

Siesta: A Complete Guide

Hand-on 3: Structural and Electronic Properties in Periodic Systems

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A Pedestrian's Guide to Solid State

Crystal Structure

The arrangement of atoms in a crystalline solid forms a periodic lattice structure, which is central to the study of solid-state physics. A crystal lattice is defined as a repeating array of points in space, where each point represents the position of an atom or group of atoms. This periodicity is the foundation for many of the unique properties of crystalline materials.

Lattice Definition

A lattice is a three-dimensional periodic array of points in space that represents the translational symmetry of a crystal. Each lattice point corresponds to an identical environment in the crystal structure.

Mathematical Description

The lattice is mathematically described by three primitive vectors, \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 , which define the unit cell. Any lattice point \mathbf{R} can be expressed as:

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3,$$

where $n_1, n_2, n_3 \in \mathbb{Z}$.

Lattice Dimensions

Lattices can exist in different dimensions:

- **1D:** Periodic arrangement along a single direction (e.g., chain of atoms).
- **2D:** Periodic arrangement in two directions (e.g., graphene).
- **3D:** Periodic arrangement in three directions (e.g., cubic or hexagonal lattices).

Example: Simple Cubic Lattice

Simple Cubic Lattice

In a simple cubic lattice, the lattice vectors are:

$$\mathbf{a}_1 = a\hat{x}, \quad \mathbf{a}_2 = a\hat{y}, \quad \mathbf{a}_3 = a\hat{z}.$$

The lattice points form a grid of cubes with side length a .

Basis

The **basis** defines the atomic or molecular arrangement at each lattice point. The complete crystal structure is formed by combining the lattice with the basis.

Atomic Basis Description

Atoms in the basis are positioned relative to lattice points using fractional coordinates:

$$\mathbf{r}_{\text{basis}} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3.$$

Where x, y, z are fractional values between 0 and 1.

Examples of Basis

Single-Atom Basis

In a simple cubic structure, each lattice point has one atom.

Multi-Atom Basis

More complex structures, like NaCl, have multiple atoms at each lattice point:

- Na atom at: $(0, 0, 0)$
- Cl atom at: $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

Crystal Structure

The combination of the lattice and basis defines the crystal structure. The position of atoms can be described as:

$$\mathbf{R}_{\text{atom}} = \mathbf{R}_{\text{lattice}} + \mathbf{r}_{\text{basis}}.$$

The lattice provides translational symmetry, and the basis defines the atomic arrangement, forming the complete crystal structure.

Unit Cell and Symmetry

The unit cell is the smallest repeating unit in a crystal that defines its symmetry and structure.

Types of Unit Cells

- **Primitive Unit Cell:** Contains one lattice point and captures the lattice symmetry.
- **Conventional Unit Cell:** Larger unit cell that may contain multiple lattice points, emphasizing symmetry.

Volume of Unit Cell

The volume of the unit cell is:

$$V_{\text{cell}} = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|.$$

Fractional Coordinates

Atomic positions are described using fractional coordinates (x, y, z) , related to the lattice vectors:

$$\mathbf{r} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3.$$

Example: Simple Cubic Unit Cell

Simple Cubic Unit Cell

For a simple cubic lattice:

$$\mathbf{a}_1 = a\hat{x}, \quad \mathbf{a}_2 = a\hat{y}, \quad \mathbf{a}_3 = a\hat{z}.$$

Each unit cell contains one lattice point and has a volume of a^3 .

Symmetry in Crystals

Symmetry plays a crucial role in determining the physical properties of crystals, reflecting the invariance of the crystal structure under certain operations.

Symmetry Operations

- **Translational Symmetry:** The structure remains unchanged when translated by a lattice vector.
- **Rotational Symmetry:** Invariance under rotation about an axis (e.g., 2-fold, 3-fold, 4-fold, 6-fold).
- **Mirror Symmetry:** Invariance under reflection across a mirror plane.
- **Inversion Symmetry:** Invariance under inversion through a point.
- **Glide Planes and Screw Axes:** Combination of translation with reflection or rotation.

Space Groups

The combination of translational symmetry and other symmetry operations leads to 230 distinct space groups in three dimensions. These groups classify the symmetry properties of all possible crystalline structures.

Example: Symmetry in Cubic Crystals

Symmetry in Cubic Crystals

Cubic crystals (e.g., FCC) exhibit:

- **4-fold Rotational Symmetry:** Along the cube's axes.
- **Mirror Planes:** Perpendicular to the cube faces.
- **Inversion Symmetry:** About the cube's center.

Impact of Symmetry

Symmetry affects various properties of crystals, such as:

- **Electronic Properties:** Determines band degeneracies and selection rules.
- **Optical Properties:** Governs phenomena like birefringence and optical activity.
- **Mechanical Properties:** Influences anisotropy in elasticity and thermal expansion.

Bravais Lattice

A **Bravais lattice** represents the periodic arrangement of points in space such that the environment around each point is identical. It is generated by integer linear combinations of three independent primitive vectors \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 .

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, \quad n_1, n_2, n_3 \in \mathbb{Z}.$$

Crystal Systems

There are **7 crystal systems**, each containing one or more Bravais lattices. The systems are categorized based on symmetry and unit cell geometry.

- **Cubic System:** SC, BCC, FCC
- **Tetragonal System:** Simple, Body-Centered
- **Orthorhombic System:** 4 types
- **Hexagonal System:** Simple
- **Trigonal System:** Simple
- **Monoclinic System:** 2 types
- **Triclinic System:** Simple

Lattice Parameters

Each Bravais lattice is characterized by the following:

- **Edge Lengths:** a, b, c
- **Angles:** α, β, γ

These parameters define the unit cell geometry, and are used to classify the crystal system.

Summary Table: Crystal Systems and Bravais Lattices

Crystal Systems and Bravais Lattices

Crystal System	Lattice Parameters	
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	Simple, Base-Centered
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	
Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	
Trigonal	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	
Monoclinic	$a \neq b \neq c, \alpha = \gamma = 90^\circ \neq \beta$	Simple
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	

Table: Crystal systems and their corresponding Bravais lattices.

Applications of Bravais Lattices

The 14 Bravais lattices are essential for:

- **Classifying Crystals:** Basis for describing all crystal structures.
- **Symmetry Analysis:** Encapsulate symmetry operations within a crystal system.
- **Material Properties:** Aid in predicting electronic, optical, and mechanical properties.

Reciprocal Space

Reciprocal Space Overview

Reciprocal space, or momentum space, is the Fourier transform of real space. It is used to describe wave-like phenomena such as electron wavefunctions, phonons, and diffraction patterns.

Reciprocal Lattice Vectors

Reciprocal lattice vectors are defined as:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}.$$

These vectors correspond to the periodicities of the real-space lattice.

Bragg's Law

The condition for constructive interference in diffraction is:

$$\mathbf{k}' - \mathbf{k} = \mathbf{G},$$

Brillouin Zone

Definition

The Brillouin zone is the Wigner-Seitz cell of the reciprocal lattice. It represents the region of reciprocal space closest to a given reciprocal lattice point.

Construction of Brillouin Zone

To construct the Brillouin zone:

- Identify reciprocal lattice points.
- Draw perpendicular bisectors between a chosen reciprocal lattice point and its neighbors.
- The enclosed region forms the Brillouin zone.

Brillouin Zone Examples

- In 1D: A line segment between $-\pi/a$ and π/a .
- In 2D: A hexagon for a hexagonal lattice.

Brillouin Zone Applications

Electronic Properties

The Brillouin zone is crucial for understanding the behavior of electron states and band structure.

Phonons

It is used to describe phonon dispersion, which affects thermal and vibrational properties.

Optical and Transport Properties

Many optical and transport phenomena, like the density of states and effective mass of electrons, depend on the Brillouin zone geometry and band structure.

Symmetry Analysis

The symmetry of the Brillouin zone corresponds to the underlying symmetry of the real-space lattice, simplifying calculations and analysis.

Definition of Stress

Stress (σ) is the internal force per unit area within a material due to external loading. It is a tensor quantity, describing both the magnitude and direction of forces.

$$\sigma = \frac{F}{A}$$

where F is the applied force and A is the cross-sectional area.

Types of Stress

Stress can be categorized as:

- **Normal Stress:** Forces perpendicular to the surface (Tensile or Compressive).
- **Shear Stress:** Forces parallel to the surface causing layers to slide.

Stress Tensor

Stress in 3D is described by the stress tensor:

$$\sigma_{ij} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix}$$

where diagonal elements are normal stresses, and off-diagonal elements are shear stresses.

Definition of Strain

Strain (ε) quantifies the deformation of a material in response to stress. It is a dimensionless quantity and measures the relative change in length or size:

$$\varepsilon = \frac{\Delta L}{L_0}$$

where ΔL is the change in length and L_0 is the original length.

Types of Strain

Strain can be classified as:

- **Normal Strain:** Results from changes in length or volume.
- **Shear Strain:** Results from angular deformation due to shear forces.

Strain Tensor

Strain in 3D is described by the strain tensor:

$$\varepsilon_{ij} = \begin{bmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} \end{bmatrix}$$

Stress-Strain Relationship

Hooke's Law

The relationship between stress and strain is governed by Hooke's Law for elastic deformation:

$$\sigma = E\varepsilon$$

where E is the Young's modulus, a measure of the material's stiffness.

Deformation Types

- **Elastic Deformation:** The material returns to its original shape after stress removal.
- **Plastic Deformation:** The material undergoes permanent deformation after exceeding the yield stress.

Poisson's Ratio

Poisson's Ratio

Poisson's ratio (ν) describes the relationship between lateral and longitudinal strains:

$$\nu = - \frac{\epsilon_{\text{lateral}}}{\epsilon_{\text{longitudinal}}}$$

Typical values range between 0 and 0.5 for most materials.

Vibrational Dynamics in Crystals

Atoms in a crystal lattice undergo oscillatory motion due to interatomic forces. At any temperature above absolute zero, these vibrations can be described using:

- Classical mechanics (coupled harmonic oscillators),
- Quantum mechanics (normal modes of vibration).

The vibrational modes depend on the symmetry and geometry of the lattice and are characterized by the wavevector \mathbf{q} and frequency $\omega(\mathbf{q})$.

Definition of Phonons

Phonons are quantized normal modes of vibration in a crystal lattice, analogous to photons in electromagnetic waves. They are bosonic quasiparticles and play a crucial role in thermal and electrical transport.

Types of Phonons

Phonons are categorized into two types based on atomic displacements:

- **Acoustic Phonons:** Atoms move in phase, producing sound waves. The frequency approaches zero as $\mathbf{q} \rightarrow 0$.
- **Optical Phonons:** Atoms in the unit cell move out of phase, typically have higher frequencies, and interact with electromagnetic radiation (e.g., infrared absorption).

Phonon Dispersion Relation

The dispersion relation connects the frequency ω with the wavevector \mathbf{q} . In a crystal with N atoms, there are $3N$ vibrational modes:

- 3 acoustic modes (1 longitudinal, 2 transverse),
- $3N - 3$ optical modes.

A negative frequency indicates dynamical instability and a possible structural phase transition.

Overview

Energy band theory is essential for understanding the electronic properties of solids. It describes how electrons in a periodic crystal lattice experience the lattice potential, forming allowed and forbidden energy regions. This theory classifies materials as conductors, semiconductors, or insulators and is critical for understanding solid-state devices.

Formation of Energy Bands

Energy Levels in Isolated Atoms

In isolated atoms, electrons occupy discrete energy levels. When atoms are brought together to form a solid, the overlap of atomic orbitals splits these levels into energy bands. The degree of overlap depends on atomic separation and orbital type.

Energy Bands

The bands are classified as:

- **Valence Band:** Highest energy levels, fully occupied at absolute zero temperature, responsible for chemical bonding.
- **Conduction Band:** Higher energy states where electrons can move freely, contributing to electrical conductivity.

Band Gap

The energy between the conduction and valence bands is called the **band gap** (E_g), defined as:

$$E_g = E_{\text{conduction}}^{\text{min}} - E_{\text{valence}}^{\text{max}}.$$

Electrical Properties Based on Band Gap

Types of Materials Based on Band Gap

- **Insulators:** Large E_g , electrons need significant energy to transition to the conduction band.
- **Semiconductors:** Moderate E_g , allowing for thermal or optical excitation of electrons.
- **Metals:** Overlapping valence and conduction bands, resulting in no band gap.

Bloch's Theorem

The wavefunction of an electron in a periodic potential is given by:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}},$$

where $u_{n\mathbf{k}}(\mathbf{r})$ is periodic with the lattice, and \mathbf{k} is the wavevector representing the crystal momentum. This leads to the **dispersion relation** between energy E and wavevector \mathbf{k} .

Kronig-Penney Model

Periodic Potential

The Kronig-Penney model simplifies band formation by considering a one-dimensional periodic potential:

$$V(x) = \begin{cases} -V_0, & 0 \leq x \leq b, \\ 0, & b < x \leq a. \end{cases}$$

Band Formation and Band Gaps

Solving the Schrödinger equation for this potential reveals:

- **Energy Bands:** Allowed energy values form bands.
- **Band Gaps:** Energy ranges where electron wavefunctions interfere destructively, forming forbidden regions.

Band Gaps in Semiconductors and Insulators

Direct vs Indirect Band Gaps

Semiconductors have either direct or indirect band gaps:

- **Direct Band Gap:** Minimum energy transition occurs at the same \mathbf{k} -point.
- **Indirect Band Gap:** Minimum energy transition involves a change in \mathbf{k} , requiring phonon interaction.

Examples of Materials

- **Silicon:** Indirect band gap ($E_g \approx 1.1 \text{ eV}$).
- **Gallium Arsenide:** Direct band gap ($E_g \approx 1.4 \text{ eV}$), ideal for optoelectronics.

Applications in Material Science

Energy band theory enables the design and optimization of materials for various applications:

- **Electronics:** Design of transistors, diodes, and integrated circuits.
- **Optoelectronics:** LEDs and lasers based on direct band gap semiconductors.
- **Photovoltaics:** Efficient light absorption in solar cells with the appropriate band gap.
- **Thermoelectrics:** Materials designed for optimal electrical conductivity and minimal thermal conductivity.

Fermi Energy

The Fermi energy (E_F) and Fermi surface are central concepts in understanding the electronic properties of materials. They describe the behavior of electrons in solids, particularly metals and semiconductors.

Fermi-Dirac Distribution

The probability of an electron occupying an energy state at temperature T is given by the Fermi-Dirac distribution:

$$f(E) = \frac{1}{1 + e^{\frac{E - E_F}{k_B T}}},$$

where:

- E is the energy of the state,
- k_B is Boltzmann's constant,
- T is the temperature.

Fermi Surface

The Fermi surface separates occupied electronic states from unoccupied states at $T = 0$ K, and it provides crucial insights into the material's electronic structure.

Fermi Surface Definition

The Fermi surface is defined by:

$$E(\mathbf{k}) = E_F,$$

where $E(\mathbf{k})$ is the energy dispersion relation and \mathbf{k} is the wavevector.

- **Electrical Conductivity:** The shape of the Fermi surface determines the electron velocities and scattering rates, impacting conductivity.
- **Thermal Properties:** The density of states near E_F affects heat capacity and thermal conductivity.
- **Magnetoresistance:** The Fermi surface topology influences quantum oscillations and other phenomena.

The optical properties of solids reveal how they interact with electromagnetic radiation. These properties are governed by the material's electronic structure and include phenomena such as absorption, reflection, refraction, and transmission.

- **Absorption:** Energy from light excites electrons between energy bands.
- **Reflection:** Light is reflected at the surface due to refractive index mismatch.
- **Refraction:** Light changes direction when passing through materials with different refractive indices.
- **Transmission:** Light passes through the material, partially absorbed and refracted.

The Optical Gap

The optical gap is the minimum energy required to excite an electron from the valence band to the conduction band via photon absorption.

- **Direct Optical Gap:** The valence band maximum (VBM) and conduction band minimum (CBM) occur at the same wavevector.
- **Indirect Optical Gap:** The VBM and CBM occur at different wavevectors, requiring phonons for momentum conservation.

Kramers-Kronig Relations

The Kramers-Kronig relations link the real and imaginary components of the dielectric function, ensuring consistency with causality.

Kramers-Kronig Relations

The relations are given by:

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\omega' \epsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega',$$

$$\epsilon_2(\omega) = -\frac{2\omega}{\pi} \mathcal{P} \int_0^\infty \frac{\epsilon_1(\omega') - 1}{\omega'^2 - \omega^2} d\omega',$$

where \mathcal{P} is the Cauchy principal value.

- These relations allow the determination of the real part of the dielectric function from experimental data.
- They are vital for analyzing optical spectra and extracting material parameters.

Optical Parameters

Refractive Index (n)

The refractive index describes the material's ability to bend light, related to the real part of the dielectric function $\epsilon(\omega)$.

Absorption Coefficient (α)

The absorption coefficient determines how light intensity decreases as it propagates through the material:

$$\alpha(\omega) = \frac{4\pi k}{\lambda}$$

Reflectivity (R)

The reflectivity is the fraction of light reflected at the surface:

$$R = \left| \frac{n - 1 + ik}{n + 1 + ik} \right|^2$$

Formation of Excitons

Excitons are bound states of an electron and a hole created during the absorption of light. Their energy is slightly less than the energy of the free electron-hole pair due to the binding energy (E_b).

- Frenkel Excitons: Tightly bound and localized.
- Wannier-Mott Excitons: Weakly bound and delocalized.
- Charge-Transfer Excitons: Electron and hole reside on different molecules or atoms.

Wannier-Mott Excitons

These excitons are weakly bound and delocalized over several lattice sites. They are typically found in inorganic semiconductors.

Symmetry Operations

Symmetry operations in a crystal are transformations that leave the crystal invariant, such as rotations, reflections, and translations.

- **Point Groups:** Symmetries that leave at least one point fixed.
- **Space Groups:** Include translational symmetry along with point group operations.

Applications of Group Theory

Group theory helps classify crystals and understand their properties, such as electronic band structure and vibrational modes.

Applications of Group Theory

Electronic Band Structure

Group theory simplifies the analysis of electronic band structure by classifying electronic states using the symmetry of the crystal.

Phonons and Vibrational Modes

Group theory classifies phonon modes as Raman-active, infrared-active, or silent, based on the symmetry of the crystal.

Magnetic Properties

Group theory extends to magnetic crystals, including time-reversal symmetry, to understand spin structures.

It's Your Turn! (1)

Task 1

Utilize the Kronig-Penney model to solve the Schrödinger equation for a one-dimensional periodic potential. Derive the transcendental equation that relates the wavevector k and energy E . Ensure the derivation captures the essential assumptions and boundary conditions of the model.

Task 2

Numerically solve the transcendental equation to compute the allowed energy bands. Plot the energy bands as a function of the wavevector k . Restrict the plot to the first Brillouin zone to highlight the periodicity of the reciprocal space. **Hint:** Implement this step using programming tools such as Python, Mathematica, or MATLAB. Ensure proper convergence of numerical solutions for accurate representation of the band structure.

Task 3

Investigate the effect of varying the barrier width on the band structure. Specifically, compute and plot the energy gap as a function of the barrier width. Analyze how the changes in barrier width influence the size of the band gap, providing physical insight into the tunability of electronic properties in periodic potentials.

Convergence Tests in SIESTA

Energy Cutoff (Mesh Cutoff)

Energy Cutoff

The energy cutoff controls the number of plane waves included in the calculation of the electronic wavefunctions. A higher cutoff results in a more accurate representation of the wavefunctions, but also increases the computational cost.

Test: Perform a series of calculations with increasing values of the energy cutoff. The calculation is considered converged when the energy difference between two successive values of the cutoff becomes negligible.

K-Point Grid

The k-point grid defines the sampling of the Brillouin zone. More k-points lead to a more accurate calculation, but at the cost of increased computational effort.

Test: Perform calculations with increasing k-point densities (e.g., $2 \times 2 \times 2$, $4 \times 4 \times 4$). The calculation is converged when the change in total energy is smaller than a specified threshold (e.g., 10^{-4} eV).

Smearing Width

SIESTA uses smearing techniques to treat the occupation of states near the Fermi level, especially in metallic systems. The smearing width affects the broadening of the Fermi surface.

Test: Perform calculations with different smearing widths (e.g., 0.1 eV, 0.2 eV) and monitor the energy and electronic properties. The system is converged when changes in total energy and electronic structure are minimal.

Force Convergence

In structural relaxation, the forces on atoms are minimized. The calculation is converged when the maximum force on any atom is below a specified threshold (e.g., 10^{-2} eV/Å).

Test: Monitor the forces during relaxation. When the maximum force is small enough, the system is considered stable.

Main Convergence Variables

- `Mesh.Cutoff`: Energy cutoff for plane wave expansion.
- `kgrid.MonkhorstPack`: Defines the k-point mesh for Brillouin zone sampling.
- `MD.MaxForceTol`: Convergence criterion for atomic forces in structural relaxation.
- `ElectronicTemperature`: Controls smearing of electronic states.

Tasks

- 1 Perform a convergence test for aluminum (Al) in the bulk FCC structure.
- 2 Perform a convergence test for gallium nitride (GaN) in the bulk wurtzite phase. **Hint:** Refer to the database or the Master's Dissertation by Carlos Maciel O. Bastos for information on the wurtzite structure of GaN.

Computing Structural Properties in SIESTA

Structural Relaxation in SIESTA

Introduction

Structural relaxation is a fundamental process to determine the equilibrium configuration of a crystal system by minimizing the total energy. This involves adjusting atomic positions, lattice parameters, or both under quantum mechanical forces.

Crystal Lattice Description

The zinc blende structure is a derivative of the FCC lattice, where Gallium (Ga) and Arsenic (As) atoms occupy two interpenetrating sublattices.

- Lattice constant of GaAs: 5.653 Å
- Gallium atom at $(0, 0, 0)$ and Arsenic atom at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$

Structural Optimization in SIESTA

Key Parameters

The following parameters control structural optimization in SIESTA:

- `MD.TypeOfRun = CG`: Specifies relaxation mode.
- `MD.VariableCell true`: Allows cell size and shape to change.
- `MD.MaxForceTol`: Sets the force tolerance for convergence.

Example: GaAs in Zinc Blende Structure

The starting point for relaxation is a zinc blende structure with a lattice constant of 7.0 \AA . Atomic coordinates are defined as:

```
%block LatticeVectors 0.0 0.5 0.5 0.5 0.0 0.5 0.5 0.5 0.0 %endblock  
LatticeVectors
```

Calculating the Bulk Modulus Using SIESTA

Definition

The bulk modulus B quantifies a material's resistance to compression:

$$B = -V \left(\frac{\partial P}{\partial V} \right)$$

where V is volume, P is pressure, and $\frac{\partial P}{\partial V}$ is the derivative of pressure with respect to volume.

Steps to Calculate Bulk Modulus

- 1 Relax the structure.
- 2 Apply volume perturbation by scaling lattice vectors.
- 3 Perform energy calculations for each volume.
- 4 Fit energy-volume data to an equation of state.

Example: Bulk Modulus of GaAs

Method

For GaAs, the expected bulk modulus is approximately 75.6 GPa. The procedure follows the steps outlined for volume perturbation and energy fitting.

Fitting the Data

Fit the energy-volume data to the Murnaghan or Birch-Murnaghan equation of state to extract the bulk modulus.

Your Turn!

Exercise 1

Obtain lattice parameters for the following systems:

- Silicon (Si) in diamond structure
- Zinc Oxide (ZnO) in wurtzite structure
- Aluminum Antimonide (AlSb) in zinc blende structure
- Calcium Titanate (CaTiO_3) in perovskite structure
- Carbon (C) in graphene structure
- Molybdenum Disulfide (MoS_2) in H_2 phase

Exercise 2

Calculate the bulk modulus for calcium titanate (CaTiO_3) and compare it with the experimental value.

Obtaining Electronic Properties Using Siesta

Band structure calculations are a cornerstone of solid-state physics, providing insights into the electronic properties of materials. This presentation will cover the following topics:

- First Brillouin Zone and k-Path Selection
- Band Structure Calculation
- Density of States (DOS) Calculation
- Visualization and Analysis

First Brillouin Zone and k-Path Selection

First Brillouin Zone

The FBZ represents the fundamental region of wavevectors in a periodic crystal lattice. For graphene, the standard high-symmetry k-points are:

- $\Gamma = (0, 0, 0)$
- $K = (\frac{1}{3}, \frac{1}{3}, 0)$
- $M = (\frac{1}{2}, 0, 0)$

k-Path Selection

For graphene, the k-path for band structure calculations is:

$$\Gamma \rightarrow M \rightarrow K \rightarrow \Gamma.$$

Calculating the Band Structure

SCF and NSCF Calculations

First, a self-consistent field (SCF) calculation is performed to obtain the converged charge density, followed by a non-self-consistent field (NSCF) calculation along the chosen k-path.

k-Path File

To define the k-path in Siesta, create the following input:

```
BandLinesScale ReciprocalLatticeVectors Bandskpoints true
%block kgrid_BandLines 3 30 0.0 0.0 0.0  Gamma 0.5 0.0 0.0  M 0.33333
0.33333 0.0  K 0.0 0.0 0.0  Gamma %endblock kgrid_BandLines
```

Extracting and Plotting the Band Structure

Extracting the Band Structure

After running the NSCF calculation, extract the band structure using the 'gnubands' utility:

```
gnubands j SYSTEM_NAME.bands j bands.dat
```

Plotting the Band Structure

To plot the band structure using Gnuplot, use the following command:

```
gnuplot plot "bands.dat" using 1:2 with lines title "Graphene Band Structure"
```

Density of States (DOS) Calculation

Density of States Formula

The DOS, $g(E)$, is defined as:

$$g(E) = \sum_i \delta(E - E_i)$$

Setting Up the DOS Calculation

In the Siesta input file, specify a dense k-point grid and projected DOS for better resolution:

```
%block PDOS.kgrid_Monkhorst_Pack 10 0 0 0.0 0 10 0 0.0 0 0 1 0.0  
%endblock PDOS.kgrid_Monkhors
```

Extracting the DOS

Use the 'fmpdos' utility to extract the DOS:
fmpdos

Visualizing the DOS

To visualize the partial DOS (e.g., for the 2s orbital), use the following Gnuplot command:
gnuplot plot "2s.dat" using 1:2 with lines title "2s partial DOS"

Your Turn!

- 1 Obtain the band structure and Density of States (DoS) for the following systems:
 - Silicon (Si) in the diamond structure.
 - Zinc Oxide (ZnO) in the wurtzite structure.
 - Aluminum Antimonide (AlSb) in the zinc blende structure.
 - Calcium Titanate (CaTiO_3) in the perovskite structure.
 - Carbon (C) in the graphene structure.
 - Molybdenum Disulfide (MoS_2) in the H2 phase.

Hit! Use the `sstranslate.x` tool to extract structural parameters.