almost 1 eV above the absorption onset. The linear fits applied to the energy range 0–1.8 eV intercept the horizontal axis at energies equal to the indirect band gaps at several temperatures. These are shown in Fig. 4.7.1(b) as red discs, and compared to experiment (grey discs). Apart from a constant offset related to our choice of the scissor shift (see Sec. 4.8), the agreement with experiment is good.

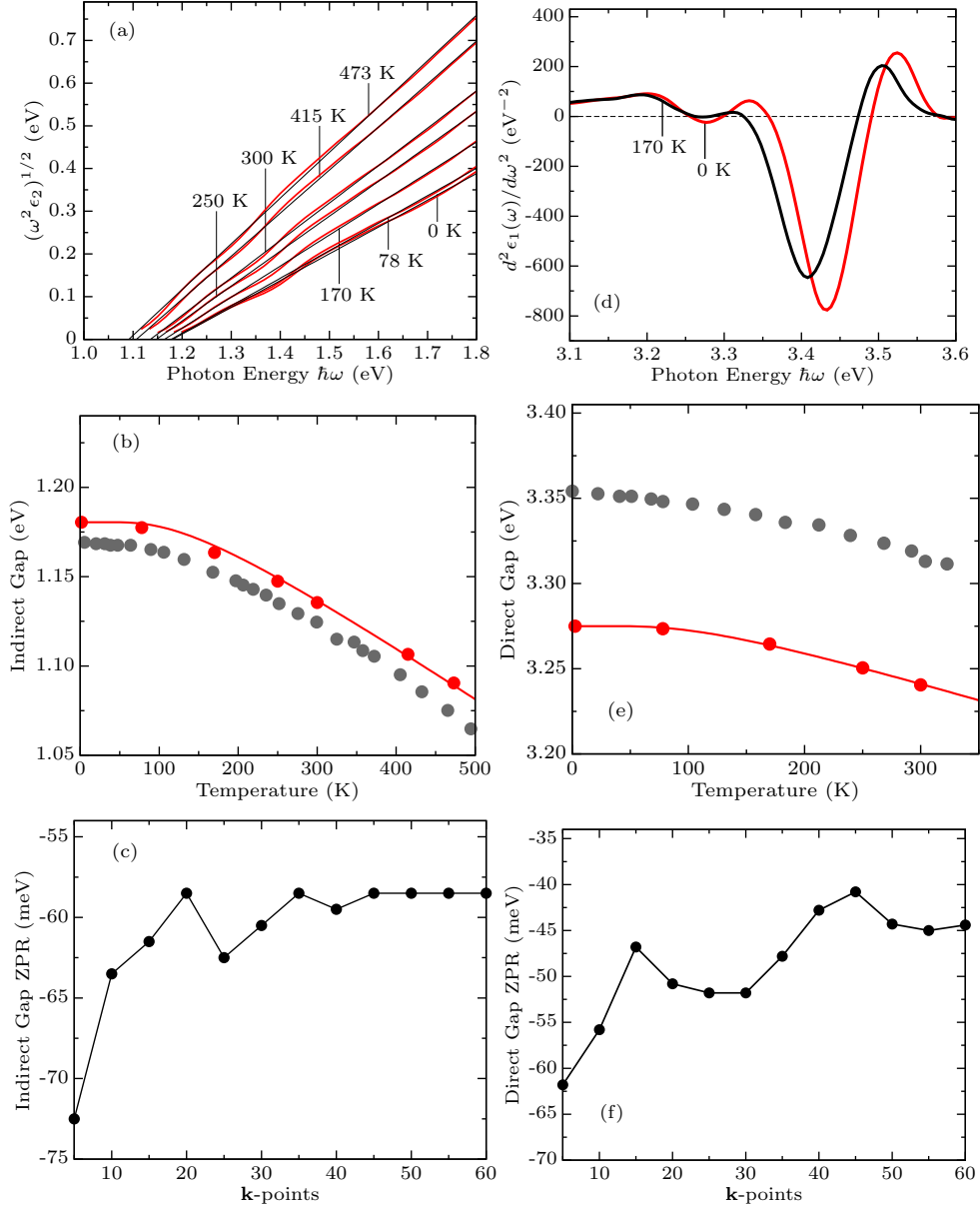


Figure 4.7.1: (a) Tauc plots for determining the temperature dependence of the indirect band gap of silicon. The red lines at each temperature vary as $(\omega^2 \epsilon_2)^{1/2}$, and the thin black lines represent the corresponding linear fits. The intercept of the linear fits with the photon energy axis yields the indirect gap. (b) Indirect band gap of silicon as a function of temperature: WL theory (red discs) and experimental data (grey discs) from Ref. [109]. The solid red line represents as a single-oscillator fit [Eq. (2.65)] and is used as a guide to the eye. The theoretical values were corrected to match the zero-point renormalisation calculated as discussed in Sec. 4.7.5. (c) Convergence of the zero-point renormalisation of the indirect gap of silicon with respect to the $\mathbf{k}$ -point sampling. (d) Second-derivative of the real part of the dielectric function of silicon at 0 K and 170 K. (e) Direct gap of silicon as a function of temperature: WL calculations (red discs) and experimental data (grey discs) from Ref. [73]. The solid red line represents as a single-oscillator fit [Eq. (2.65)] and is used as a guide to the eye. (f) Convergence of the zero-point renormalisation of the direct gap of silicon with respect to the $\mathbf{k}$ -point sampling. All calculations in this figure refer to $8 \times 8 \times 8$ supercells.

In order to minimise numerical inaccuracies, we determine the zero-point renormalisation (ZPR) of the band gap, ΔE_g , as the offset between the square root of the joint-density of states calculated at equilibrium and that at $T = 0$ K. This refinement is discussed in Sec 4.7.5. In this case we find $\Delta E_g = 57$ meV. Small changes of this value are expected for larger supercells and denser Brillouin zone sampling. For completeness we show in Fig. 4.7.1(c) the convergence of the ZPR with respect the Brillouin zone sampling.

Our calculated ZPR of the indirect gap of silicon compares well with experiment and previous calculations. In fact, Ref. [93] reported a ZPR of 60 meV using finite-differences supercell calculations; Ref. [96] obtained 58 meV using the Monte Carlo technique; Ref. [94] reported renormalisation of 56 meV employing the AH approach. Experimental values of the ZPR lie between 62 and 64 meV [70, 102, 113].

In Fig. 4.7.1(d) we present the calculated $\partial^2 \varepsilon_1(\omega; T)/\partial \omega^2$ for silicon at 0 K and 170 K. Based on Ref. [73], we identify the energy of the E'_0 transition considering the first dip in the second-derivative spectra. Figure 4.7.1(e) compares the temperature dependence of the direct band gap with the experimental data. Except of the vertical offset the agreement with experiment is good. In order to obtain the ZPR of the direct gap, we considered the difference between the dips of $\partial^2 \varepsilon_1(\omega)/\partial \omega^2$ calculated at $T = 0$ K and at equilibrium. We obtained a zero-point renormalisation of 44 meV, which is in good agreement with the experimental range 25 ± 17 meV. [73] Previous calculations reported values in the same range: 42 meV from Ref. [94] and 28 meV from Ref. [120]. Ref. [120] reported that GW corrections on a $4 \times 4 \times 4$ supercell yield a renormalisation of 53 meV. Finally, in Fig. 4.7.1(f) we show the convergence of the ZPR with respect to the $\mathbf{k}$ -point sampling.

4.7.2 Indirect semiconductors: C

In Fig. 4.7.2(a) we show the Tauc plots calculated for diamond in the WL theory. As as before, we determined the temperature dependence of the indirect gap by using the

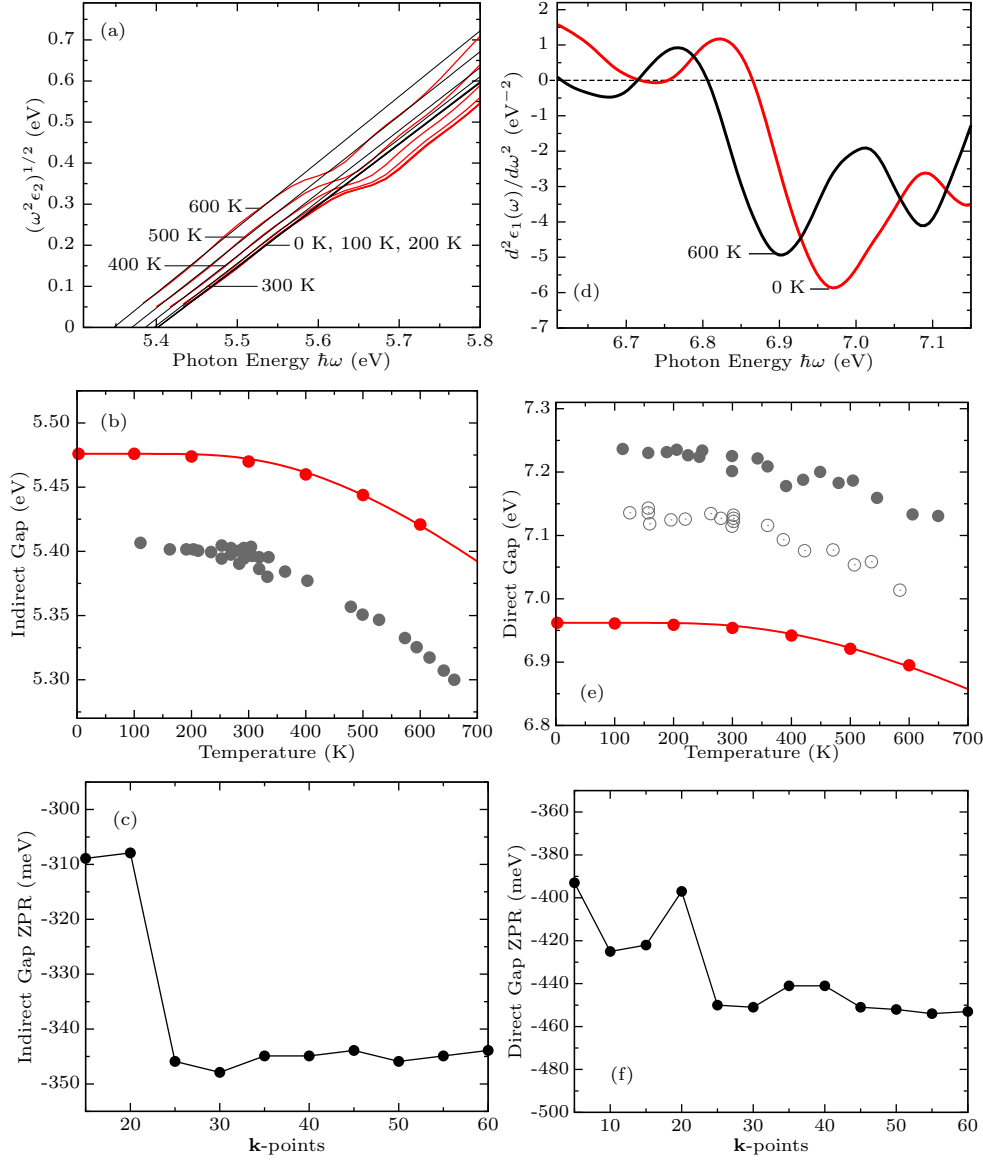


Figure 4.7.2: (a) Tauc plots to determine the temperature dependence of the indirect gap of diamond. The red and black lines represent $(\omega^2 \epsilon_2)^{1/2}$ calculated at each temperature and the corresponding linear fits, respectively. The intercept of the fits, taken in the range of $\hbar\omega = 0$ -5.6 eV, with the horizontal axis yields the indirect gap. (b) Indirect gap of diamond vs temperature: WL values (red discs) and experimental data (grey discs) from Ref. [163]. The solid red line indicates a single-oscillator fit [Eq. (2.65)] and is used as a guide to the eye. The theoretical values were shifted to match the ZPR calculated as discussed in Sec. 4.7.5. (c) Convergence of the zero-point indirect gap renormalisation of diamond as a function of the Brillouin zone sampling. (d) WL second-derivative spectra, $\partial^2 \epsilon_1(\omega; T) / \partial \omega^2$, for diamond at 0 K and 600 K. The E'_0 transition is determined from the deep minimum, according to Ref. [74]. (e) Temperature-dependence of the direct band gap of diamond: WL calculations (red discs) and experimental values from Ref. [74]. The experimental data refer to both diamond samples IIa (grey circles) and IIb (grey discs) examined in Ref. [74]. (f) Convergence of the ZPR of the direct band gap of diamond as a function of the k-point sampling. All calculations were performed using $8 \times 8 \times 8$ supercells.

intercept of the fits with the energy axis. The results are compared to the experimental data of Ref. [163] in Fig. 4.7.2(b). Here, we see that we obtain reasonable agreement with the measured values, but our calculations underestimate the experimental renormalisation. This effect has been assigned to the fact that DFT/LDA underestimates the electron-phonon coupling coefficients because of the DFT band gap problem [92]. Our calculated ZPR of the indirect gap is 345 meV. This result was determined following the procedure in Sec. 4.7.5. Our calculated value for the ZPR is compatible with previously reported values based on DFT/LDA, namely 330 meV [94], 334 meV [93], 343 meV [95], and 344 meV [96]. Our calculations compare well with the experimental values of 340 meV and 370 meV measured in Refs. [102, 113]. However, the use of a recent extrapolation of the experimental data reveals a renormalisation of 410 meV [111], which is 65 meV larger than our result. Since the GW corrections increase the ZPR as compared to DFT/LDA [92, 120], we expect that if we perform our WL calculations in a GW framework, our results to exhibit better agreement with experiment. In Fig. 4.7.2(c) we also show the convergence of the ZPR with respect to the Brillouin zone sampling (for an $8 \times 8 \times 8$ supercell).

Figure 4.7.2(d) shows the WL second-derivative spectra, $\partial^2 \varepsilon_1(\omega; T)/\partial \omega^2$, of diamond at two temperatures. The direct gap of diamond was identified in Ref. [74] from the deep minimum in the corresponding experimental curves. Here we adopt the same method, and we show our results in Fig. 4.7.2(e). These are compared to the experimental values from Ref. [74]. Except of the vertical offset due to our choice of the scissor correction, the calculations compare well with experiment. In particular, we obtained a ZPR of 450 meV close to the experimental values of 180 ± 150 meV (sample IIa of Ref. [74]) and 450 ± 370 meV (sample IIb of Ref. [74]). Our ZPR is compatible with previous calculations at the DFT/LDA level: Ref. [95] obtained 400 meV, Ref. [91] reported 409 meV, Ref. [120] obtained 410 meV (value extracted from Fig.3) and Ref. [94] reported 416 meV.

We also point out that in Ref. [16], the calculations on the electron-phonon renor-

malisation in diamond revealed a renormalisation to the direct gap of 615 meV using DFT/LDA. The origin of this overestimation might be related to numerical noise when calculating electron-phonon matrix elements for unoccupied Kohn-Sham states at very high-energy. Recent studies [92, 120] demonstrated that the GW corrections lead to an increase of the ZPR of the direct band gap. Calculations of optical spectra using the WL theory in conjunction with the GW method are certainly desirable, but lie beyond the scope of this thesis.

For completeness, in Appendix D.5 we also investigate multi-phonon effects. In particular, we prove that WL calculations correctly yield the generalisation of the adiabatic AH theory to the case of two-phonon processes, and we demonstrate that multi-phonon effects provide a negligible contribution to the band gap renormalisation.

4.7.3 Direct semiconductors: GaAs

In Fig. 4.7.3 we show our WL calculations for the temperature-dependent absorption onset and band gap of GaAs. Since this semiconductor is polar, we included the non-analytical part of the dynamical matrix in order to calculate the phonon frequencies and eigenmodes [168]. In this case we also considered the lattice thermal expansion, which is not negligible for GaAs [169]. To this aim we performed calculations within the *quasi-harmonic* approximation [64], that is we repeated the calculations of the normal modes at each temperature, by varying the lattice constant according to the measured thermal lattice expansion coefficient [170, 171].

In Fig. 4.7.3(a) we show the Tauc plots calculated for GaAs in the WL theory. In this case we determine the band gap from the linear fits of $(\omega^2 \varepsilon_2)^2$, after Eq. (4.19). Because the energy range where the function $(\omega^2 \varepsilon_2)^2$ varies linearly is narrow, we refine the calculation of the ZPR by employing the more accurate procedure, discussed in Sec. 4.7.5.

In Fig. 4.7.3(b) we report the extracted band gaps vs temperature (red discs), and we compare them to experimental data (grey discs) from Ref. [75]. For completeness

we present the results obtained without taking into account the lattice thermal expansion (blue discs). Here we conclude that our calculations are in reasonable agreement with experiment, and that the effect of thermal expansion of the lattice is definitely not

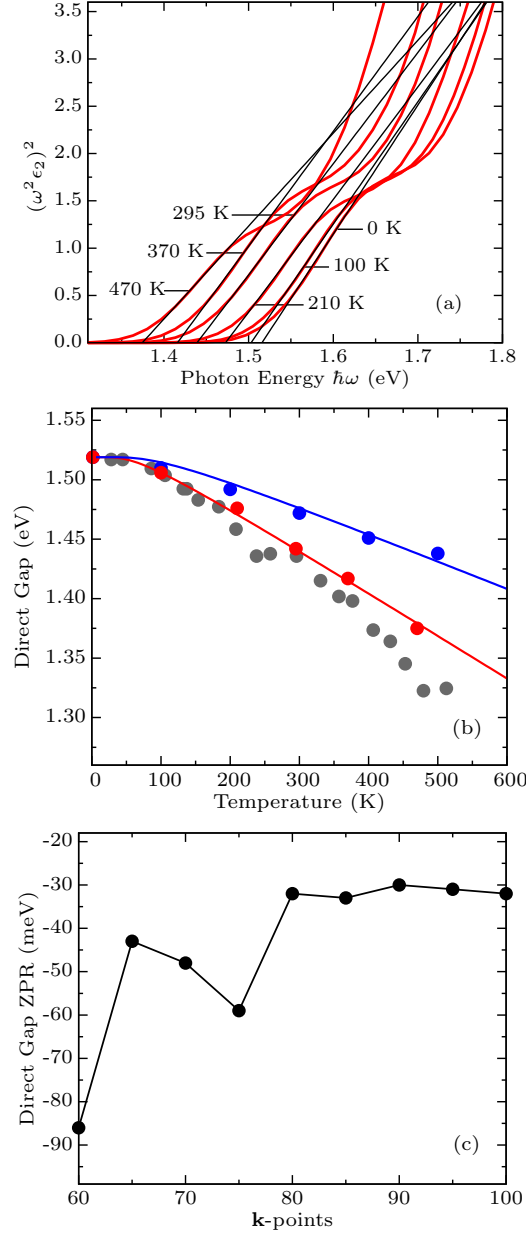


Figure 4.7.3: (a) Tauc plots of GaAs for various temperatures, as calculated using the WL theory in a $8 \times 8 \times 8$ supercell. For our calculations we employed the quasi-harmonic approximation. The red spectra correspond to $(\omega^2 \epsilon_2)^2$ and the thin black lines represent the corresponding linear fits taken in the energy range 1.42-1.62 eV. (b) Direct band gap of GaAs as a function of temperature: calculations in the quasi-harmonic approximation (red discs), calculations without considering the lattice thermal expansion (blue discs), and experimental values (grey discs) from Ref. [75]. The lines are single-oscillator fits [Eq. (2.65)], which are used as guides to the eye. (c) Convergence of the zero-point renormalisation as a function of the number of k-points, in a $8 \times 8 \times 8$ supercell.

negligible. We found a zero-point renormalisation of 32 meV from our calculations in an $8 \times 8 \times 8$ supercell. Our result is in good agreement with previous calculations, yielding 23 meV [92], as well as with the experimental range of 57 ± 29 meV. We expect that GW corrections will further increase the zero-point correction by ~ 10 meV [92]. For completeness in Fig. 4.7.3(c) we show the convergence of the ZPR with the $\mathbf{k}$ -point sampling.

Recently it was pointed out that, in the case of polar semiconductors, calculations within the Allen-Heine theory reveal a divergence when the quasiparticle lifetimes are set to zero [94, 97]. This artefact is related to the Fröhlich electron-phonon coupling [125, 126], discussed in Sec. 2.3.6. In the present supercell calculations, it is practically impossible to examine whether we would have a singularity in the limit of a very large simulation cell. However, we speculate that our supercell calculations should eliminate this problem, because the BvK boundary conditions effectively short-circuit the electric field generated by the displacement of atoms along the LO mode. This aspect requires separate investigation and its beyond the scopus of this thesis.

In order to account for the influence of the Fröhlich polar coupling on the band gap renormalisation of GaAs we employ Eq. (2.66). More computational details are provided in Sec. 4.8. We find that at 0 K, the effect is a shift of -1.9 meV and 4.5 meV to the hole and electron states, respectively. This leads to the refinement of the total zero-point renormalisation by -6.4 meV. We also report that the temperature dependence of the Fröhlich contribution to the band gap renormalisation is negligible, varying from -6.4 meV at 0 K to -7.5 meV at 300 K. This reflects the weak Fröhlich interaction in GaAs that results from the small difference between the static permittivity ($\kappa_0 = 12.5$) and high-frequency dielectric constant ($\kappa_\infty = 10.9$) [128].

In Table 5.2.1 we give a summary of all our calculated zero-point renormalisation values for Si, C, and GaAs, and compare them with previous theory and experiment.

Table 4.7.1: Vibrational zero-point renormalisation of the band gaps of silicon, diamond, and gallium arsenide. Our present results based on the WL theory and Tauc plots are compared with previous DFT/LDA calculations and with experiment. The grids within the brackets indicate the sampling of the Brillouin zone or the supercell size employed in previous calculations.

Indirect gap			
	Present	Previous	Experiment
Si	57	56 ¹ , 58 ² , 60 ³	62 ⁴ , 64 ⁵
C	345	330 ¹ , 334 ⁶ , 343 ⁷ , 344 ²	370 ⁵ , 410 ⁸
Direct gap			
	Present	Previous	Experiment
Si	44	28 ⁹ , 42 ¹	25 ± 17 ¹⁰
C	450	409 ¹¹ , 410 ⁶ , 416 ¹ , 430 ⁹	180 ± 150 ¹² , 450 ± 370 ¹²
GaAs	32	23 ¹³	57 ± 29 ¹⁴

¹Ref. [94] (75×75×75), ²Ref. [96] (6×6×6), ³Ref. [93] (5×5×5), ⁴Ref. [113], ⁵Ref. [102], ⁶Ref. [93] (6×6×6), ⁷Ref. [95] (48×48×48), ⁸Ref. [111], ⁹Ref. [120] (4×4×4), ¹⁰Ref. [73], ¹¹Ref. [91], ¹²Ref. [74], ¹³Ref. [92], ¹⁴Ref. [75].

4.7.4 Zero-point renormalisation of degenerate band edges: C

Here in this small section, we point out that, when small supercells are employed, the zero-point renormalisation incorporates an extra spurious contribution in the case of degenerate band edges. This problem arises from a linear-order electron-phonon coupling which lifts the band degeneracy, and has already been observed in path-integral molecular dynamics calculations on diamond using a supercell with 64 atoms [172]. This effect is reflected in the density of states shown in Fig. 4.7.4, where three separate peaks near the valence band maximum are revealed. In the limit of large supercells this effect should disappear, since it arises from zone-centre phonons, whose weight becomes negligibly small as $M \rightarrow \infty$. Indeed, our calculations for the density of states referring to $8 \times 8 \times 8$ (blue) supercells show that this spurious contribution is eliminated, and therefore the zero-point renormalisation of the band gap can be safely determined.

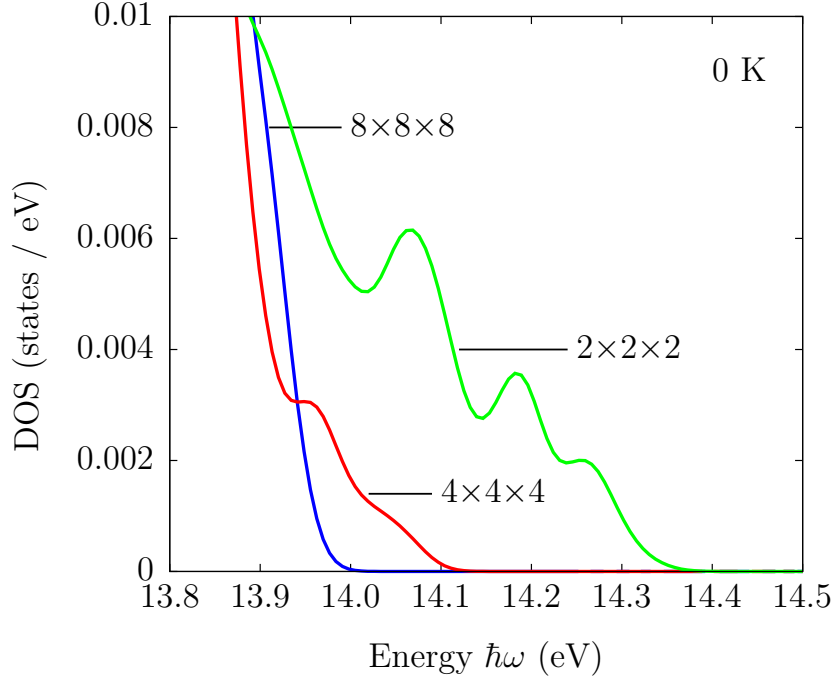


Figure 4.7.4: Density of states near the valence band edge of diamond at 0 K. Calculations were performed on $2 \times 2 \times 2$ (green), $4 \times 4 \times 4$ (red) and $8 \times 8 \times 8$ (blue) supercells using the one-shot WL method. We used 2560, 320 and 40 $\mathbf{k}$ -points, respectively, and a Gaussian broadening of 15 meV. The broken degeneracy of the valence band top, which can be seen for the $2 \times 2 \times 2$ supercell, tends to vanish with increasing supercell size.

4.7.5 Zero-point renormalisation of the band gap from the joint-density of states: Si, C, and GaAs

In this section we present an accurate procedure for determining the zero-point band gap renormalisation within a supercell calculation, following our discussion in Sec. 4.5.2.

Here we use Eqs. (4.21) and (4.22) to calculate the zero-point renormalisation of the band gap. This is determined by the horizontal offset between the curves $J(\omega)^{1/2}$ and $J(\omega; T = 0)^{1/2}$. This procedure is very accurate because we are comparing two calculations executed under identical conditions; therefore the numerical errors arising from the choice of the energy range, the Gaussian broadening and the Brillouin zone sampling tend to cancel out.

In Figs. 4.7.5 (a), (b) and (c) we show the square-root of the joint-density of states

of silicon, diamond and gallium arsenide, calculated with the atoms in their relaxed positions (red lines), and the corresponding one-shot WL calculations at 0 K (blue lines). In all cases the two curves are parallel, and the horizontal offset between the

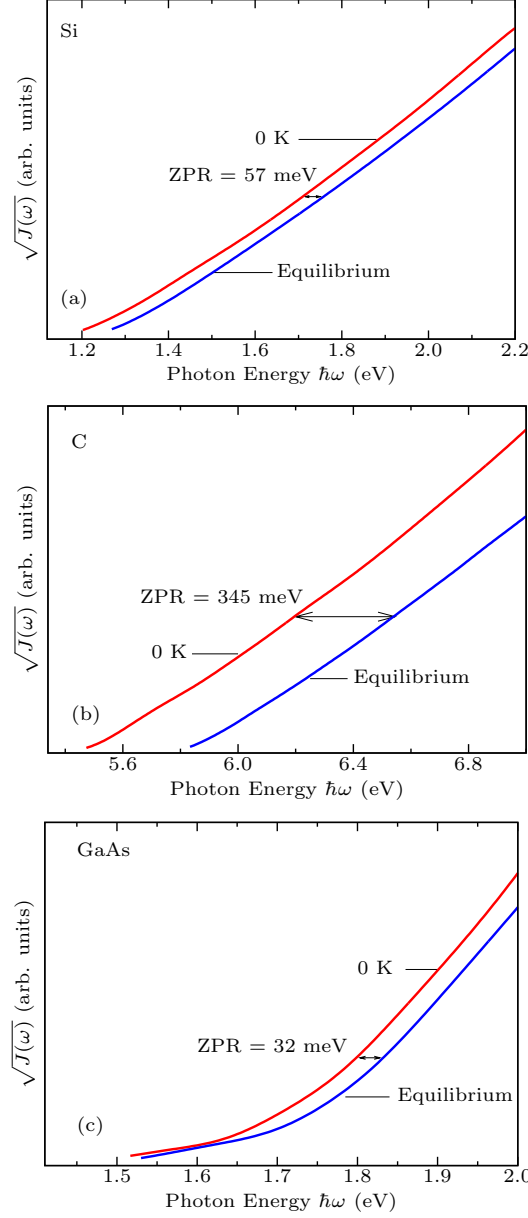


Figure 4.7.5: Square-root of the joint-density of states of (a) silicon, (b) diamond, and (c) gallium arsenide. The calculations were performed with nuclei clamped in their equilibrium positions (blue lines), and using the one-shot WL method at $T = 0$ K (red lines). The horizontal offset between blue and red curves corresponds to the zero-point renormalisation of the band gap in each case. The calculations for the equilibrium structures were performed in the primitive unit cells, using 20480, 20480 and 51200 random $\mathbf{k}$ -points for Si, C, and GaAs, respectively. The WL calculations were performed on $8 \times 8 \times 8$ supercells, using 40, 40, and 100 random $\mathbf{k}$ -points for Si, C, and GaAs, respectively. A Gaussian broadening of 30 meV was used in all plots.

curves gives the zero-point renormalisation. Using this method, our values of the zero-point renormalisation of the band gaps of Si, C and GaAs are 57 meV, 345 meV and 32 meV, respectively. For completeness, in Fig. D.4.2 we also report the temperature dependence of the joint-density of states of these three semiconductors.

We should point out that this new procedure for calculating the zero-point renormalisation critically requires the JDOS as opposed to the optical spectra. The reason is that in the case of indirect-gap materials, no optical absorption is revealed below the direct gap in the equilibrium structure.

4.8 Computational setup

Here we present the computational setup used for obtaining the results presented in this Chapter. All calculations were performed in the DFT/LDA framework [49, 135]. We employed norm-conserving pseudopotentials [136], as implemented in the Quantum ESPRESSO package [32]. The KS wavefunctions were expanded using plane-wave basis sets with kinetic energy cutoffs of 40 Ry, 50 Ry, and 120 Ry for Si, GaAs and C, respectively. At variance with the frozen-phonon calculations used for our results in the previous chapter, here the interatomic force constants, and hence the phonons, were calculated in the primitive unit cells via density functional perturbation theory [64]. This reduced the computational cost significantly.

For calculating the band gap renormalisation, we used two atomic configurations: our optimal configuration, given by Eq. (4.4), and its antithetic pair, i.e. by swapping the signs of all normal coordinates. As shown in Sec. 4.6.2, this choice ensures high accuracy in the spectra near the absorption onset. The absorption coefficients shown in Fig. 4.6.1 were calculated using Eq. (B.9). The contribution from the nonlocal part of the pseudopotential [see Appendix B.2] was included in our calculations for the optical matrix elements using Yambo [103]. To account for the DFT band gap problem, we applied a rigid shift to the unoccupied bands so as to mimic GW corrections [see Sec. 3.3.2]. The scissor corrections were determined based on previous GW calcula-

tions [142, 173]. In particular, we used $\Delta = 0.74$ eV, 1.64 eV, [142] and 0.53 eV [173] for Si, C, and GaAs, respectively. The nonlocality of the scissor operator was considered in the oscillator strengths [77] via the normalising factor given in Eq. (3.9). As discussed in Sec. 3.3.2, this ensures that the f -sum rule is correctly fulfilled.

The WL dielectric functions were evaluated by replacing the Dirac deltas appearing in Eq. (2.73) with Gaussians of width 30 meV for Si and C, and 50 meV, for GaAs. All calculations presented in this work were performed using $8 \times 8 \times 8$ supercells of the primitive unit cell, unless specified otherwise. In order to sample the $8 \times 8 \times 8$ supercells of Si, C and GaAs we used 40, 40, and 100 random $\mathbf{k}$ -points, respectively. The weights were determined by Voronoi triangulation [79]. This sampling procedure was discussed in Sec. 3.3.

The expansion of the lattice with temperature was only considered for GaAs. This is justified by the fact that the band gaps of Si and C change by less than 2 meV when using the lattice constants at $T = 0$ K and $T = 300$ K. The temperature dependence of the lattice constants of Si and C was taken from Refs. [140, 174].

In the case of GaAs, the influence of Fröhlich coupling on the band extrema was evaluated by substituting into Eq. (2.66) the values $\kappa_0 = 12.5$, $\kappa_\infty = 10.9$, $\hbar\omega_{LO} = 36$ meV, $m_e^* = 0.067$ and $m_h^* = 0.6$ [128]. We also considered a radius of integration equivalent to the radius of the Debye sphere with volume equal to the Brillouin zone of the $8 \times 8 \times 8$ GaAs supercell.

4.9 Conclusions

In this Chapter we introduced a new first principles method for the calculation of temperature-dependent optical spectra and quantum zero-point renormalisation of semiconductors, based on the Williams-Lax theory. The work presented here, significantly expands the scope of our previous investigation in Chapter 3, by completely removing the complexity of the stochastic sampling over the nuclear wavefunctions. In particular, we demonstrated using both, a formal proof and explicit *ab-initio* calcu-

lations, that in order to evaluate WL dielectric functions and band gaps at finite temperature it is sufficient to perform only one calculation in a supercell with the atoms in a well-defined configuration, specified by Eq. (4.23).

Using this new method we reported the first *ab-initio* calculations of the *complete* phonon-assisted absorption spectra of C and GaAs, and we confirmed our results obtained for silicon in Chapter 3. Our calculated absorption coefficients compare well with experiment regarding the lineshape, location of the absorption onset, and magnitude of oscillator strengths. From our optical spectra we extracted the zero-point renormalisation and the temperature dependence of the indirect and direct band gaps of Si, C, and GaAs. This was achieved using standard experimental procedures, described in Sec. 4.5. Our results are in good agreement with experiment and previous theoretical studies.

The significance of using the optimal configuration specified by Eq. (4.4) is reflected by the fact that it allows us to calculate optical spectra at finite temperature using a *single* nuclear configuration. This represents an important advance over alternative methods, including importance-sampling Monte Carlo, path-integrals molecular dynamics, or the direct evaluation of each term in Eq. (4.3) using frozen-phonon calculations for each vibrational mode.

We stress that, although we have proven the limit in Eq. (4.8), we cannot specify the convergence rate of $\epsilon_2^{1C}(\omega; T)$ towards the exact WL dielectric function. In principle this rate could be estimated *a priori* by checking the convergence of the Eliashberg spectral function, given by Eq. (2.63), in a calculation within the primitive unit cell. In practice we found it easier to directly check the convergence of $\epsilon_2^{1C}(\omega; T)$ for supercells of increasing size.

In Sec. 4.4 we reported for the first time the formal relation between the Williams-Lax theory of optical transitions, the Allen-Heine theory of phonon-induced renormalisation of the band structures, and the Hall-Bardeen-Blatt theory of indirect optical absorption. In particular, we proved that both the AH theory and the HBB theory can

be derived as low-order approximations of the WL theory, as well as we derived an expression [see Eq. (4.15)] that includes seamlessly the AH and HBB theories on the same footing.

Finally we summarise the key advantages of the WL approach: (i) The method of calculating optical spectra is simple and can be performed as a post-processing tool on top of any electronic structure package. (ii) The formalism is *agnostic* of the level of theory used to describe optical excitations. Therefore the same procedure can be used within the theories of independent-particle approximation, random-phase approximation [175–177], Hartree-Fock [38], and GW/Bethe-Salpeter [159]. (iii) The method combines the AH theory and the HBB theory. (iv) It enables calculations of *full* temperature-dependent optical spectra, capturing correctly direct and indirect optical transitions, as well as the interference between these two processes up to all orders.

Chapter 5

Inverse Varshni effect in lead halide perovskites

The photovoltaic applications of lead halide perovskites have been a big field of research over the last five years with energy-conversion efficiencies up to 22.1%. An important characteristic of the organic-inorganic lead halide perovskites is the blue-shift of the absorption edge with increasing temperature, known as the “inverse Varshni effect”, introduced in Sec. 2.3.5. This differs from the behaviour found in conventional semiconductors, like Si, C and GaAs, investigated in the two previous chapters. The underlying physics driving the “inverse Varshni effect” has not been well understood. Here we show that the band gap opening of the metal-halide perovskites with temperature strongly correlates to the local distortion of the octahedra induced from modes with metal-halide-metal bending or rocking character. We attempt to rationalise this behaviour by calculating separately the Debye-Waller and Fan electron-phonon contributions to the band gap renormalisation of well-defined vibrational modes. To support our findings we calculate the optical gap of the low and room temperature phases of methylammonium lead triiodide (MAPbI_3) and we find good agreement with experiments. The present work is under preparation for publication.

5.1 Introduction

During recent years, methylammonium lead triiodide (MAPbI_3) perovskite has attracted great attention in the field of high efficient photovoltaics [178–181], because of its outstanding light-harvesting properties. In fact, MAPbI_3 exhibits large absorption coefficients and a direct band gap of ~ 1.6 eV [122, 182–187] close to the optimum value of 1.34 eV predicted by the Shockley-Queisser theory [188]. Other promising applications include light-emitting diodes, thermoelectrics, and devices for solar-to-fuel energy conversion [189–192].

The band gap and structure of metal-halide perovskites are highly dependent on the temperature [122, 183, 187, 193, 194]. For example, MAPbI_3 undergoes a phase transition from orthorhombic (space group: $Pnma$) to tetragonal (space group: $I4/m$) at 160 K and from tetragonal to cubic (space group: $Pm\bar{3}m$) at 310 K. These phase transitions are accompanied by band gap changes, which are attributed to the degree of tilting of the corner-sharing octahedra network [194–196]. In fact, in Ref. [196], first principles calculations demonstrate that the band gap of perovskites strongly correlates to the metal-halide-metal bond angles and therefore to the hybridisation between the metal and halide orbitals.

Despite the permanent distortion of the octahedral network at each structural phase, band gap changes are also induced from the atomic vibrations and thermal lattice expansion. In MAPbI_3 crystals, the absorption edge is gradually blue shifted as the temperature increases [122, 182, 187] and a similar behaviour has been measured for some other perovskite compounds [197–199]. This intriguing phenomenon is known as the “inverse Varshni effect”, meaning a positive renormalisation of the gap with temperature, and opposes to what is experienced in typical semiconductors. [104] *Ab-initio* calculations [200, 201] attribute the anomalous temperature dependence of the band gap in CsSnI_3 to the thermal expansion of the lattice and to the additional stretching of the Sn-I bonds induced from atomic vibrations. For the case of MAPbI_3 crystals, the authors of Ref. [199] attribute this behaviour to the thermal expansion of the lattice

without taking into account vibrational effects. In Ref. [121], band gap calculations were performed for the cubic phase of MAPbI_3 and CsPbI_3 , including both thermal expansion and vibrational motion, showing good agreement with experiment. However, the physical origin that leads to this unusual behaviour is still unclear.

In this Chapter we elucidate the physical mechanisms that underpin the “inverse Varshni effect” in structural phases of MAPbI_3 . The organisation of the Chapter is as follows: In Sec. 5.2.1 we calculate the temperature dependence of the band gap in the low and room temperature phases of MAPbI_3 . Our results exhibit good agreement with experiment and a positive renormalisation of the band gap with temperature. We also show that electron-phonon coupling is the most important contribution driving the “inverse Varshni effect”. In order to shed light on the origin of this behaviour we present, in Sec 5.2.2, the Eliashberg spectral function in the orthorhombic phase and classify the phonon modes in two different groups. These include phonon modes with Pb-I-Pb bending or rocking character and Pb-I stretching character. In Sec. 5.2.3, we extend our analysis by presenting a separate set of calculations using modes with well-defined character. These show that there is a linear correlation between the local distortion of the PbI_6 octahedra and the decrease (increase) of the valence band top (conduction band bottom). In Sec. 5.2.3, we analyse the Debye-Waller and Fan electron-phonon contributions calculated for the modes with well-defined character and identify the key physical mechanisms that lead to the magnitude and sign of the energy level renormalisation. Our analysis admits that the main mechanisms driving the band gap opening in MAPbI_3 are the vibrational modes with Pb-I-Pb bending or rocking character. Section 5.3 reports all computational details of the calculations presented in this Chapter. In Sec. 5.4, we summarise our main results. Supporting findings and discussions are left to Appendices E.1-E.3.

5.2 Results: MAPbI₃

5.2.1 Temperature dependence of the band gap

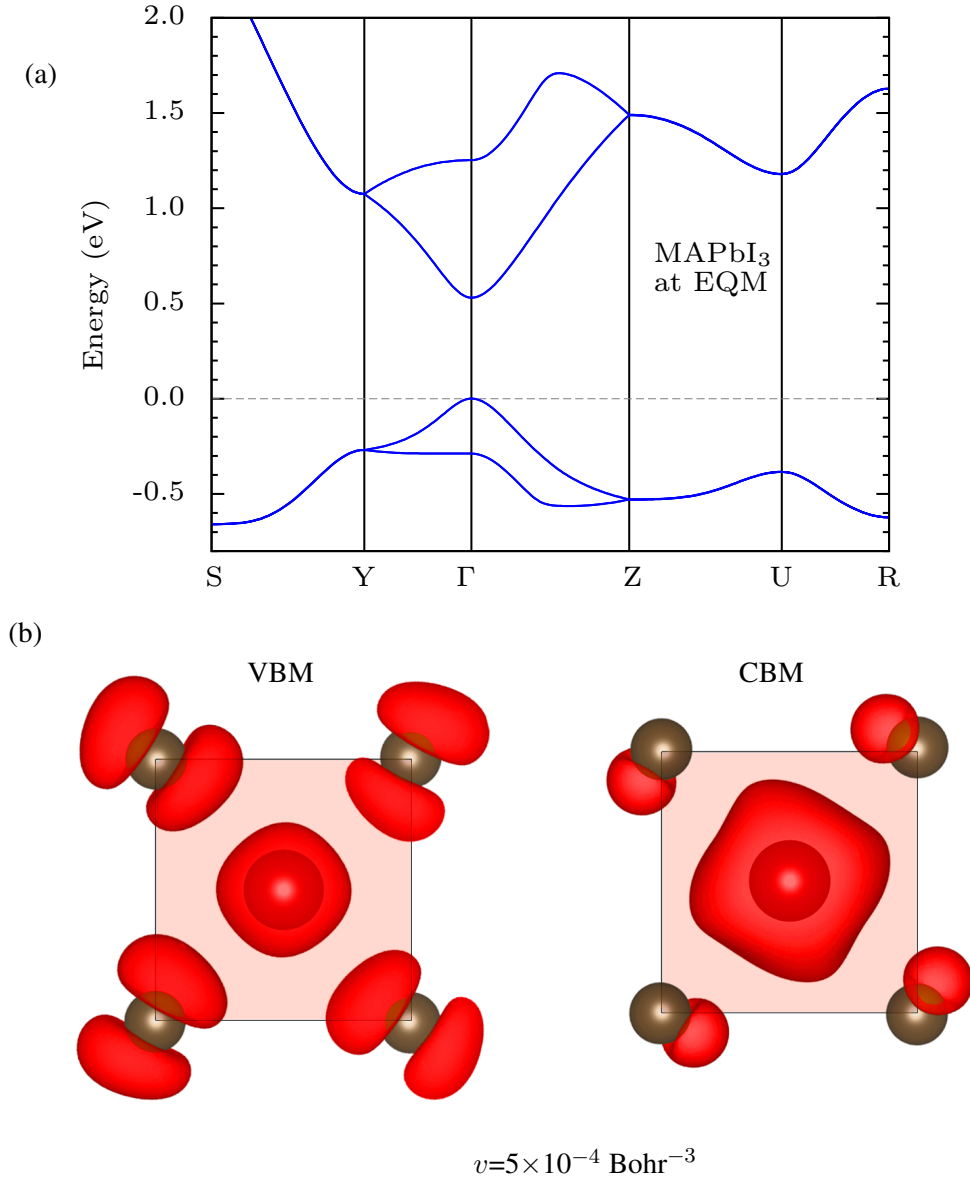


Figure 5.2.1: (a) Electronic band structure of MAPbI₃ in the orthorhombic phase with the atoms fixed at their equilibrium positions. For clarity we present only the two doubly degenerate occupied (unoccupied) states which are higher (lower) in energy. (b) Spatial distribution of the unperturbed charge density $|\psi_{n\mathbf{k}}(\mathbf{r})|^2$ in the valence band maximum (VBM) and conduction band minimum (CBM). Pb and I atoms lie at the centre and the corners of the octahedron, respectively. The iso-value v used for to plot charge density is also shown.

Figure 5.2.1(a) shows the band structure of MAPbI₃ in the orthorhombic phase. MAPbI₃ is a direct band gap semiconductor with the valence band maximum (VBM)

and conduction band minimum (CBM) at the Γ -point. In the presence of spin-orbit coupling the VBM is formed by a two-fold spin degenerate state. This state is associated to hybridisations of Pb 6s-orbitals and I 5p-orbitals forming weak σ -antibonding interactions [202, 203]. The CBM is also two-fold spin degenerate and is predominantly associated to Pb 6p-orbitals with small contributions of I 5p-orbitals forming weak π -antibonding interactions [202, 203]. The states associated with the cation (MA) are well above (below) the CBM (VBM) [196]. In Fig. 5.2.1(b), we show the charge density distribution in the VBM and CBM. Owing to the σ -bonding in the VBM, the charge density lies along the internuclear axis connecting the Pb and I atoms. In contrast, the charge density around the I atoms in the CBM is directed perpendicular to the internuclear axis reflecting the π -bonds.

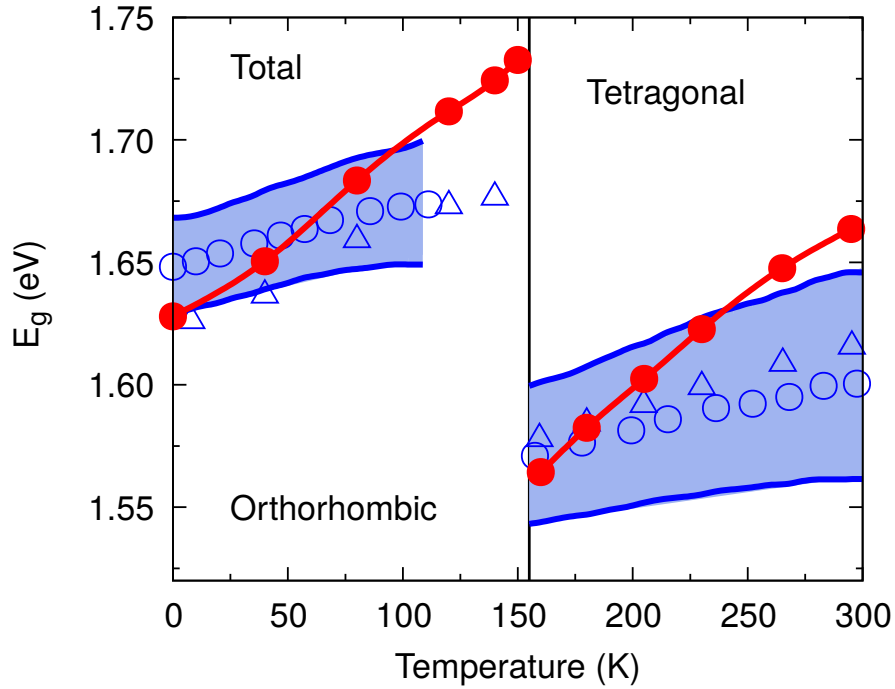


Figure 5.2.2: Temperature-dependence of the direct band gap of MAPbI₃ in the orthorhombic (0-155 K) and tetragonal (155-300 K) phases: red discs correspond to the present calculations; blue triangles and circles are experimental data from Refs. [122] and [199], respectively. The blue shading corresponds to the linewidth of the measured photoluminescence peak used to determine the band gap [199]. The calculations include contributions to the band gap renormalisation induced from atomic vibrations, thermal lattice expansion and Fröhlich electron-phonon coupling. A rigid shift of 1.13 eV is used for the calculated band gaps of the orthorhombic and tetragonal phases. This value is close to the GW quasiparticle corrections calculated in Refs. [194, 204].

In Fig. 5.2.2 we compare our calculations (red circles) for the temperature dependence of the band gap of MAPbI₃ in the orthorhombic and tetragonal phases to the experimental data (blue circles and triangles) from Refs. [122] and [199]. For our calculations we employ density functional theory in the local density approximation including spin-orbit coupling (SOC). The band gap E_g is evaluated as the sum of four different contributions: $E_g = E_B + E_{ph} + E_{Fr} + E_{LE}$, where E_B , E_{ph} , E_{Fr} and E_{LE} stand for the energy contributions coming from the bare (equilibrium) structure, atomic vibrations, Fröhlich polar coupling and thermal lattice expansion, respectively. For both phases our results reveal an increase of the band gap with temperature compatible with the experimental values. Discrepancies between theory and experiment are attributed to various effects coming from the four contributions which are analysed separately in the following.

Figure 5.2.3(a) shows the band gap of MAPbI₃ in the orthorhombic and tetragonal phases with the atoms and lattice parameters fixed at their equilibrium positions. At the phase transition temperature the band gap closes by 175 meV. This can qualitatively be explained with tight binding arguments and linked with the change in the hybridisation between the metal-halide orbitals [195, 196]. In fact, the change of the apical Pb-I-Pb angle from 150° towards 180° leads to the increase in the head-on overlap between σ_{sp}^* bonds, thereby increasing the energy of the VBM. An opposite effect results in lowering the energy of the CBM, as π_{pp}^* interactions are weakened upon opening of the Pb-I-Pb angle. Another structural characteristic which leads to the decrease of the band gap at the phase transition is the orientation of the methylammonium (MA) cations [199, 205]. In the orthorhombic phase the MA cations are orientationally aligned [206–209]. In contrast, in the tetragonal structure, the MA cations are partially disordered because of symmetry, and can exhibit up to 8 different orientations [209]. DFT calculations have shown that the disordered cations lead to the relative increase of the VBM, thereby closing the band gap [199]. The variability of the band gap due to the MA orientations has been examined in Ref. [205]. This aspect is beyond the scope of this thesis, as we

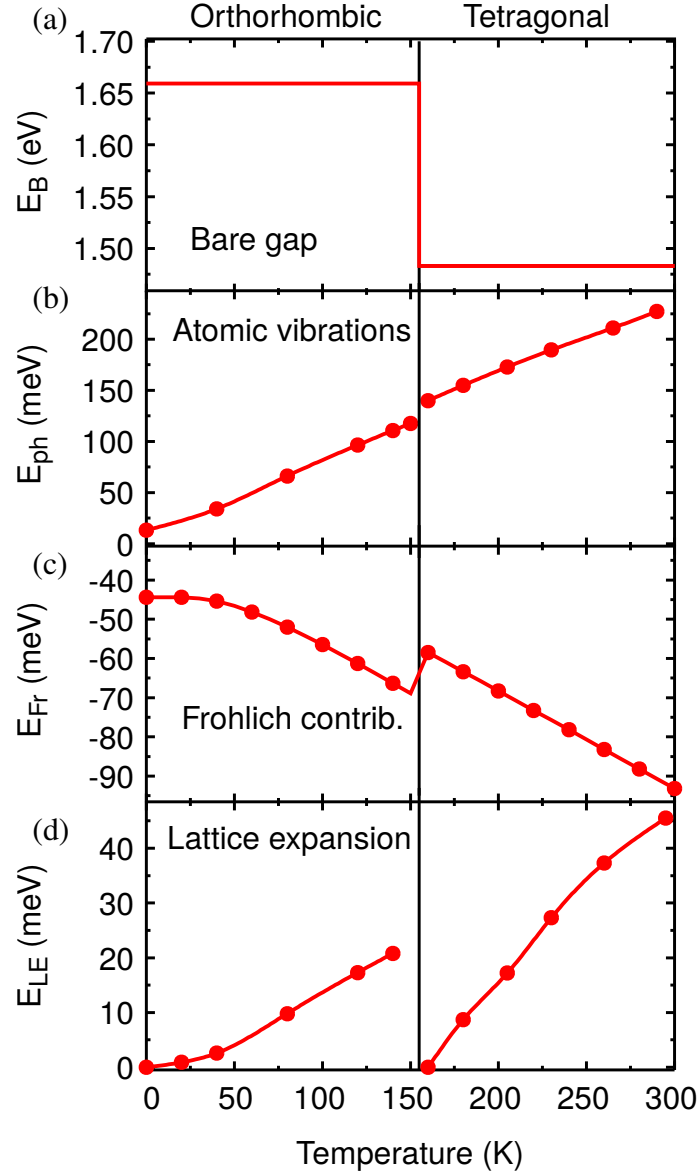


Figure 5.2.3: Contributions to the band gap of MAPbI_3 in the orthorhombic (0-155 K) and tetragonal (155-300 K). (a) Band gap of MAPbI_3 with atoms and lattice constants fixed at their equilibrium values. (b) Temperature-dependence of the band gap renormalisation due to atomic vibrations. The calculations were performed within the Williams-Lax theory [22, 23], using the optimal configuration and its antithetic pair as analysed in Sec. 4.6.1. Convergence tests with respect the supercell size are left to Appendix E.1. (c) Temperature-dependence of the band gap renormalisation due to the Fröhlich polar coupling. The data was evaluated using the analytic expression in Eq. (2.66). (d) Temperature-dependence of the band gap renormalisation due to thermal lattice expansion. The lattice constants were varied according to the experimental values [209].

concentrate mainly on the effect of the atomic vibrations.

Figure 5.2.3(b) shows the band gap renormalisation of MAPbI_3 induced from vibrational atomic motion (E_{ph}) as a function of temperature. Our calculations were

performed using the one-shot procedure described in Sec. 4.6.1, and based on the Williams-Lax theory in the harmonic approximation [22, 23]. The vibrational eigenmodes and eigenfrequencies were calculated using density functional perturbation theory [64]. All information about the computational details is presented in Sec. 5.3. In Fig. E.1.1 of Appendix E.1, we also show convergence tests of the band gap as a function of the supercell size. Our computations reveal a positive zero-point renormalisation of 13 meV. We emphasise that our calculations do not capture correctly the influence of the Fröhlich polar coupling, which is analysed below. In addition, our calculations do not include anharmonic and quasiparticle effects which are also expected to refine the effect of electron-phonon coupling on the band gap renormalisation. In both, the orthorhombic and tetragonal phases, the harmonic electron-phonon coupling leads to the opening of the band gap. The same dependence of the band gap energy on the atomic vibrations was calculated for the cubic phase of MAPbI₃ in Ref. [121]. This behaviour opposes to the one calculated in conventional semiconductors, like Si, C and GaAs, and its physical origin is addressed later in Sec. 5.2.4. Figure 5.2.3(b) also reveals that there is a small discontinuity of the band gap renormalisation at the phase transition. This shows that E_{ph} is almost agnostic to the MAPbI₃ structural phases.

As discussed in Sec. 2.3.4, for polar materials, the vibrational motion along the longitudinal optical (LO) mode induces electric fields which scatter the electrons leading to an extra correction for the energy level renormalisation. In the case of MAPbI₃, photoluminescence measurements, supported by theoretical calculations, reveal that the scattering of electrons from LO phonons is the most important source of electron-phonon coupling [197]. Our calculations in Fig. 5.2.3(b) do not include correctly this effect, discussed in Sec. 2.3.6. In order to account for this effect in our calculations we combine the analytic expression in Eq. (2.66) and first principle calculations (see Sec. 5.3). In Fig. 5.2.3(c) we present the influence of the Fröhlich coupling on the band gap as a function of temperature. We find that at 0 K the effect is a shift of -22 meV and 23 meV to the hole and electron states, respectively. This decreases

the zero-point renormalisation by 45 meV. In contrast to the case of GaAs, examined in Sec. 4.7.3, such a large renormalisation is a direct consequence of the large difference between the dielectric permittivity ($\kappa_0 = 25.3$) and the high-frequency dielectric constant ($\kappa_\infty = 5.8$). The small discontinuity of the contribution from the Fröhlich coupling at the orthorhombic to tetragonal phase transition is related to the small differences between the dielectric permittivity, the high-frequency dielectric constant [210, 211] and the frequency of the LO mode at the two phases (see Sec. 5.3).

Figure 5.2.3(d) shows our calculations for the band gap change of MAPbI₃ due to the thermal lattice expansion in the temperature range 0–300 K. The lattice parameters were varied according to their experimental values from Ref. [209]. The opening of the band gap with the volume expansion is characteristic for hybrid perovskites [199, 212, 213] and opposes to the trend calculated in typical semiconductors. This behaviour can be attributed to the changes in the overlap between the Pb and I atomic orbitals with the volume expansion of the system [195, 196, 199]. In fact, our calculations show that both the VBM and CBM decrease in energy as the volume of the structure increases. As explained in Ref. [199], the expansion of the crystal reduces the antibonding interactions between the Pb and I atomic orbitals, lowering the energy of both band edges. However, the decrease in VBM is slightly larger than the one in CBM, leading to the overall band gap opening in both phases. This difference can qualitatively be explained by the stronger head-on overlap of σ_{sp}^* bonds in the VBM. We note that other anharmonic effects, such as anharmonic electron-phonon and phonon-phonon couplings, are not included in our calculations.

To facilitate comparison we present in Appendix Fig. E.1.2 the contributions of E_{ph} , E_{Fr} and E_{LE} to the band gap renormalisation at 80 K and 230 K. We find that in both the orthorhombic and tetragonal phases, E_{ph} , is the most important contribution that leads to the band gap opening with temperature. In the rest of this Chapter, we focus on explaining the influence of vibrational motion on the energy renormalisation of the band extrema.

5.2.2 Eliashberg spectral function and mode characterisation

In order to analyse the contribution from each vibrational mode to E_{ph} , we calculate the Eliashberg spectral function for the low temperature phase. The Eliashberg spectral function is given by Eq. (2.63) and therefore the band gap correction coming from the vibrational motion is obtained as $E_{\text{ph},T} = \int d\omega g^2 F(\omega, T)$. For the evaluation of the second derivatives with respect to the nuclear displacement $\frac{\partial^2 E_{\text{ph}}}{\partial x_\nu^2}$, we used finite-difference formulas. This operation requires the displacement of the nuclei along the phonon mode ν by the zero-point amplitude l_ν , defined in Eq. (A.6).

Figure 5.2.4 shows the Eliashberg spectral function $g^2 F(\omega, T)$ for temperatures 0–140 K in the phonon frequency range 0–15 meV. Our calculations refer to the orthorhombic unit cell and to a total of 144 normal modes. All features that appear in the spectrum are mainly associated to the lead-iodide vibrational modes. This is in agreement with the analysis in Ref. [214]. The dominant contribution is positive and comes from the normal modes with frequencies < 9.0 meV. This explains our results in Fig. 5.2.3(b), which are compatible with the experimental observation that the band gap opens with temperature [122, 187, 199]. In the frequency range 11.5–14.0 meV

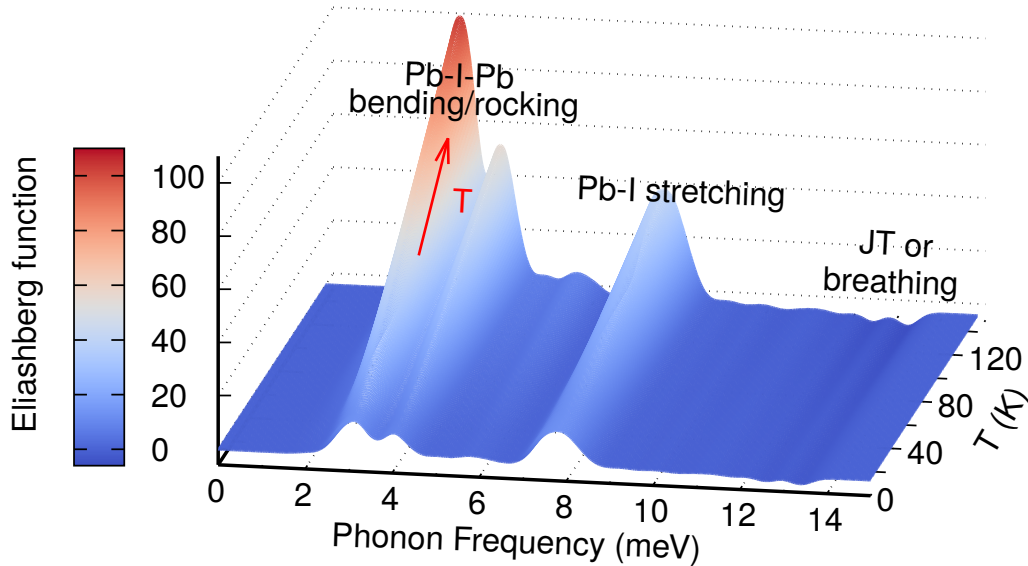


Figure 5.2.4: Eliashberg spectral function of MAPbI₃ in the orthorhombic phase in the temperature range 0–140 K. The legends stand for the character of the vibrational modes for different phonon frequency ranges.

the spectral function is slightly negative. At higher frequencies (not shown), that correspond to vibrations of the MA cations, the Eliashberg spectral function is found to be relatively small. In fact, our calculations reveal that the zero-point renormalisation associated with the lead-iodide vibrational modes is 28.7 meV and to the MA vibrational modes is -5.3 meV. This leads to a total zero-point renormalisation of 23.4 meV, close to the value calculated within the Williams-Lax theory using the same size of simulation cell (see Fig. E.1.1). It can be readily seen in Fig. 5.2.4 that as the temperature increases, the band gap renormalisation is dominated by the vibrational degrees of freedom with frequencies between 1.5-5 meV. This should not come as a surprise, since the low frequency modes are first populated according to the Bose-Einstein distribution $n_\nu(\omega, T)$.

To provide a rationale for the picture derived from $g^2F(\Omega)$, we correlate the variations of the band gap to the character of each phonon mode. Then, in Sec. 5.2.3 we explain how these correlations can qualitatively be connected to the Debye-Waller and Fan electron-phonon contributions to the energy renormalisation of the band edges.

We correlate E_{ph} to the structural distortion induced by each vibrational degree of freedom using the measures of the bond angle variance [215]:

$$\sigma^2 = \frac{1}{11} \sum_{i=1}^{12} (\theta_i - \theta_0)^2 \quad (5.1)$$

and the deviation from the equilibrium bond lengths [215]:

$$\Delta = \frac{1}{6} \sum_{i=1}^6 [(l_i - l_0)]^2. \quad (5.2)$$

Here θ_i/l_i are the bond angles/lengths of an octahedron and the subscript 0 indicates quantities that are evaluated at their equilibrium geometry. These measures describe the local distortions of an octahedron. The choice of quadratic structural parameters is motivated by the quadratic dependence of E_{ph} on the atomic displacements [see Eq. (2.60)].

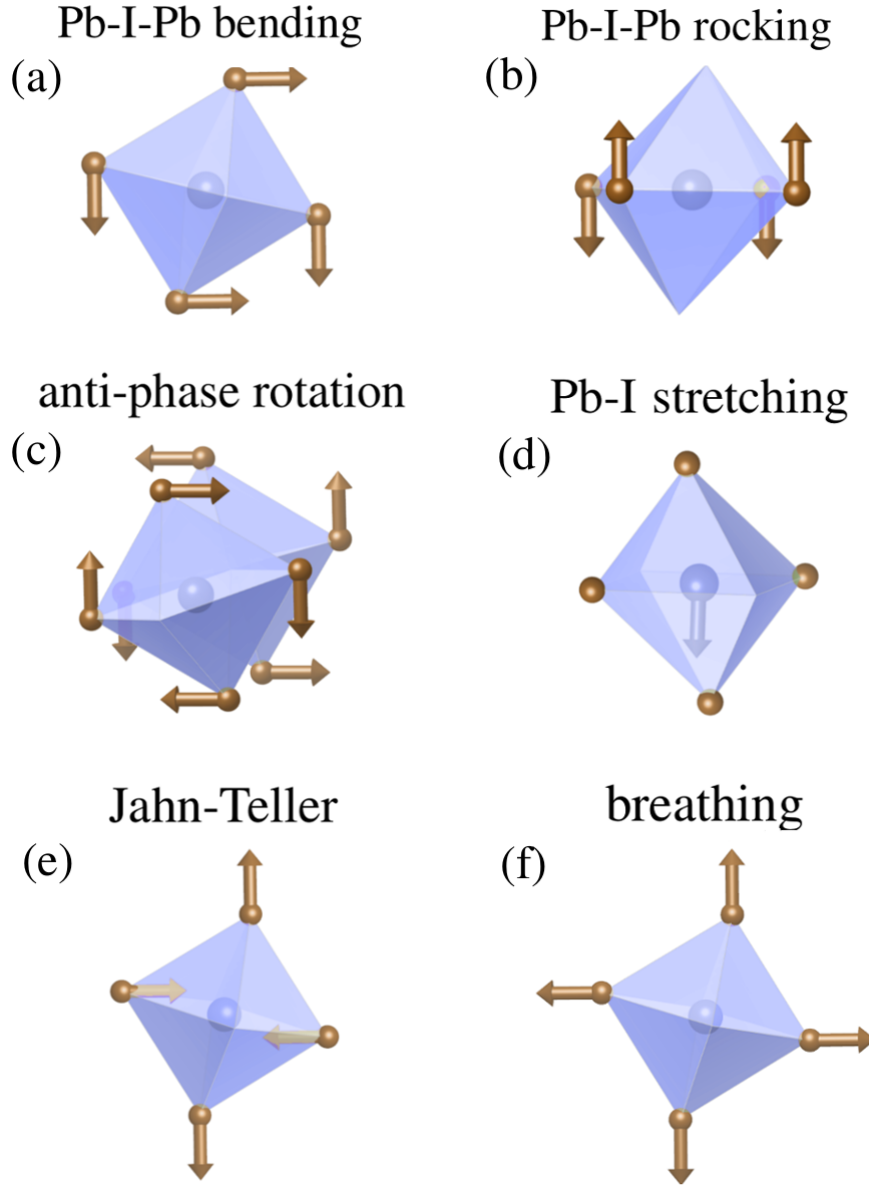


Figure 5.2.5: Schematic representation of the modes with different character. Pb-I-Pb bending, rocking, Jahn-Teller (d-type) and breathing modes have symmetry A_g . The anti-phase rotation of the octahedra and the Pb-I stretching mode have symmetries B_{1g} and B_{3u} , respectively. I atoms (brown spheres) and Pb atoms (grey spheres) lie at the corners and centre of the octahedron, respectively.

In Appendix E.2, Fig. E.2.1, we show that σ^2 and Δ have to be considered separately for explaining the influence of the vibrational degrees of freedom on the band gap. This is mainly due to the normal mode character which is classified as follows [214]. 1) Pb-I-Pb bending or rocking character shown in Figs. 5.2.5(a)-(c): These

modes involve rotations of the I atoms around the Pb atoms, so that the I-Pb-I angles (θ_i) are oscillating around their equilibrium values. The measure used to describe the effect of the Pb-I-Pb bending/rocking modes on each octahedron is given by Eq. (5.1). Specific cases include the in-phase or anti-phase rotation of the PbI_6 octahedra. Along the in-phase mode, the two corner sharing octahedra rotate in the *same* direction around the long axis of the orthorhombic structure. Along the anti-phase mode, the two octahedra rotate in opposite directions around the long axis. The latter rotation is shown schematically in Fig. 5.2.5(c). 2) Pb-I stretching character shown in Figs. 5.2.5(d)-(f): These modes involve the off-centre displacement of the Pb atoms and/or the displacement of I atoms towards to the Pb atoms, so that the Pb-I bond lengths (l_i) oscillate around their equilibrium values. The effect of the Pb-I stretching modes on each octahedron is described by the measure given in Eq. (5.2). Special cases include the breathing and Jahn-Teller distortions [216], shown in Figs. 5.2.5(e) and (f). Jahn-Teller distortion of d-type represents the two-in, two-out displacement of I atoms. Along the breathing mode, the I atoms move either towards to, or away from the Pb atoms.

In Fig. 5.2.6 we show the character of each vibrational mode in the frequency range

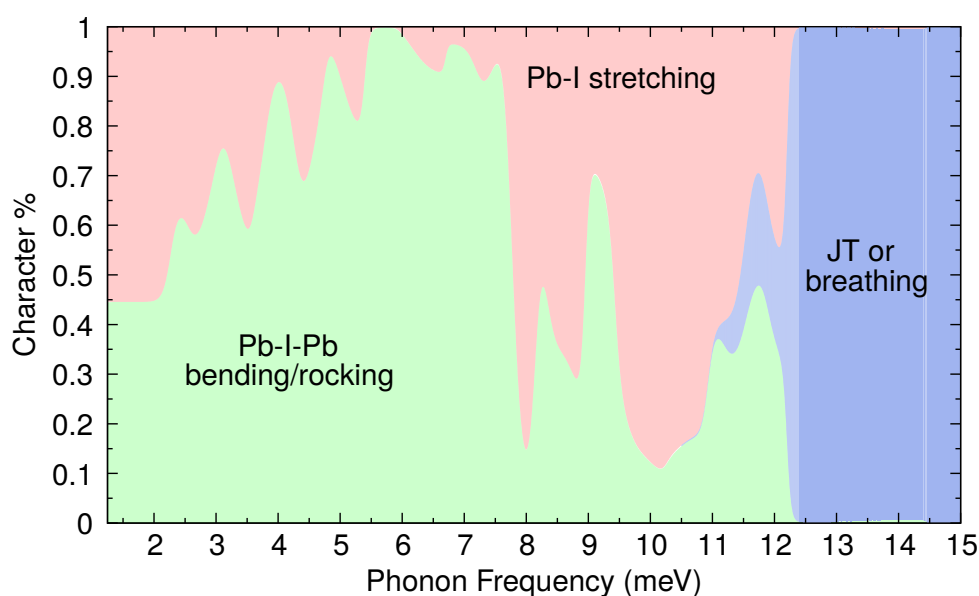


Figure 5.2.6: Character of the vibrational modes for different phonon frequency ranges. Light green, red and blue shadings correspond to modes with Pb-I-Pb bending/rocking, Pb-I stretching and Jahn-Teller/breathing character, respectively.

0–15 meV, determined using the nuclear site analysis method [217, 218]. Details about this method are presented in Sec. 5.3. Following this procedure, the vibrational modes of the PbI₃ network are decomposed into separate atomic displacements of the Pb and the three inequivalent I atoms (one apical and two equatorial). This decomposition results in a new basis containing 48 modes with well-defined character. We find that the low frequency phonons, which dominate the band gap renormalisation as the temperatures increases, correspond to normal modes with Pb-I-Pb bending or rocking character. In the frequency range 7.0–15 meV, the phonons have Pb-I stretching character. The special cases of Jahn-Teller and breathing modes are assigned to phonons in the frequency range 11.5–14.0 meV. It is essential to decompose the mixed character of the calculated normal modes into well-defined atomic displacements to understand the origin of the energy level renormalisation.

5.2.3 Band-gap renormalisation along well-defined normal modes

Now we explore the underlying mechanisms responsible for the picture derived in Fig. 5.2.4. For the new basis, described in Sec. 5.3, we calculate the renormalisation of the energy levels using finite-difference formulas. We find that all modes with well-defined character induce an opening to the band gap except the anti-phase rotation of the octahedra, the anti-phase off-centre displacement of the Pb atoms, the Jahn-Teller and the breathing modes which tend to close the gap. The in-phase rotation of the octahedra induces a negligible renormalisation to the energy levels.

In Figs. 5.2.7(a)-(f), we show the energy renormalisation of the VBM (blue discs), CBM (green discs) and band gap (red discs) as a function of different structural distortion measures. The choice of these measures is determined from the well-defined character of the 6 modes presented here. The schematic representation of the modes is shown in Fig. 5.2.5. To support our results, discussed below in Sec. 5.2.4, we also calculate explicitly the Debye-Waller (DW) and Fan (or self-energy) contributions to the energy level renormalisation. These are reported in Table 5.2.1. Then we attribute

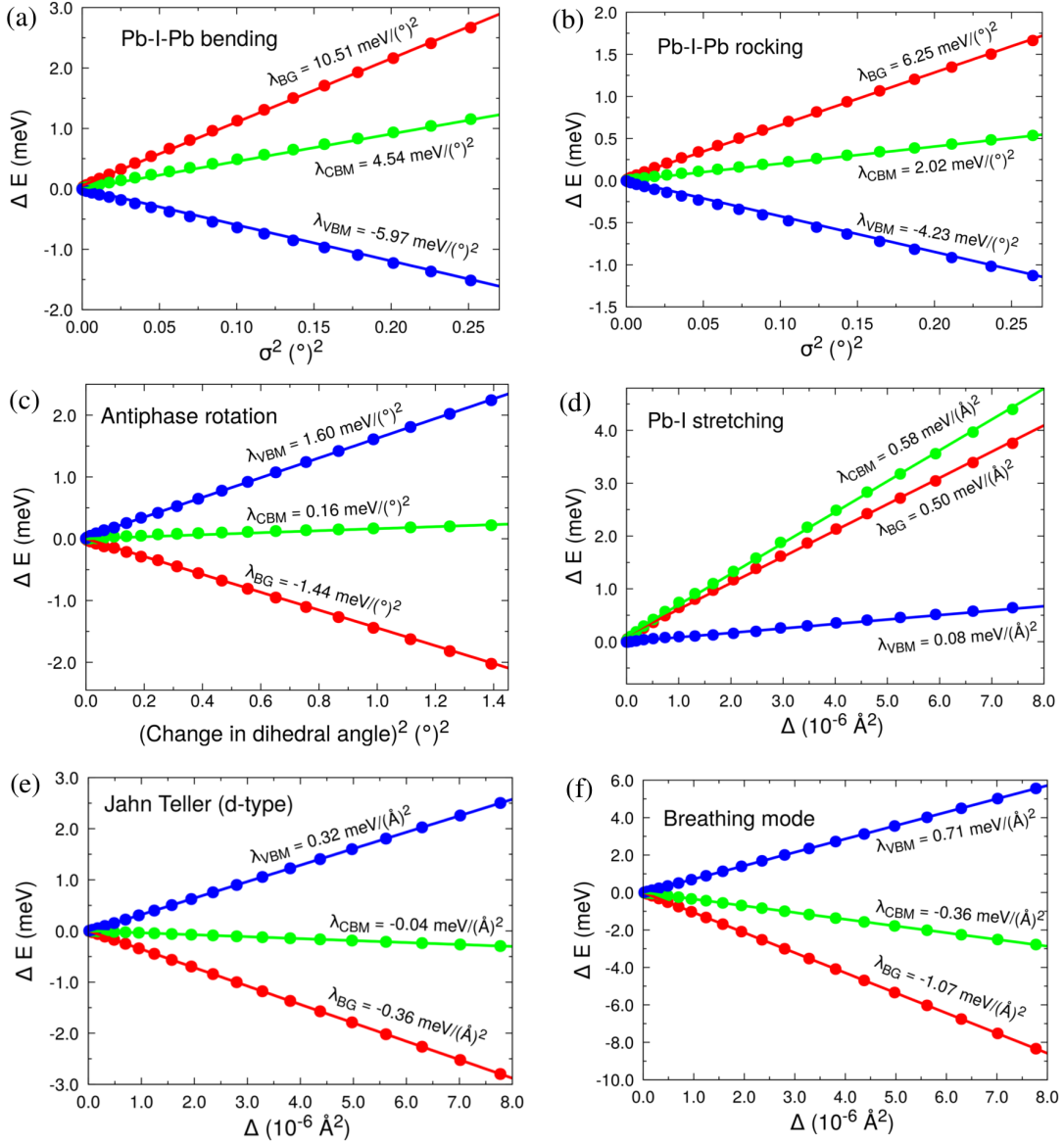


Figure 5.2.7: (a)-(f) Energy renormalisation of the valence band maximum (blue discs), conduction band minimum (green discs) and band gap (red discs) induced from the modes with different character. The schematic representation of the modes is shown in Fig 5.2.5. The distortion measures (see main text) are chosen according to the character of the vibrational mode. The solid lines represent the linear regression to the data with slopes λ .

the changes in the VBM and CBM to the dominant term. For more details about the calculation of the DW and Fan terms we refer the reader to Sec. 5.3. In the following we combine our results shown in Figs. 5.2.7(a)-(f) with those reported in Table 5.2.1 in order to give the physical insight of the “inverse Varshni effect”.

Table 5.2.1 shows the contributions of the DW and Fan terms to the renormalisa-

Table 5.2.1: Contributions of the Debye-Waller (DW) and Fan terms to the energy renormalisation of the valence band maximum (top panel) and conduction band minimum (bottom panel) induced from selective degrees of freedom. Units are in meV.

VBM				
	DW	Fan	DW+Fan	Renorm.
Pb-I-Pb bend.	2.51	-2.85	-0.34	-0.38
Pb-I-Pb rock.	2.60	-2.86	-0.26	-0.28
Anti-phase rot.	2.51	-1.96	0.55	0.56
In-phase rot.	2.59	-2.58	0.01	0.01
Pb-I stretch.	4.34	-4.22	0.12	0.13
Jahn-Teller	6.67	-6.00	0.67	0.63
Breathing	6.64	-5.17	1.47	1.40

CBM				
	DW	Fan	DW+Fan	Renorm.
Pb-I-Pb bend.	1.97	-1.77	0.20	0.29
Pb-I-Pb rock.	1.31	-1.24	0.07	0.13
Anti-phase rot.	1.97	-1.96	0.01	0.05
In-phase rot.	2.07	-2.06	0.01	0.05
Pb-I stretch.	6.07	-4.68	1.39	1.10
Jahn-Teller	0.41	-0.50	-0.09	-0.07
Breathing	0.35	-1.10	-0.75	-0.70

tion of the energy levels induced from the modes shown in Fig. 5.2.5. Here we also report results for the in-phase rotation of the octahedra. We find that for all the modes, the two terms tend to cancel each other, since the DW term is positive and the Fan term is negative. The total contribution of the two terms (DW+Fan) to the energy renormalisation is sufficient to explain qualitatively the energy shifts in the VBM, CBM and band gap. The difference between the sum DW+Fan (4th column of Table 5.2.1) and the calculated renormalisation (5th column of Table 5.2.1) is attributed to the fact that the DW and Fan terms refer only to single-phonon processes, as well as that we do not account correctly for the extra contribution coming from the nonlocal part of the Kohn-Sham potential (see Sec. 5.3).

From Table 5.2.1, it is evident that the energy level renormalisation due to the in-phase rotation of the octahedra is negligible. This is because of the cancellation be-

tween the DW and Fan contributions. On the other hand the downward (upward) shift of the VBM (CBM) induced from the modes with Pb-I-Pb bending or rocking character is a consequence of the larger (smaller) Fan contribution. The concurrent decrease and increase of the VBM and CBM energies, respectively, leads to the opening of the band gap, as shown in Figs. 5.2.7(a) and (b). This is in line with the positive Eliashberg spectral function in the frequency range 1-5 meV, shown in Fig. 5.2.4. The calculated slopes of the linear relationships between the band gap and the bond angle variance are $10.51 \text{ meV}/(^{\circ})^2$ and $6.25 \text{ meV}/(^{\circ})^2$ for Pb-I-Pb bending and rocking, respectively. These values are compatible with those reported in Fig. E.2.1 for the calculated normal modes. We restate here that the same trend is obtained for the rest of the modes with Pb-I-Pb bending or rocking character, except for the in-phase and anti-phase rotations of the octahedra.

In Figs. 5.2.7(c), we show that the band gap decreases due to the anti-phase rotation of the octahedra. This is explained by the upward shift of the VBM, as the DW is larger than the Fan term. Regarding the CBM, the large cancellation between the two terms leads to a negligible energy renormalisation. It is clear that the measure of bond angle variance, given in Eq. (5.1), remains zero due to either the clockwise or anticlockwise rotation of the I atoms (around the Pb atom) in the same octahedron. Although this measure can describe correctly the negligible renormalisation induced by the in-phase rotation of the octahedra, it fails to correlate the energy variations due to the anti-phase rotation. In order to quantify the latter kind of vibrational distortion we consider the changes in the I-Pb-Pb-I dihedral angle [194]. At variance with σ^2 , this measure is not related to the local distortion of an octahedron, and accounts for the simultaneous motion of the two octahedra. In Fig. 5.2.7(c) we obtain a linear relationship between the change in the energy levels and the square of the change in the dihedral angle. The calculated slopes of $\lambda_{\text{VBM}} = 1.60 \text{ meV}/(^{\circ})^2$ and $\lambda_{\text{CBM}} = 0.16 \text{ meV}/(^{\circ})^2$ shows that the up-shift of the VBM dominates over the small up-shift of the CBM. Hence, we conclude that any change in the dihedral angle due to the anti-phase rotation of the

octahedra leads to the closing of the band gap.

Figure 5.2.7(d) shows the relationship between the band gap opening and the Pb-I bond stretching due to the off-centre displacement of the Pb atoms. Here, we find that the increase of the band gap is dominated by the upward shift of the CBM, since the DW term exceeds in magnitude the Fan term (5th row of Table 5.2.1). The calculated slope of $\lambda_{\text{BG}} = 0.58 \text{ meV}/(^{\circ})^2$ is close to the value $\lambda_{\text{BG}} = 0.96 \text{ meV}/(^{\circ})^2$, shown in Fig. E.2.1. We stress that a similar picture is derived for the rest of the Pb-I stretching modes, except for the out-phase off-centre Pb displacements (not shown).

Finally, in Figs. 5.2.7(e) and (f) we show the renormalisation of the band extrema induced from the Jahn-Teller and breathing modes, respectively. The decrease in the band gap results mainly from the upward shift of the VBM as the DW exceeds the Fan term. This is in agreement with the negative Eliashberg spectral function in the energy range 11.5–14 meV, shown in Fig. 5.2.4.

5.2.4 Analysis of the Debye-Waller and Fan terms

In order to understand the physical origin of the sign and magnitude of the DW and self-energy terms presented in Table 5.2.1, we analyse separately the electron density and the self-consistent potential, as well as their variations due to the atomic displacements. We focus on the modes with Pb-I-Pb bending or rocking character which are first populated with temperature and *dominate* the opening of the band gap.

For the calculation of the Debye-Waller and Fan terms, we do not take into account the nonlocality of the self-consistent potential. That is we write the electron-phonon coupling coefficient at Γ -point as:

$$\frac{\partial^2 \varepsilon_n}{\partial x_\nu^2} = \int d\mathbf{r} \frac{\partial^2 V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu^2} |\psi_n(\mathbf{r})|^2 + \int d\mathbf{r} \frac{\partial V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu} \frac{\partial |\psi_n(\mathbf{r})|^2}{\partial x_\nu}, \quad (5.3)$$

where x_ν is the amplitude of the atomic displacements along the normal mode ν and ε_n refers to the Kohn-Sham energy of the state n . The above expression readily derives

from Eq. (2.55) and from neglecting the nonlocal part of the Kohn-Sham potential. The first and second terms on the right hand side of Eq. (5.3) are analogous to the DW and Fan electron-phonon coupling coefficients, respectively. We see that the DW term depends on the second order variations of the self-consistent potential $\frac{\partial^2 V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu^2}$ and on the electron density calculated with the atoms at their equilibrium geometry $|\psi_{n\mathbf{k}}(\mathbf{r})|^2$. The Fan term depends on the linear-order variation of the self-consistent potential $\frac{\partial V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu}$ and the linear-order redistribution of the charge density induced due to the vibrational motion $\frac{\partial |\psi_{n\mathbf{k}}(\mathbf{r})|^2}{\partial x_\nu}$.

Figures 5.2.8(a) and (b) show the spatial distribution of the Debye-Waller (left panel) and Fan contributions (right panel) to the energy renormalisation of the VBM and CBM, respectively, induced from the mode with Pb-I-Pb bending character. For the sake of clarity we also present the DW and Fan contributions to the CBM in the case of one iodine atom in Fig. 5.2.8(c).

We start our discussion with the left panel of Fig. 5.2.8 and the DW term. This term depends on the charge density at equilibrium $|\psi_{n\mathbf{k}}(\mathbf{r})|^2$ and the second order variations in the self-consistent potential $\frac{\partial^2 V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu^2}$. The latter is obtained as an average over the two possible replicas of the mode (see Sec. 5.3). For this reason $\frac{\partial^2 V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu^2}$ is *symmetric* around the atoms and is oriented along the direction of the atomic motion which is perpendicular to the internuclear Pb-I axis. Because the variations in the self-consistent potential are agnostic to the Kohn-Sham states, the difference in the DW terms calculated for the VBM and CBM relies on the distribution of the electron density at each state. In the VBM the charge density around I atoms is directed along the internuclear Pb-I axis, as shown in Fig. 5.2.8(a). In the CBM the charge density around I atoms is directed perpendicular to the internuclear Pb-I axis, as shown in Fig. 5.2.8(b).

In the left panel of Fig. 5.2.8(c) we show that the product of $|\psi_{n\mathbf{k}}(\mathbf{r})|^2$ with $\frac{\partial^2 V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu^2}$ can explain the spatial distribution and the sign of the DW term calculated for the CBM. It is immediate to see that the distribution of the DW term follows the distribution of $|\psi_{n\mathbf{k}}(\mathbf{r})|^2$, because $\frac{\partial^2 V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu^2}$ is symmetric. The sign of the DW term depends

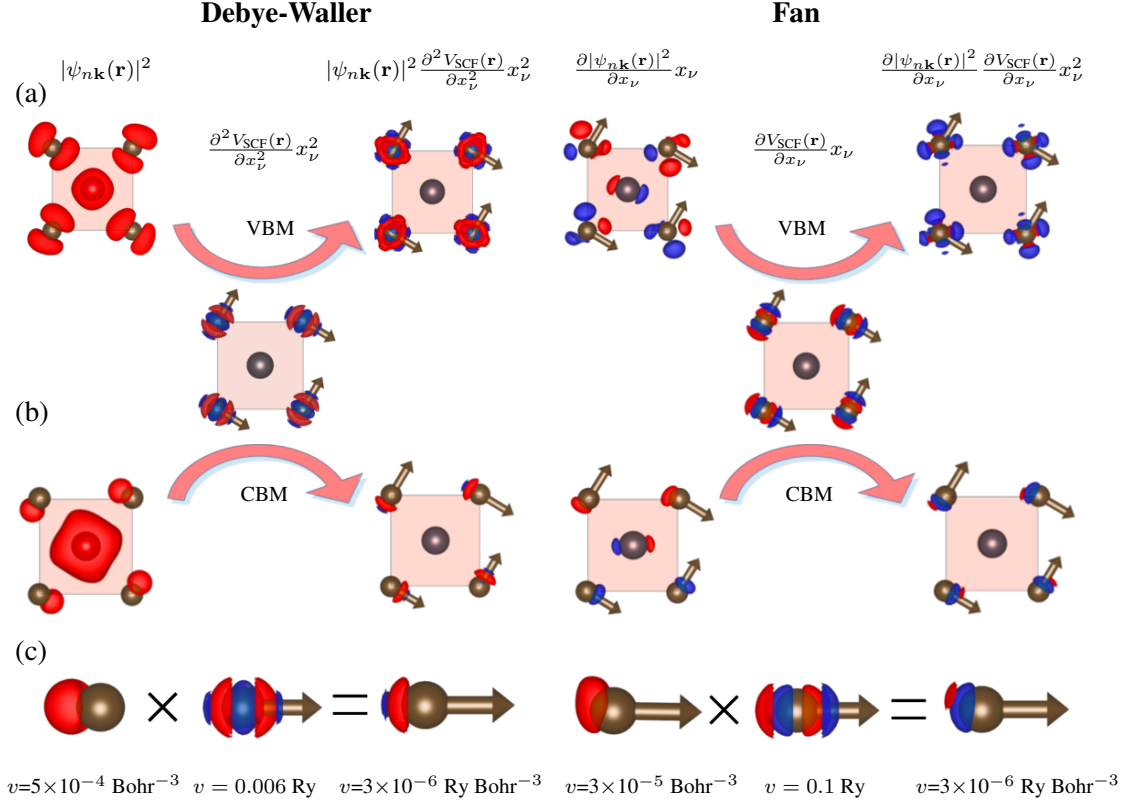


Figure 5.2.8: Spatial distribution of the Debye-Waller and Fan contributions to the energy level renormalisation induced from the mode with Pb-I-Pb bending character. Left panel shows the spatial distribution of the Debye-Waller term $\frac{\partial^2 V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu^2} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 x_\nu^2$, the second order variation in the self-consistent potential $\frac{\partial^2 V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu^2} x_\nu^2$ and the unperturbed charge density $|\psi_{n\mathbf{k}}(\mathbf{r})|^2$ in the: (a) valence band maximum and (b) conduction band maximum. Right panel shows the spatial distribution of the Fan term $\frac{\partial V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu} \frac{\partial |\psi_{n\mathbf{k}}(\mathbf{r})|^2}{\partial x_\nu} x_\nu^2$, the linear-order variation in the self-consistent potential $\frac{\partial V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu} x_\nu$ and the linear-order variation in the charge density $\frac{\partial |\psi_{n\mathbf{k}}(\mathbf{r})|^2}{\partial x_\nu} x_\nu$ at (a) valence band maximum and (b) conduction band maximum. The lower panel (c) shows the same quantities as in (b), but only for one iodine atom. The isovalues v and the corresponding units are shown in each case. The arrows represent the mode with Pb-I-Pb bending character. I and Pb atoms are shown as brown and grey spheres, respectively. Red and blue regions indicate positive and negative signs of the corresponding observable, respectively.

on the orientation and localisation of the electron density around the I atoms. Here the electron concentration follows the orientation of the p-orbitals leading mainly to the overlap with the positive variations of $\frac{\partial^2 V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu^2}$, and therefore to a positive DW term. Similar conclusions can be derived for the positive DW term calculated for the VBM. Owing to the small contribution of I p-orbitals in the formation of the CBM, the DW term calculated for the CBM renormalisation is smaller than the one calculated for the

VBM renormalisation, both reported in Table 5.2.1.

The right panel of Figure 5.2.8 shows the self-energy (Fan) term calculated for the Pb-I-Pb bending mode. This term depends on the linear redistribution of the charge density $\frac{\partial |\psi_{n\mathbf{k}}(\mathbf{r})|^2}{\partial x_\nu}$ and the linear-order variations in the self-consistent potential $\frac{\partial V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu}$. Figure 5.2.8(c) shows that $\frac{\partial V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu}$ is *antisymmetric* around the I atoms and is oriented along the direction of the atomic motion, perpendicular to the inter-nuclear Pb-I axis. It is also evident that the electron density is transferred from the I atoms moving anticlockwise to the I atoms moving clockwise and vice versa. In particular, the charge accumulated/depleted around the I atoms moving clockwise is depleted/accumulated around the I atoms moving in the anticlockwise direction. This holds for both the VBM and CBM. The linear charge redistribution in combination with the antisymmetric variations in the self consistent potential result in a negative Fan term, as illustrated in the right panel of Fig. 5.2.8(c).

In the case of the VBM, the negative Fan term exceeds in magnitude the positive DW term, reported in Table 5.2.1. In the case of the CBM the magnitude of the negative Fan term is less than the positive DW term, reported in Table 5.2.1. These lead to the decrease of the VBM and the increase of the CBM, and therefore to the opening of the band gap in MAPbI₃. The trends described above are mainly attributed to the amount of charge and its distribution around the I atoms at each of the band edges. We emphasise here that similar arguments can be used to explain the distributions and signs of the DW and self-energy terms calculated for the other five well-defined modes. There are presented in Appendix E.3. For example, due to the spatial symmetry of $|\psi_{n\mathbf{k}}(\mathbf{r})|^2$ and $\frac{\partial^2 V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu^2}$, the DW contributions to the renormalisation of the VBM remain nearly constant for phonon modes with the same character, like Pb-I-Pb rocking, anti-phase and in-phase rotation of the octahedra, reported in Table 5.2.1.

5.3 Computational setup

Here we present the computational details used to obtain the results presented in this Chapter. All calculations were performed within the local density approximation to density functional theory [49, 135] including spin-orbit coupling as implemented in the Quantum ESPRESSO software package [32]. At variance with the materials studied in Chapter 4, the effect of spin-orbit coupling is important for lead halide perovskites, because it leads to a large down-shift of the conduction band minimum [203]. We used fully relativistic norm-conserving pseudopotentials [58], and for Pb atoms we included the 5d semicore states. The electron wavefunctions were expanded in planewave basis sets with a kinetic energy cutoff of 100 Ry.

For our simulations on the orthorhombic structure we use the primitive unit cell which contains four PbI_3 formula units and four inequivalent MA cations that follow the symmetry properties of the $Pnma$ space group. We fixed the lattice constants to the experimental values [206] and we optimised the atomic positions by sampling the Brillouin zone using a $4 \times 4 \times 4$ grid centred at Γ . For the tetragonal phase we use a primitive unit cell consisting of two PbI_3 formula units. We relaxed both the lattice constants and atomic positions so that the residual stresses are minimised. The calculated short and long lattice parameters underestimate the experimental values [209] by 0.03% and 0.01%, respectively. The apical Pb-I-Pb angles were relaxed to 175.5° close to the ideal 180° . For our calculations in the tetragonal structure, we considered one combination of the 8-fold MA orientations [209]. These multiple possible orientations are due to the $I4/mcm$ symmetry of the tetragonal structure.

All electronic structure calculations on the orthorhombic primitive cell (48 atoms) and $2 \times 2 \times 2$ supercell were performed using $6 \times 6 \times 6$ and $2 \times 2 \times 2$ Brillouin zone grids, respectively. The supercells used for the tetragonal structure are multiples of the primitive cell consisting of 24 atoms. The lattice dynamics for the two phases were calculated on $\mathbf{q}$ -grids commensurate with the supercell size using density functional perturbation theory [64]. In Appendix Fig. E.1.1 we show the convergence of the band

gap renormalisation with the size of the simulation cell. In order to reduce the error in our calculations for the band gap renormalisation, we use the optimal configuration and its antithetic counterpart, defined in Sec. 4.6.1.

To account for the effect of polar coupling on the band gap renormalisation we use Eq. (2.66). For the low temperature phases of MAPbI₃, DFT/LDA calculations [214] yield $\kappa_0 = 25.3$, $\kappa_\infty = 5.8$ and $\hbar\omega_{LO} = 13$ meV. The GW corrected effective mass for the electrons at the minimum of the conduction band is $m_e^* = 0.16$ and for the holes at the top of the valence band is $m_h^* = 0.18$ [219]. For the tetragonal phase we find $\kappa_0 = 22.4$, $\kappa_\infty = 6.6$ and $\hbar\omega_{LO} = 10$ meV. The effective masses are found to be equal to those calculated for the orthorhombic structure. We should point out that the temperature dependence of the dielectric permittivity and dielectric constant is not included in our calculations.

Among the calculated 144 normal modes of the orthorhombic primitive cell, 48 correspond to vibrations of PbI₃ network and the rest to the MA cations. We determine the symmetry of the normal modes by using the nuclear site analysis (NSA) method, since it requires the least amount of information about the unit cell: the space group and the Wyckoff positions [217, 218]. Within the NSA method, the calculated normal modes are projected on a normalised basis containing the contribution of the atoms occupying the different Wyckoff positions to the normal modes. Therefore, the sum of the square coefficients of the projected normal modes add up to 48. In particular, the new normalised basis consists of 22 degrees of freedom with Pb-I stretching character. Among them, the 12 represent off-centre displacements of the Pb atoms, 4 represent displacements of the I atoms, and 6 are Jahn-Teller or breathing like distortions. We also identify 26 modes with Pb-I-Pb bending or rocking character, of which two represent in-phase and anti-phase rotations of the octahedra. For our calculations shown in Fig. 5.2.7, we chose 6 modes from the new basis. These modes have different character and are schematically presented in Fig. 5.2.5.

In order to obtain explicitly the DW and Fan coefficients appearing in Eq. (5.3) we

calculate the linear and second order variations in the self consistent potential as:

$$\frac{\partial V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu} = \frac{V_{\text{SCF}}(\mathbf{r}, x_\nu) - V_{\text{SCF}}(\mathbf{r}, -x_\nu)}{2x_\nu}, \quad (5.4)$$

$$\frac{\partial^2 V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu^2} = \frac{V_{\text{SCF}}(\mathbf{r}, x_\nu) + V_{\text{SCF}}(\mathbf{r}, -x_\nu) - 2V_{\text{SCF}}(\mathbf{r})}{x_\nu^2} \quad (5.5)$$

and similarly for the electron density $|\psi_n(\mathbf{r})|^2$. For the calculation of the DW and Fan terms in Table 5.2.1 we choose x_ν to be equal to 0.5 Å. The energy level renormalisation in Fig. 5.2.7 is calculated for x_ν between 0.05–1 Å in steps of 0.05 Å. This range of values is chosen such that the modes of the new basis drive a distortion similar in magnitude to the distortion induced from the calculated vibrational modes at 0K (see Appendix Fig. E.2.1). To keep the discussion simple we focus only on the displacements of the Pb and I atoms that lie in the equatorial plane (perpendicular to the long axis of the orthorhombic structure) as shown in the schematic representations of Fig. 5.2.5. We note that a more accurate calculation of the Debye-Waller and Fan terms would involve a separate treatment to the nonlocal part of the self consistent potential [77]. Upon comparing the values appearing in the 4th and 5th columns of Table 5.2.1, we conclude that the correct treatment of the nonlocality of the potential will have a small effect on our DW+Fan values.

5.4 Conclusions

In this Chapter we identified the main atomistic mechanisms leading to the “inverse Varshni effect” in lead halide perovskites. This was achieved by investigating separately the Debye-Waller and Fan electron-phonon contributions to the energy level renormalisation induced from modes with different character, i.e. bending, rocking and stretching. To our knowledge, this is the first time that an *ab-initio* study attempts to explain the vibrational renormalisation based on the changes induced on the electron density and potential. In fact, we reported calculations of the Debye-Waller and

Fan terms of the main vibrational mechanisms and we confirmed the opening of the band gap due to the down-shift of the valence band maximum and to the up-shift of the conduction band minimum. This anomalous picture is attributed to the symmetry and amount of the charge concentrated around the I atoms at each state, as well as to the distribution of the potential felt by electrons.

In contrast to the atomic vibrations, the band gap renormalisation induced from phase transitions and thermal volume expansion is related to the changes in the overlap of the atomic orbitals forming the band extrema. This can be justified using tight binding arguments. We calculated the volume expansion with temperature up to 150 K and we reported an opening of the gap by 1–20 meV. These values are not enough to quantify the total “inverse Varshni effect” measured in experiments, because of the extra renormalisation coming from the vibrational motion. At the phase transition temperature we also calculated a decrease in the band gap energy of 175 meV related to the change of the apical Pb-I-Pb angle from 150° to 175° .

The influence of the Fröhlich electron-phonon coupling to the zero-point renormalisation of the band gap was found to be -45 meV, which is 7 times larger than the corresponding value reported for GaAs in Sec. 4.7.3. This is attributed to the relatively large difference between the dielectric permittivity and the high-frequency dielectric constant of MAPbI_3 . We also reported the temperature dependence of the Fröhlich coupling contribution to the band gap, varying from -45 to -90 meV in the temperature range 0–300 K. This T -dependent renormalization is clearly not negligible and must be considered in polar materials that exhibit similar dielectric properties.

Finally, in this Chapter we demonstrate that the band gap opening with increasing temperature is dominated by the vibrational modes with Pb-I-Pb bending and rocking character. Pb-I stretching vibrations play a secondary role in the increase of the band gap energy. Special cases such as Jahn-Teller and breathing distortions, as well as the anti-phase rotation of the octahedra lead to the closing of the band gap. We also confirm that the in-phase rotation of the octahedra induces negligible renormalisation

5.4. CONCLUSIONS

to the energy levels due to the large cancellation between the Debye-Waller and Fan terms. Although the latter degree of freedom does not affect the thermal renormalisation of the band gap is known to be the origin of the phase transition from orthorhombic to tetragonal and from tetragonal to cubic in metal-halide perovskites [\[220\]](#).

Chapter 6

Conclusions

In this thesis, we introduced the Williams-Lax theory as a *new theory* for the calculation of optical absorption at finite temperatures. In fact, our first-principles methodology incorporates for the first time the quantum zero-point renormalisation and the temperature dependence of the band structure, as well as phonon-assisted transitions in the calculation of optical spectra. Such a unified description of electron-phonon interactions in optical absorption constitutes a significant step forward over previous work.

In its original formulation the Williams-Lax theory was used to study the vibrational broadening of the photoluminescence spectra of defects in solids [22, 23]. Here we showed that the same theory can successfully be employed for predicting the temperature dependence of absorption coefficients and band gaps in semiconductors. The reason for this success is that a perturbative treatment of the Williams-Lax theory naturally leads to the adiabatic approximations of the Allen-Heine and the Hall-Bardeen-Blatt theories. We demonstrated our technique by comparing calculations and measurements for the case of silicon, diamond, and gallium arsenide and we confirmed the accuracy of this new method being capable of yielding absorption coefficients in agreement with experiment over several orders of magnitude and for a wide spectral range.

Furthermore, we developed an efficient computational strategy for performing *one-*

shot finite-temperature calculations. Simply put, our methodology only requires the evaluation of the optical matrix elements of a system described by a well-defined atomic configuration in a large supercell. To reach this striking result, a stochastic method was employed initially, which was found to be very efficient to the point that a single calculation was sufficient to compute accurate optical spectra. This key observation eventually opened the way for further investigation in our approach of sampling the nuclear wavefunctions. In fact, we replaced the Importance Sampling Monte Carlo evaluation of the dielectric function at finite temperatures by a fully deterministic choice. The validity of this replacement was demonstrated by a mathematical, as well as a numerical proof that led to the conclusion: the *exact* Williams-Lax dielectric function is obtained by a *single* calculation in a sufficiently large supercell with the atoms in well-defined positions. We note that an identical statement can be derived and used for the evaluation of temperature-dependent band-structures. In both cases the one-shot calculation includes electron-phonon interactions beyond the quadratic order.

Our method does not come without drawbacks: The calculations presented in this thesis require the use of supercells in order to accommodate enough phonon wavevectors within the first Brillouin zone. Therefore, the evaluation of the absorption coefficients in some complex systems can be proved to be prohibitively expensive. The Williams-Lax theory upon which our method is based is critically linked to the adiabatic approximation, therefore our technique cannot yield electron lifetimes and scattering rates in the sense of the Fermi Golden Rule. For example, our calculations include an adiabatic broadening given by Eq. (4.13). This adiabatic broadening is essentially the same as what one would find from path-integral molecular dynamics simulations, but does not coincide with the electron-phonon linewidth obtained in time-dependent perturbation theory. In addition, the Williams-Lax theory does not predict correctly the fine structure close to the absorption onset, at variance with the non-adiabatic Hall-Bardeen-Blatt theory which captures two different slopes for phonon

absorption and emission processes [20, 166].

Last but not least, in this thesis we identified the key atomistic mechanism underlying the opening of the band gap with temperature in

Last but not least, in this thesis we identified the key atomistic mechanism underlying the opening of the band gap with temperature in lead halide perovskites, using the example of MAPbI_3 . The electron coupling to vibrational modes with metal-halide-metal bending or rocking character was shown to be the dominant contribution to the “inverse Varshni effect”. Metal-halide stretching modes were found to play a secondary role. In order to obtain these results, we firstly calculated the Eliashberg spectral function and then we assigned the character to each vibrational degree of freedom using the nuclear site analysis method. To provide more insights in understanding the origin of the band gap opening with temperature we analysed separately the Debye-Waller and Fan electron-phonon contributions to the renormalisation of the band edges. In particular, we explained the energy level renormalisation based on the symmetry and changes induced on the electron density and the potential felt by electrons. We also calculated the influence of the Fröhlich electron-phonon coupling on the zero-point correction. At variance with GaAs, such effect was found to be important in the case of MAPbI_3 due to the large difference between the dielectric permittivity and the high-frequency dielectric constant.

Chapter 7

Future directions

The main appeal of the methodology developed in this thesis is that it is completely agnostic of the theory and methods employed for calculating optoelectronic properties at clamped nuclei. As a result, while the calculations reported in this thesis were performed using the simplest level of theory, the independent particle approximation and the density functional theory in the local density approximation, we anticipate that our technique may be used in conjunction with higher-level electronic-structure calculations, such as for example the GW and the Bethe-Salpeter approaches. On the contrary, the extension of the Hall-Bardeen-Blatt theory to account for electron-hole effects would be cumbersome and computationally difficult. Since the present approach requires only one calculation in a large supercell, we hope that calculations including exciton-phonon coupling [221] will soon become feasible. In this regard we note that, Ref. [95] proposed the so-called “non-diagonal” supercells for performing accurate supercell calculations at a reduced computational cost. In the future, it will be interesting to examine how to exploit nondiagonal supercells in order to make our methodology even more efficient.

In future work it will be important to test the role of additional correction terms, such as nonadiabaticity [18] and anharmonicity [124]. While these further refinements will modify the precise values of the zero-point renormalisation, it is expected that the features of our calculated spectra in Fig. 4.6.1 will not change. We note that the anhar-

monicity of the potential energy surface can be incorporated by using the appropriate nuclear wavefunctions [123]. In fact, Eq. (4.1) could be evaluated using the nuclear wavefunctions obtained from the solution of the nuclear Schrödinger equation with electrons in their ground state. This choice would lead to the automatic inclusion of anharmonic effects.

We emphasise that our approach in the WL theory revealed calculations of *full* optical spectra at finite temperature, including direct and indirect optical transitions, as well as interference between the two processes. This feature is useful in order to calculate spectra which are directly comparable to experiment in absolute terms, i.e. without arbitrarily rescaling the absorption coefficient or shifting the absorption onset to fit experiment. In addition, the one-shot procedure presented in Sec. 4.6.1, is very simple and can straightforwardly be implemented in any electronic structure code as a post-processing step. In these regards, we hope that the methodology presented in this thesis will also be useful for *predictive* calculations of optical spectra, for example in the context of high-throughput computational screening of materials.

We also note that the mathematical formulas used for the derivation of the Williams-Lax dielectric function and the one-shot method are consistent with a supercell formulation i.e. all phonon and electron states are considered to have zero wavevectors $\mathbf{k}$ and $\mathbf{q}$. As a future development, our theory will be re-expressed in the conventional reciprocal space formulation. Another task that remains a challenge to us is to assign a physical meaning to the optimal configuration of the nuclei. Preliminary mathematical analysis shows that our optimum set of nuclear coordinates contains all the necessary information for thermal ellipsoids and Debye-Waller factors [81] used to describe the interaction of x-ray scattering with thermal motion. We anticipate to address and finalise this aspect soon.

Finally, it should be possible to generalise our present method to other important optical and transport properties. In fact, the WL theory is completely general and can be used with any property which can be described by the Fermi Golden Rule.

Indeed, it should be clear from Eq. (4.2), that it is possible to calculate transition rates with the atoms fixed at coordinates determined by our optimal configuration. In this regard, we expect that generalisations to properties such as photoluminescence and Auger recombination [222], as well as non-linear effects due to two-photon absorption and Kerr coefficients [223] to be within reach.

Appendix A

Dynamical Matrix and vibrational normal modes

Here we introduce the dynamical matrix related to the interatomic force constant matrix elements [Eq. (2.29)] through:

$$D_{lI\alpha, l'J\beta} = \frac{1}{\sqrt{M_I M_J}} C_{lI\alpha, l'J\beta}, \quad (\text{A.1})$$

where the indices l , I , and α have the same meaning as in Eq. (2.28). For the diagonalisation of the dynamical matrix, is convenient to apply the transformation of the displacements to normal mode coordinates given by:

$$u_{lI\alpha} = \sqrt{\frac{M_P}{M_I}} \sum_{\nu} e_{lI\alpha}^{\nu} x_{\nu}, \quad (\text{A.2})$$

where M_P is a reference mass and x_{ν} stands for the normal mode coordinates. The normalised polarisation vector $e_{lI\alpha}^{\nu}$ and frequency ω_{ν} of the mode ν are obtained by solving the secular equation:

$$\sum_{l'J\beta} D_{lI\alpha, l'J\beta} e_{l'J\beta}^{\nu} = \omega_{\nu}^2 e_{lI\alpha}^{\nu}. \quad (\text{A.3})$$

The dynamical matrix is Hermitian and therefore admits real eigenvalues ω_ν^2 . Moreover, the translational invariance of the crystal imposes that 3 normal modes must have zero frequency. The eigenvectors of the dynamical matrix are chosen such that:

$$\sum_{\nu} e_{IJ\alpha}^{\nu} (e_{I'J\beta}^{\nu})^* = \delta_{II'} \delta_{JJ'} \delta_{\alpha\beta}, \quad (\text{A.4a})$$

$$\sum_{II'} e_{II\alpha}^{\nu} (e_{II'\alpha}^{\nu'})^* = \delta_{\nu\nu'}. \quad (\text{A.4b})$$

For completeness we also introduce the quantised version of the normal coordinates [9]:

$$\hat{x}_\nu = l_\nu (\hat{a}_\nu^\dagger + \hat{a}_\nu), \quad (\text{A.5})$$

where l_ν represents the zero-point amplitude and is given by:

$$l_\nu = \sqrt{\frac{\hbar}{2M_P\omega_\nu}}. \quad (\text{A.6})$$

In Eq. (A.5), $a_\nu^\dagger$ and a_ν indicate the standard creation and annihilation operators (or ladder operators). The action of these operators on the quantum harmonic oscillators $|\chi_{n_\nu}\rangle$, defined in Eq. (2.35), and their commutation relation are given by [69, 224]:

$$a_\nu^\dagger |\chi_{n_\nu}\rangle = \sqrt{n_\nu + 1} |\chi_{n_\nu+1}\rangle, \quad (\text{A.7a})$$

$$a_\nu |\chi_{n_\nu}\rangle = \sqrt{n_\nu} |\chi_{n_\nu-1}\rangle, \quad (\text{A.7b})$$

$$[a_\nu, a_\mu^\dagger] = \delta_{\nu,\mu}, \quad (\text{A.7c})$$

$$a_\nu^\dagger a_\nu |\chi_{n_\nu}\rangle = n_\nu |\chi_{n_\nu}\rangle. \quad (\text{A.7d})$$

The above properties of the ladder operators are used for the derivation of the Allen-Heine and Hall-Bardeen-Blatt theories in Secs. 2.3.3 and 2.3.4, respectively. Taken together, Eqs. (A.7) and (A.5), then the expectation value of the square position operator reads:

$$\langle \chi_{n_\nu} | \hat{x}_\nu^2 | \chi_{n_\nu} \rangle = l_\nu^2 (2n_\nu + 1). \quad (\text{A.8})$$

The temperature dependence of the energy levels and optical spectra is introduced by assuming that each phonon state has a finite chance to be occupied according to the Gibbs distribution law:

$$\langle n_\nu \rangle_T = \frac{1}{Z} \sum_n e^{\frac{-E_{n_\nu}}{k_B T}} \langle \chi_{n_\nu} | n_\nu | \chi_{n_\nu} \rangle = [\exp(\hbar\omega_\nu/k_B T) - 1]^{-1}, \quad (\text{A.9})$$

where $Z = \sum_n e^{\frac{-E_{n_\nu}}{k_B T}}$ is the partition function and k_B is the Boltzmann constant. The term in the right hand side of this equation represents the Bose-Einstein distribution. To reach the Bose-Einstein expression we use Eq. (2.38) and the formula for the geometric series to find for $Z = q^{1/2}Q$, where $q = \exp(-\hbar\omega_\nu/k_B T)$ and $Q = 1/(1 - q)$. We also rewrite the summation over n as $q^{3/2} \frac{\partial Q}{\partial q}$. Throughout this thesis we will refer to the operation in Eq. (A.9) as the thermal average of a given quantity.

Appendix B

Optical properties

B.1 Weak electromagnetic field and response functions

By adopting the Coulomb gauge [71], where the scalar potential Φ and the divergence of the vector potential $\nabla \cdot \mathbf{A}$ vanish, we can replace $\mathbf{p}$ with the generalised momentum $\mathbf{p} + \frac{e}{c}\mathbf{A}$. Therefore, the perturbed Hamiltonian reads:

$$H' = \frac{1}{2m_e} \left[\mathbf{p} + \frac{e}{c}\mathbf{A} \right]^2 + V(\mathbf{r}) \simeq H + \frac{e}{m_e c} \mathbf{A} \cdot \mathbf{p}, \quad (\text{B.1})$$

where e and c stand for the electronic charge and the speed of light in vacuum, respectively. This expression is obtained by considering the Coulomb gauge and neglecting the non-linear term (i.e. we assume a weak electromagnetic field).

The power absorbed in the medium from the weak electromagnetic field can be expressed as:

$$P = \hbar\omega \Gamma(\boldsymbol{\xi}, \omega), \quad (\text{B.2})$$

where $\Gamma(\boldsymbol{\xi}, \omega)$ is the total absorption rate given by Eq. (2.43). An alternative form for the power delivered to the system can be obtained from [2]:

$$P = \int_{\Omega} \mathbf{J} \cdot \mathbf{E} \, d\mathbf{r} = 2\sigma_1(\boldsymbol{\xi}, \omega) \frac{\omega^2}{c^2} A_0^2 \Omega, \quad (\text{B.3})$$

where $\mathbf{J}$ is the current density that flows in the system of volume Ω and is given by the product of the complex conductivity σ and the electric field defined as $\mathbf{E} = -i \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}$. The right-hand side of Eq. (B.3) is obtained by assuming an isotropic medium and taking the real part of the integration $\int_{\Omega} \mathbf{J} \cdot \mathbf{E} \, d\mathbf{r}$. If we combine Eqs. (B.2) and (B.3) we find for the real part of the conductivity:

$$\sigma_1(\boldsymbol{\xi}, \omega) = \frac{c^2}{2\omega^2} \frac{\hbar\omega\Gamma(\boldsymbol{\xi}, \omega)}{\Omega A_0^2}, \quad (\text{B.4})$$

which is related to the complex dielectric function through the equation [2]:

$$\epsilon(\boldsymbol{\xi}, \omega) = 1 + \frac{4\pi i}{\omega} \sigma(\boldsymbol{\xi}, \omega). \quad (\text{B.5})$$

If we substitute Eqs. (2.43) and (B.4) into (B.5), the imaginary part of the dielectric function in the independent particle picture is given by:

$$\epsilon_2(\boldsymbol{\xi}, \omega) = 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{v,c} |\langle \psi_c | e^{i\boldsymbol{\xi} \cdot \mathbf{r}} \hat{\mathbf{e}} \cdot \mathbf{p} | \psi_v \rangle|^2 \delta(\epsilon_c - \epsilon_v - \hbar\omega), \quad (\text{B.6})$$

where the factor 2 accounts for spin degeneracy. The real part of the dielectric function ϵ_1 is linked to $\epsilon_2(\boldsymbol{\xi}, \omega)$ by the Kramers-Kronig relation [10]:

$$\epsilon_1(\boldsymbol{\xi}, \omega) = 1 + \frac{2}{\pi} \mathbb{P} \int_0^{\infty} \frac{\omega' \epsilon_2(\boldsymbol{\xi}, \omega')}{\omega'^2 - \omega^2} d\omega', \quad (\text{B.7})$$

where $\mathbb{P}$ indicates the Principal value of the integral.

The optical absorption coefficient is related to the imaginary part of the dielectric function by the equation [10]:

$$\kappa(\omega) = \frac{\omega}{cn(\omega)} \epsilon_2(\omega), \quad (\text{B.8})$$

where $n(\omega)$ is the refractive index of the material. For *ab-initio* calculations it is convenient to express the absorption coefficient in terms of both components of the complex

dielectric function as:

$$\kappa(\omega) = \frac{\sqrt{2}\omega}{c} \left[\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} - \epsilon_1(\omega) \right]. \quad (\text{B.9})$$

The optical spectra for $\kappa(\omega)$ and $\epsilon_2(\omega)$ exhibit similar peaks and lineshapes. In both cases a logarithmic scale is used to display the weak absorption features close to the band gap energy. Finally, we present here some other useful definitions that are used throughout this thesis:

$$\omega_{cu} = \frac{\varepsilon_c - \varepsilon_v}{\hbar}, \quad (\text{B.10})$$

and

$$f_{cu} = \frac{2|p_{cu}|^2}{m_e \hbar \omega_{cu}}, \quad (\text{B.11})$$

where ω_{cu} , f_{cu} are the resonance frequency and oscillator strength, respectively [10]. The former represents the frequency at which an optical transition takes place and the oscillator strength is a dimensionless quantity, corresponding to the number of oscillators with frequency ω_{cu} .

B.2 Non-local Pseudopotentials

As discussed in Sec. 2.1.8, the pseudopotential approach is employed in electronic structure calculations in order to simplify computations and avoid the explicit description of the core electrons. The constructed pseudopotential and pseudo-wavefunctions coincide outside the core region with the all-electron wavefunction and potential [225], but they differ inside the core radius. The term "local" is used when the pseudopotential is common for all the angular momenta, l , and therefore it is expressed as a function of the distance r from the nucleus. In the case where each angular momentum is treated separately inside the core radius, the pseudopotential is termed as "semi-local" [226], meaning that is nonlocal in the angular, but local in the radial coordinates. For practical calculations on the optical properties of solids a fully nonlocal form, as proposed by Kleinman and Bylander [227], is used.

Based on the above discussion, we can separate the Kohn-Sham potential into a local, $\hat{V}_{\text{loc}}$ and nonlocal part $\hat{V}_{\text{nl}}$, i.e.:

$$\hat{V} = \hat{V}_{\text{loc}} + \hat{V}_{\text{nl}}, \quad (\text{B.12})$$

where we drop the index KS for notational convenience. In the presence of an electromagnetic field, the nonlocal term must be treated separately in order to preserve gauge invariance [77, 228]. In particular, we need to modify the interaction Hamiltonian in Eq. (2.41) as:

$$\Delta\hat{H} = \frac{e}{m_e c} \mathbf{A} \cdot \left\{ \mathbf{p} + \frac{im_e}{\hbar} [\hat{V}_{\text{nl}}, \mathbf{r}] \right\}. \quad (\text{B.13})$$

In view of Eq. (2.44), it is immediate to see that we can replace the optical matrix elements with the expression [78]:

$$\langle \psi_v | \mathbf{p} | \psi_c \rangle \rightarrow \langle \psi_v | \mathbf{p} | \psi_c \rangle + \frac{im_e}{\hbar} \langle \psi_v | [\hat{V}_{\text{nl}}, \mathbf{r}] | \psi_c \rangle. \quad (\text{B.14})$$

It becomes clear that the matrix elements of $[\hat{V}_{\text{nl}}, \mathbf{r}]$ contribute an extra term to the

formula for the dielectric function. These matrix elements are well defined within periodic boundary conditions and have to be explicitly evaluated [229].

In conjunction with the pseudopotential approach we employ the plane wave representation of the wavefunction, introduced in Sec. 2.1.7. We combine Eq. (2.21) and the closure relation $\int |\mathbf{r}\rangle \langle \mathbf{r}| d\mathbf{r} = \mathbb{1}$ twice, to obtain for the matrix elements of $\hat{V}_{\text{nl}}$:

$$\langle \psi_{u\mathbf{k}} | \hat{V}_{\text{nl}} | \psi_{c\mathbf{k}} \rangle = \sum_{\mathbf{G}, \mathbf{G}'} \int d^3\mathbf{r}' \int d^3\mathbf{r} e^{-i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}'} c_{v\mathbf{k}}^*(\mathbf{G}') \langle \mathbf{r} | \hat{V}_{\text{nl}} | \mathbf{r}' \rangle e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} c_{c\mathbf{k}}(\mathbf{G}). \quad (\text{B.15})$$

Now it is straightforward to prove that the matrix elements of the commutator $[\hat{V}_{\text{nl}}, \mathbf{r}]$ are related to the above quantity by the expression [230]:

$$\langle \psi_{u\mathbf{k}} | [\hat{V}_{\text{nl}}, \mathbf{r}] | \psi_{c\mathbf{k}} \rangle = -i(\nabla_{\mathbf{K}} + \nabla_{\mathbf{K}'}) \langle \psi_{u\mathbf{k}} | \hat{V}_{\text{nl}} | \psi_{c\mathbf{k}} \rangle, \quad (\text{B.16})$$

where $\nabla_{\mathbf{K}}$ stands for the derivative with respect to $\mathbf{K} = \mathbf{k} + \mathbf{G}$. Based on this relation, the matrix elements of the commutator can be calculated by considering only the action of $\hat{V}_{\text{nl}}$ on the wavefunctions.

Typically, norm-conserving pseudopotentials (semilocal) are employed for the evaluation of the right hand side of Eq. (B.16). However, this involves costly operations, especially when we study large systems. Kleinman and Bylander [227] proposed a different form of $\hat{V}_{\text{nl}}$, and replaced the semilocal operator [49] by a fully nonlocal operator given by:

$$\hat{V}_{\text{nl}}^{\text{KB}} = \sum_{\ell, m} |\psi_{\ell, m} V_{\text{nl}, \ell} \rangle \alpha_{\ell} \langle V_{\text{nl}, \ell} \psi_{\ell, m} |, \quad (\text{B.17})$$

which is separable in radial variables. In the above expression m stands for the magnetic quantum number. $V_{\text{nl}, \ell}$ represents the momentum dependent part of the pseudopotential and α_{ℓ} is given by $\alpha_{\ell} = \langle \psi_{\ell, m} | V_{\text{nl}, \ell} | \psi_{\ell, m} \rangle^{-1}$. The one electron wavefunction can then be expressed as a product of its radial and spherical harmonic part, i.e. $\psi_{\ell, m} = R_{\ell} Y_{\ell m}$. The reason for this decomposition is that a spherically symmetric pseudopotential is assumed [58].

The advantage of the Kleinman-Bylander formalism is that the calculation of the matrix elements involves only products of projection operations. This results in significant computational savings [8]. An explicit form of the matrix elements of $[\hat{V}_{\text{nl}}, \mathbf{r}]$, that involves the Legendre polynomials and Kleinman-Bylander structure factors, is given in Ref. [231]. This form is referred in the literature as the Kleinman-Bylander separable form for norm-conserving pseudopotentials and has been implemented successfully in electronic structure calculations [103, 230]. It is also the one adopted for the calculation of the optical spectra presented in this thesis.

We note that another efficient method of calculating the matrix elements of $[\hat{V}_{\text{nl}}, \mathbf{r}]$ is described in Ref. [232]. In this method, second order $\mathbf{k} \cdot \mathbf{p}$ expressions with Vanderbilt pseudopotentials [59] are employed to evaluate the contribution from the nonlocal part of the pseudopotential at reduced computational cost.

B.3 Perturbative expansions

In perturbation theory we use approximate methods to predict the evolution of a quantum mechanical system in the presence of a small change. For the purposes of our work we consider that this change is either due to an external electromagnetic field or due to first order variations of the self-consistent potential as a result of atomic vibrations. These perturbations are described by adding to the Hamiltonian an additional term. Depending whether we encounter a static or a dynamic change in the state of the system we employ time-independent or time-dependent perturbation theory, respectively.

In the first instance we present the main results of time-independent perturbation theory or Rayleigh-Schrödinger perturbation theory [233, 234]. We express the perturbation as $\Delta\hat{H}$, so that the eigenvalues and eigenstates of the perturbed Hamiltonian $\hat{H}'$ satisfy: $\hat{H}'|\psi'_c\rangle = \varepsilon'_c|\psi'_c\rangle$. In the case of non-degenerate states, the second-order perturbative expansion of the energy is given by:

$$\varepsilon'_c = \varepsilon_c + \Delta H_{cc} + \sum'_\beta \frac{|\Delta H_{\beta c}|^2}{\varepsilon_c - \varepsilon_\beta} + \mathcal{O}(3), \quad (\text{B.18})$$

where $\Delta H_{\beta c} = \langle\psi_\beta|\Delta\hat{H}|\psi_c\rangle$ represents the matrix elements of the perturbation and the primed summation indicates that we skip the term such that $c = \beta$. The linear perturbative expansion of the eigenstate is:

$$|\psi'_c\rangle = |\psi_c\rangle + \sum'_\beta \frac{\Delta H_{\beta c}}{\varepsilon_c - \varepsilon_\beta} |\psi_\beta\rangle + \mathcal{O}(2). \quad (\text{B.19})$$

In both equations the notation $\mathcal{O}(m)$ indicates that the neglected terms are proportional to m and higher powers of $\Delta H_{\beta c}$.

In order to calculate transition rates in a quantum mechanical system we employ the Fermi Golden Rule, which derives directly from time-dependent perturbation theory in the interaction picture [234]. The transition probability that the system in an initial

B.3. PERTURBATIVE EXPANSIONS

state $|\psi_v\rangle$ will be found in a final state $|\psi_c\rangle$ (i.e. $v \neq c$) at time t is given to first order by:

$$P_{v \rightarrow c}^{(1)}(t) = |c_{v \rightarrow c}^{(1)}(t)|^2, \quad (\text{B.20a})$$

$$c_{v \rightarrow c}^{(1)}(t) = \frac{1}{i\hbar} \int_0^t dt' \Delta H_{cv}(t') e^{i(\omega_c - \omega_v)t'}. \quad (\text{B.20b})$$

Now $\Delta H_{cv}(t)$ represents the matrix elements of the time-dependent perturbation $\Delta \hat{H}(t)$.

If we assume that the system is driven by a harmonic perturbation [as the weak electromagnetic field in Eq. (2.42)] of the form $\Delta \hat{H}(t) = \Delta \hat{H} e^{-i\omega t}$ and solve the integral in Eq. (B.20b) we obtain the *Fermi Golden Rule* [233]:

$$P_{v \rightarrow c}^{(1)}(t) = \frac{2\pi}{\hbar} t |\Delta H_{cv}|^2 \delta(\varepsilon_c - \varepsilon_v - \hbar\omega). \quad (\text{B.21})$$

The delta function here arises by assuming that the duration of the perturbation is large (i.e. $t \rightarrow \infty$) and hence the energy of the final state after the transition is well defined.

In the case where two processes are involved to complete the transition, such as in phonon-assisted optical absorption, we resort to second order perturbation theory. We assume now that the system is driven by two harmonic perturbations: $\Delta \hat{H}^{(1)}(t) = \Delta \hat{H}^{(1)} e^{-i\omega_1 t}$ followed by $\Delta \hat{H}^{(2)}(t) = \Delta \hat{H}^{(2)} e^{-i\omega_2 t}$. The transition probability to second order reads:

$$P_{v \rightarrow c}^{(2)}(t) = |c_{v \rightarrow c}^{(2)}(t)|^2, \quad (\text{B.22a})$$

$$c_{v \rightarrow c}^{(2)}(t) = \frac{-1}{\hbar^2} \int_0^t dt' \int_0^{t'} dt'' \sum_{\beta} e^{i(\omega_c - \omega_{\beta})t'} e^{i(\omega_{\beta} - \omega_v)t''} \Delta H_{c\beta}^{(2)}(t') \Delta H_{\beta v}^{(1)}(t''). \quad (\text{B.22b})$$

In contrast to the transition probability to first order [Eq. (B.20)], here the intermediate states $|\psi_{\beta}\rangle$ are involved in the transitions and there is no direct coupling between the

states $|\psi_c\rangle$ and $|\psi_v\rangle$. If we perform the double integration in Eq. (B.22b) we find [83]:

$$P_{v \rightarrow c}^{(2)}(t) = \left| \frac{1}{\hbar^2} \sum_{\beta} \frac{1}{\Omega_{\beta v 1}} \left[\frac{e^{i\Omega_{cv21}t} - 1}{\Omega_{cv21}} - \frac{e^{i\Omega_{c\beta 2}t} - 1}{\Omega_{c\beta 2}} \right] \Delta H_{c\beta}^{(2)} \Delta H_{\beta v}^{(1)} \right|^2, \quad (\text{B.23})$$

where for notation simplicity we use $\Omega_{\beta v 1} = \omega_{\beta} - \omega_v - \omega_1$ and $\Omega_{cv21} = \omega_c - \omega_v - \omega_2 - \omega_1$. The first term in the square brackets dominates over the second and therefore we neglect the second term from our analysis [83, 84, 224, 233]. This is because Ω_{cv21} is recognised as the resonant denominator which reduces to zero if conservation of energy is satisfied. We make the substitution $e^{i\Omega t} - 1 = i\Omega t e^{i\Omega t/2} \text{sinc}(\Omega t/2)$ and take the limit $t \rightarrow \infty$ as before to obtain the standard textbook formula for the transition probability to second order [2]:

$$P_{v \rightarrow c}^{(2)}(t) = \frac{2\pi}{\hbar} t \left| \sum_{\beta} \frac{\Delta H_{c\beta}^{(2)} \Delta H_{\beta v}^{(1)}}{\varepsilon_{\beta} - \varepsilon_v - \hbar\omega_1} \right|^2 \delta(\varepsilon_c - \varepsilon_v - \hbar\omega_2 - \hbar\omega_1). \quad (\text{B.24})$$

If the perturbation order is not important and both $\Delta \hat{H}^{(1)}(t)$ and $\Delta \hat{H}^{(2)}(t)$ can take place first, then the transition probability is given by:

$$P_{v \rightarrow c}^{(2)}(t) = \frac{2\pi}{\hbar} t \left| \sum_{\beta} \frac{\Delta H_{c\beta}^{(2)} \Delta H_{\beta v}^{(1)}}{\varepsilon_{\beta} - \varepsilon_v - \hbar\omega_1} + \frac{\Delta H_{c\beta}^{(1)} \Delta H_{\beta v}^{(2)}}{\varepsilon_{\beta} - \varepsilon_v - \hbar\omega_2} \right|^2 \delta(\varepsilon_c - \varepsilon_v - \hbar\omega_2 - \hbar\omega_1). \quad (\text{B.25})$$

Now we consider the realistic scenario where one of the perturbations has the harmonic form: $\Delta \hat{H}^{(1)}(t) = 2\Delta \hat{H}^{(1)} \cos(\omega_1 t) = \Delta \hat{H}^{(1)} e^{-i\omega_1 t} + \Delta \hat{H}^{(1)} e^{i\omega_1 t}$, as for a vibrational Hamiltonian that drives phonon emission and absorption. In this case the transition probability reads [233]:

$$\begin{aligned} P_{v \rightarrow c}^{(2)}(t) &= \frac{2\pi}{\hbar} t \left| \sum_{\beta} \frac{\Delta H_{c\beta}^{(2)} \Delta H_{\beta v}^{(1)}}{\varepsilon_{\beta} - \varepsilon_v - \hbar\omega_1} + \frac{\Delta H_{c\beta}^{(1)} \Delta H_{\beta v}^{(2)}}{\varepsilon_{\beta} - \varepsilon_v - \hbar\omega_2} \right|^2 \delta(\varepsilon_c - \varepsilon_v - \hbar\omega_2 - \hbar\omega_1) \\ &+ \frac{2\pi}{\hbar} t \left| \sum_{\beta} \frac{\Delta H_{c\beta}^{(2)} \Delta H_{\beta v}^{(1)}}{\varepsilon_{\beta} - \varepsilon_v + \hbar\omega_1} + \frac{\Delta H_{c\beta}^{(1)} \Delta H_{\beta v}^{(2)}}{\varepsilon_{\beta} - \varepsilon_v - \hbar\omega_2} \right|^2 \delta(\varepsilon_c - \varepsilon_v - \hbar\omega_2 + \hbar\omega_1). \end{aligned} \quad (\text{B.26})$$

To reach this expression we omitted the cross terms arising from the expansion of the square modulus. As we will explain in Appendix B.4, these terms do not contribute to the temperature dependence of the absorption rate [84]. The above formula is employed for the derivation of the Hall-Bardeen-Blatt expression for phonon-assisted optical absorption, presented in Appendix B.4.

Finally, we combine $c_{v \rightarrow c}^{(1)}(t)$ and $c_{v \rightarrow c}^{(2)}(t)$ given by Eqs. (B.20b) and (B.22b) to write for the transition probability *up to* second order [233]:

$$P_{v \rightarrow c}(t) = \left| c_{v \rightarrow c}^{(1)}(t) + c_{v \rightarrow c}^{(2)}(t) \right|^2 \quad (\text{B.27a})$$

$$= P_{v \rightarrow c}^{(1)}(t) + c_{v \rightarrow c}^{(1)*}(t)c_{v \rightarrow c}^{(2)}(t) + c_{v \rightarrow c}^{(1)}(t)c_{v \rightarrow c}^{(2)*}(t) + P_{v \rightarrow c}^{(2)}(t). \quad (\text{B.27b})$$

In the last expression, by expanding the square modulus of Eq. (B.27a) we obtain the standard contributions from first and second order transitions probabilities given by Eqs. (B.21) and (B.26), respectively. In addition, we obtain two cross-coupling terms representing the contributions to the total transition probability coming from the interference of first and second order processes.

B.4 Derivation of the Hall-Bardeen-Blatt expression

In second quantisation [9] the normal coordinates take the form of an operator:

$$\hat{x}_{\nu\mathbf{q}} = l_{\nu\mathbf{q}}(\hat{a}_{\nu\mathbf{q}}^\dagger + \hat{a}_{\nu\mathbf{q}}), \quad (\text{B.28})$$

where $\hat{a}_{\nu\mathbf{q}}^\dagger$ and $\hat{a}_{\nu\mathbf{q}}$ indicate the standard creation and annihilation operators, respectively. The zero-point amplitude associated with the phonon of wavevector $\mathbf{q}$, branch ν and frequency $\omega_{\nu\mathbf{q}}$ is given by $l_{\nu\mathbf{q}} = \sqrt{\frac{\hbar}{2M_p\omega_{\nu\mathbf{q}}}}$, similar to Eq. (A.6). In the interaction picture [234] the time evolution of the normal coordinates is given by [9]:

$$\hat{x}_{\nu\mathbf{q}}(t) = l_{\nu\mathbf{q}}(\hat{a}_{\nu\mathbf{q}}^\dagger e^{i\omega_{\nu\mathbf{q}}t} + \hat{a}_{\nu\mathbf{q}} e^{-i\omega_{\nu\mathbf{q}}t}). \quad (\text{B.29})$$

Taken together Eqs. (B.26), (2.41), (2.49) and (B.29), the transition rate of an electron from a valence state ($|\psi_{v\mathbf{k}_v}\rangle, \varepsilon_{v\mathbf{k}_v}$) to a conduction state ($|\psi_{c\mathbf{k}_c}\rangle, \varepsilon_{c\mathbf{k}_c}$) associated with the absorption of a photon and emission or absorption of a phonon is given by [84]:

$$\begin{aligned} \Gamma_{v,\mathbf{k}_v \rightarrow c,\mathbf{k}_c}^{(2)} = & \left[\left| \sum_{\beta,\mathbf{k}_\beta} \frac{\Delta H_{c\beta}^{(2)}(\mathbf{k}_c, \mathbf{k}_\beta) \Delta H_{\beta v}(\mathbf{k}_\beta, \mathbf{k}_v)}{\varepsilon_{\beta,\mathbf{k}_\beta} - \varepsilon_{v,\mathbf{k}_v} - \hbar\omega_{\nu\mathbf{q}}} + \frac{\Delta H_{c\beta}(\mathbf{k}_c, \mathbf{k}_\beta) \Delta H_{\beta v}^{(2)}(\mathbf{k}_\beta, \mathbf{k}_v)}{\varepsilon_{\beta,\mathbf{k}_\beta} - \varepsilon_{v,\mathbf{k}_v} - \hbar\omega} \right|^2 \right. \\ & \times \delta(\varepsilon_{c,\mathbf{k}_c} - \varepsilon_{v,\mathbf{k}_v} - \hbar\omega - \hbar\omega_{\nu\mathbf{q}}) \\ & + \left| \sum_{\beta,\mathbf{k}_\beta} \frac{\Delta H_{c\beta}^{(2)}(\mathbf{k}_c, \mathbf{k}_\beta) \Delta H_{\beta v}^\dagger(\mathbf{k}_\beta, \mathbf{k}_v)}{\varepsilon_{\beta,\mathbf{k}_\beta} - \varepsilon_{v,\mathbf{k}_v} + \hbar\omega_{\nu\mathbf{q}}} + \frac{\Delta H_{c\beta}^\dagger(\mathbf{k}_c, \mathbf{k}_\beta) \Delta H_{\beta v}^{(2)}(\mathbf{k}_\beta, \mathbf{k}_v)}{\varepsilon_{\beta,\mathbf{k}_\beta} - \varepsilon_{v,\mathbf{k}_v} - \hbar\omega} \right|^2 \\ & \left. \times \delta(\varepsilon_{c,\mathbf{k}_c} - \varepsilon_{v,\mathbf{k}_v} - \hbar\omega + \hbar\omega_{\nu\mathbf{q}}) \right] \frac{2\pi}{\hbar} \left(\frac{eA_0}{m_e c} \right)^2, \end{aligned} \quad (\text{B.30a})$$

where [13]:

$$\Delta H_{\beta v}(\mathbf{k}_\beta, \mathbf{k}_v) = \sum_{\nu\mathbf{q}} l_{\nu\mathbf{q}} \langle \psi_{\beta\mathbf{k}_\beta} | \frac{\partial \hat{H}}{\partial x_{\nu\mathbf{q}}} \hat{a}_{\nu\mathbf{q}} | \psi_{v\mathbf{k}_v} \rangle \delta_{\mathbf{k}_\beta, \mathbf{k}_v + \mathbf{q}}, \quad (\text{B.30b})$$

$$\Delta H_{\beta v}^\dagger(\mathbf{k}_\beta, \mathbf{k}_v) = \sum_{\nu\mathbf{q}} l_{\nu\mathbf{q}} \langle \psi_{\beta\mathbf{k}_\beta} | \frac{\partial \hat{H}}{\partial x_{\nu\mathbf{q}}} \hat{a}_{\nu\mathbf{q}}^\dagger | \psi_{v\mathbf{k}_v} \rangle \delta_{\mathbf{k}_\beta, \mathbf{k}_v + \mathbf{q}}, \quad (\text{B.30c})$$

and

$$\Delta H_{c\beta}^{(2)}(\mathbf{k}_c, \mathbf{k}_\beta) = \langle \psi_{c\mathbf{k}_c} | \mathbf{p} | \psi_{\beta\mathbf{k}_\beta} \rangle \delta_{\mathbf{k}_c, \mathbf{k}_\beta} \quad (\text{B.30d})$$

Now, by assuming the system to be in thermal equilibrium, we can account for the temperature dependence of the transition rate by taking the thermal average as in Eq. (A.9) [235]. Within the Born-Oppenheimer approximation, the electron states are associated to phonon states $|\chi_{n_{\nu\mathbf{q}}}\rangle$ with occupation number $n_{\nu\mathbf{q}}$ and obey the orthonormality relation $\langle\chi_{n_{\nu'\mathbf{q}'}}|\chi_{n_{\nu\mathbf{q}}}\rangle = \delta_{\nu',\nu}\delta_{\mathbf{q}',\mathbf{q}}$. If we expand the square modulus of the two terms in Eq. (B.30a), consider the action of the ladder operators on the quantum harmonic oscillator on $|\chi_{n_{\nu\mathbf{q}}}\rangle$ [see Eq. (A.7)], and regroup the terms to get back the square modulus form, then the total transition rate can be obtained by summing over all valence, conduction and phonon branches, as well as integrate separately over the wavevectors $\mathbf{q}$, $\mathbf{k}_v$ and $\mathbf{k}_c$. After some straightforward manipulations, and using Eqs. (B.4) and (B.5), we obtain the HBB expression [Eq. (2.50)] for the imaginary part of the dielectric function. To make the notation more compact we define the optical matrix elements as $\mathbf{p}_{c\beta}(\mathbf{k}) = \langle\psi_{c\mathbf{k}}|\mathbf{p}|\psi_{\beta\mathbf{k}}\rangle$ and the electron-phonon matrix elements as $g_{\beta c\nu}(\mathbf{k}, \mathbf{q}) = l_{\nu\mathbf{q}} \langle\psi_{\beta\mathbf{k}}|\frac{\partial\hat{H}}{\partial x_{\nu\mathbf{q}}}|\psi_{c,\mathbf{k}+\mathbf{q}}\rangle$. In view of Eq. (2.40), we note that $\frac{\partial\hat{H}}{\partial x_{\nu\mathbf{q}}} = \frac{\partial V_{\text{KS}}}{\partial x_{\nu\mathbf{q}}}$.

To this end, we stress that the cross terms omitted from Eq. (B.26) will not contribute to the total absorption rate [84]. It can be readily seen that these terms do not survive upon taking the thermal average, since they include the product of the same ladder operators, i.e. $\hat{a}_{\nu\mathbf{q}}\hat{a}_{\nu\mathbf{q}}$ and $\hat{a}_{\nu\mathbf{q}}^\dagger\hat{a}_{\nu\mathbf{q}}^\dagger$. We also note that the HBB theory neglects contributions to the dielectric function coming from direct transitions, i.e. the first order transition probability in Eq. (B.27b). Finally, the cross-coupling terms appearing in Eq. (B.27b) will not survive the thermal average, because they are linear in ladder operators.

B.5 Derivation of the Allen-Heine expression

Starting from Eq. (2.52) we differentiate the expectation value of the Hamiltonian with respect to one normal-mode coordinate and obtain:

$$\frac{\partial \varepsilon_c^x}{\partial x_\nu} = \langle \psi_c | \frac{\partial \hat{H}}{\partial x_\nu} | \psi_c \rangle + \langle \frac{\partial \psi_c}{\partial x_\nu} | \hat{H} | \psi_c \rangle + \langle \psi_c | \hat{H} | \frac{\partial \psi_c}{\partial x_\nu} \rangle. \quad (\text{B.31})$$

If we combine the fact that $|\psi_c\rangle$ is an eigenstate of $\hat{H}$ with real eigenvalues and the Hellmann-Feynman theorem we come up with Eq. (2.54). We differentiate now Eq. (B.31) again with respect to one normal-mode coordinate to find:

$$\begin{aligned} \frac{\partial^2 \varepsilon_c^x}{\partial x_\nu \partial x_\mu} = & \langle \frac{\partial^2 \psi_c}{\partial x_\nu \partial x_\mu} | \hat{H} | \psi_c \rangle + \langle \frac{\partial \psi_c}{\partial x_\nu} | \frac{\partial \hat{H}}{\partial x_\mu} | \psi_c \rangle + \langle \frac{\partial \psi_c}{\partial x_\nu} | \hat{H} | \frac{\partial \psi_c}{\partial x_\mu} \rangle \\ & + \langle \frac{\partial \psi_c}{\partial x_\mu} | \frac{\partial \hat{H}}{\partial x_\nu} | \psi_c \rangle + \langle \psi_c | \frac{\partial^2 \hat{H}}{\partial x_\nu \partial x_\mu} | \psi_c \rangle + \langle \psi_c | \frac{\partial \hat{H}}{\partial x_\nu} | \frac{\partial \psi_c}{\partial x_\mu} \rangle \\ & + \langle \frac{\partial \psi_c}{\partial x_\mu} | \hat{H} | \frac{\partial \psi_c}{\partial x_\nu} \rangle + \langle \psi_c | \frac{\partial \hat{H}}{\partial x_\mu} | \frac{\partial \psi_c}{\partial x_\nu} \rangle + \langle \psi_c | \hat{H} | \frac{\partial^2 \psi_c}{\partial x_\nu \partial x_\mu} \rangle. \end{aligned} \quad (\text{B.32})$$

The 3rd and 7th terms on the R.H.S. will lead to the simplification of the above expression. We consider the derivatives of $\frac{\partial}{\partial x_\mu} (\hat{H}^x |\psi_c^x\rangle)$ and $\frac{\partial}{\partial x_\nu} (\langle \psi_c^x | \hat{H}^x)$ and we multiply from the left with $\langle \frac{\partial \psi_c}{\partial x_\nu} |$ and from the right with $|\frac{\partial \psi_c}{\partial x_\mu}\rangle$, respectively. By rearranging and adding the two expressions we obtain for the 3rd term :

$$\begin{aligned} \langle \frac{\partial \psi_c}{\partial x_\nu} | \hat{H} | \frac{\partial \psi_c}{\partial x_\mu} \rangle = & \frac{1}{2} \left[\frac{\partial \varepsilon_c^x}{\partial x_\nu} \langle \psi_c | \frac{\partial \psi_c}{\partial x_\mu} \rangle + \frac{\partial \varepsilon_c^x}{\partial x_\mu} \langle \frac{\partial \psi_c}{\partial x_\nu} | \psi_c \rangle \right. \\ & \left. - \langle \frac{\partial \psi_c}{\partial x_\nu} | \frac{\partial \hat{H}}{\partial x_\mu} | \psi_c \rangle - \langle \psi_c | \frac{\partial \hat{H}}{\partial x_\nu} | \frac{\partial \psi_c}{\partial x_\mu} \rangle \right] + \varepsilon_c^x \langle \frac{\partial \psi_c}{\partial x_\nu} | \frac{\partial \psi_c}{\partial x_\mu} \rangle. \end{aligned} \quad (\text{B.33})$$

For the 7th term we obtain the same expression by exchanging x_μ and x_ν . If we substitute Eq. (B.33) into Eq. (B.32) and apply the Hellmann-Feynman theorem twice we obtain Eq. (2.55).

B.6 Derivation of the Williams-Lax expression

Here we start the derivation of the Williams-Lax expression for optical absorption from Eq. (2.68):

$$\Gamma_{\alpha n \rightarrow \beta}(\omega) = \sum_m \frac{2\pi}{\hbar} |\langle X_{\alpha n} | P_{\alpha\beta}^x | X_{\beta m} \rangle|^2 \delta(E_{\beta m}^T - E_{\alpha n}^T - \hbar\omega), \quad (\text{B.34})$$

which we rewrite here to keep the discussion compact. In order to facilitate algebraic manipulations, we express the transition rate in the time domain, using the inverse Fourier transform [23, 69]:

$$\Gamma_{\alpha n \rightarrow \beta}(\omega) = \int_{-\infty}^{\infty} \Gamma_{\alpha n \rightarrow \beta}(t) e^{-i\omega t} dt, \quad (\text{B.35})$$

where:

$$\Gamma_{\alpha n \rightarrow \beta}(t) = \sum_m \frac{2\pi}{\hbar} \langle X_{\alpha n} | P_{\alpha\beta}^x | X_{\beta m} \rangle \langle X_{\beta m} | e^{iE_{\beta m}^T t/\hbar} P_{\alpha\beta}^{x*} e^{-iE_{\alpha n}^T t/\hbar} | X_{\alpha n} \rangle. \quad (\text{B.36})$$

Now we observe that from Eq. (2.32) we can write $e^{-i\hat{H}_{\alpha N} t/\hbar} |X_{\alpha n}\rangle = e^{-iE_{\alpha n}^T t/\hbar} |X_{\alpha n}\rangle$. For notation simplicity we redefine the nuclear kinetic energy operator in Eq. (2.25) as T^x and the nucleus-nucleus Coulomb interaction in Eq. (2.26) as W^x , so that $\hat{H}_{\alpha N} = E_{\alpha}^x + T^x + W^x$ and $U_{\alpha}^x = E_{\alpha}^x + W^x$. If we use the closure relation $\sum_m |X_{\beta m}\rangle \langle X_{\beta m}| = \mathbb{1}$ and assume that the kinetic energy operator commutes with the adiabatic PES, i.e. $[T^x, U_{\alpha}^x] = 0$, then we have:

$$\Gamma_{\alpha n \rightarrow \beta}(t) = \frac{2\pi}{\hbar} \langle X_{\alpha n} | P_{\alpha\beta}^x e^{iU_{\beta}^x t/\hbar} e^{iT^x t/\hbar} P_{\alpha\beta}^{x*} e^{-iT^x t/\hbar} e^{-iU_{\alpha}^x t/\hbar} | X_{\alpha n} \rangle. \quad (\text{B.37})$$

We also consider the operator identity [234]:

$$e^{\tau A} B e^{-\tau A} = B + \tau[A, B] + \frac{\tau^2}{2!}[A, [A, B]] + \frac{\tau^3}{3!}[A, [A, [A, B]]] + \dots, \quad (\text{B.38})$$

and make the additional approximation of neglecting the matrix elements that involve $[T^x, P_{\alpha\beta}^{x*}]$ to obtain the expression:

$$\Gamma_{\alpha n \rightarrow \beta}(t) = \frac{2\pi}{\hbar} \langle X_{\alpha n} | |P_{\alpha\beta}^x|^2 e^{\frac{it}{\hbar}(E_\beta^x - E_\alpha^x)} | X_{\alpha n} \rangle. \quad (\text{B.39})$$

Now we use Eq. (B.35) and return back to the frequency domain to obtain the Williams-Lax semiclassical expression for the transition rate [23, 69]:

$$\Gamma_{\alpha n \rightarrow \beta}^{(\text{SC})}(\omega) = \frac{2\pi}{\hbar} \langle X_{\alpha n} | |P_{\alpha\beta}^x|^2 \delta(E_\beta^x - E_\alpha^x - \hbar\omega) | X_{\alpha n} \rangle. \quad (\text{B.40})$$

This step completes the proof for deriving Eq. (2.69). In simple words, the WL approximation is equivalent to replacing the Herzberg-Teller transition energies with the adiabatic potential-energy surfaces of the initial and final electronic states.

To account for the temperature dependence of the WL transition rate, we set the initial electronic state to the ground state and perform a thermal average similarly to Eq. (A.9). That is:

$$\Gamma_{0 \rightarrow \beta}^{(\text{SC})}(\omega; T) = \frac{1}{Z} \sum_n e^{\frac{-E_{0n}^T}{k_B T}} \int dx |X_{0n}|^2 |P_{0\beta}^x|^2 \delta(E_\beta^x - E_0^x - \hbar\omega). \quad (\text{B.41})$$

In order to evaluate this quantity, we combine first Eqs. (2.38) and (2.39) to rewrite the summation as:

$$\Gamma_{0 \rightarrow \beta}^{(\text{SC})}(\omega; T) = \frac{1}{Z} e^{-\frac{U_0^{\mathbf{R}^0}}{k_B T}} \prod_\nu q_\nu^{1/2} \sum_n q_\nu^n \int dx |X_{0n}|^2 |P_{0\beta}^x|^2 \delta(E_\beta^x - E_0^x - \hbar\omega), \quad (\text{B.42})$$

where we follow the same prescription as in Appendix A and simplify the notation using the definition $q_\nu = \exp(-\hbar\omega_\nu/k_B T)$. Ideally we should have used the notation $q_{\nu,T}$ to indicate the temperature dependence in the right hand side of the Eq. (B.42). Now we recall that in the harmonic approximation, the many body nuclear quantum state can be expressed as a product of Hermite functions [Eqs. (2.35) and (2.37)]. By

exploiting the property of the Hermite polynomials and Mehler's formula [69, 236]:

$$\sum_{n=0}^{\infty} \frac{e^{-(x_1^2+x_2^2)/2}}{2^n n! \sqrt{\pi}} q^n \mathbf{H}_n(x_1) \mathbf{H}_n(x_2) = \frac{1}{\sqrt{\pi(1-q^2)}} \exp \left[\frac{4x_1 x_2 q - (x_1^2 + x_2^2)(1+q^2)}{2(1-q^2)} \right], \quad (\text{B.43})$$

we obtain:

$$\Gamma_{0 \rightarrow \beta}^{(\text{SC})}(\omega; T) = \frac{1}{Z} e^{-\frac{U_0^{\mathbf{R}^0}}{k_{\text{B}} T}} \int dx \prod_{\nu} \frac{q_{\nu}^{1/2} e^{-x_{\nu}^2/2\sigma_{\nu,T}^2}}{\sqrt{2\pi l_{\nu}^2(1-q_{\nu}^2)}} |P_{0\beta}^x|^2 \delta(E_{\beta}^x - E_0^x - \hbar\omega), \quad (\text{B.44})$$

where we have used that $\frac{q_{\nu}+1}{1-q_{\nu}} = \sigma_{\nu,T}^2$ and $\sigma_{\nu,T}^2$ is given by Eq. (2.61). Finally, following Appendix A, we write the partition function as $Z = e^{-\frac{U_0^{\mathbf{R}^0}}{k_{\text{B}} T}} \prod_{\nu} \frac{q_{\nu}^{1/2}}{1-q_{\nu}}$ and we derive the compact expression for the temperature dependence of the transition rate:

$$\Gamma_{0 \rightarrow \beta}^{(\text{SC})}(\omega; T) = \prod_{\nu} \int dx_{\nu} \frac{\exp(-x_{\nu}^2/2\sigma_{\nu,T}^2)}{\sqrt{2\pi}\sigma_{\nu,T}} |P_{0\beta}^x|^2 \delta(E_{\beta}^x - E_0^x - \hbar\omega). \quad (\text{B.45})$$

Appendix C

Stochastic approach

C.1 Supplemental material

In this Appendix we provide supporting information of our results presented in Chapter 3.

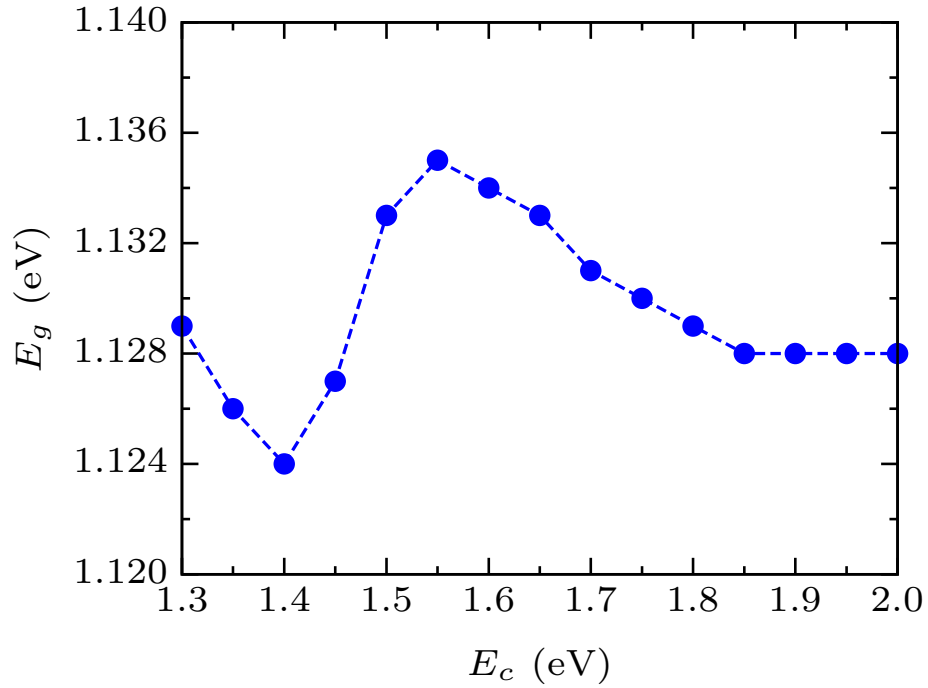


Figure C.1.1: Indirect band gap of silicon E_g as a function of the energy cutoff E_c used in the linear fits of Fig. 3.2.4. The fits were applied in the energy range $[0, E_c]$, and the temperature considered in this case is 300 K.

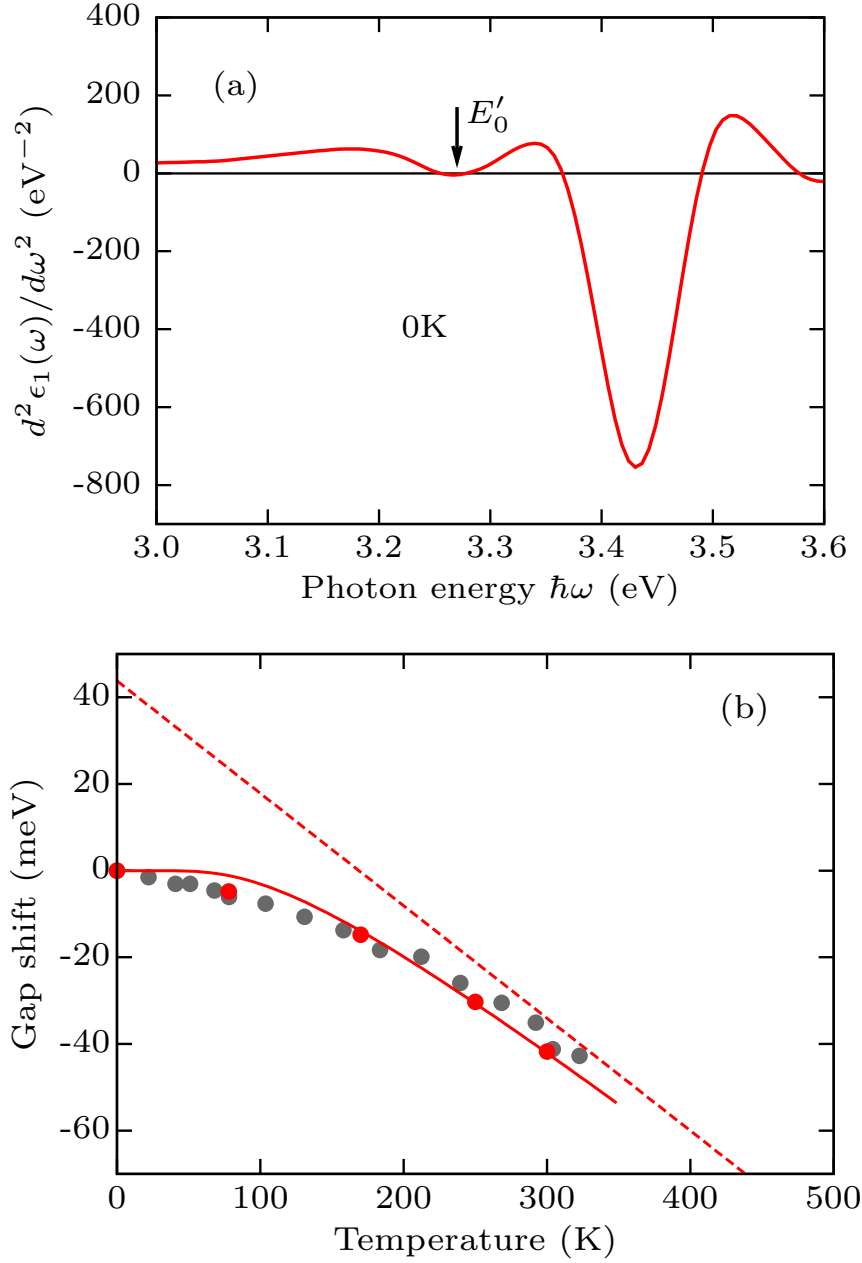


Figure C.1.2: (a) Williams-Lax second-derivative spectra of the real part of the dielectric function of silicon at $T = 0$ K. In experiment, the first dip in this spectrum was assigned to the E'_0 transition [73]. This dip is used to determine the direct band gap of silicon. (b) Temperature dependence of the direct gap of silicon within the WL theory (red filled discs), extracted from the second-derivative spectra illustrated in panel (a). We compare our values with the experimental data from Ref. [73], shown as grey filled discs. A single-oscillator fit [Eq. (2.65)] to the calculated temperature dependence (thin red line) yields $a_B = 44$ meV and $\Theta = 337.5$ K. These values are compatible with the experimental ranges 25 ± 17 meV and 267 ± 123 K [73], respectively. The high-temperature asymptote to the fit is represented by straight red dashed line. For $T > 350$ K the transitions E'_0 and E_1 merge (both in our calculations and experimental spectra) and therefore the direct band gap cannot be extracted using this method.

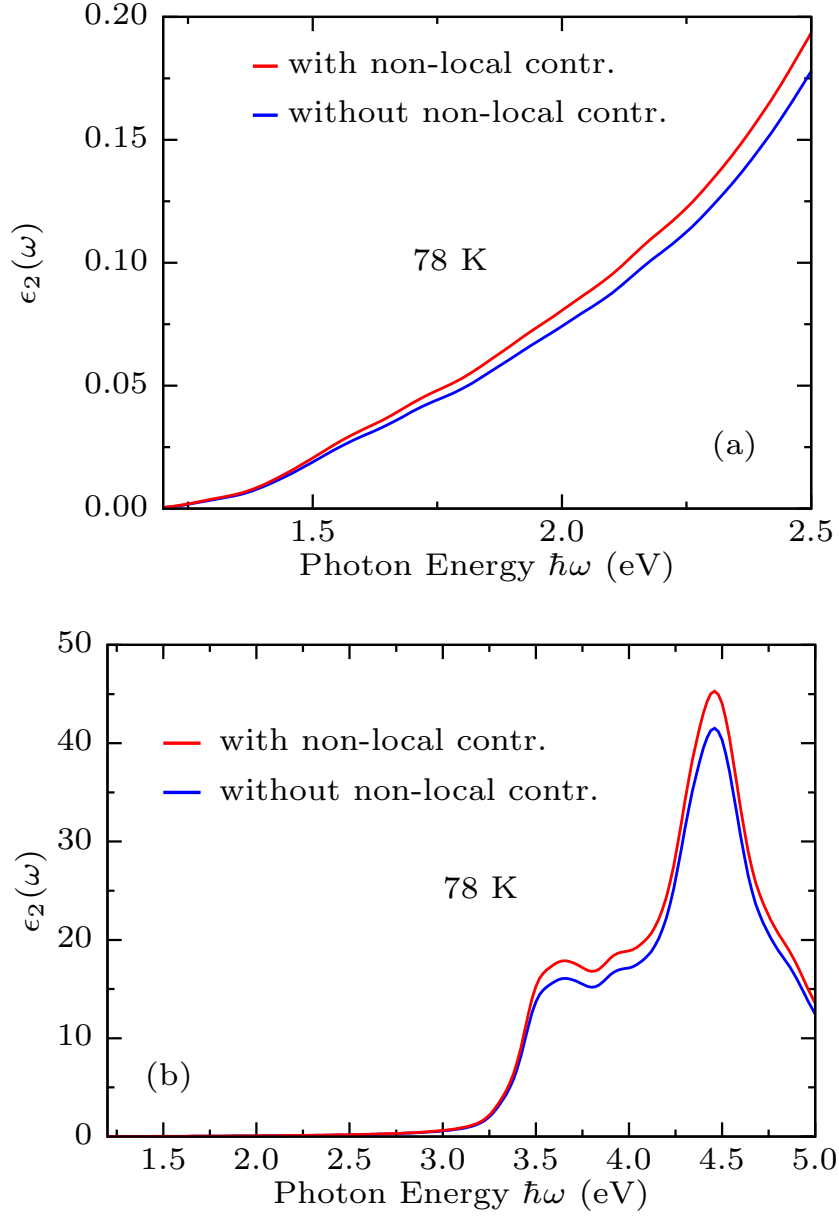


Figure C.1.3: (a) and (b) Imaginary part of the dielectric function of silicon calculated at 78 K, with (red) or without (blue) including the contributions to the optical matrix elements arising from the nonlocal components of the pseudopotential. We point out that the scale in Fig. 3.2.2 is logarithmic, while here we use a linear scale for clarity. The inclusion of the nonlocal components of the pseudopotential leads to a modification of the oscillator strengths in the order of 10–15%. We note that in Figs. 3.2.1 and 3.2.4 of the main text, the nonlocal contributions are correctly included. The pseudopotential used for these calculations has the local component in the d channel.

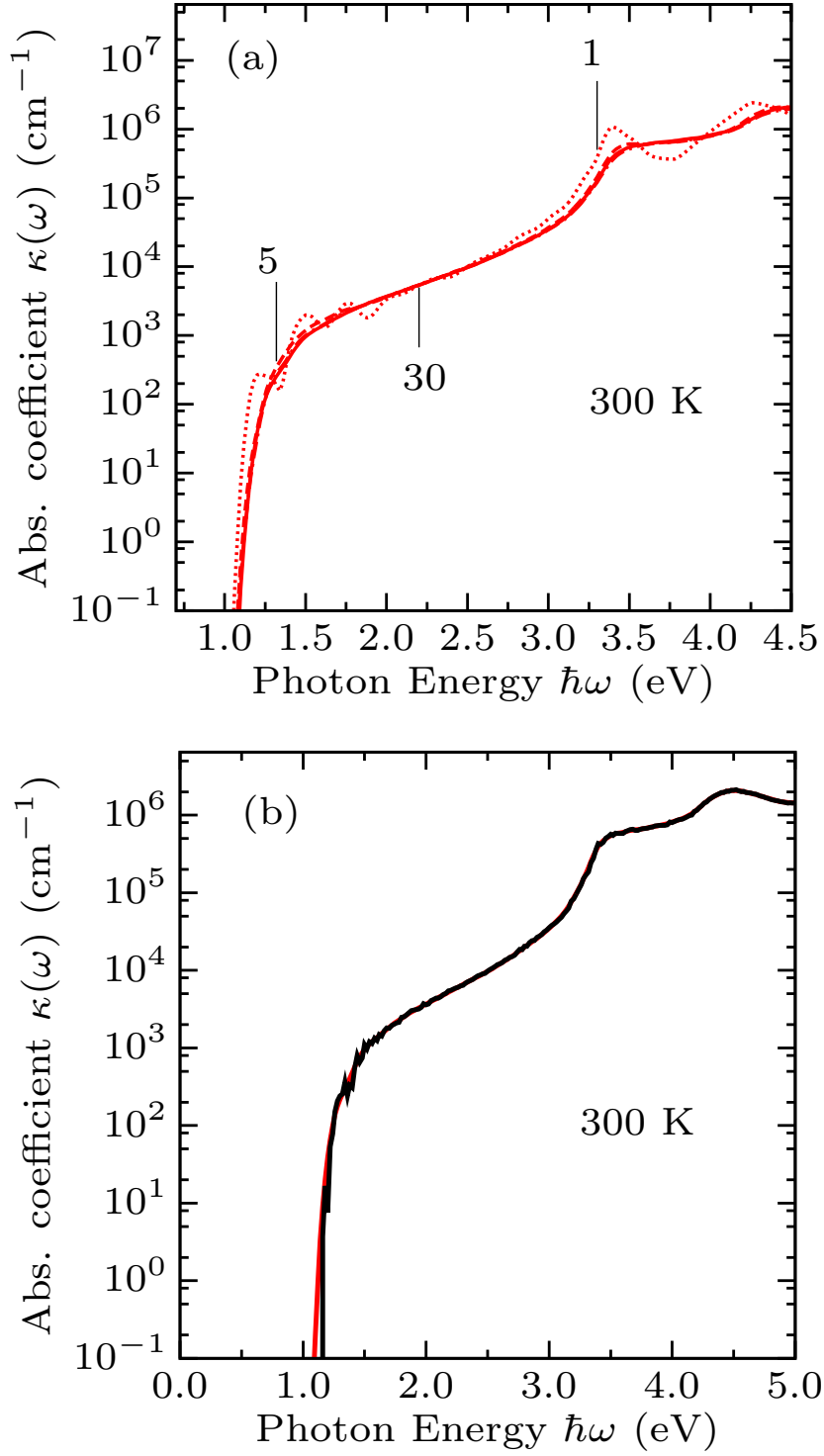


Figure C.1.4: (a) Numerical convergence of the calculated absorption coefficient of silicon with respect to the sampling of the Brillouin zone. The red lines indicate spectra calculated using an $8 \times 8 \times 8$ BVK supercell using 1 (dotted), 5 (dashed), 30 (solid) random k -points. (b) Absorption coefficient of silicon calculated using two different Gaussian broadening parameters, 30 meV (red line) and 1 meV (black line). These calculations are for an $8 \times 8 \times 8$ BVK supercell and $T = 300$ K.

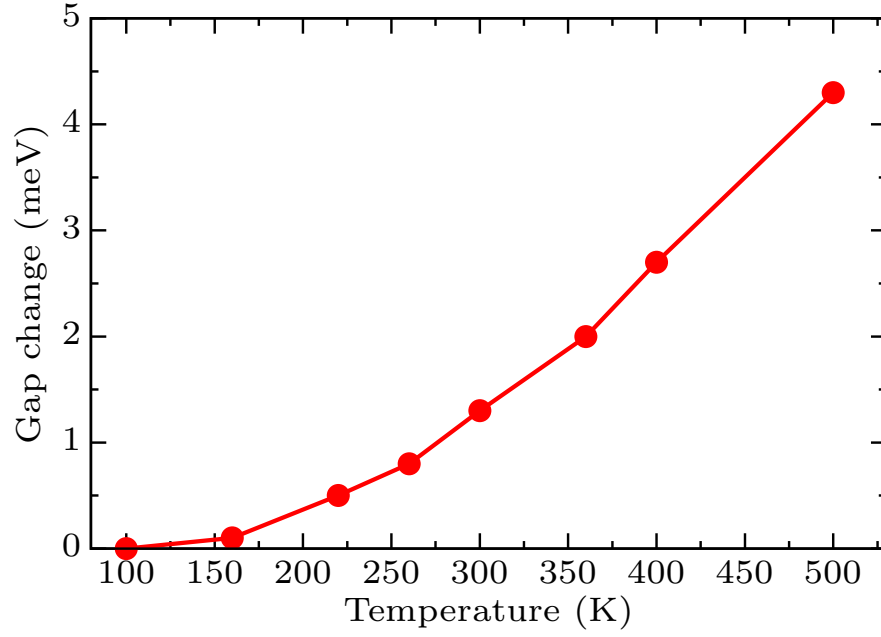


Figure C.1.5: Indirect band gap of silicon at clamped nuclei as a function of temperature considering only the effect of thermal lattice expansion. For each temperature we used the experimental lattice parameters from Ref. [140]. The discs show the change in band gap relative to the value at 100 K, and the lines are guides to the eye. As expected the effect of thermal lattice expansion between 100 K and 500 K is very small (< 5 meV) when compared to the variation due to electron-phonon renormalisation [~ 100 meV, see Fig. 3.2.4(b)].

Appendix D

One-shot calculation of optical spectra

D.1 Williams-Lax expression for direct absorption

In this Appendix we outline the steps leading from Eq. (4.11) to Eq. (4.12). We start by introducing the compact notation:

$$\Delta\varepsilon_{cv}^x = \sum_{\nu} A_{cv\nu} x_{\nu} + \sum_{\mu\nu} B_{cv\mu\nu} x_{\mu} x_{\nu} + \mathcal{O}(x^3), \quad (\text{D.1})$$

where the coefficients $A_{cv\nu}$ and $B_{cv\mu\nu}$ are obtained from Eq. (4.10):

$$A_{cv\nu} = \frac{1}{l_{\nu}} (g_{cc\nu} - g_{vv\nu}), \quad (\text{D.2})$$

$$B_{cv\mu\nu} = \frac{1}{l_{\mu} l_{\nu}} \sum_{\beta}' \left[\left(\frac{g_{c\beta\mu} g_{\beta c\nu}}{\varepsilon_c - \varepsilon_{\beta}} + h_{c\mu\nu} \right) - \left(\frac{g_{v\beta\mu} g_{\beta v\nu}}{\varepsilon_v - \varepsilon_{\beta}} + h_{v\mu\nu} \right) \right]. \quad (\text{D.3})$$

Equation (4.11) can be simplified by using the Taylor expansion of the Dirac delta with respect to the energy argument. In general, if we expand $\delta(\epsilon + \eta)$ around ϵ , we have [161, 237]:

$$\delta(\epsilon + \eta) = \sum_{n=0}^{\infty} \frac{1}{n!} \left. \frac{\partial^n \delta}{\partial \epsilon^n} \right|_{\epsilon} \eta^n, \quad \text{where } \eta \rightarrow 0. \quad (\text{D.4})$$

Therefore we can set $\epsilon = \epsilon_{cv} - \hbar\omega$ and $\eta = \Delta\epsilon_{cv}^x$, and replace inside Eq. (4.11). We find:

$$\begin{aligned} \epsilon_2(\omega; T) &= 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{cv} |p_{cv}|^2 \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \left. \frac{\partial^n \delta}{\partial (\hbar\omega)^n} \right|_{\hbar\omega - \epsilon_{cv}} \\ &\times \prod_{\nu} \int dx_{\nu} \frac{\exp(-x_{\nu}^2/2\sigma_{\nu,T}^2)}{\sqrt{2\pi}\sigma_{\nu,T}} (\Delta\epsilon_{cv}^x)^n. \end{aligned} \quad (\text{D.5})$$

We note that if we consider the case $n = 0$ we recover the expression for the dielectric function with the nuclei clamped at their equilibrium positions [Eq. (2.44)]. Now we replace $\Delta\epsilon_{cv}^x$ from Eq. (D.1) and carry out the integrals in the coordinates x_{ν} using the Gaussian integrals:

$$\int dx \frac{x^{2n} e^{(-x^2/2\sigma^2)}}{\sqrt{2\pi}\sigma} = \sigma^{2n} (2n-1)!! , \quad (\text{D.6})$$

where n is an integer and the double factorial is $(2n-1)!! = (2n-1)(2n-3)\cdots 1$. The resulting expression does not contain the normal coordinates any more, and the various derivatives of the delta function that are multiplied with powers of $\sum_{\mu} B_{cv\mu\mu} \sigma_{\mu}^2$ can be regrouped using Eq. (D.4) in reverse. Now the dielectric function is:

$$\begin{aligned} \epsilon_2(\omega; T) &= 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{cv} |p_{cv}|^2 \times \left[\delta(\epsilon_{cv,T}^{\text{AH}} - \hbar\omega) + \frac{1}{2} \sum_{\nu} A_{cv\nu}^2 \sigma_{\nu,T}^2 \frac{\partial^2 \delta(\hbar\omega - \epsilon_{cv})}{\partial (\hbar\omega)^2} \right] \\ &+ \mathcal{O}(\sigma^4), \end{aligned} \quad (\text{D.7})$$

where $\epsilon_{cv,T}^{\text{AH}} = \epsilon_{c,T}^{\text{AH}} - \epsilon_{v,T}^{\text{AH}}$, and $\epsilon_{m,T}^{\text{AH}}$ is the temperature-dependent electron energy given by Eq. (3.5).

In order to make Eq. (D.7) more compact, it is convenient to rewrite the second term inside the square brackets by performing a Taylor expansion of the Dirac delta around $\epsilon_{cv,T}^{\text{AH}}$, and group the terms proportional to $\sigma_{\nu,T}^4$ and higher order inside the term

$\mathcal{O}(\sigma^4)$ at the end. This step leads to:

$$\epsilon_2(\omega; T) = 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{cv} |p_{cv}|^2 \times \left[1 + \frac{1}{2} \Gamma_{cv}^2 \frac{\partial^2}{\partial(\hbar\omega)^2} \right] \delta(\varepsilon_{cv,T}^{\text{AH}} - \hbar\omega) + \mathcal{O}(\sigma^4), \quad (\text{D.8})$$

having defined:

$$\Gamma_{cv}^2 = \sum_{\nu} A_{cv\nu}^2 \sigma_{\nu,T}^2 = \sum_{\nu} (g_{c\nu\nu} - g_{v\nu\nu})^2 (2n_{\nu,T} + 1). \quad (\text{D.9})$$

In the final step we note that the term $\partial^2/\partial(\hbar\omega)^2$ in Eq. (D.8) acts so as to broaden the lineshape. This is seen by using the Fourier representation of the Dirac delta, $\delta(\hbar\omega) = (2\pi\hbar)^{-1} \int dt \exp(-i\omega t)$. We find:

$$\begin{aligned} & \left[1 + \frac{1}{2} \Gamma_{cv}^2 \frac{\partial^2}{\partial(\hbar\omega)^2} \right] \delta(\varepsilon_{cv,T}^{\text{AH}} - \hbar\omega) = \\ & \frac{1}{2\pi\hbar} \int dt \left[1 - \frac{\Gamma_{cv}^2}{2\hbar^2} t^2 \right] \exp\left(-i \frac{\varepsilon_{cv,T}^{\text{AH}} - \hbar\omega}{\hbar} t\right). \end{aligned} \quad (\text{D.10})$$

The term $\left[1 - \frac{\Gamma_{cv}^2}{2\hbar^2} t^2 \right]$ corresponds to the first order Taylor expansion of a Gaussian (or alternatively a Lorentzian), and therefore, if we assume that Γ_{cv}^2 is small, the last expression can be rewritten as:

$$\frac{1}{2\pi\hbar} \int dt \exp\left[-\frac{\Gamma_{cv}^2}{2\hbar^2} t^2\right] \exp\left(-i \frac{\varepsilon_{cv,T}^{\text{AH}} - \hbar\omega}{\hbar} t\right) + \mathcal{O}(\sigma^4). \quad (\text{D.11})$$

Here we recognise the Fourier transform of a Gaussian which we can evaluate explicitly using:

$$\int e^{-at^2+bt+c} dt = \sqrt{\pi/a} e^{b^2/4a+c}, \quad (\text{D.12})$$

and setting $a = \frac{\Gamma_{cv}^2}{2\hbar^2}$, $b = -i \frac{\varepsilon_{cv,T}^{\text{AH}} - \hbar\omega}{\hbar}$, $c = 0$. This completes the proof and the final result is Eq. (4.12).

D.2 Williams-Lax expression for indirect absorption

In this Appendix we outline the derivation of Eq. (4.15) starting from Eq. (4.14). It is convenient to introduce the notation:

$$C_{cv\mu} = \frac{\partial p_{cu}}{\partial x_\mu} = \sum_\beta' \left[\frac{p_{c\beta} g_{\beta v\mu}}{\varepsilon_v - \varepsilon_\beta} + \frac{g_{c\beta\mu} p_{\beta v}}{\varepsilon_c - \varepsilon_\beta} \right] \frac{1}{l_\mu}, \quad (\text{D.13})$$

so that Eq. (4.14) can be written as:

$$\begin{aligned} \epsilon_2(\omega; T) &= 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{cv} \prod_\nu \int dx_\nu \frac{\exp(-x_\nu^2/2\sigma_{\nu,T}^2)}{\sqrt{2\pi}\sigma_{\nu,T}} \\ &\times \sum_{\mu\mu'} C_{cv\mu} C_{cv\mu'} x_\mu x_{\mu'} \delta(\varepsilon_{cv} + \Delta\varepsilon_{cv}^x - \hbar\omega) + \mathcal{O}(\sigma^4). \end{aligned} \quad (\text{D.14})$$

We now write explicitly the expansion of the Dirac delta to second order in x_ν , using Eqs. (D.1)-(D.4):

$$\begin{aligned} \delta(\varepsilon_{cv} + \Delta\varepsilon_{cv}^x - \hbar\omega) &= \delta(\varepsilon_{cv} - \hbar\omega) - \frac{\partial \delta}{\partial(\hbar\omega)} \bigg|_{\hbar\omega - \varepsilon_{cv}} \left[\sum_\nu A_{cv\nu} x_\nu + \sum_{\mu\nu} B_{cv\mu\nu} x_\mu x_\nu \right] \\ &+ \frac{1}{2} \frac{\partial^2 \delta}{\partial(\hbar\omega)^2} \bigg|_{\hbar\omega - \varepsilon_{cv}} \left[\sum_{\mu\nu} A_{cv\mu} A_{cv\nu} x_\mu x_\nu \right] + \mathcal{O}(x^3). \end{aligned} \quad (\text{D.15})$$

Retaining only the first term in the above expression and substituting into Eq. (D.14) corresponds effectively to neglecting the dependence of the band structure on the nuclear coordinates. This is along the same lines with the argument used in Sec. 3.2.1 to derive the adiabatic version of the HBB expression [see Eq. (3.2)]. Instead, by substituting Eq. (D.15) into Eq. (D.14) and performing the integration using Eq. (D.6), after a few lengthy but straightforward manipulations we have:

$$\begin{aligned} \epsilon_2(\omega; T) &= 2 \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{cv} \sum_\nu |C_{cv\nu}|^2 \sigma_{\nu,T}^2 \\ &\times \left[1 - \sum_\mu B_{cv\mu\mu} \sigma_{\mu,T}^2 \frac{\partial}{\partial(\hbar\omega)} + \frac{1}{2} \sum_\mu |A_{cv\mu}|^2 \sigma_{\mu,T}^2 \frac{\partial^2}{\partial(\hbar\omega)^2} \right] \delta(\varepsilon_{cv,T}^{\text{AH}} - \hbar\omega) \\ &+ \mathcal{O}(\sigma^6). \end{aligned} \quad (\text{D.16})$$

In this expression we neglected the interference terms $\sum_{\mu\nu \neq \lambda\kappa} C_{cv\mu} C_{cv\lambda} B_{cv\nu\kappa} \sigma_{\nu,T}^2 \sigma_{\kappa,T}^2$ next to positive-definite terms of the same order, i.e. $\sum_{\mu\nu} |C_{cv\mu}|^2 B_{cv\nu\nu} \sigma_{\mu,T}^2 \sigma_{\nu,T}^2$. Similarly we neglected the terms $\sum_{\mu \neq \nu} C_{cv\mu} C_{cv\nu} A_{cv\mu} A_{cv\nu} \sigma_{\mu,T}^2 \sigma_{\nu,T}^2$ next to the terms $\sum_{\mu\nu} |C_{cv\mu}|^2 |A_{cv\nu}|^2 \sigma_{\mu,T}^2 \sigma_{\nu,T}^2$. Both cases are justified since in the case of extended solids the sum of interference terms tends to zero as the phases of each term cancel out in average. In a similar spirit, we neglected terms like $2 \sum_{\mu} |B_{cv\mu\mu}|^2 \sigma_{\mu,T}^4$ next to $\sum_{\mu,\nu} B_{cv\mu\mu} B_{cv\nu\nu} \sigma_{\mu,T}^2 \sigma_{\nu,T}^2$. This is justified by grouping the two terms together as $\sum_{\mu} B_{cv\mu\mu} \sigma_{\mu,T}^2 [2B_{cv\mu\mu} \sigma_{\mu,T}^2 + \sum_{\nu} B_{cv\nu\nu} \sigma_{\nu,T}^2]$ and noting that $2B_{cv\mu\mu} \sigma_{\mu,T}^2 \ll \sum_{\nu} B_{cv\nu\nu} \sigma_{\nu,T}^2$ for an extended system.

Now Eq. (D.16) can be recast in the form given by Eq. (4.15) by using the Fourier representation of the Dirac delta, and following the same steps as in Appendix D.1, Eqs. (D.10)-(D.12). In particular, the term $\partial\delta/\partial(\hbar\omega)$ yields a shift of the excitation energies which coincides with the energy renormalisation in the Allen-Heine theory, see Eq. (3.5). Similarly, the term $\partial^2\delta/\partial(\hbar\omega)^2$ yields a broadening of the absorption peak, which corresponds to the linewidth Γ_{cv} of Eq. (4.13).

D.3 Deterministic reduction of cross terms to even order

We have explained in Sec. 4.6.2, that there might be cases where the supercell size, and thus the number of normal modes, cannot be large enough due to the computational complexity of the material under examination. Therefore, one has to resort to an approximation and use a smaller system size. In this case, the optimum configuration defined by Eq. (4.23) will not lead to cancellation of the extra terms appear in Eq. (4.5) and therefore is not anymore the optimum choice. In this appendix we describe how we can choose deterministically the configurations in order to reduce the error to even order systematically. We show for example that only 32 configurations with their antithetic pairs are sufficient to reduce the number of the extra terms down to 3.13 %.

For the following discussion we consider reduction of the extra terms to the quadratic order, but the approach can be generalised to all higher orders. We start with the configuration $\mathbf{x}^{(1)} = \mathbf{M}_1 \bar{\mathbf{x}}$, where $\bar{\mathbf{x}}$ is a column vector with elements $\{\sigma_1, \sigma_2, \dots, \sigma_{d-1}, \sigma_d\}$, $\mathbf{M}_1$ is a diagonal sign matrix of size d and arbitrary entries. The temperature index has been dropped to keep the notation light. The error to the second order compared to the exact WL dielectric function now reads:

$$\Delta\epsilon_2^{(1)} = \sum_{\nu \neq \mu}^d \sigma_\nu \sigma_\mu, \quad (\text{D.17})$$

where for notation simplicity the signs and coefficients $\frac{1}{2} \frac{\partial^2 \epsilon_2}{\partial x_\nu \partial x_\mu}$ are absorbed into the cross terms $\sigma_\nu \sigma_\mu$. Now we choose new configurations of the form:

$$\mathbf{x}^{(i)} = \mathbf{M}_i \mathbf{M}_1 \bar{\mathbf{x}}, \quad (\text{D.18})$$

where the action of $\mathbf{M}_i$ is such that it alters the signs of our initial set of nuclear coordinates. We choose $\mathbf{M}_2$ with the diagonal entries given by the set $\{+\dots+|-$

$\cdots - \}$, where the vertical line represents the bisection of the set. This allocation of the signs, although is not the only choice, will yield maximum reduction of the extra terms. The remaining error of the average spectrum obtained from the two configurations is given by:

$$\frac{1}{2}[\Delta\epsilon_2^{(1)} + \Delta\epsilon_2^{(2)}] = \sum_{\nu \neq \mu}^{\leq d/2} \sigma_\nu \sigma_\mu + \sum_{\nu \neq \mu=d/2}^{\leq d} \sigma_\nu \sigma_\mu. \quad (\text{D.19})$$

Here we have eliminated $\sim 50\%$, i.e. $\frac{d^2}{2}$, of the cross terms that appear in Eq. (D.17). In same spirit, we further bisect the previous set so that the diagonal entries of $\mathbf{M}_3$ are $\{+\cdots+ | -\cdots- | +\cdots+ | -\cdots-\}$ and $\mathbf{M}_4 = \mathbf{M}_2\mathbf{M}_3$. Now the error of the average spectrum reduces to:

$$\frac{1}{4} \sum_i^4 \Delta\epsilon_2^{(i)} = \sum_{\nu \neq \mu}^{\leq d/4} \sigma_\nu \sigma_\mu + \sum_{\nu \neq \mu=d/4}^{\leq 2d/4} \sigma_\nu \sigma_\mu + \sum_{\nu \neq \mu=2d/4}^{\leq 3d/4} \sigma_\nu \sigma_\mu + \sum_{\nu \neq \mu=3d/4}^{\leq d} \sigma_\nu \sigma_\mu, \quad (\text{D.20})$$

which corresponds to $\sim 75\%$, i.e. $\frac{3d^2}{4}$, decrease of the total number of the extra terms, by using only 4 configurations. It becomes apparent that our next step is to decompose each subset of $\mathbf{M}_3$ into $\{+\cdots+ | -\cdots-\}$ and obtain $\mathbf{M}_5$. Now $\mathbf{M}_6 = \mathbf{M}_2\mathbf{M}_5$, $\mathbf{M}_7 = \mathbf{M}_3\mathbf{M}_5$ and $\mathbf{M}_8 = \mathbf{M}_4\mathbf{M}_5$. Taking the average of these 8 configurations, the number of the cross terms is now reduced to 12.5%. Therefore, we can conclude that for reducing the cross terms at each step by 50 %, we need to double the effort (configurations) involved in the previous step.

We can easily generalise Eq. (D.20) and write for a number of n_c configurations:

$$\frac{1}{n_c} \sum_i^{n_c} \Delta\epsilon_2^{(i)} = \sum_{\nu \neq \mu}^{\leq d/n_c} \sigma_\nu \sigma_\mu + \cdots + \sum_{\substack{\nu \neq \mu = \\ \frac{n_c-1}{n_c}d}}^{\leq d} \sigma_\nu \sigma_\mu, \quad (\text{D.21})$$

where n_c is an integer power of 2 and indicates how many calculations we need to run for eliminating $(1 - 1/n_c)\%$ of the total cross terms in Eq. (D.17). The diagonal entries

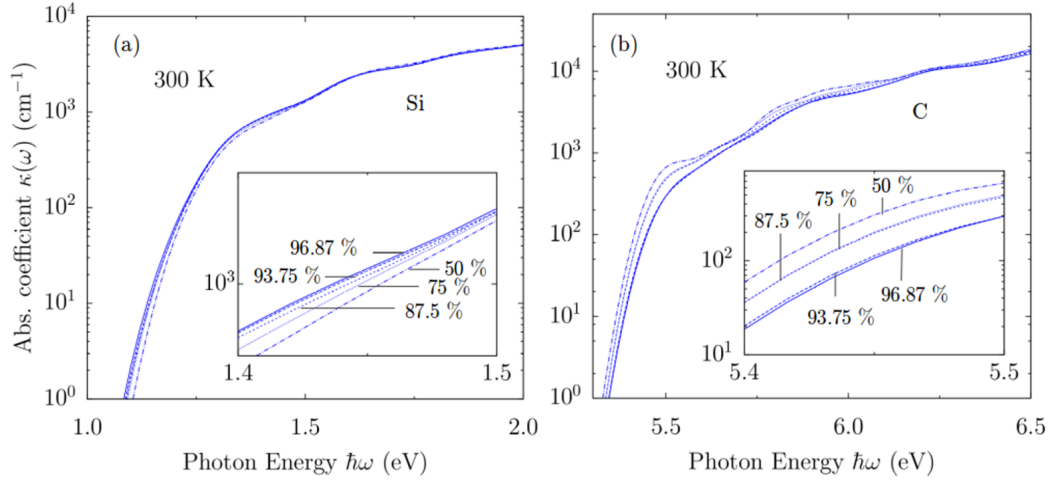


Figure D.3.1: Numerical convergence of the absorption coefficient of (a) silicon and (b) diamond at 300 K with the reduction of the cross terms to the even order. The inset shows a magnified part of the spectra and the labels correspond to the percentage of the eliminated terms to the even order. The configurations and their antithetic pairs were generated according to Eqs. (4.24), (D.22) and (D.23). Calculations were performed on $4 \times 4 \times 4$ BvK supercells and a Gaussian broadening of width 50 meV was used.

of the matrix $\mathbf{M}_{\frac{n_c}{2}+1}$ are divided into n_c disjoint index subsets:

$$\mathbf{S}_1 \oplus \mathbf{S}_2 \oplus \cdots \oplus \mathbf{S}_{n_c}, \quad (\text{D.22})$$

where subsets with successive index, i.e. $\mathbf{S}_{2k-1}$ and $\mathbf{S}_{2k}$, have opposite signs. The rest of the diagonal sign matrices are generated according to:

$$\mathbf{M}_{\frac{n_c}{2}+1+j} = \mathbf{M}_{1+j} \mathbf{M}_{\frac{n_c}{2}+1}, \quad (\text{D.23})$$

where j is an integer running between 1 and $\frac{n_c}{2}-1$. The only a priori information which is required for this method is the initial signs of the matrix $\mathbf{M}_1$.

Now we demonstrate this method by calculating the optical spectra of silicon and diamond in $4 \times 4 \times 4$ BvK supercells. We consider 32 sets of nuclear coordinates and their antithetic pairs, in order to retain only 3.13 % of the cross terms to the even order. The signs of $\mathbf{M}_1$ are chosen as for our optimum configuration defined in Eq. (4.23). Our results are shown in Fig. D.3.1.

We emphasise here that the choice made above for the matrices $\mathbf{M}_{\frac{n_c}{2}+1}$ is not

unique. One could also choose for example the following diagonal sign matrices with index $\frac{n_c}{2}+1$:

$$\begin{aligned}
 \mathbf{M}_2 &= \left(\begin{array}{c|c|c|c|c} + & - & & & \\ \hline & + & - & & \\ \hline & & \dots & & \\ \hline & & & + & - \\ \hline & & & & + & - \end{array} \right), \\
 \mathbf{M}_3 &= \left(\begin{array}{c|c|c|c|c} + & + & & & \\ \hline & - & - & & \\ \hline & & \dots & & \\ \hline & & & + & + \\ \hline & & & & - & - \end{array} \right), \\
 \mathbf{M}_5 &= \left(\begin{array}{c|c|c|c|c} + & + & + & + & \\ \hline & - & - & - & \\ \hline & & \dots & & \\ \hline & & & + & + & + & + \\ \hline & & & & - & - & - \end{array} \right),
 \end{aligned} \tag{D.24}$$

and so on. The rest of the sign matrices are still constructed from Eq. (D.23). The formula for the remaining cross terms if we use n_c configurations, then is given by:

$$\frac{1}{n_c} \sum_i^{n_c} \Delta \epsilon_2^{(i)} = \sum_{\substack{\nu \neq \mu, \\ |\mu - \nu| \equiv 0 \pmod{n_c}}}^d \sigma_\nu \sigma_\mu. \tag{D.25}$$

The above equation states that if we use n_c configurations, then we are left with $(1 - 1/n_c)\%$ of the total cross terms, whose indices satisfy $|\mu - \nu| \equiv 0 \pmod{n_c}$. Here mod represents the "modulo" function.

D.4 Comparison of Tauc plots and joint-density of states.

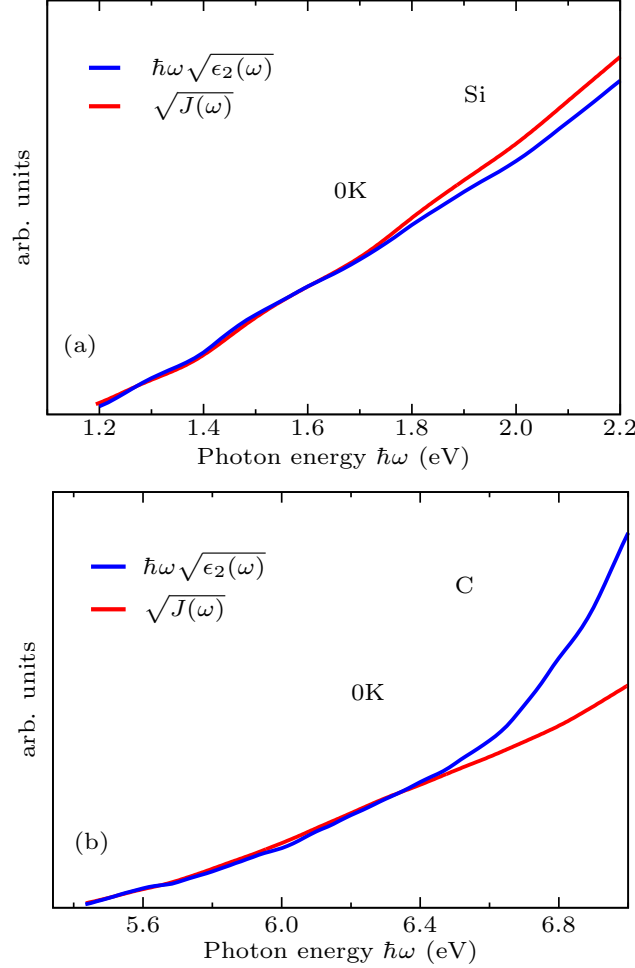


Figure D.4.1: Comparison between the square root of the joint-density of states, $\sqrt{J(\omega)}$, (red solid line) and the Tauc plot, $\hbar\omega\sqrt{\epsilon_2(\omega)}$, (blue solid line) of (a) Si, (b) C. All curves were calculated using the Williams-Lax approach. The calculations were performed using $8 \times 8 \times 8$ supercells and Gaussians of width 30 meV. The electronic Brillouin zone was sampled using 40 **k**-points. In order to facilitate the comparison between the two curves, $\sqrt{J(\omega)}$ was multiplied by a constant. It is immediate to see here that the optical matrix elements calculated for silicon and diamond are approximately constant in the energy range 0.5 eV and 1.1 eV above the absorption onset, respectively. Beyond this range the Tauc plots deviate from $\sqrt{J(\omega)}$ because the optical matrix elements are no longer constant. This is more pronounced in the case of diamond. For direct gap materials, $J(\omega)^2$ and $[\omega^2\epsilon_2(\omega)]^2$ cannot be practically compared, because $\epsilon_2(\omega)$ is dominated by direct transitions. The states that account for direct transitions cannot be easily distinguished in a supercell calculation. In order to achieve this, we need to apply a separate technique for unfolding the band structure of a supercell calculation [238]. This technique will also lead to the calculation of temperature-dependent band structures in reciprocal space.

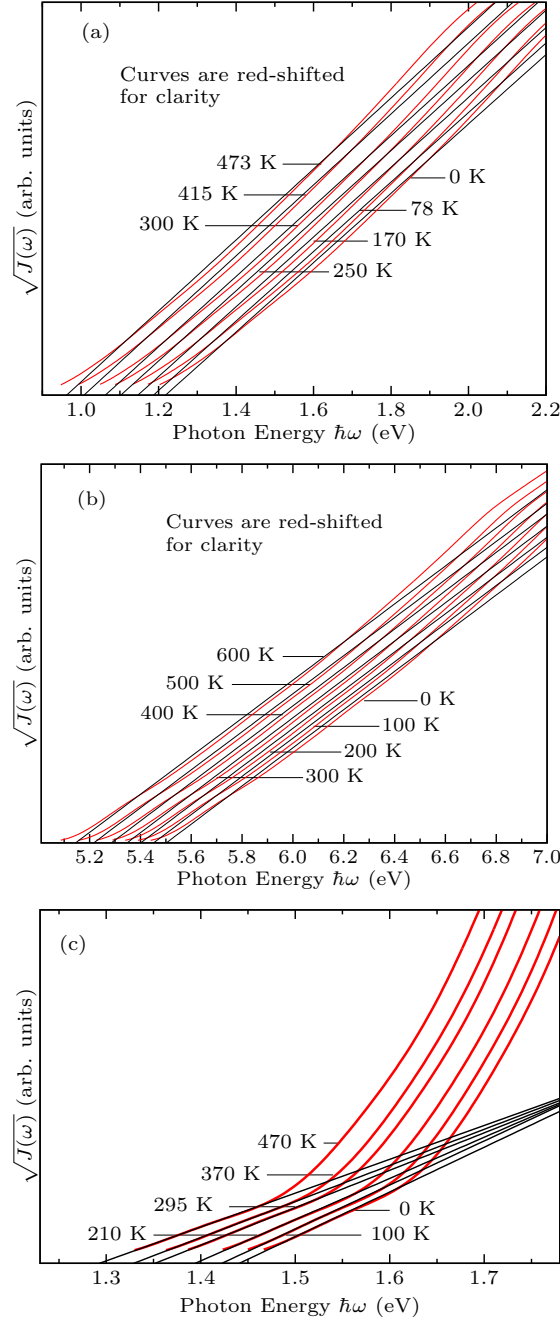


Figure D.4.2: Temperature dependence of the square root of the joint-density of states, $\sqrt{J(\omega)}$, for silicon (a), diamond (b) and gallium arsenide (c). The red and black lines represent $\sqrt{J(\omega)}$ and the corresponding linear fits, respectively, at each temperature. The band gap in all cases is determined from the intercept with the horizontal axis. The results extracted here are in agreement with those shown in Figs. 4.7.1, 4.7.2 and 4.7.4. For the sake of clarity, curves calculated for Si and C are red-shifted with respect to the joint-density of states at 0K.

D.5 Analysis of multi-phonon contributions to the band gap renormalisation of diamond

In this Appendix we first establish the link between our one-shot WL calculation and multi-phonon processes in the AH theory, and then show that multi-phonon effects are essentially negligible in diamond.

We perform an expansion of the Kohn-Sham energy ε_n^x in terms of normal-mode coordinates to obtain:

$$\begin{aligned} \varepsilon_c^x &= \varepsilon_c + \sum_{\nu} \frac{\partial \varepsilon_c^x}{\partial x_{\nu}} x_{\nu} + \frac{1}{2} \sum_{\mu\nu} \frac{\partial^2 \varepsilon_c^x}{\partial x_{\mu} \partial x_{\nu}} x_{\mu} x_{\nu} + \frac{1}{3!} \sum_{\mu\nu\lambda} \frac{\partial^3 \varepsilon_c^x}{\partial x_{\mu} \partial x_{\nu} \partial x_{\lambda}} x_{\mu} x_{\nu} x_{\lambda} \\ &+ \frac{1}{4!} \sum_{\mu\nu\lambda\kappa} \frac{\partial^4 \varepsilon_c^x}{\partial x_{\mu} \partial x_{\nu} \partial x_{\lambda} \partial x_{\kappa}} x_{\mu} x_{\nu} x_{\lambda} x_{\kappa} + \mathcal{O}(x^5). \end{aligned} \quad (\text{D.26})$$

Likewise with the WL expression for the dielectric function in Eq. (4.2), the AH theory is obtained by taking the thermal averages of x_{ν} , $x_{\mu} x_{\nu}$, $x_{\mu} x_{\nu} x_{\lambda}$, and $x_{\mu} x_{\nu} x_{\lambda} x_{\kappa}$. Using Eq. (D.6), the result up to fourth order is:

$$\varepsilon_{c,T}^{\text{AH}} = \varepsilon_c + \frac{1}{2} \sum_{\nu} \frac{\partial^2 \varepsilon_c^x}{\partial x_{\nu}^2} \sigma_{\nu,T}^2 + \frac{3}{4!} \sum_{\mu \neq \nu} \frac{\partial^4 \varepsilon_c^x}{\partial x_{\mu}^2 \partial x_{\nu}^2} \sigma_{\mu,T}^2 \sigma_{\nu,T}^2 + \frac{3}{4!} \sum_{\nu} \frac{\partial^4 \varepsilon_c^x}{\partial x_{\nu}^4} \sigma_{\nu,T}^4. \quad (\text{D.27})$$

The second term on the r.h.s. represents the energy-level renormalisation within the AH theory, and accounts only for single-phonon processes. This was discussed in Sec. 4.4. The third and fourth terms of the r.h.s. represent the two-phonon contribution to the energy-level renormalisation in the AH theory.

Now we show how our one-shot calculation correctly captures the two-phonon contribution. By replacing our “optimal configuration” from Sec. 4.6.1 inside Eq. (D.26), and taking the limit of $M \rightarrow \infty$, we find up to fourth order:

$$\varepsilon_{c,T}^{1\text{C}} = \varepsilon_c + \frac{1}{2} \sum_{\nu} \frac{\partial^2 \varepsilon_c^x}{\partial x_{\nu}^2} \sigma_{\nu,T}^2 + \frac{3}{4!} \sum_{\mu \neq \nu} \frac{\partial^4 \varepsilon_c^x}{\partial x_{\mu}^2 \partial x_{\nu}^2} \sigma_{\mu,T}^2 \sigma_{\nu,T}^2 + \frac{1}{4!} \sum_{\nu} \frac{\partial^4 \varepsilon_c^x}{\partial x_{\nu}^4} \sigma_{\nu,T}^4. \quad (\text{D.28})$$

By comparing Eqs. (D.27) and (D.28) we see that the one-shot method and the fourth-order AH theory give the same result, except for a contribution $\frac{2}{4!} \sum_{\nu} \frac{\partial^4 \varepsilon_n^x}{\partial x_{\nu}^4} \sigma_{\nu,T}^4$. In the limit of $M \rightarrow \infty$ this contribution is negligible as compared to the other terms. This reasoning is analogous to the discussion in Appendix D.2.

Therefore we can conclude that the one-shot WL method captures not only the standard one-phonon processes of the AH theory, but also multi-phonon contributions. The two-phonon contributions are identical to what one would obtain from carrying the AH theory to fourth-order in the atomic displacements. For completeness, and as a future reference we write the result here:

$$\begin{aligned} \frac{\partial^4 \varepsilon_c^x}{\partial x_{\nu}^2 \partial x_{\mu}^2} = & \frac{2}{l_{\nu}^2 l_{\mu}^2} \left[2 \left(\sum_n' \frac{|g_{cn\nu}|^2}{\varepsilon_c - \varepsilon_n} + h_{cc\nu\nu} \right) \sum_n' \frac{|g_{cn\mu}|^2}{(\varepsilon_c - \varepsilon_n)^2} \right. \\ & + 4 \left(\sum_n' \frac{|g_{cn\mu}|^2}{\varepsilon_c - \varepsilon_n} + h_{cc\nu\mu} \right) \sum_n' \frac{g_{cn\nu} g_{cn\mu}}{(\varepsilon_c - \varepsilon_n)^2} + 4 g_{cc\nu} \sum_n' \frac{g_{cn\nu} h_{cn\mu\mu}}{(\varepsilon_c - \varepsilon_n)^2} \\ & + 8 g_{cc\nu} \sum_n' \frac{g_{cn\mu} h_{cn\nu\mu}}{(\varepsilon_c - \varepsilon_n)^2} + 8 \sum_n' \frac{g_{cn\mu} K_{cn\nu\mu}}{\varepsilon_c - \varepsilon_n} + 8 \sum_n' \frac{|h_{cn\nu\mu}|^2}{\varepsilon_c - \varepsilon_n} \\ & \left. + 4 \sum_n' \frac{h_{cn\nu\nu} h_{cn\mu\mu}}{\varepsilon_c - \varepsilon_n} + M_{cc\nu\nu\mu\mu} \right], \end{aligned} \quad (\text{D.29})$$

where:

$$\begin{aligned} g_{cn\nu} &= l_{\nu} \langle c | \frac{\partial V}{\partial x_{\nu}} | n \rangle, \\ h_{cn\nu\mu} &= \frac{1}{2} l_{\nu} l_{\mu} \langle c | \frac{\partial^2 V}{\partial x_{\nu} \partial x_{\mu}} | n \rangle, \\ K_{cn\nu\mu\lambda} &= \frac{1}{2} l_{\nu} l_{\mu} l_{\lambda} \langle c | \frac{\partial^3 V}{\partial x_{\nu} \partial x_{\mu} \partial x_{\lambda}} | n \rangle, \\ M_{cn\nu\mu\lambda\kappa} &= \frac{1}{2} l_{\nu} l_{\mu} l_{\lambda} l_{\kappa} \langle c | \frac{\partial^4 V}{\partial x_{\nu} \partial x_{\mu} \partial x_{\lambda} \partial x_{\kappa}} | n \rangle. \end{aligned} \quad (\text{D.30})$$

The derivation of the above expression is laborious and can be obtained by following the same prescription as in Appendix B.5, but now to fourth order in atomic displacements. As expected this expression involves variations of the self-consistent potential up to the fourth order.

D.5. ANALYSIS OF MULTI-PHONON CONTRIBUTIONS TO THE BAND GAP RENORMALISATION OF DIAMOND

In order to investigate the energy-level renormalisation coming from two-phonon and higher multi-phonon processes, we calculated the density of states (DOS) of diamond within (i) the standard (one-phonon) AH theory, and (ii) the one-shot WL method. These quantities are shown in Fig. D.5.1, for $T = 300$ K, in blue and red, respectively. For comparison, we also show the DOS calculated with the atoms in their equilibrium positions (green). The AH correction to the DOS was obtained by evaluating the derivatives $\partial^2 \varepsilon_n^x / \partial x_\nu^2$ by means of finite differences. This required $6M - 3$ frozen-phonon calculations.

Figure D.5.1 shows that the DOS obtained from the standard AH theory and from the one-shot WL method (which includes multi-phonon effects) essentially coincide. This demonstrates that multi-phonon contributions to the band gap renormalisation are negligible in diamond.

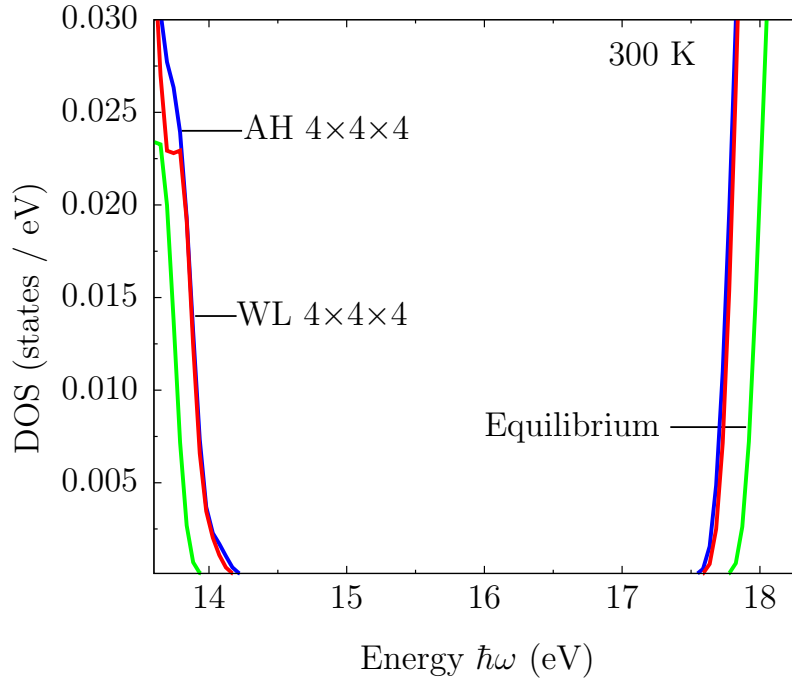


Figure D.5.1: Density of states of diamond close to the valence and conduction band extrema: calculation at the equilibrium geometry (green line), one-shot WL calculation (red line), and AH calculation (blue line). The latter two calculations were performed for $T = 300$ K, using a $4 \times 4 \times 4$ supercell and 65 $\mathbf{k}$ -points in the Brillouin zone of the supercell. The calculation with the atoms at their equilibrium geometry was carried out within the primitive unit cell, using 4160 $\mathbf{k}$ -points. A Gaussian smearing of 30 meV was used for all curves.

Appendix E

Inverse Varshni effect in lead halide perovskites

E.1 Temperature dependence of the band gap

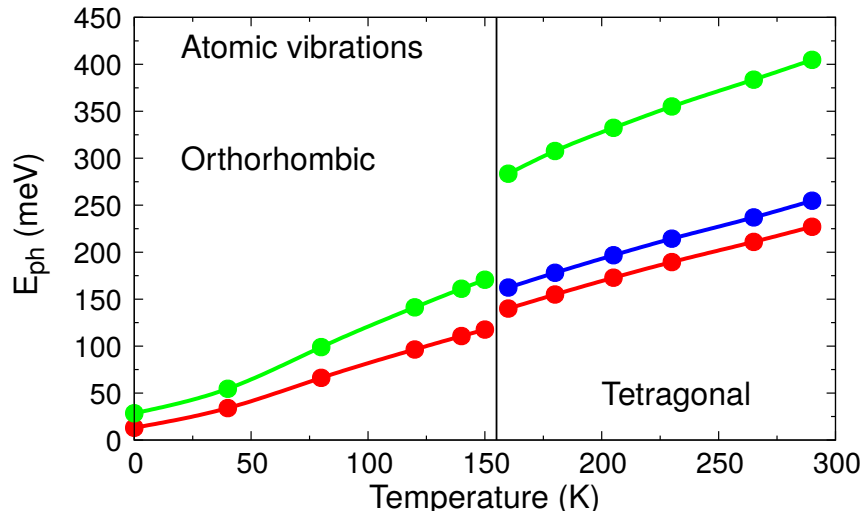


Figure E.1.1: Convergence of the temperature dependence of the band gap renormalisation induced from the atomic vibrational motion (E_{ph}) in the orthorhombic and tetragonal phases of MAPbI_3 as a function of the supercell size: For the orthorhombic phase green and red discs are for calculations using $1 \times 1 \times 1$ supercells (48 atoms) and $2 \times 2 \times 2$ supercells (384 atoms), respectively. For the tetragonal phase green, blue, and red discs correspond to $1 \times 1 \times 2$ supercells (48 atoms), $2 \times 2 \times 2$ supercells (192 atoms), and $2 \times 3 \times 2$ supercells (288 atoms), respectively. The zero-point renormalisation is 27 meV and 13 meV for the $1 \times 1 \times 1$ and $2 \times 2 \times 2$ orthorhombic supercells, respectively. For the lattice dynamics of the tetragonal phase, our calculations revealed that 1 degree of freedom corresponds to a soft mode. Because of this small fraction we decided to exclude the soft mode from our calculations.

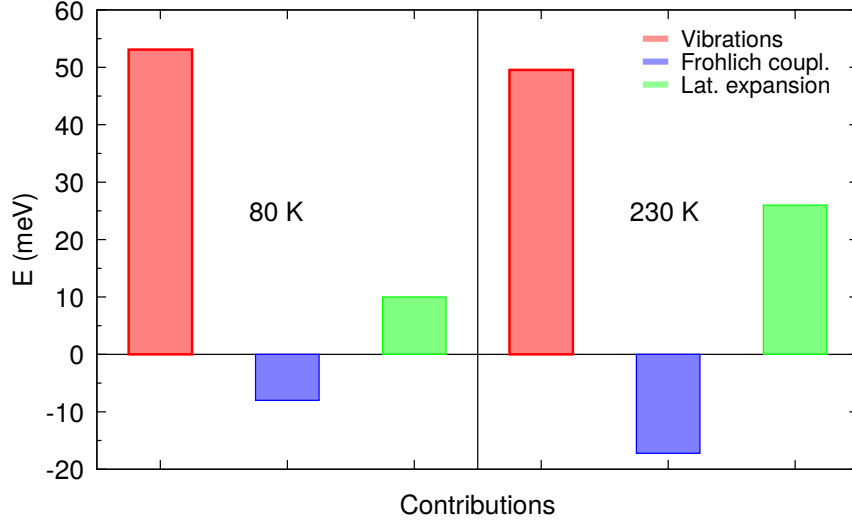


Figure E.1.2: Contributions to the band gap renormalisation at 80 K and 230 K coming from atomic vibrations (red), Fröhlich polar coupling (blue) and thermal lattice expansion (green). The gap renormalisation at 80 K and 230 K of each contribution is taken with respect to their calculated values at 0 K and 160 K, respectively.

E.2 Energy renormalisation vs structural distortion

Figure E.2.1(a) shows that there is a strong positive linear correlation between the change in the energy of the CBM and the oscillations of the Pb-I bond lengths. The bond angle variance measure (σ^2), given in Eq. (5.1), is found to be nearly zero. The modes that induce relatively large distortion ($\Delta > 0.5 \times 10^{-5}$) lie in the energy range 7.0–9.0 meV. Here, we conclude that the oscillations of the Pb-I bond lengths increase the energy of the CBM leading to the opening to the band gap. There are also subtle variations in the energy of the VBM (ranging from -0.4–0.4 meV) which decrease the correlation between the band gap and Δ as shown in Fig. E.2.1(b). These variations are attributed to the mix character of the vibrational modes which mainly influence the bond lengths but also induce small angular distortions.

In Figs. E.2.1(c) and (d) we present the energy renormalisation of the VBM, CBM and band gap as a function of the bond angle variance, σ^2 , calculated for the normal modes with Pb-I-Pb bending or rocking character. The correlation between the band gap change and the measure Δ for Pb-I bond stretching is negligible. It should not come as a surprise that σ^2 provides a unified correlation for Pb-I-Pb bending and rock-

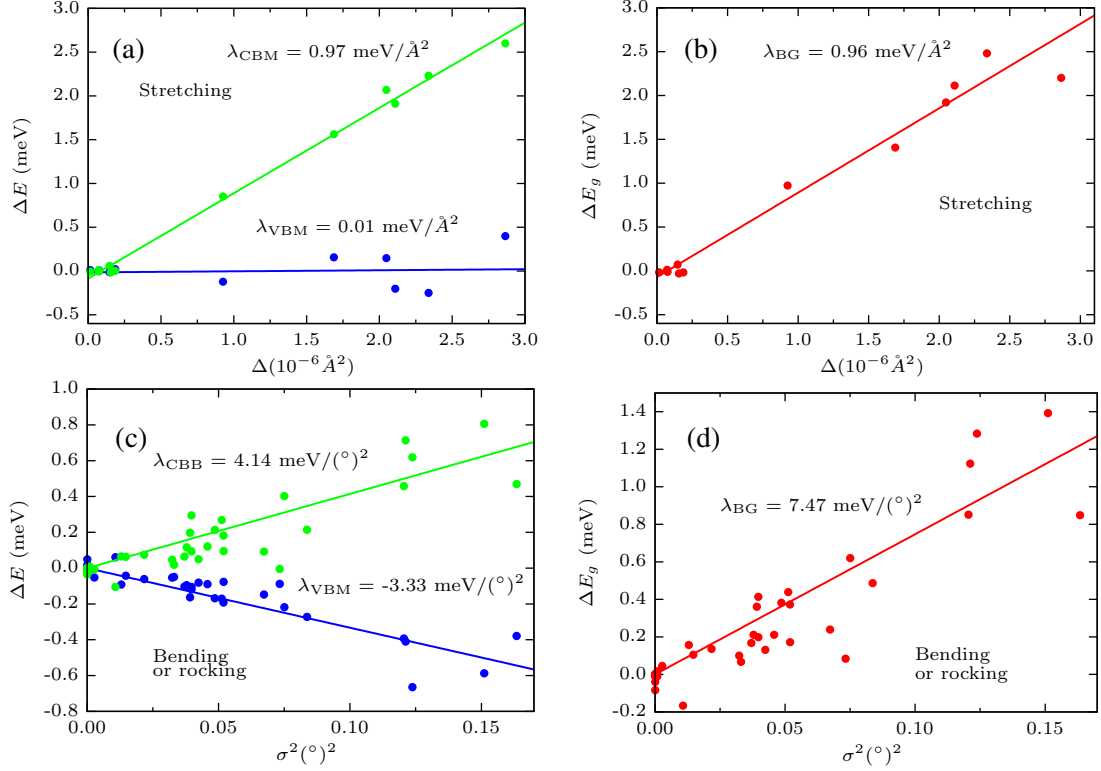


Figure E.2.1: Top panel: Energy level renormalisation of (a) the valence band maximum (blue discs), the conduction band bottom (green discs), and (b) the band gap (red discs) as a function of the Pb-I stretching induced from the phonon modes with frequencies between 7–11 meV (see Fig. 5.2.4). Bottom panel: Energy level renormalisation of (c) the valence band maximum (blue discs), the conduction band bottom (green discs), and (d) the band gap, as a function of the octahedra distortion induced from the phonon modes with Pb-I-Pb bending or rocking character and frequencies between 0–7 meV (see Fig. 5.2.4). The lines represent the linear regression to the data with slopes λ . The distortion measures σ^2 and Δ refer to the measures given in Eqs. (5.1) and (5.2), respectively.

ing modes, since these distortions are directly related to the variations of the twelve I-Pb-I angles of the octahedra [θ_i in Eq. (5.1)]. The vast majority of the vibrational modes lowers the energy of the VBM and increases the energy of the CBM leading to an overall opening of the band gap. Surprisingly, the mode that corresponds to the in-phase rotation of the octahedra induce a negligible energy renormalisation. In Figs. E.2.1(d) we can identify one vibrational distortion [$\sigma^2 = 0.015 (^\circ)^2$] that results in a negative electron-phonon coupling coefficient, opposing to the trend found for the other vibrational distortions of the same character. This mode corresponds to the anti-phase rotation of the octahedra which we examine in Appendix E.3.

E.3 Analysis of the Debye-Waller and Fan terms

In this Appendix we discuss the Debye-Waller and Fan terms calculated for the Pb-I-Pb rocking, Pb-I stretching, Jahn-Teller and breathing modes, as well as the antiphase rotation of the octahedra. The results for the Pb-I-Pb rocking are similar to the mode with Pb-I-Pb bending character and therefore are presented here. The rest of the modes discussed here do not play as important a role to the band gap renormalisation as the Pb-I-Pb bending/rocking modes [see Fig. 5.2.4]. However, the investigation of the DW and Fan terms calculated for these modes reveals interesting physics.

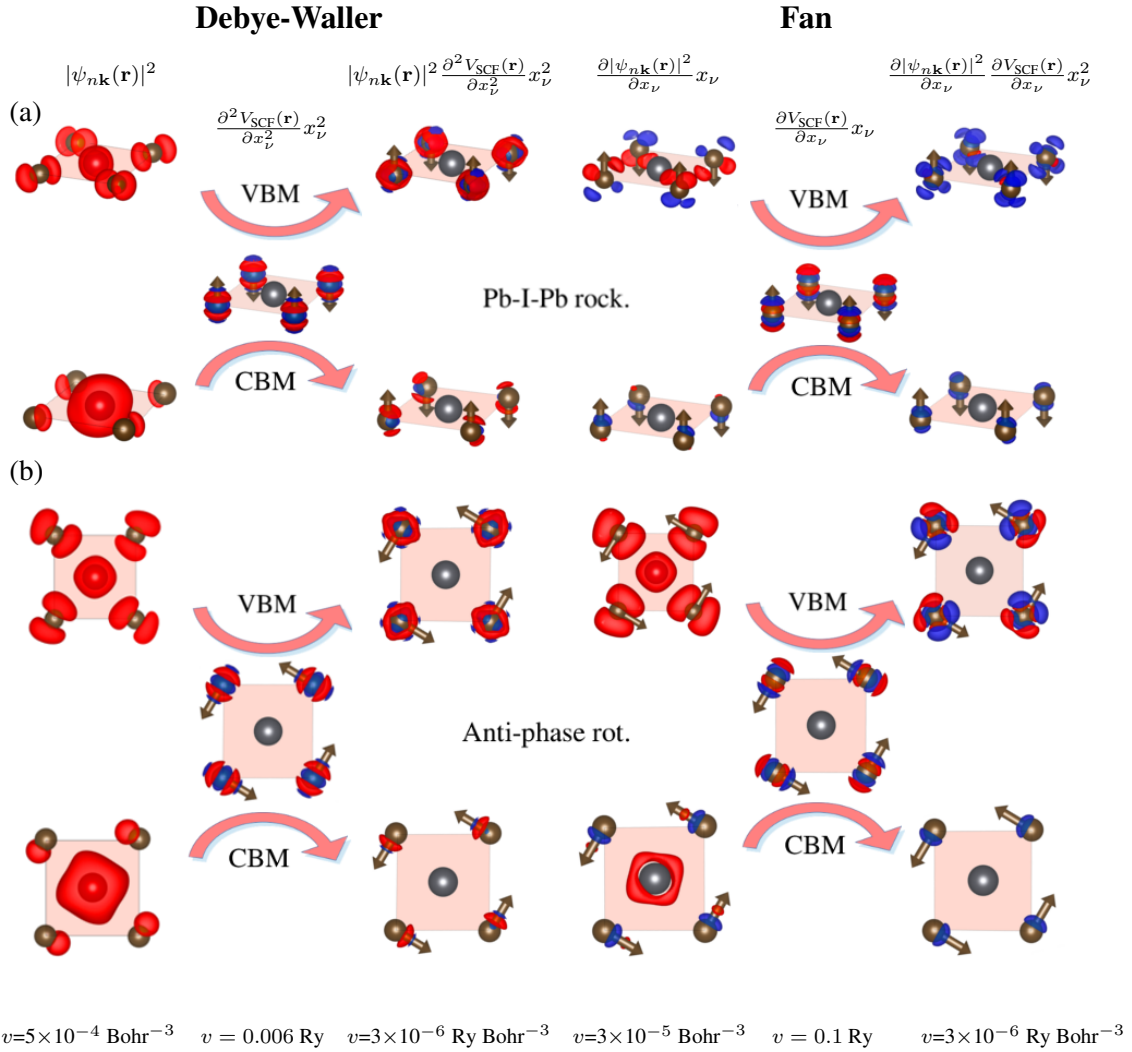


Figure E.3.1: Spatial distribution of the Debye-Waller (left panel) and Fan (right panel) contributions to the energy level renormalisation induced from the mode with Pb-I-Pb rocking character (a) and the antiphase rotation of the octahedra (b). Legends and schematic representation are as in Fig. 5.2.8 of the main text.

Figure E.3.1 shows the Debye-Waller (left panel) and Fan (right panel) terms calculated for the Pb-I-Pb rocking mode (a) and the antiphase rotation of the octahedra (b). Regarding the Pb-I-Pb rocking mode, we can derive similar conclusions for the DW and Fan contributions as for the mode with Pb-I-Pb bending character. This is because the charge is redistributed in a similar manner. However, the positive renormalisation of the CBM reported in Table 5.2.1 is not as large as in the case for the Pb-I-Pb bending mode. The reason is that now the atomic motion is not along the orientation of the charge density in the CBM leading to a smaller overlap between $|\psi_{n\mathbf{k}}(\mathbf{r})|^2$ and $\frac{\partial^2 V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu^2} x_\nu^2$, and thereby to a smaller DW correction.

For the antiphase rotation of the octahedra the DW terms calculated for the VBM and CBM are equal to the DW terms calculated for the mode with Pb-I-Pb bending character (see Table 5.2.1). This should not come as a surprise, since the second order variations in the self-consistent potential remain the same in both cases, as revealed from the left panel of Fig. E.3.1(b). However, when the octahedra rotate out-of-phase, a positive renormalisation of the VBM is reported. The mechanism that differentiates the picture between this mode and the bending or rocking modes is the linear redistribution of the charge density. Now, the electron density is depleted from one plane (not shown) and is accumulated in the upper plane as shown in the right panel of Fig. E.3.1(b). This charge redistribution leads to a smaller self-energy contribution to the renormalisation of the VBM than the one calculated for bending and rocking modes. Moreover, the fact that the charge is not locally redistributed, but instead migrates from one octahedron to another, explains the choice of correlating the band gap renormalisation with the dihedral angle [see Fig. 5.2.7(c)]. In the case of the CBM, the electron density migrates from the I atoms to the Pb atom in the centre of the octahedron as illustrated in the right panel of Fig. E.3.1(b). Exactly the opposite picture is found for the lower plane (not shown). The depleted charge around the I atoms results in a negative Fan correction which is equal in magnitude to the DW term. This leads to a negligible renormalisation reported in Table 5.2.1.

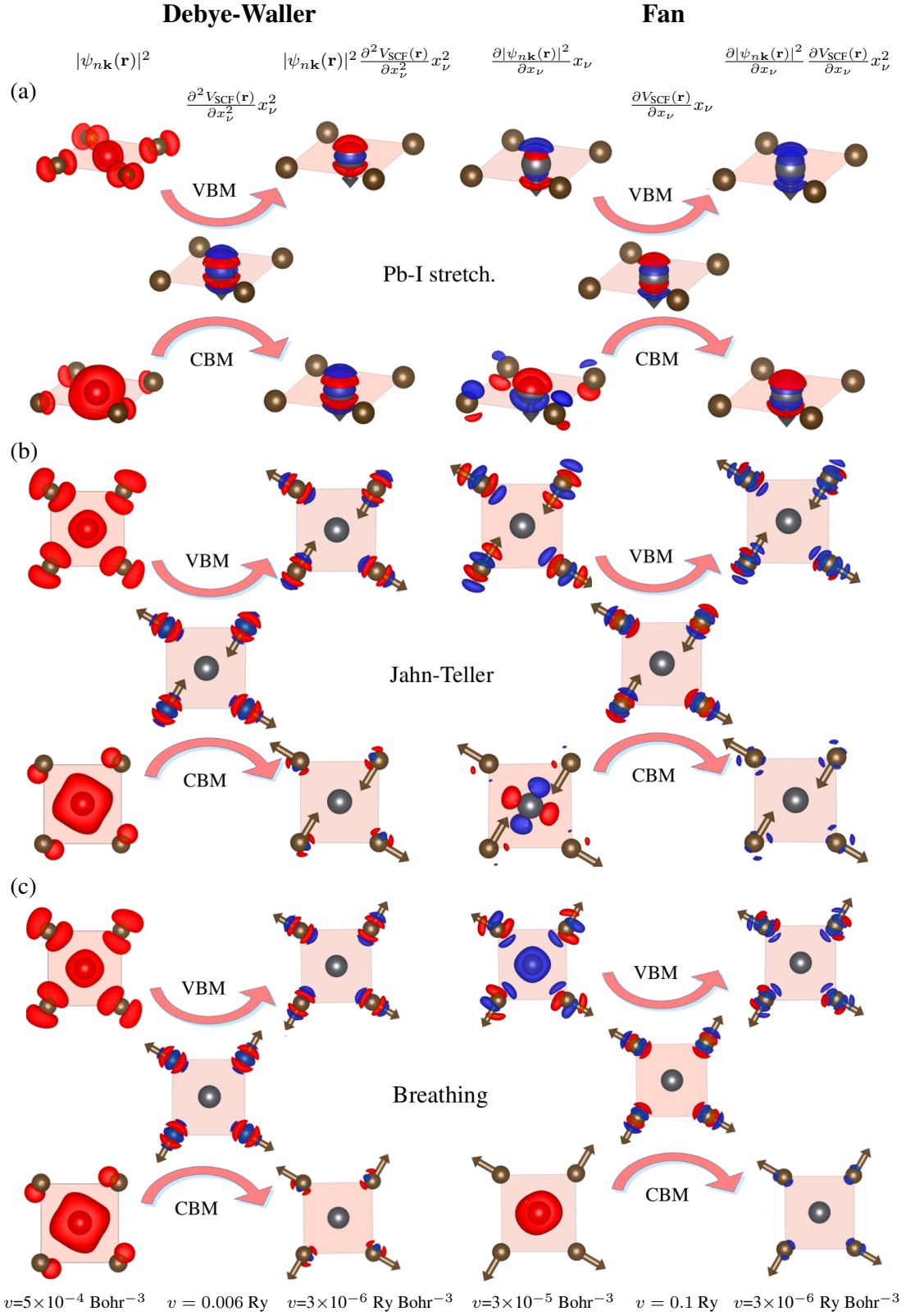


Figure E.3.2: Spatial distribution of the Debye-Waller (left panel) and Fan (right panel) contributions to the energy level renormalisation induced from the Pb-I stretching mode (a), the Jahn-Teller (b), and breathing (c) distortions. Legends and schematic representation are as in Fig. 5.2.8 of the main text.

Figure E.3.2 shows the Debye-Waller (left panel) and Fan (right panel) terms calculated for the Pb-I stretching mode (a), the Jahn-Teller (b), and breathing (c) distortions. In the case of the Pb-I stretching mode, the renormalisation of the VBM is small owing to the large cancellation between the calculated DW and Fan terms (see Table 5.2.1). At variance with the VBM, the positive renormalisation of the CBM is not negligible due to a larger DW term (see Table 5.2.1). The reason is that the charge density at the CBM is less localised around the Pb atoms [see Fig. E.3.2(a)]. This leads to a significant overlap of $|\psi_{nk}(\mathbf{r})|^2$ with the positive variations of $\frac{\partial^2 V_{\text{SCF}}(\mathbf{r})}{\partial x_\nu^2} x_\nu^2$. The fact that the charge density is not strongly localised around the Pb atoms is the main mechanism that leads to the up-shift of the CBM and therefore to the opening of the band gap in MAPbI₃ due to off-centre displacements of the Pb atoms. In the main text, we do not discuss extensively this mechanism because we concentrate only on the charge localisation around the I atoms which are displaced along the modes with Pb-I-Pb bending/rocking character.

In the case of the Jahn-Teller and breathing modes [Fig. E.3.2(b) and (c)], the DW contribution to the renormalisation of the CBM is small (see Table 5.2.1) owing to the direction of motion of the I atoms. This motion leads to a small overlap between the second order variations of the self consistent potential and the small equilibrium charge density concentrated around the I atoms. On the other hand, the DW contribution to the renormalisation of the VBM is much larger because the second order variations of the self consistent potential are directed parallel to the equilibrium electron density. The relatively large Fan term calculated for the VBM is due to the overlap between the positive (negative) charge redistribution and the negative (positive) variations of the self consistent potential. Finally, the relatively small Fan contribution to the renormalisation of the CBM is because the charge around the I atoms varies very little. In conclusion, we find for the Jahn-Teller and breathing modes that the band gap closes owing to the large DW calculated for the VBM. At variance with vibrations along the Pb-I-Pb bending/rocking mode, which lower the VBM, here the atoms are moving par-

allel to the distribution of the electron density. Therefore, the direction of motion of the atoms is another mechanism that determines the sign of the band gap renormalisation. In the main text, we do not discuss extensively this mechanism because we concentrate only on the direction along the Pb-I-Pb bending/rocking modes, which are dominating the band gap renormalisation at finite temperatures.

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