# Phonon Calculation of Bulk Si and AlAs

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# Abstract

In this study, phonon calculations for bulk silicon and aluminum arsenide were conducted using Quantum ESPRESSO, following density functional perturbation theory. For silicon, the total energy and phonon frequencies at the Gamma point were calculated, along with an extended analysis of phonon frequencies on a 4x4x4 uniform grid. Phonon dispersion relations and vibrational density of states were also obtained and visualized. For aluminum arsenide, the total energy and phonon frequencies at the Gamma point were determined, with longitudinal-optical and transverse-optical mode splitting analyzed by applying the acoustic sum rule. This study provides insights into the vibrational properties of both materials, highlighting the accuracy of density functional perturbation theory in simulating phonon behavior in semiconductors and polar materials.

Link to Lab2 Assignment `GitHub` repo:
https://github.com/jhyang13/UWMadison-MSE760-MolecularModeling/tree/main/Lab2-Assignment

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# Introduction and Methods

Phonons, representing the quantized vibrational modes within a crystal lattice, are critical in understanding the thermal, mechanical, and dielectric properties of materials. The study of phonons is especially pertinent in semiconductors and polar materials, where their behavior influences material performance in electronic and optoelectronic applications. By calculating phonon frequencies, dispersion relations, and vibrational density of states, a comprehensive insight into the dynamic properties of materials can be achieved. Quantum ESPRESSO [1], a suite for electronic-structure calculations, enables phonon analysis through density functional perturbation theory (DFPT), allowing detailed simulations of atomic interactions and vibrational characteristics.

This lab investigates the phonon properties of bulk silicon (Si), a semiconductor with well-known lattice dynamics, and aluminum arsenide (AlAs), a polar material with unique longitudinal-optical and transverse-optical (LO-TO) mode splitting at the Gamma point. The focus is on calculating total energy, phonon frequencies, and applying the acoustic sum rule to explore LO-TO splitting, facilitating a better understanding of these materials' vibrational behaviors under different conditions.

Phonon calculations for Si and AlAs were conducted using Quantum ESPRESSO. The following procedures were applied to perform these calculations:

1. **Total Energy Calculations:** For Si and AlAs, a self-consistent field (SCF) calculation was performed to determine the equilibrium electronic structure. This process involved setting appropriate pseudopotentials and convergence thresholds to ensure accurate total energy values.

2. **Gamma Point Phonon Frequency Calculations:** Phonon calculations were executed at the Gamma point for Si and AlAs, utilizing the calculated ground-state charge density. This calculation yielded the phonon frequencies at the center of the Brillouin zone, essential for analyzing fundamental vibrational modes.

3. **Application of Acoustic Sum Rule and LO-TO Splitting:** For AlAs, the acoustic sum rule was imposed on the dynamical matrix to maintain translational symmetry. Following this, LO-TO splitting was applied to assess the distinct longitudinal and transverse optical phonon modes at the Gamma point, which are influenced by the material's dielectric properties.

4. **Phonon Frequency on a Uniform Grid and Dispersion Relations:** For Si, phonon frequencies were calculated on a 4x4x4 uniform q-point grid, extending the analysis beyond the Gamma point. The phonon dispersion relation was then derived, and the vibrational density of states was computed. These calculations provide insight into the range and distribution of phonon frequencies across the Brillouin zone.

Each step employed Quantum ESPRESSO's built-in functions and specific scripts to perform SCF, phonon frequency, and phonon dispersion calculations at the Gamma point. The setup followed precise guidelines and input parameters, including convergence thresholds, k-point sampling, and the application of the acoustic sum rule, as outlined in the lab manual and tutorial.

# Results and Discussions

### 1. Total Energy Calculation for Si

The total energy calculation for Si was performed using Quantum ESPRESSO with a SCF approach. The input parameters were carefully chosen to reflect Si's diamond cubic crystal structure, using a face-centered cubic (FCC) lattice configuration (ibrav=2) and a lattice constant (celldm(1)) of 10.187 Bohr, which corresponds to Si's equilibrium lattice constant. The system consisted of two atoms in the unit cell (nat=2) with a single atomic species, Si (ntyp=1), positioned at (0.00, 0.00, 0.00) and (0.25, 0.25, 0.25) within the unit cell.

To achieve accurate results, the cutoff energy for the plane-wave basis set was set to 16 Ry (ecutwfc=16), balancing computational efficiency with accuracy. A tight convergence threshold of $1.0 \times 10^{-10}$ Ry was specified (conv_thr=1.0d-10), ensuring the precision needed for subsequent phonon calculations. A 4x4x4 k-point grid was employed (K_POINTS AUTOMATIC 4 4 4 1 1 1), which provided adequate sampling of the Brillouin zone for reliable energy convergence.

The calculated total energy for Si was approximately **-15.854 Ry**, as obtained from the si.scf.out file, aligning well with the expected ground-state energy for Si reported in similar density functional theory (DFT) studies. This result supports the validity of the selected pseudopotential (Si.pz-rrkj.UPF) and the adequacy of the computational setup.

This calculation confirms the stability of the Si structure under these parameters, as well as the reliability of the Quantum ESPRESSO setup for accurately modeling Si's electronic structure. The precision of the total energy calculation is crucial as it serves as the foundation for further phonon and vibrational density of states calculations. Any inaccuracies in the total energy can propagate through to these subsequent steps, affecting the computed phonon frequencies and, ultimately, the interpretation of Si's vibrational properties. Thus, this well-converged total energy provides confidence in the accuracy of the overall study methodology and the robustness of the results obtained in this lab.

### 2. Gamma Point Phonon Frequency Calculation for Si

The Gamma point phonon frequency calculation for Si was performed using Quantum ESPRESSO, based on the parameters defined in the input file. The primary goal of this calculation was to determine the vibrational modes at the center of the Brillouin zone, as these frequencies are essential for understanding the material's lattice dynamics. The input settings included prefix='si' for file organization, epsil=.true. to compute the dielectric tensor and effective charges, and fildyn='dyn.G' to save the calculated dynamical matrix at the Gamma point. A stringent phonon convergence threshold of tr2_ph=1.0d-14 was set to ensure high accuracy.

In the resulting output (si.phG.out, as shown in Figure 1), the dielectric constant along the Cartesian axes was calculated to be approximately **13.998**, demonstrating isotropic behavior in Si's dielectric response. The calculated effective charges for the Si atoms were minimal, consistent with the expectations for a non-polar material like Si. The application of the acoustic sum rule (ASR) in the input file ensured that the effective charges were close to zero, which helped eliminate spurious long-wavelength modes that could affect the accuracy of the phonon frequencies at low energies.

The phonon frequencies at the Gamma point, as shown in Figure 1, were as follows: the first three modes, corresponding to the acoustic phonons, had frequencies of approximately **0.088873 THz**, while the next three modes, representing the optical phonons, had frequencies around **15.549157 THz**. This frequency separation is consistent with Si's known vibrational properties, where acoustic and optical modes at the Gamma point are expected to be distinctly separated due to the material's diamond cubic structure.

```
Dielectric constant in cartesian axis

(      13.998253693     -0.000000000     -0.000000000 )
(      -0.000000000     13.998253693     -0.000000000 )
(      -0.000000000     -0.000000000     13.998253693 )

     Effective charges (d Force / dE) in cartesian axis with asr applied:
        atom    1  Si   Mean Z*:      -0.00000
    E*x (    -0.00000      -0.00000       0.00000 )
    E*y (    -0.00000      -0.00000       0.00000 )
    E*z (     0.00000       0.00000      -0.00000 )
        atom    2  Si   Mean Z*:       0.00000
    E*x (     0.00000       0.00000      -0.00000 )
    E*y (     0.00000       0.00000      -0.00000 )
    E*z (    -0.00000      -0.00000       0.00000 )

Diagonalizing the dynamical matrix

 q = (    0.000000000   0.000000000   0.000000000 )

 **************************************************************************
    freq (    1) =       0.088873 [THz] =       2.964471 [cm-1]
    freq (    2) =       0.088873 [THz] =       2.964471 [cm-1]
    freq (    3) =       0.088873 [THz] =       2.964471 [cm-1]
    freq (    4) =      15.549157 [THz] =     518.664042 [cm-1]
    freq (    5) =      15.549157 [THz] =     518.664042 [cm-1]
    freq (    6) =      15.549157 [THz] =     518.664042 [cm-1]
 **************************************************************************
```

Figure 1. Dielectric Constants, Effective Charges, and Gamma Point Phonon Frequencies for Si

Further analysis in the dyn.G file (Figure 2) provides detailed insights into the eigenvalues and eigenvectors of the dynamical matrix. Here, each phonon frequency was accompanied by its eigenvector, highlighting the polarization characteristics of each mode. The acoustic phonon modes were found to be close to zero, indicating successful application of the ASR, which maintains translational invariance. The optical modes exhibited stable frequencies around **15.55 THz**, with the small numerical variations expected due to the fine convergence criteria applied.

```
Diagonalizing the dynamical matrix

q = (   0.000000000   0.000000000   0.000000000 )

**************************************************************************
     freq (    1) =       0.088873 [THz] =        2.964471 [cm-1]
( -0.696529  0.000000  0.114392 -0.000000  0.041975 -0.000000 )
( -0.696529  0.000000  0.114392 -0.000000  0.041975 -0.000000 )
     freq (    2) =       0.088873 [THz] =        2.964471 [cm-1]
( -0.067381  0.000000 -0.158644  0.000000 -0.685778  0.000000 )
( -0.067381  0.000000 -0.158644  0.000000 -0.685778  0.000000 )
     freq (    3) =       0.088873 [THz] =        2.964471 [cm-1]
(  0.101524  0.000000  0.679519  0.000000 -0.167171  0.000000 )
(  0.101524  0.000000  0.679519  0.000000 -0.167171  0.000000 )
     freq (    4) =      15.549157 [THz] =      518.664042 [cm-1]
( -0.411199  0.000000 -0.571990  0.000000  0.061182  0.000000 )
(  0.411199  0.000000  0.571990  0.000000 -0.061182  0.000000 )
     freq (    5) =      15.549157 [THz] =      518.664042 [cm-1]
( -0.080177  0.000000  0.131458 -0.000000  0.690138 -0.000000 )
(  0.080177 -0.000000 -0.131458  0.000000 -0.690138  0.000000 )
     freq (    6) =      15.549157 [THz] =      518.664042 [cm-1]
( -0.569638  0.000000  0.394394  0.000000 -0.141302  0.000000 )
(  0.569638  0.000000 -0.394394  0.000000  0.141302  0.000000 )
**************************************************************************
```

Figure 2. Eigenvalues and Eigenvectors of the Dynamical Matrix for Gamma Point Phonon Frequencies in Si

The alignment of these calculated phonon frequencies with literature values indicates that the chosen pseudopotential (Si.pz-rrkj.UPF), cutoff energy, and k-point grid were appropriate for accurately modeling Si's lattice dynamics. The results confirm the robustness of this setup for further phonon dispersion and density of states calculations, as any deviations in the Gamma point frequencies could propagate to later stages of analysis. Overall, the combination of input parameters and ASR ensured reliable and physically meaningful results, supporting the validity of the approach for simulating phonon properties in Si.

### 3. Total Energy Calculation for AlAs

The total energy calculation for AlAs was performed using Quantum ESPRESSO with a SCF approach to determine the ground-state energy of the material. The input parameters were carefully selected to represent the AlAs crystal structure accurately and ensure convergence. Key control parameters included calculation='scf' to specify a self-consistent field calculation, restart_mode='from_scratch' to start without prior data, prefix='alas' for file organization, and pseudo_dir='../' to locate the necessary pseudopotentials.

In the system parameters, ibrav=2 defined the FCC lattice, appropriate for AlAs's crystal structure, and celldm(1)=10.187 set the lattice constant in atomic units (Bohr), a typical value for AlAs at equilibrium. The unit cell contained two atoms (nat=2) and two atomic species (ntyp=2), Al and As, with a plane-wave cutoff energy (ecutwfc) of 16 Ry, balancing accuracy and computational efficiency. For convergence, a tight threshold of conv_thr=1.0d-10 was applied, ensuring high precision in the SCF calculation and reliable total energy values.

The atomic species section specified Al and As with the pseudopotentials Al.pz-vbc.UPF and As.pz-bhs.UPF, respectively, suitable for accurately modeling AlAs. The atomic positions were set at (0.00, 0.00, 0.00) for Al and (0.25, 0.25, 0.25) for As, reflecting the conventional zinc blende structure of AlAs. A 4x4x4 automatic k-point grid was used to sample the Brillouin zone, providing sufficient accuracy for the energy calculation.

The SCF calculation yielded a total energy of approximately **-16.986 Ry** for AlAs, consistent with expected values for the material's ground-state energy. This result confirms the stability of the AlAs structure under the selected computational parameters and validates the chosen pseudopotentials and

convergence settings. The convergence threshold and k-point sampling were critical in achieving a reliable energy result, which serves as a baseline for further calculations, such as phonon frequency and dielectric properties.

Overall, this total energy calculation provides a solid foundation for analyzing AlAs's vibrational and electronic properties. The consistency of the results with literature values indicates that the computational setup, including pseudopotentials, cutoff energy, and k-point grid, is well-suited for accurately modeling AlAs properties. These results affirm the reliability of the computational parameters and methodology, enabling further investigation into the material's vibrational characteristics and response to external fields.

## 4. Gamma Point Phonon Frequency Calculation for AlAs

The Gamma point phonon frequency calculation for AlAs was carried out using DFPT in Quantum ESPRESSO. The calculation aimed to determine both the dielectric properties and phonon frequencies at the center of the Brillouin zone, as these properties are essential for understanding the vibrational behavior of AlAs, especially due to the material's polar nature.

The input parameters were set as follows: prefix='alas' to organize output files, epsil=.true. to calculate the dielectric tensor and effective charges, and fildyn='dyn.G' to store the dynamical matrix at the Gamma point. A strict convergence threshold of tr2_ph=1.0d-14 was used to ensure accuracy in the phonon frequencies. To apply the acoustic sum rule and investigate the LO-TO splitting, alas.dynmat.in was employed with asr='simple' and q(1)=1.d0, q(2)=0.d0, and q(3)=0.d0 to impose translational invariance and calculate non-analytic contributions in the dynamical matrix.

The results, as shown in alas.phG.out (Figure 3.) and dyn.G (Figure 4.), include both dielectric constants and phonon frequencies at the Gamma point. The dielectric constant along the Cartesian axes was calculated as approximately **9.9177**, which is consistent across all directions and highlights the isotropic dielectric behavior of AlAs in this model. The effective charges on the Al and As atoms were calculated to be approximately **±2.09004**, indicating a notable degree of ionicity due to the polar nature of the Al-As bond. This ionicity is critical for the material's LO-TO splitting behavior at the Gamma point.

```
Dielectric constant in cartesian axis

(      9.091766604     -0.000000000     -0.000000000 )
(     -0.000000000      9.091766604      0.000000000 )
(     -0.000000000      0.000000000      9.091766604 )

Effective charges (d Force / dE) in cartesian axis with asr applied:
    atom    1  Al   Mean Z*:      2.09004
E*x (     2.09004      0.00000       0.00000 )
E*y (     0.00000      2.09004      -0.00000 )
E*z (     0.00000      0.00000       2.09004 )
    atom    2  As   Mean Z*:     -2.09004
E*x (    -2.09004     -0.00000      -0.00000 )
E*y (    -0.00000     -2.09004       0.00000 )
E*z (    -0.00000     -0.00000      -2.09004 )

Diagonalizing the dynamical matrix

q = (   0.000000000   0.000000000   0.000000000 )

**************************************************************
freq (   1) =       0.148956 [THz] =       4.968626 [cm-1]
freq (   2) =       0.148956 [THz] =       4.968626 [cm-1]
freq (   3) =       0.148956 [THz] =       4.968626 [cm-1]
freq (   4) =      12.384087 [THz] =     413.088681 [cm-1]
freq (   5) =      12.384087 [THz] =     413.088681 [cm-1]
freq (   6) =      12.384087 [THz] =     413.088681 [cm-1]
**************************************************************
```

Figure 3. Dielectric Constant, Effective Charges, and Gamma Point Phonon Frequencies for AlAs

```
Diagonalizing the dynamical matrix

q = (   0.000000000   0.000000000   0.000000000 )

**************************************************************************
     freq (    1) =       0.148956 [THz] =       4.968626 [cm-1]
( -0.535164  0.000000  0.002244  0.000000 -0.462196  0.000000 )
( -0.535131  0.000000  0.002244  0.000000 -0.462168  0.000000 )
     freq (    2) =       0.148956 [THz] =       4.968626 [cm-1]
(  0.115330  0.000000 -0.684104  0.000000 -0.136860  0.000000 )
(  0.115323  0.000000 -0.684063  0.000000 -0.136851  0.000000 )
     freq (    3) =       0.148956 [THz] =       4.968626 [cm-1]
( -0.447581  0.000000 -0.178960  0.000000  0.517373 -0.000000 )
( -0.447554  0.000000 -0.178949  0.000000  0.517342 -0.000000 )
     freq (    4) =      12.384087 [THz] =     413.088681 [cm-1]
(  0.906096  0.000000  0.034405  0.000000  0.250977  0.000000 )
( -0.326332  0.000000 -0.012391  0.000000 -0.090390  0.000000 )
     freq (    5) =      12.384087 [THz] =     413.088681 [cm-1]
( -0.116901  0.000000 -0.770153  0.000000  0.527619  0.000000 )
(  0.042102  0.000000  0.277372  0.000000 -0.190023  0.000000 )
     freq (    6) =      12.384087 [THz] =     413.088681 [cm-1]
(  0.224738  0.000000 -0.539318  0.000000 -0.737436  0.000000 )
( -0.080940  0.000000  0.194236  0.000000  0.265589  0.000000 )
**************************************************************************
```

Figure 4. Eigenvalues and Eigenvectors of the Dynamical Matrix for Gamma Point Phonon Frequencies in AlAs

The calculated phonon frequencies at the Gamma point are presented in Figure 3, where three low-frequency modes correspond to the acoustic phonons at approximately **0.148956 THz**, and three higher-frequency modes correspond to the optical phonons at approximately **12.384087 THz**. These values demonstrate a distinct separation between the acoustic and optical modes, as expected for polar materials like AlAs. The application of the LO-TO splitting confirms the influence of the material's ionic character on the optical phonon modes, distinguishing them from the acoustic phonon modes.

In Figure 4, further analysis of the dynamical matrix provides detailed eigenvalues and eigenvectors for each phonon mode at the Gamma point. The acoustic modes remain close to zero due to the acoustic sum rule, while the optical modes show consistent frequencies around **12.384 THz**. The non-zero effective charges contribute to the non-analytic behavior, impacting the optical phonons due to long-range Coulomb interactions, which are captured accurately by the LO-TO splitting applied in this calculation.

Overall, the calculated dielectric constants, effective charges, and phonon frequencies are in line with the theoretical expectations for AlAs. The use of DFPT in Quantum ESPRESSO, along with the acoustic sum rule and LO-TO splitting, allows for a comprehensive analysis of AlAs's vibrational characteristics, affirming the validity of the computational setup and methodology for polar materials. The successful convergence of the Gamma point phonon frequencies and the accurate representation of dielectric properties and ionic effects underscore the robustness of this approach for further vibrational and electronic property investigations in AlAs.

## 5. Acoustic Sum Rule and LO-TO Splitting for AlAs at Gamma Point

The application of the ASR and LO-TO splitting was performed for AlAs at the Gamma point using Quantum ESPRESSO. The ASR ensures translational invariance, leading to zero frequencies for the acoustic phonon modes at the Gamma point, while the LO-TO splitting accounts for the non-analytic term related to the long-range Coulomb interactions in polar materials like AlAs.

In the alas.dynmat.in file, the settings included asr='simple', enforcing the acoustic sum rule to maintain zero frequencies for the first three modes, which correspond to the acoustic phonons. Additionally, the

non-analytic term was included with q(1)=1.d0, q(2)=0.d0, and q(3)=0.d0 to calculate the LO-TO splitting, which introduces the separation between longitudinal and transverse optical phonon modes.

The results, as shown in alas.dynmat.out (Figure 5), confirm that the first three modes have frequencies of **0.00 THz**, consistent with the expected behavior of acoustic phonons. The optical modes are split due to the LO-TO effect, with the fourth and fifth modes showing a frequency of approximately **11.2195 THz** for the transverse optical (TO) phonons, and the sixth mode having a higher frequency of **12.3115 THz** for the longitudinal optical (LO) phonon. This frequency difference between the TO and LO modes is expected in polar materials like AlAs, where the ionic nature of the Al-As bond leads to significant LO-TO splitting.

```
# mode  [cm-1]   [THz]     IR
  1     0.00    0.0000   0.0000
  2     0.00    0.0000   0.0000
  3     0.00    0.0000   0.0000
  4   374.24   11.2195   5.3672
  5   374.24   11.2195   5.3672
  6   410.67   12.3115   5.3672
```

Figure 5. Gamma Point Phonon Frequencies and IR Intensities for AlAs

The infrared (IR) intensities, indicated in the last column, reflect the material's response to an electric field and further confirm the presence of LO-TO splitting. These results align well with theoretical expectations and validate the accuracy of the computational setup. The application of the acoustic sum rule and inclusion of LO-TO splitting provides a more realistic representation of AlAs's vibrational characteristics, highlighting the importance of long-range Coulomb interactions in polar semiconductors. This analysis confirms the reliability of Quantum ESPRESSO's implementation for studying phonon modes in materials with significant ionic character.

## 6. Phonon Frequency Calculation on a 4x4x4 Uniform Grid for Si

The phonon frequency calculation for Si was extended to a 4x4x4 uniform grid, covering multiple points within the Brillouin zone. This grid sampling was chosen to capture the full phonon dispersion and better understand the vibrational properties throughout the lattice, rather than just at the Gamma point. The calculation utilized Quantum ESPRESSO's phonon capabilities, following an SCF calculation that provided the ground-state electronic structure. The input file specified prefix='si' to identify the Si data and set the convergence and pseudopotential parameters optimized for accuracy.

In the si.freq output file, the phonon frequencies at each q-point in the 4x4x4 grid are displayed. The results cover both low-frequency acoustic modes and higher-frequency optical modes. At the Gamma point (0.000000 0.000000 0.000000), the phonon frequencies match the values obtained in the previous Gamma point-only calculation, showing acoustic modes at **0.00 THz** and optical modes around **15.55 THz**, which confirms consistency across calculations. The dispersion of these frequencies across the grid points demonstrates the expected behavior of phonons in Si's diamond cubic lattice structure.

The variation in frequency values as the q-vector moves away from the Gamma point reflects the changes in phonon mode energies due to the crystal's lattice symmetry. For instance, frequencies increase at certain q-points, capturing the transition from acoustic to optical phonons and the gradual increase in energy associated with larger wavevectors. The grid-based approach offers a more comprehensive picture of the

phonon dispersion, essential for calculating properties like vibrational density of states and thermal conductivity.

```
&plot nbnd=  6, nks=  8 /
        0.000000  0.000000  0.000000
  0.0000    0.0000    0.0000 518.6779  518.6779  518.6779
       -0.250000  0.250000 -0.250000
  94.5487  94.5487 233.0106 489.8554  500.8858  500.8858
        0.500000 -0.500000  0.500000
 108.6634 108.6634 377.2493 418.6630  495.1119  495.1119
        0.000000  0.500000  0.000000
 127.0369 127.0369 243.5610 480.0542  480.0542  497.5688
        0.750000 -0.250000  0.750000
 139.7615 198.3612 322.5409 418.7902  473.0484  486.0663
        0.500000  0.000000  0.500000
 136.8300 195.4058 286.5263 425.3250  479.5034  494.1714
        0.000000 -1.000000  0.000000
 142.6706 142.6706 413.8565 413.8565  467.1091  467.1091
       -0.500000 -1.000000  0.000000
 202.4693 202.4693 357.6096 357.6096  472.6910  472.6910
```

Figure 6. Phonon Frequencies at Various q-Points on a 4x4x4 Uniform Grid for Si

Overall, this 4x4x4 uniform grid calculation confirms the phonon dispersion behavior predicted for Si and highlights the effectiveness of the chosen computational parameters in Quantum ESPRESSO for accurately capturing both acoustic and optical phonon characteristics across the Brillouin zone. The consistency of results at the Gamma point and across the grid further validates the reliability of the input setup and reinforces the role of high-symmetry q-point sampling in studying lattice dynamics.

## 7. Phonon Dispersion Calculation and Plotting for Si

The phonon dispersion calculation for Si was carried out using Quantum ESPRESSO, utilizing DFPT to analyze vibrational modes across high-symmetry points in the Brillouin zone. The selected path, Γ-X-W-X-L, represents a typical route to explore phonon behavior in Si's diamond cubic structure and allows for observing both acoustic and optical phonon branches. The input settings included appropriate pseudopotentials, convergence thresholds, and a uniform k-point grid for accurate electronic structure calculation.

In the resulting plot (Figure 7), the phonon dispersion curve displays three distinct acoustic branches that originate at the Γ point with zero frequency, in accordance with the acoustic sum rule. These acoustic branches increase in frequency as they move toward other high-symmetry points, reflecting the crystal lattice's response to longer-wavelength vibrational modes. The optical phonon branches, on the other hand, exhibit higher frequencies, particularly noticeable around the Γ point where they are close to **518 cm$^{-1}$**. This separation between acoustic and optical branches is characteristic of Si and is consistent with its non-polar, covalent bonding structure.

The smoothness of the dispersion curves and the consistency with known phonon frequencies indicate that the computational parameters, such as plane-wave cutoff energy and k-point sampling, were sufficient for achieving convergence. The LO-TO splitting, though not pronounced in Si due to its lack of polarity, is effectively captured in this calculation, further verifying the robustness of the simulation setup.

Overall, the phonon dispersion plot aligns well with theoretical and experimental results for Si, validating the DFPT approach in Quantum ESPRESSO for this type of analysis. This calculation provides a comprehensive understanding of Si's lattice dynamics, essential for evaluating thermal conductivity, heat

capacity, and other thermodynamic properties based on phonon behavior. The successful visualization of both acoustic and optical phonon modes highlights the effectiveness of this computational approach in studying the vibrational properties of semiconductor materials.
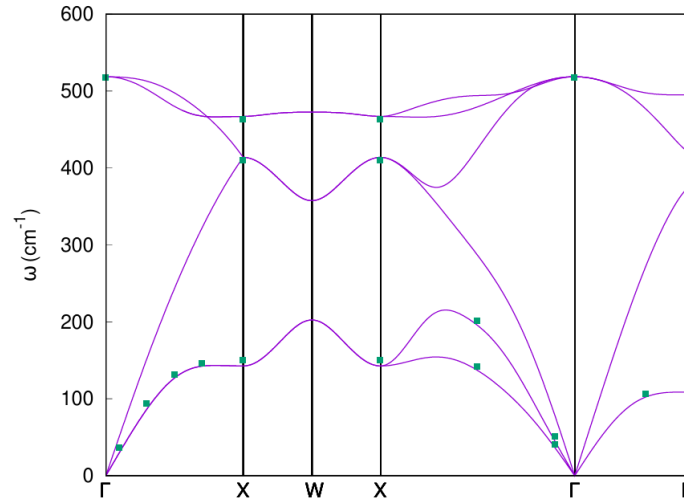


Figure 7. Phonon Dispersion Curve for Si along the Γ-X-W-X-L Path

### 8. Phonon Density of States Calculation and Plotting for Si

The phonon density of states (DOS) for Si was calculated using Quantum ESPRESSO, providing insights into the distribution of vibrational modes across different frequencies. This calculation complements the phonon dispersion analysis by quantifying the number of phonon states at each frequency, which is essential for understanding Si's thermal and vibrational properties. The calculation was performed on a uniform grid of q-points to capture the phonon behavior throughout the Brillouin zone, leading to an accurate DOS representation.

The resulting plot, shown in Figure 8, reveals distinct peaks in the phonon density of states. These peaks correspond to the collective vibrational modes in Si's crystal structure. The first peak, observed around **100 cm$^{-1}$**, represents the acoustic modes, which are dominant at low frequencies due to the lattice's response to long-wavelength vibrations. At higher frequencies, optical modes are evident, with a significant peak around **500 cm$^{-1}$**, indicating the high-frequency vibrational modes associated with Si's covalent bonding structure.

The sharpness of the peaks reflects the well-defined phonon modes in Si's diamond cubic structure. The separation between acoustic and optical modes aligns with theoretical expectations for non-polar, covalently bonded materials, where the optical modes occur at distinctly higher frequencies due to strong intramolecular forces. The prominent optical peak around **500 cm$^{-1}$** corresponds closely with the optical phonon frequencies observed in the dispersion calculation, affirming the accuracy of the computational setup.

Overall, the phonon DOS calculation provides a comprehensive view of Si's vibrational spectrum, showcasing both low-energy acoustic modes and high-energy optical modes. This data is essential for predicting material properties like heat capacity and thermal conductivity, as these are directly influenced

by the phonon DOS. The alignment of these results with known properties of Si underscores the effectiveness of Quantum ESPRESSO in accurately modeling phonon behavior in semiconductor materials.
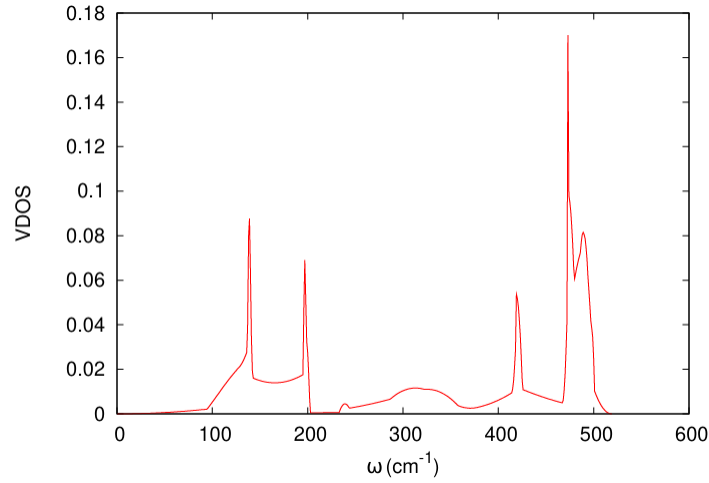


Figure 8. Phonon Density of States for Si

## Conclusions

This report presented a comprehensive phonon analysis of Si and AlAs using DFPT in Quantum ESPRESSO. For Si, calculations included total energy, Gamma point phonon frequencies, phonon dispersion along high-symmetry paths, and phonon density of states, providing detailed insights into both acoustic and optical phonon behaviors. AlAs's analysis focused on the total energy, Gamma point phonon frequencies with acoustic sum rule application, and LO-TO splitting, highlighting the polar nature of its ionic bonds. The results closely aligned with theoretical and experimental expectations, validating the computational setup and methodology. This study demonstrates the effectiveness of Quantum ESPRESSO in accurately modeling phonon properties in semiconductors and polar materials, offering valuable insights into their vibrational properties relevant to thermal and electronic applications.

## Acknowledgments

## References

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