Phonons and Lattice Dynamics

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Outline

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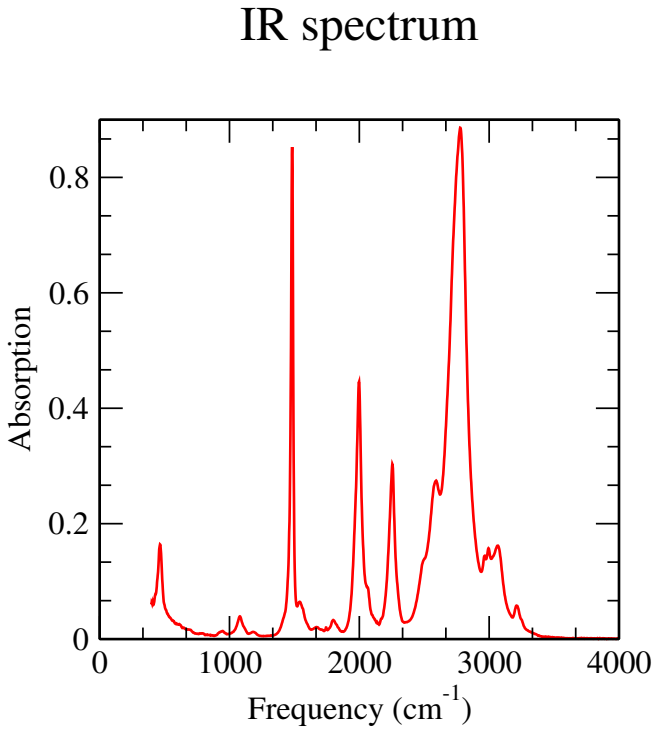
Motivation

Spectroscopy

- Experiments measure response of a system to a perturbation
  - Probes dynamic properties of crystal
  - Not ground state directly!
- Spectroscopic techniques provide incomplete information
  - IR and Raman have inactive modes
  - Hard to distinguish fundamental and overtones processes in spectra
  - Little information on which atoms involved means that mode assignment is difficult
- Would like a predictive technique that does not rely on intuition to calculate vibrational responses within a crystal.



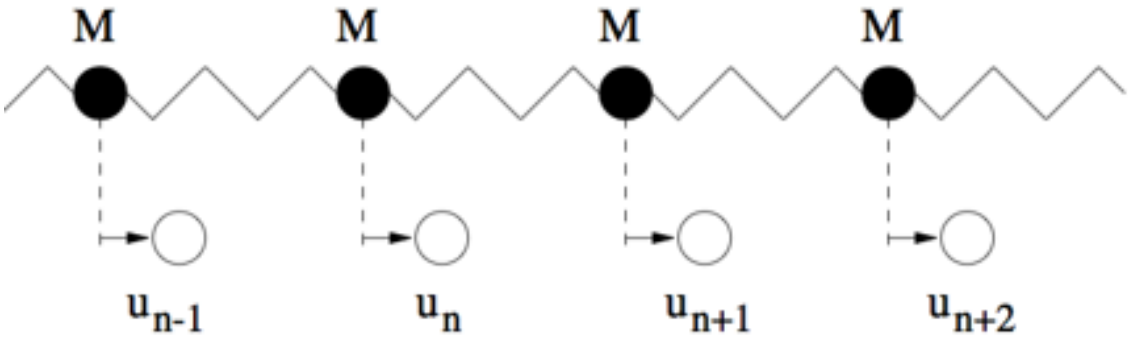
Why *ab initio*?

- *ab initio* methods give us a highly transferable, parameter-free probe of the experimental results.
  - Calculate vibrational properties on the same theoretical basis as electronic properties.
  - Can probe whether a structure is stable wrt perturbations
  - Can compute zero point energy and phonon entropy contributions to free energy.
  - Predict Raman and IR peaks
  - Captures the effects of electron-phonon interactions

Lattice Dynamics of Crystals

1d Chain of Atoms – I

Start with infinite 1d chain of atoms connected by springs (force constant K)



Equilibrium separation is a. u_n is the displacement of an atom from equilibrium position.
Assuming only nearest neighbours interact, the force between neighbors i and $i+1$ is

$$F_{n,n+1} = -K(u_{n+1} - u_n)$$

1d Chain of Atoms – II

The total force on an atom i is the sum of both nearest neighbours which pull in opposite directions

$$F_n = F_{n,n+1} - F_{n-1,n} = -K(u_{n+1} - u_n) + K(u_n - u_{n-1}) = K(2u_n - u_{n+1} - u_{n-1})$$

We use Newton's second law, $F = ma$ so,

$$M\frac{d^2u_n}{dt^2} = K(2u_n - u_{n+1} - u_{n-1})$$

A known solution of this differential equation is a travelling wave

$$u_{n,q}(t) = \widetilde{u}_{n,q}e^{i(qx-\omega_q t)}$$

where $q = \frac{2\pi}{\lambda}$ is a wavenumber and ω_q is an angular frequency. $\widetilde{u}_{n,q}$ is a vector representing the motion of atom n.

1d Chain of Atoms – III

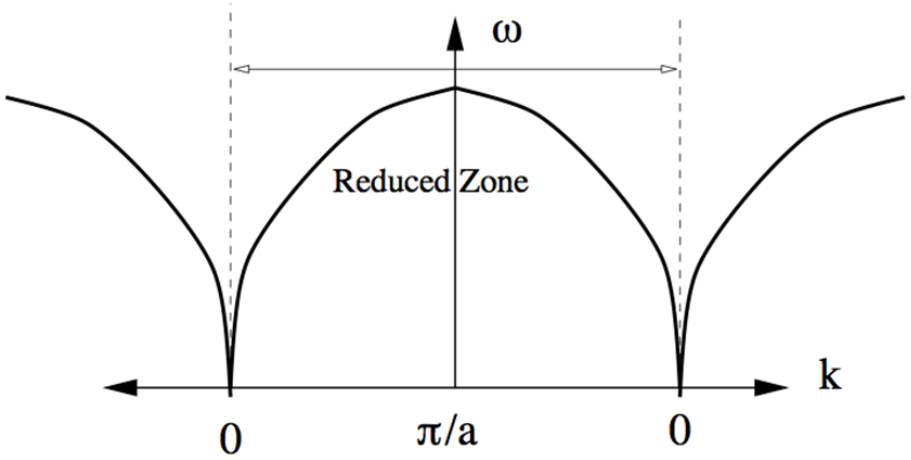
Substituting this into the differential equation gives us

$$M\omega_q^2 = 2K\,[1 + cos(qa)]$$

This leads to the dispersion relation:

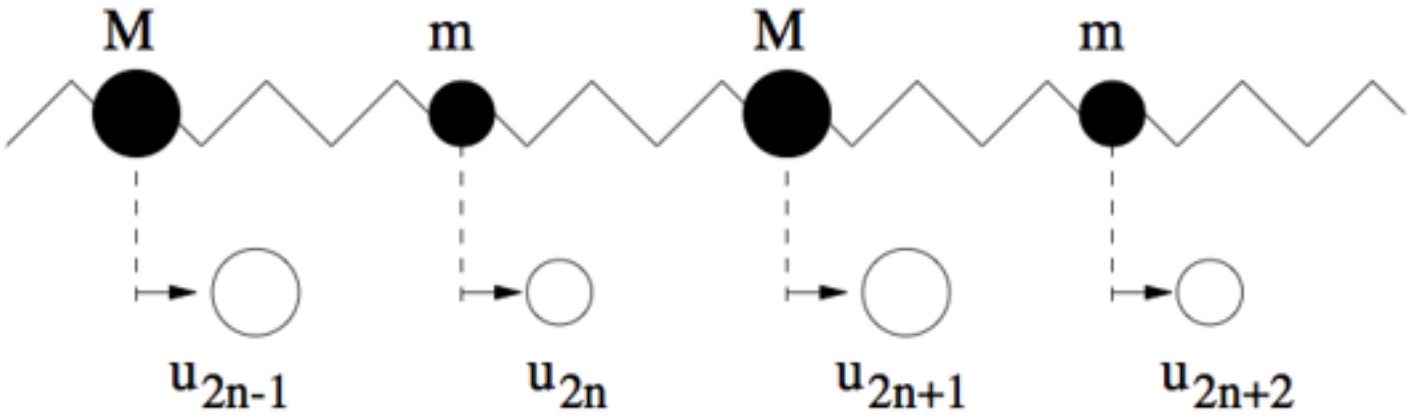
$$\omega_q = \sqrt{\frac{4K}{M}}\,|sin(qa/2)|$$

Single solution or *branch* for each value of q.



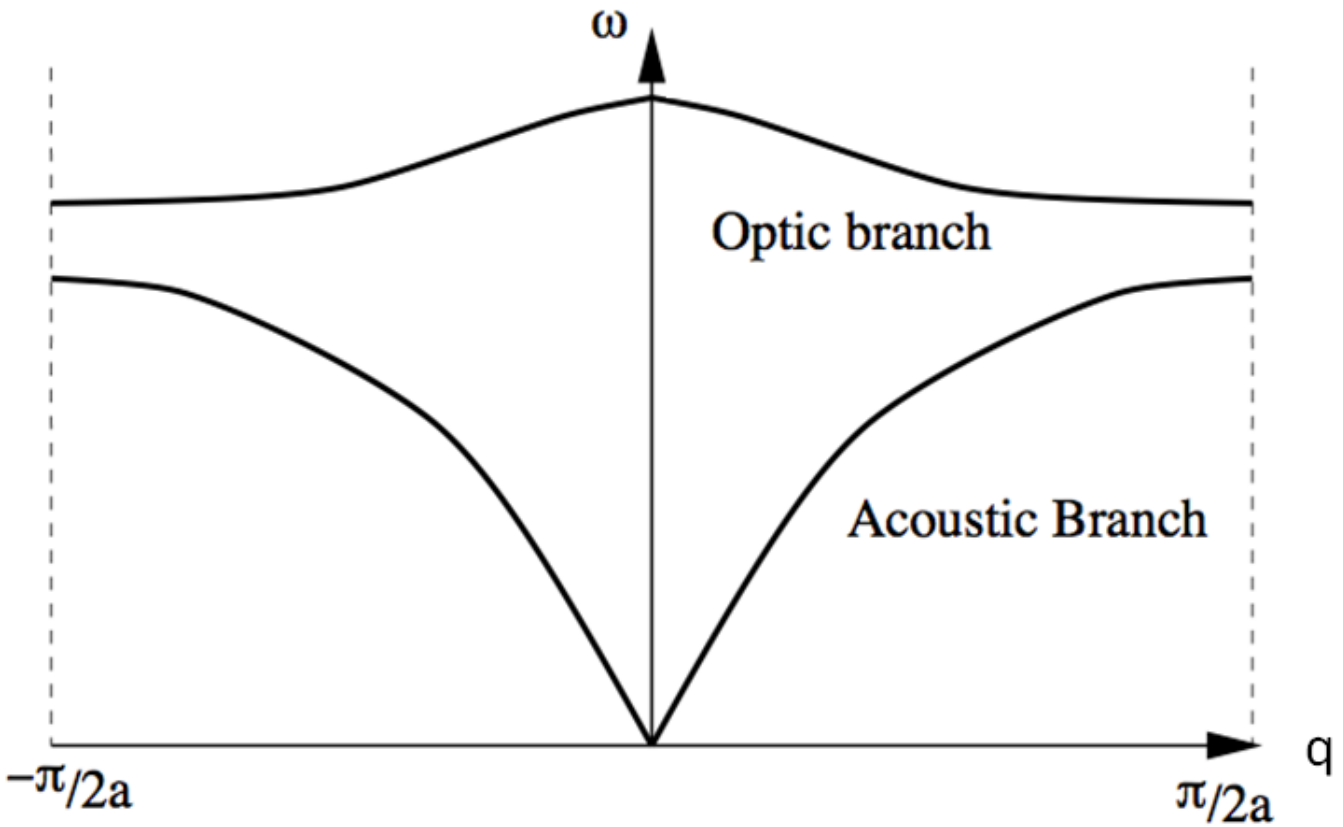
Diatomic Crystal – Optic modes I

If instead, we attempt to determine the modes for a crystal with two different masses of atoms:



We find that there are now multiple values for ω that will satisfy the differential equation for each q

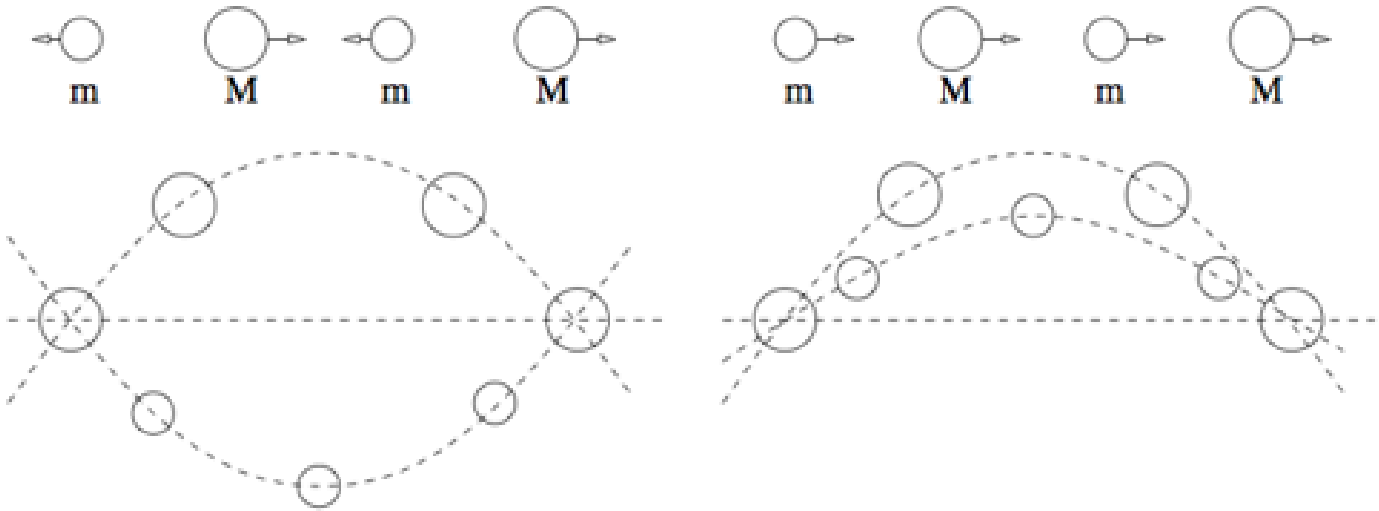
Diatomic Crystal – Optic modes II



More than one atom per unit cell gives rise to *optic modes* with different characteristic dispersion.

Diatomic Crystal – Optic modes III

Reminder from earlier: $\widetilde{u}_{n,q}$ is a vector representing the motion of atom n.
If we examine these for both modes at the $\Gamma = (0, 0, 0)$ point, we see

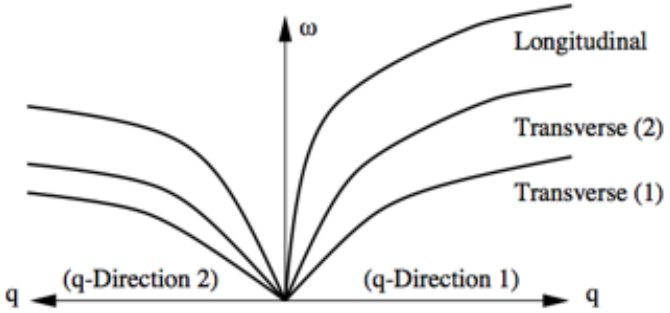


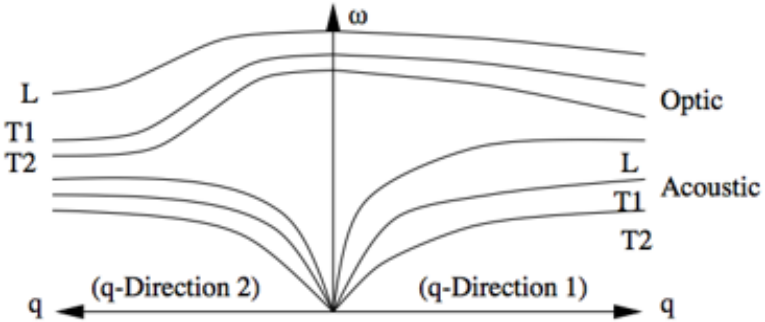
Accoustic Modes Atoms move in-phase (same direction at the same time)

Optical Modes Atoms move anti-phase

Characterization of Vibrations in 3D Crystals

- Vibrational modes in solids take form of *waves* with wavevector-dependent frequencies (just like electronic energy levels).
- $\omega(\boldsymbol{q})$ relations known as *dispersion curves*
- N atoms in prim. cell $\Rightarrow$ $3N$ *branches*.
- 3 *acoustic* branches corresponding to sound propagation as $\boldsymbol{q} \to 0$ and $3N - 3$ *optic* branches.





Setting up the 3d problem

- Firstly, we will fill space with periodically repeating unit cells in 3 dimensions
- Take one as an (arbitrary) origin
- Label the rest with respect to this
- Label the unit cells

$$a = (a_1, a_2, a_3)$$

where a_1, a_2 and a_3 are integers

Coordinate axes

- The shape of each unit cell is defined by 3 linearly independent vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$
- The origin of the a^{th} unit cell can be defined as

$$\mathbf{r}_a = a_1\mathbf{a}_1 + a_2\mathbf{a}_2 + a_3\mathbf{a}_3$$

  relative to the origin a=(0,0,0)
- This co-ordinate system gives us the origin of any of the periodically repeating unit cells throughout space

Placement of Atoms

- Within each unit cell we will place n atoms
- We will label these atoms $\kappa = 1, 2, \ldots, n$
- Relative to the origin of a given unit cell (position $\mathbf{r}_l$) the atoms will be placed at positions $\mathbf{r}_\kappa$
- So that each atom will have position

$$\mathbf{r}_{\kappa,a} = \mathbf{r}_a + \mathbf{r}_\kappa$$

relative to our “origin” of the unit cells

Atomic Motion

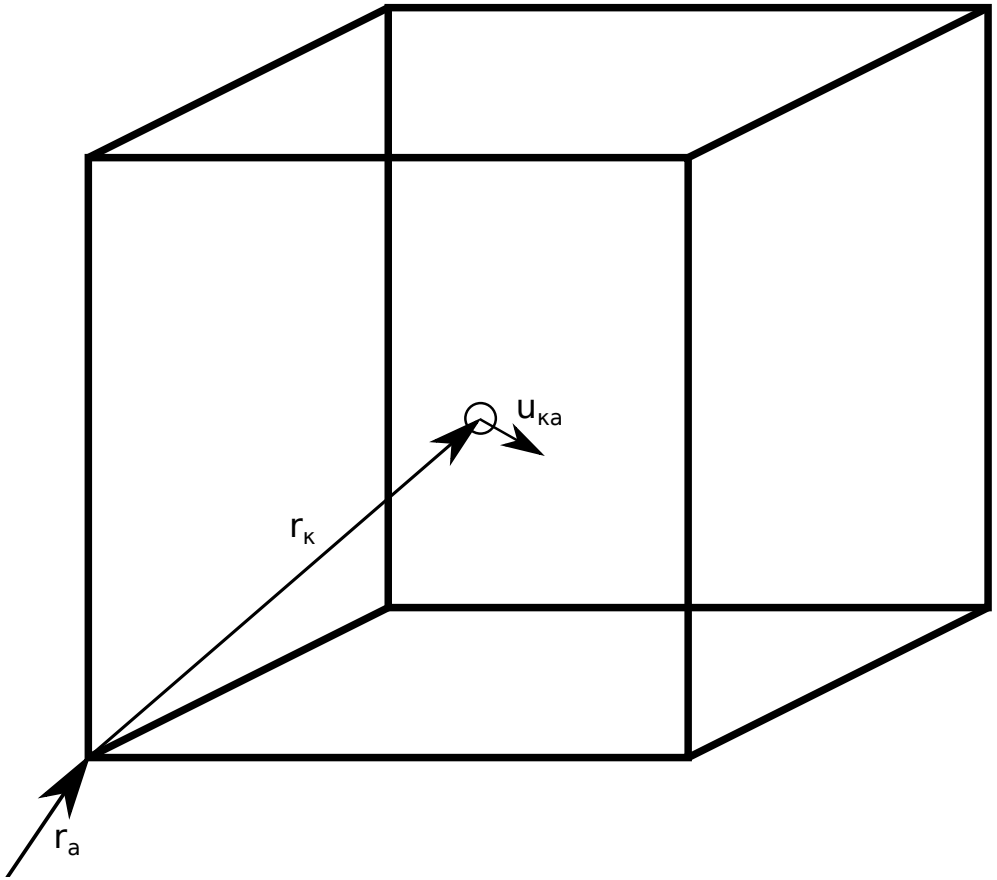
- Now we've defined the equilibrium positions of the atoms, we need to move them to describe thermal motion
- The atoms move an amount

$$\mathbf{u}_{\kappa,a} = (u_{x,\kappa,a}, u_{y,\kappa,a}, u_{z,\kappa,a})$$

  from their equilibrium position $\mathbf{r}_{a,\kappa}$
- The actual position of atom (a, κ) under thermal motion is then

$$R_{\kappa,a} = \mathbf{r}_{\kappa,a} + \mathbf{u}_{\kappa,a}$$

Diagram of coordinate system



Formal Theory of Lattice Dynamics

- Based on expansion of total energy about structural equilibrium co-ordinates

$$E = E_0 + \frac{\partial E}{\partial u}.u + \frac{1}{2!}\frac{\partial^2 E}{\partial u^2}.u^2 + \frac{1}{3!}\frac{\partial^3 E}{\partial u^3}u^3 + ...$$

- At equilibrium the forces $F_{\alpha,\kappa} = -\frac{\partial E}{\partial u}$ are all zero so 1^{st} term vanishes.

$$E = E_0 + \frac{1}{2}\sum \boldsymbol{u}_{\alpha,\kappa,a}.\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}.\boldsymbol{u}_{\kappa',\alpha',a} + ...$$

  where $\boldsymbol{u}_{\alpha,\kappa,a}$ is the displacement of atom κ in unit cell a in Cartesian direction α.

- In the *Harmonic Approximation* the 3^{rd} and higher order terms are assumed to be negligible

- $\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a)$ is the matrix of *force constants*

$$\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a) = \frac{\partial^2 E}{\partial \boldsymbol{u}_{\alpha,\kappa}\partial \boldsymbol{u}_{\kappa',\alpha'}}$$

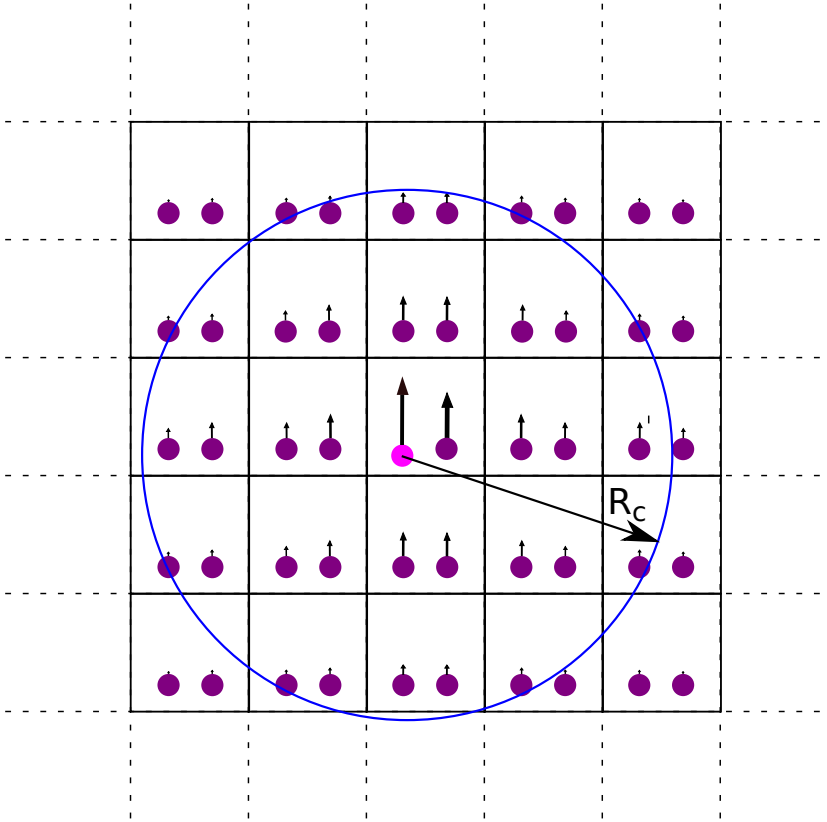
The Force Constant Matrix (FCM)

This matrix represents all the effective 3d spring constants between atoms

$$\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a) = \frac{\partial^2 E}{\partial \boldsymbol{u}_{\alpha,\kappa} \partial \boldsymbol{u}_{\kappa',\alpha'}}$$

$$= -\frac{\partial F_{\boldsymbol{u}_{\alpha,\kappa,a}}}{\partial \boldsymbol{u}_{\kappa',\alpha',a}}$$

Alternative view is change on force on atoms due to displacing an atom



The Dynamical Matrix (DM)

Solution in 1d can be reused with a few modifications for 3d:

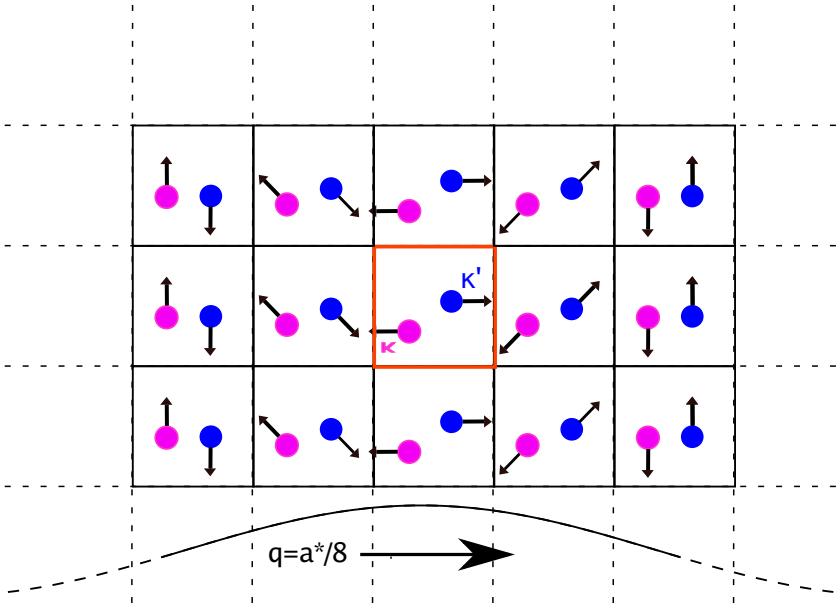
$$\boldsymbol{u}_{\alpha,\kappa} = \varepsilon_{m\alpha,\kappa\boldsymbol{q}} e^{i\boldsymbol{q}.\boldsymbol{R}_{\alpha,\kappa} - \omega t}$$

Taking the derivative of the total energy equation to get the force, F and substituting this trial solution, we have

$$D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q})\varepsilon_{m\alpha,\kappa\boldsymbol{q}} = \omega^2_{m,\boldsymbol{q}}\varepsilon_{m\alpha,\kappa\boldsymbol{q}}$$

where

$$D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q}) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} C^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q}) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_a \Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a) e^{-i\boldsymbol{q}.\boldsymbol{R}_a}$$



- The **dynamical matrix** $D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q})$ is the Fourier transform of the force constant matrix.
- The solutions of the eigenvalue equation correspond to vibrational **modes**
- Mode frequency is square root of corresponding eigenvalue $\omega_{m,\boldsymbol{q}}$.

Formal Theory of Lattice Dynamics II

- The dynamical matrix is a $3N \times 3N$ matrix at each wavevector $\boldsymbol{q}$.
- $D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q})$ is a hermitian matrix $\Rightarrow$ eigenvalues $\omega^2_{m,\boldsymbol{q}}$ are real.
- $3N$ eigenvalues $\Rightarrow$ modes at each $\boldsymbol{q}$ leading to $3N$ branches in dispersion curve.
- The mode eigenvector $\varepsilon_{m\alpha,\kappa}$ gives the atomic displacements, and its symmetry can be characterised by group theory.
- Given a force constant matrix $\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a)$ we have a procedure for obtaining mode frequencies and eigenvectors over entire BZ.

Ab initio Lattice Dynamics

The Finite-Displacement method

The **finite displacement** method:

- Displace ion κ' in direction α' by small distance $\pm u$.
- Use single point energy calculations and evaluate *forces* on *every* ion in system $F^{+}_{\kappa,\alpha}$ and $F^{+}_{\kappa,\alpha}$ for +ve and -ve displacements.
- Compute numerical derivative using central-difference formula

$$\frac{dF_{\kappa,\alpha}}{du} \approx \frac{F^{+}_{\kappa,\alpha} - F^{-}_{\kappa,\alpha}}{2u} = \frac{d^2E}{du_{\kappa,\alpha}du_{\kappa',\alpha'}}$$

- Have calculated entire *row* k', α' of $D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q} = 0)$
- Only need $6N_{\text{at}}$ SPE calculations to compute entire dynamical matrix.
- This is a *general* method, applicable to any system.
- Can take advantage of space-group symmetry to avoid computing symmetry-equivalent perturbations.
- Works only at $\boldsymbol{q} = 0$.

Non-diagonal supercell method

- New method by J. Lloyd-Williams and B. Monserrat, Phys Rev B, 92, 184301 (2015).
- Extension of finite displacement method
- Old "Direct" Supercell method calculates the FCM for each atom
  - Construct supercell big enough that we can ignore periodicity
  - Supercell needs to be big enough that interactions fall to zero
  - Often requires very large calculations with lots of atoms
- Non-diagonal supercell method takes advantage of periodicity of system
  - Calculates response at $\mathbf{q}$ by constructing a minimal supercell.
  - Supercells are much smaller than those in the supercell method.
  - Very efficient and can calculate DM on arbitrary grid.

Second derivatives in QM

Goal is to calculate the *2nd derivatives* of energy to construct FCM or $D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q})$.

- Energy $E = \langle\Psi|\,\hat{H}\,|\Psi\rangle$ with $\hat{H} = -\frac{1}{2}\nabla^2 + V_{\text{SCF}}$
- Forces (first derivative) can be shown to be

$$F = -\frac{dE}{d\lambda} = -\langle\psi|\,\frac{dV}{d\lambda}\,|\psi\rangle$$

- Force constants are the *second* derivatives of energy

$$k = \frac{d^2E}{d\lambda^2} = -\frac{dF}{d\lambda} = \left\langle \frac{d\Psi}{d\lambda}\middle|\,\frac{dV}{d\lambda}\,|\Psi\rangle + \langle\Psi|\,\frac{dV}{d\lambda}\middle|\frac{d\Psi}{d\lambda}\right\rangle - \langle\Psi|\,\frac{d^2V}{d\lambda^2}\,|\Psi\rangle$$

- None of the above terms vanishes.
- Need **linear response** of wavefunctions *wrt* perturbation (ie $\left\langle \frac{d\Psi}{d\lambda}\right|$).
- In general n^{th} derivatives of wavefunctions needed to compute $2n+1^{th}$ derivatives of energy. This result is the "$2n+1$ *theorem*".

Density-Functional Perturbation Theory

- In DFPT need *first-order* KS orbitals $\phi^{(1)}$, the *linear response* to λ.
- λ may be a displacement of atoms with wavevector $\boldsymbol{q}$ (or an electric field E.)
- If $\boldsymbol{q}$ incommensurate $\phi^{(1)}$ have Bloch-like wavefunction: $\phi^{(1)}_{\boldsymbol{k},\boldsymbol{q}}(\boldsymbol{r}) = e^{-i(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{r}} u^{(1)}(\boldsymbol{r})$ where $u^{(1)}(\boldsymbol{r})$ has periodicity of unit cell.
- First-order density $n^{(1)}(\boldsymbol{r})$ and potential $v^{(1)}$ have similar Bloch representation.
- First-order response orbitals are solutions of **Sternheimer equation**

$$\left(H^{(0)} - \epsilon_m^{(0)}\right) \left|\phi_m^{(1)}\right\rangle = -v^{(1)} \left|\phi_m^{(0)}\right\rangle$$

- First-order potential $v^{(1)}$ includes response terms of Hartree and XC potentials and therefore depends on first-order *density* $n^{(1)}(\boldsymbol{r})$ which depends on $\phi^{(1)}$.
- Finding $\phi^{(1)}$ is therefore a *self-consistent* problem just like solving the Kohn-Sham equations for the ground state.

Variational and Green function approaches

- Two major approaches to finding $\phi^{(1)}$ are suited to plane-wave basis sets:

  Variational DFPT (X. Gonze (1997) PRB **55** 10377-10354).
  Conjugate-gradient minimization of variational 2$^{\text{nd}}$-order energy expression subject orthogonality constraint $\left\langle \phi_n^{(1)} | \phi_m^{(0)} \right\rangle = 0$

  Green function (S. Baroni *et al* (2001), Rev. Mod. Phys **73**, 515-561).
  Solve Sternheimer equation in self-consistent loop with 1$^{\text{st}}$-order density mixing.

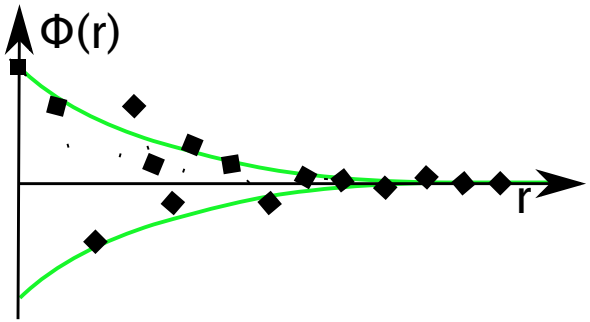
  CASTEP implements both DFPT methods (`phonon_dfpt_method`).

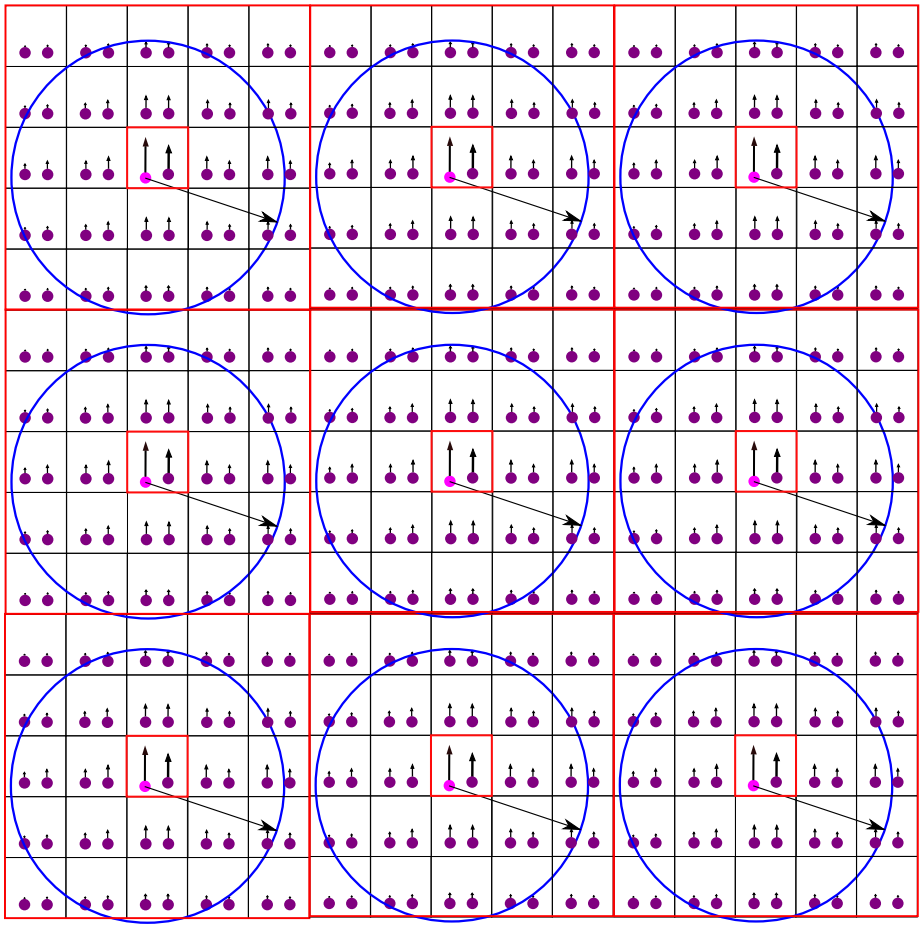
  Variational DFPT implemented for insulators only, Green function/DM for both insulators and metals.

- DFPT has huge advantage - can calculate response to *incommensurate* ***q*** from a calculation on primitive cell.
- Disadvantages of DFPT:
  - Needs derivatives for the XC functional – only works for some functionals (LDA, PBE, etc)
  - Not implemented for ultrasoft pseudopotentials – have to use NCP

Fourier Interpolation of dynamical Matrices

- FCM decays quickly
- Approximate by reverse Fourier transform of DM
- Use forward transform to get DM at arbitrary **q**
- Handle Coulomb analytically





Acoustic Sum Rule

- At the Γ point, the 3 lowest energy modes should be exactly zero
  - This corresponds to the 3 translational symmetries in a periodic crystal
  - Atomic motion becomes more and more like a rigid shift as $\boldsymbol{q} \rightarrow 0$
- Insufficient convergence may lead to this not being true
  - Numerical noise can affect this
  - Insufficient sampling in real or reciprocal space
- We can "fix" solution to enforce this sum rule

  REALSPACE Correct the FCM in real space.

  RECIPROCAL Correct the DM at $\boldsymbol{q} = 0$ and then apply this correction to all DMs.
- Select method by `phonon_sum_rule_method`

Break

Lattice Dynamics in CASTEP

Methods in CASTEP

CASTEP can perform *ab initio* lattice dynamics using

- Primitive cell finite-displacement at $\boldsymbol{q} = 0$
- Supercell finite-displacement for any $\boldsymbol{q}$
- DFPT at arbitrary $\boldsymbol{q}$.
- DFPT on MP grid of $\boldsymbol{q}$ with Fourier interpolation to arbitrary fine set of $\boldsymbol{q}$.
- Finite displacements using non-diagonal supercells with Fourier interpolation.

Full use is made of space-group symmetry to only compute only

- symmetry-independent elements of $D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q})$
- $\boldsymbol{q}$-points in the irreducible Brillouin-Zone for interpolation
- electronic k-points adapted to symmetry of perturbation.

k-points and **q**-points

For phonons we have two sets of points in the Brillouin zone which are both defined in the *.cell* file

k-points These are the points where we solve the Kohn-Sham equations to obtain wavefunctions and total energies. These are specified by:
kpoint_<tag>
spectral_kpoint_<tag>
supercell_kpoint_<tag>

q-points These are the points that we calculate the phonons modes on. They are specified by:
phonon_kpoint_<tag> phonon_fine_kpoint_<tag>

where <tag> is one of

mp_grid A Monkhurst-Pack grid specification (n_x, n_y, n_z)

mp_offset An offset to apply to the above grid

list A list of points to sample

spacing Use a grid with at most this spacing

path Generate a path between this list of points

A CASTEP calculation I - simple DFPT

Lattice dynamics assumes atoms at mechanical equilibrium.
Golden rule: *The first step of a lattice dynamics calculation is a high-precision geometry optimisation*

- Parameter `task = phonon` selects lattice dynamics calculation.
- Iterative solver tolerance is `phonon_energy_tol`. Value of 10^{-5} eV/Ang**2 usually sufficient. Sometimes need to increase `phonon_max_cycles`
- Need very accurate *ground-state* as prerequisite for DFPT calculation `elec_energy_tol` needs to be roughly *square* of `phonon_energy_tol`
- $D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q})$ calculated at $\boldsymbol{q}$-points specified in *cell* file by `phonon_kpoint_<tag>`

Example Phonon Output – Si2


```
================================================================================
+                           Vibrational Frequencies                            +
+                           -----------------------                            +
+                                                                              +
+ Performing frequency calculation at   3 wavevectors (q-pts)                  +
+ ========================================================================== +
+                                                                              +
+ -------------------------------------------------------------------------- +
+  q-pt=    1 (  0.000000  0.000000  0.000000)     0.1250000000               +
+ -------------------------------------------------------------------------- +
+  Acoustic sum rule correction <  11.519522 cm-1 applied                      +
+     N      Frequency irrep.    ir intensity active            raman active +
+                (cm-1)          ((D/A)**2/amu)                                +
+                                                                              +
+     1      -0.026685   a           0.0000000  N                      N      +
+     2      -0.026685   a           0.0000000  N                      N      +
+     3      -0.026685   a           0.0000000  N                      N      +
+     4     514.731729   b           0.0000000  N                      Y      +
+     5     514.731729   b           0.0000000  N                      Y      +
+     6     514.731729   b           0.0000000  N                      Y      +
+ ..........................................................................   +
+        Character table from group theory analysis of eigenvectors           +
+                           Point Group =  32, Oh                              +
+ ..........................................................................   +
+  Rep   Mul |    E   4   2  2'   3   I  -4 m_h m_v  -3                       +
+            | ---------------------------------------                         +
+ a T1u    1 |    3   1  -1  -1   0  -3  -1   1   1   0                       +
+ b T2g    1 |    3  -1  -1   1   0   3  -1  -1   1   0                       +
+ -------------------------------------------------------------------------- +
```

CASTEP phonon calculations II - Fourier Interpolation

- Specify grid of $\boldsymbol{q}$-points using `phonon_kpoint_mp_grid` $p\ q\ r$.
- To select interpolation `phonon_fine_method = interpolate`
- **Golden rule of interpolation:** Always include the Γ point (0,0,0) in the interpolation grid. For even p, q, r use *shifted* grid `phonon_fine_kpoint_mp_offset` $\frac{1}{2p}\ \frac{1}{2q}\ \frac{1}{2r}$ to shift one point to Γ
- $D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q})$ interpolated to $\boldsymbol{q}$-points specified in *cell* file by `phonon_fine_kpoint_<tag>`
- Can calculate fine dispersion plot and DOS on a grid rapidly from one DFPT calculation.
  - Real-space force-constant matrix is stored in `.check` file.
  - All `fine_kpoint` parameters can be changed on a continuation run.
  - Interpolation is very fast.

CASTEP phonon calculations III - Non-diagonal Supercell

- To select set both `phonon_method = finite_displacement` and `phonon_fine_method = interpolation`
- Specify grid of $\boldsymbol{q}$-points using `phonon_kpoint_mp_grid` $p\ q\ r$ - as for DFPT. CASTEP will automatically determine supercells to use - no need to explicitly set supercell in `.cell` file.
- K-points for supercell set using spacing or grid keywords `supercell_kpoint_mp_spacing`
- CASTEP automatically chooses a series of non-diagonal (skew) supercells and performs FD phonons and computes $D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q})$ on grid of $\boldsymbol{q}$-points specified in *cell* file by one of same `phonon_kpoint` keywords.
- From there calculation proceeds exactly as for supercell or DFPT interpolation.

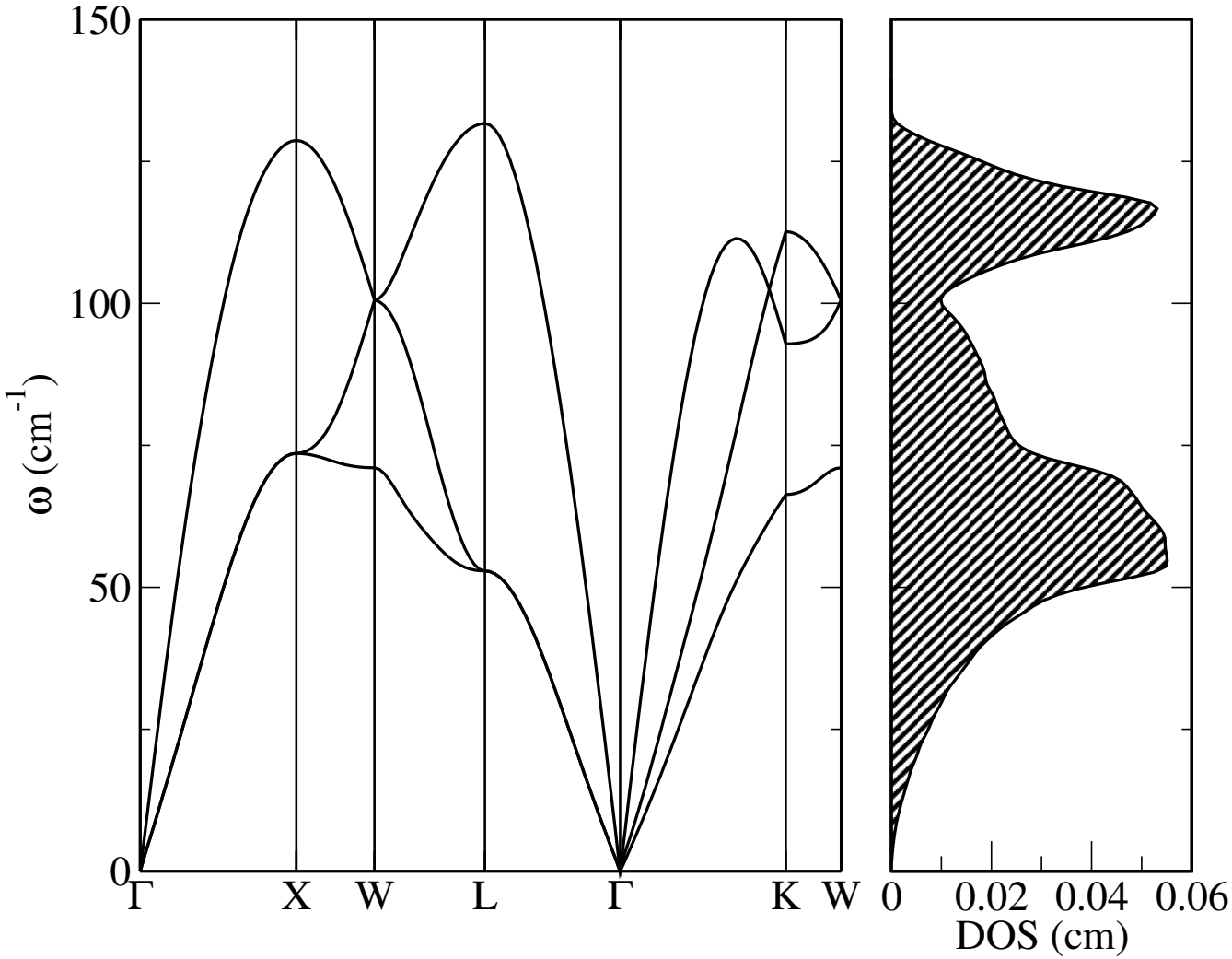
Running a phonon calculation

- Phonon calculations can be lengthy. CASTEP saves partial calculation periodically in `.check` file:

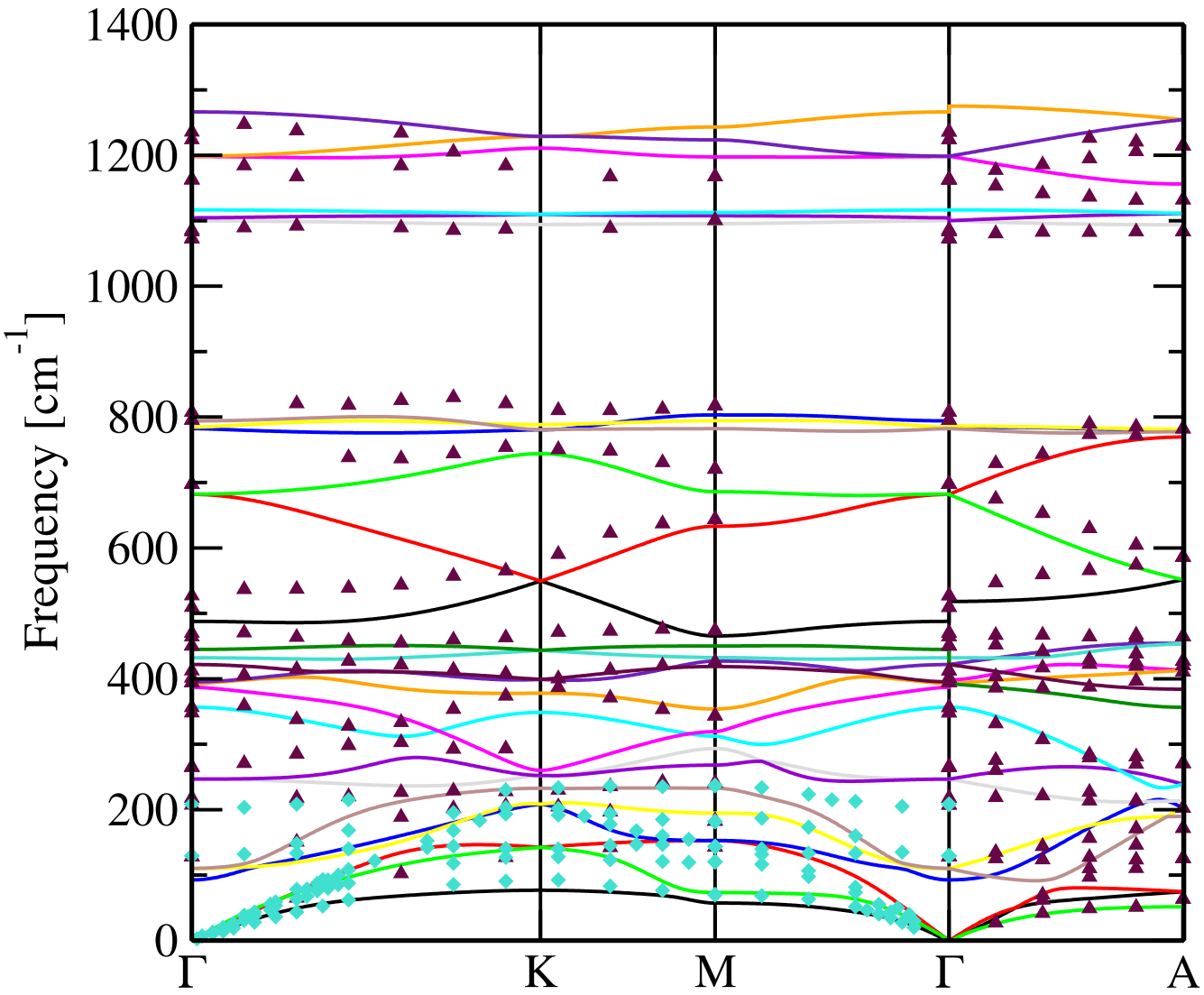
  `num_backup_iter` n – Backup every n **q**-vectors
  `backup_interval` t – Backup every t seconds
- Phonon calculations have high inherent parallelism. Because perturbation breaks symmetry relatively large electronic **k**-point sets are used.
- Number of **k**-points varies depending on symmetry of perturbation.
- Try to choose number of processors to make best use of k-point parallelism. If N_k not known in advance choose N_P to have as many different prime factors as possible - **not** just 2!

Phonon Examples

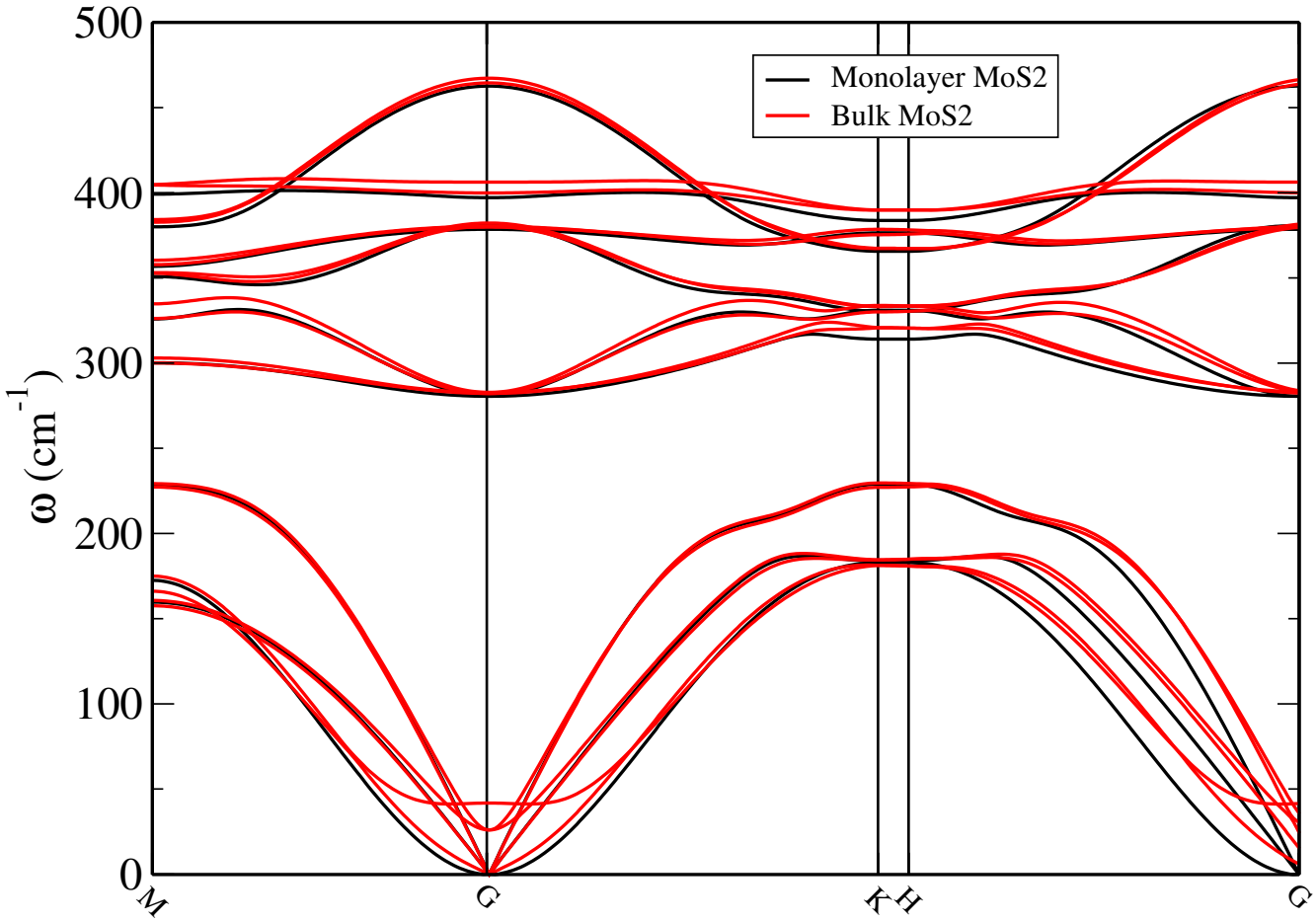
DFPT with interpolation for Au



α-quartz



MoS2 – Bulk vs monolayer



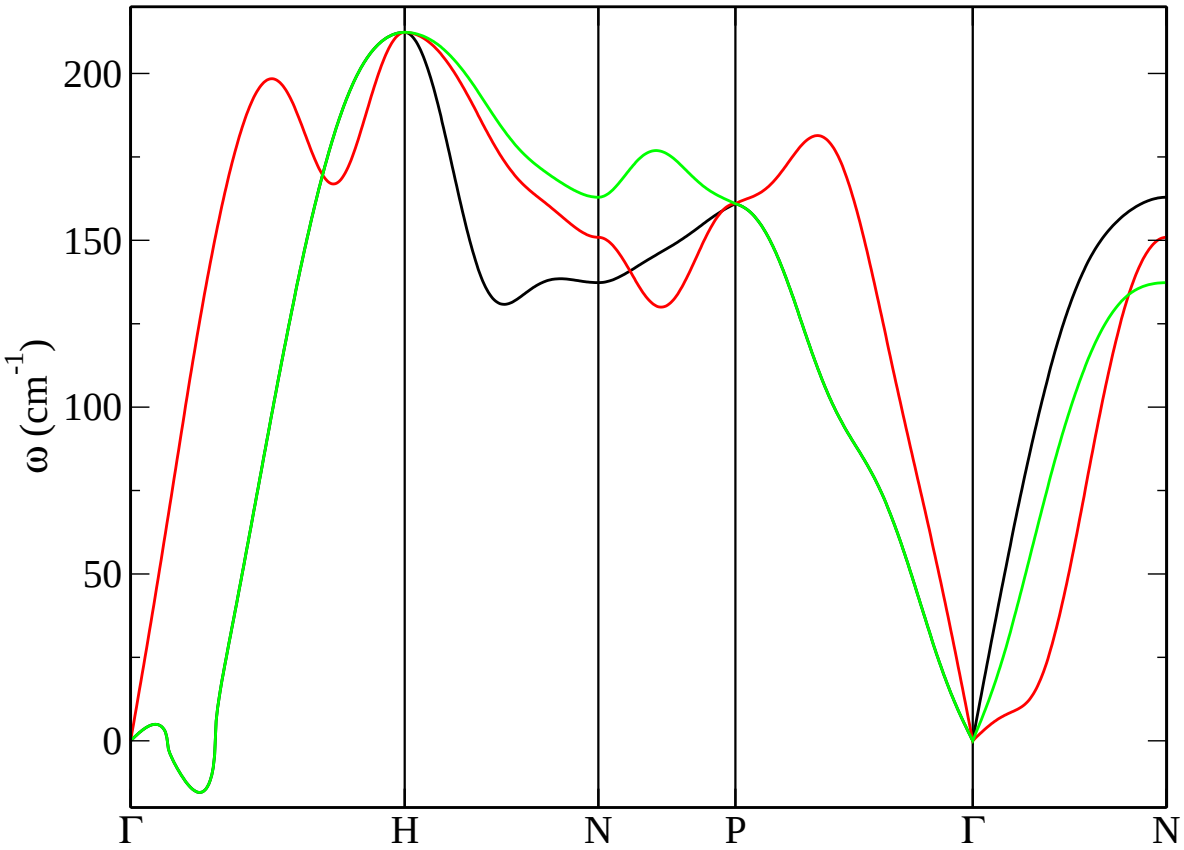
Convergence issues for lattice dynamics

ab initio lattice dynamics calculations are very sensitive to convergence issues. A good calculation must be well converged as a function of

1. plane-wave cutoff
2. electronic kpoint sampling of the Brillouin-Zone (for crystals) (under-convergence gives poor acoustic mode dispersion as $\boldsymbol{q} \rightarrow 0$
3. geometry. Co-ordinates must be well converged with forces close to zero (otherwise calculation will return *imaginary* frequencies.)
4. For DFPT calculations need high degree of SCF convergence of ground-state wavefunctions.
5. supercell size for “molecule in box” calculation and slab thickness for surface/s lab calculation.
6. Fine FFT grid for finite-displacement calculations.

- Accuracy of 25-50 cm^{-1} usually achieved or bettered with DFT.
- need GGA functional *e.g.* PBE, PW91 for hydrogenous and H-bonded systems.
- When comparing with experiment remember that disagreement may be due to *anharmonicity*.

Nb – Imaginary Phonon Modes/Negative Frequencies



Quantities from Phonons

Thermodynamics

- Given the phonon frequencies, the phonon density of states, $g(\omega)$ can be obtained
- This is straightforward: just count the number of frequencies in the range w to $\omega + d\omega$
- This histogram is the phonon density of states
- Finite temperature information is obtained by manipulating $g(\omega)$

Thermal Energy

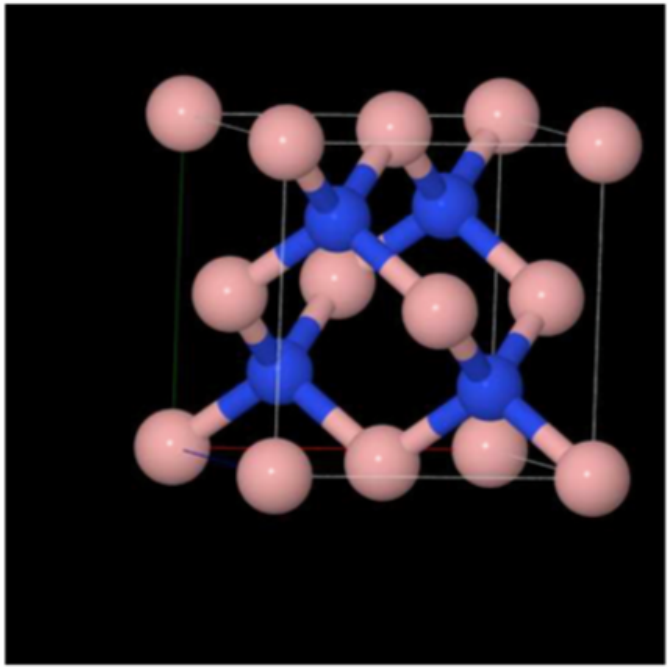
- The total thermal energy due to atomic motion is given by

$$E_{vib}(T) = E + k_B T \sum_q \log \left[2 \sinh \left(\frac{\hbar \omega(q)}{2 k_B T} \right) \right]$$

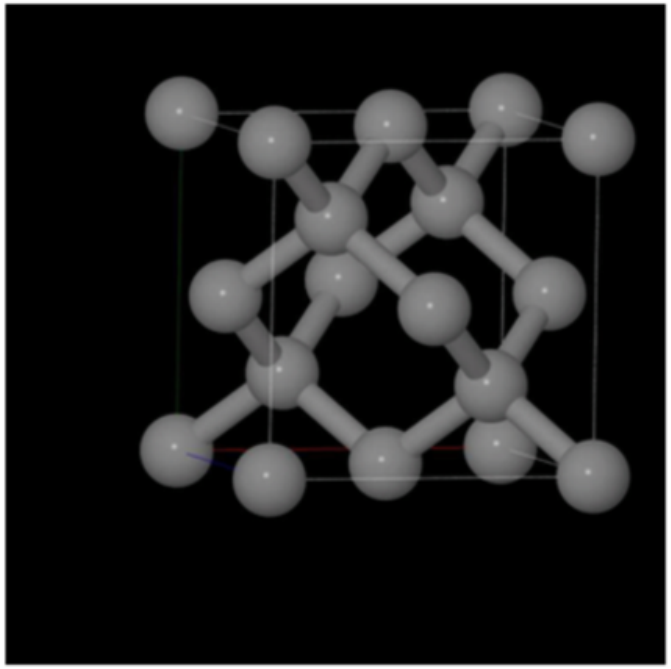
- Many thermodynamic properties can be calculated from this such as entropy, specific heat, etc. which you are free to investigate on your own

LO/TO Splitting

Two similar structures



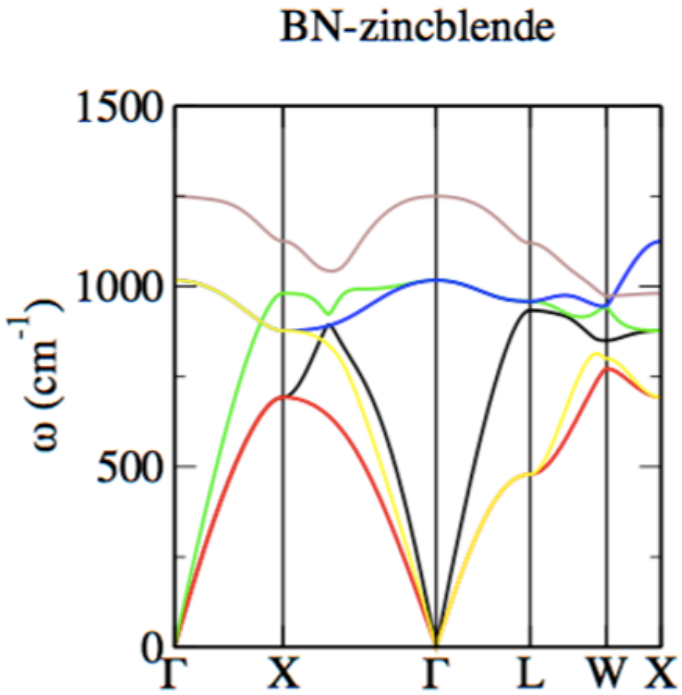
Zincblende BN

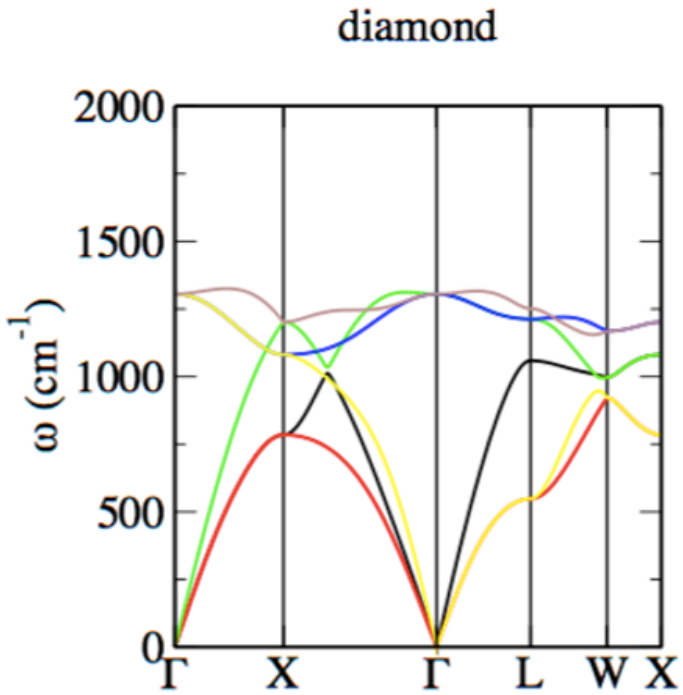


Diamond

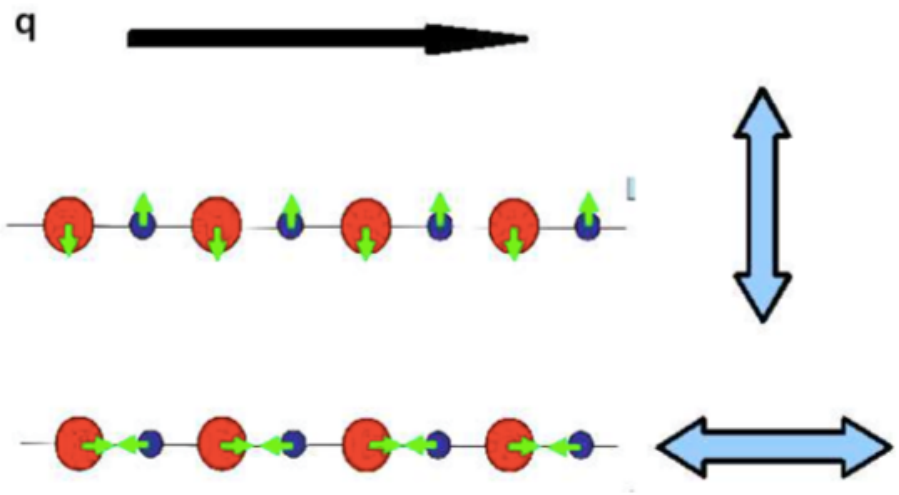
BN and Diamond

Note degeneracies of optical modes at Γ?





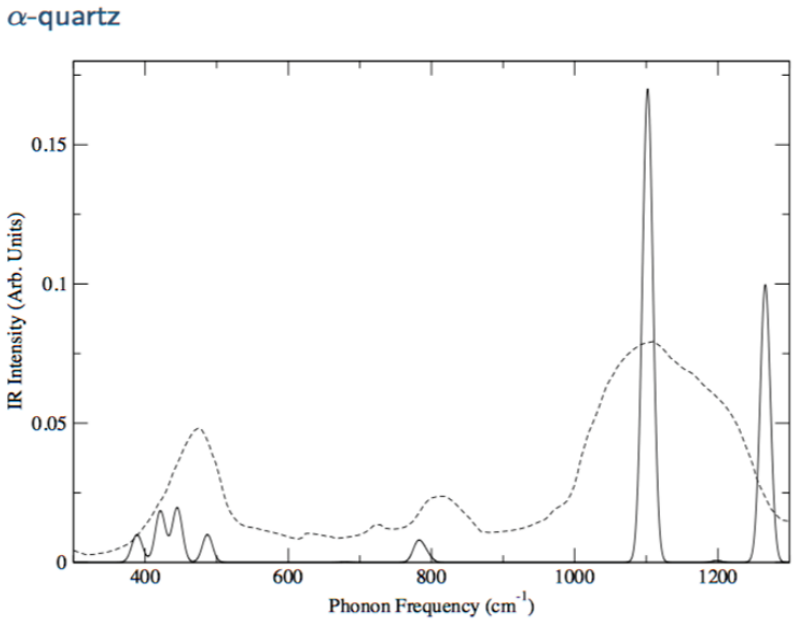
LO/TO Splitting



- Dipole created by displacement of charges of long-wavelength LO mode creates induced electric field.
- For TO motion, $E \perp q$ so $E.q = 0$
- For LO motion, $E \parallel q$ and $E.q$ adds additional restoring force
- Energy (and so frequency) of LO mode is increased
- This is included in the formalism of DFPT.

Powder infra-red

- IR absorption is governed by the change in polarisation due to a phonon at the Γ point.
- Can calculate which modes are IR active and how strongly they will interact.

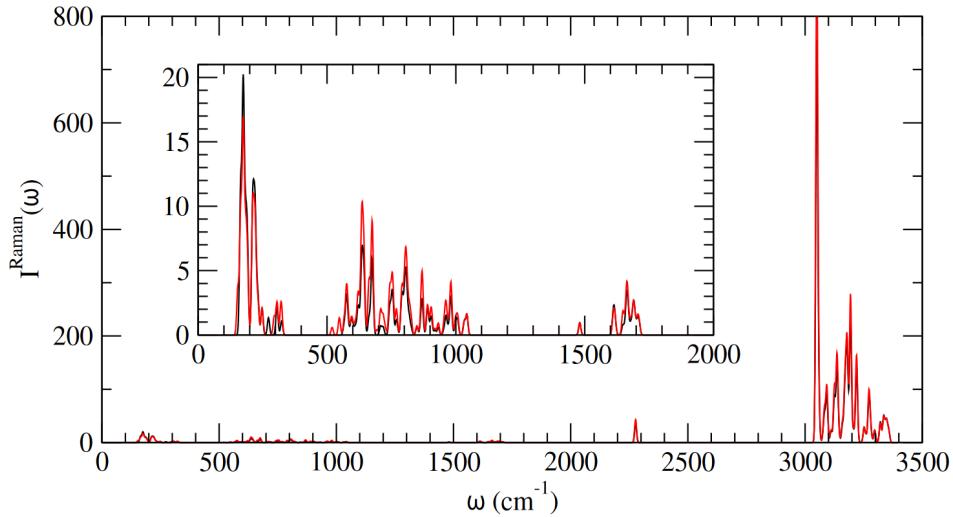


Raman Spectroscopy

- Raman scattering depends on raman activity tensor

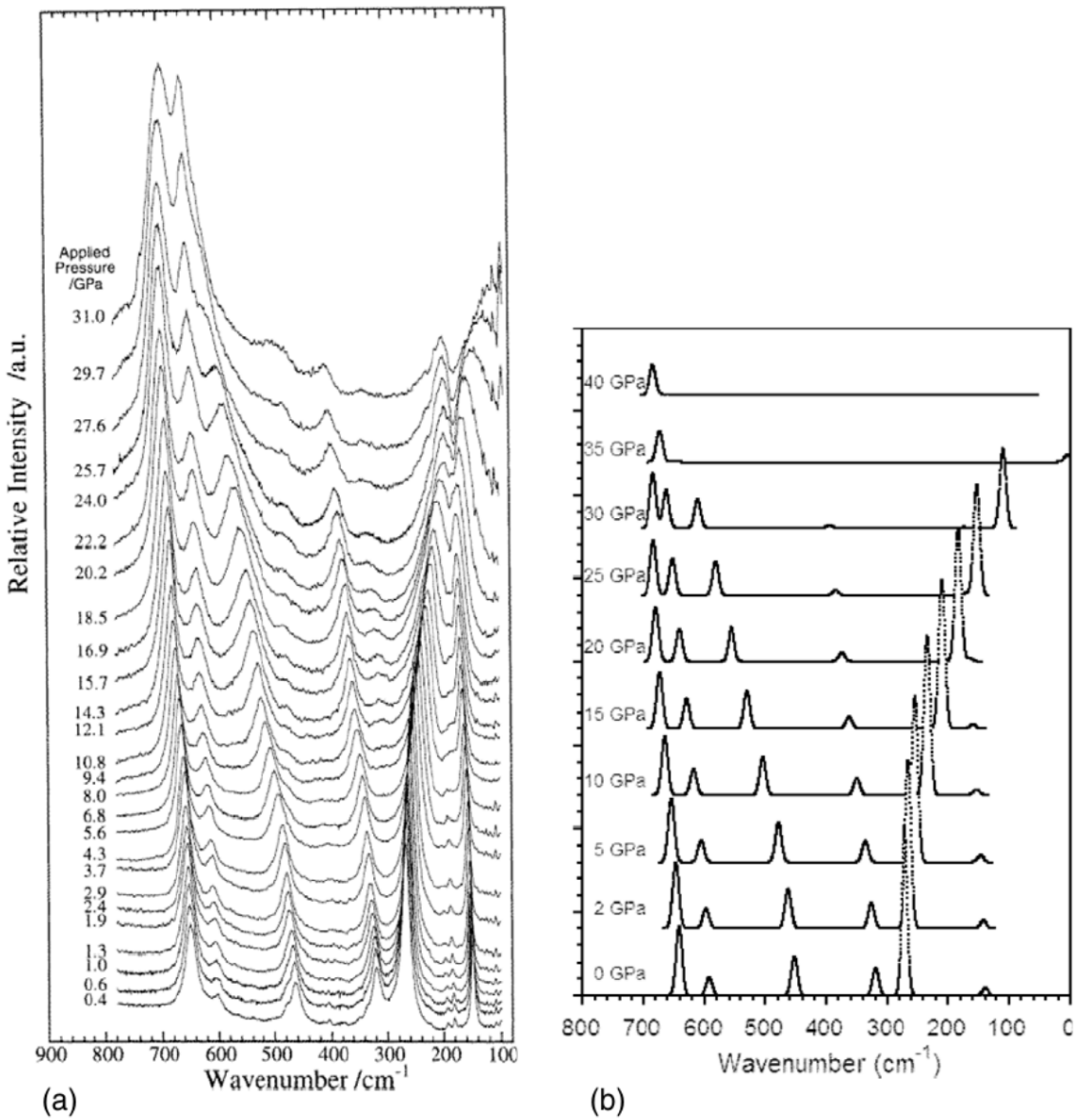
$$I_{\alpha\beta}^{\text{raman}} = \frac{d^3E}{d\varepsilon_\alpha d\varepsilon_\beta dQ_m} = \frac{d\epsilon_{\alpha\beta}}{dQ_m}$$

- Can do this by displacing the atoms and doing an e-field calculation at each point or by the $2n+1$ theorem



- Both methods give similar results but the perturbative method is much faster (ice13 – 16,000 s vs 80,000 s)

Raman Spectra of ZrO2



Conclusion

- Phonons can be calculated by either
  - Finite displacement with
    - Primitive cell at $\boldsymbol{q} = 0$
    - Non-diagonal supercell on MP grid
    - Direct supercell to calculate FCM
  - Density functional perturbation theory
    - At arbitrary $\boldsymbol{q}$
- Interpolation is very useful for finely sampling phonons.
- Acoustic sum rule can help correct frequencies at $\boldsymbol{q} = 0$
- Thermodynamic properties available!
- Raman and and IR can be calculated

Thanks for listening!

References

Books on Lattice Dynamics

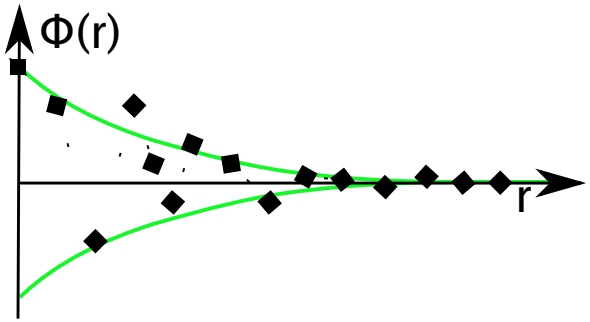
- M. T. Dove *Introduction to Lattice Dynamics*, CUP. - elementary introduction.
- J. C. Decius and R. M. Hexter *Molecular Vibrations in Crystals* - Lattice dynamics from a spectroscopic perspective.
- Horton, G. K. and Maradudin A. A. *Dynamical properties of solids* (North Holland, 1974) A comprehensive 7-volume series - more than you'll need to know.
- Born, M and Huang, K *Dynamical Theory of Crystal Lattices*, (OUP, 1954) - The classic reference, but a little dated in its approach.

References on *ab initio* lattice dynamics

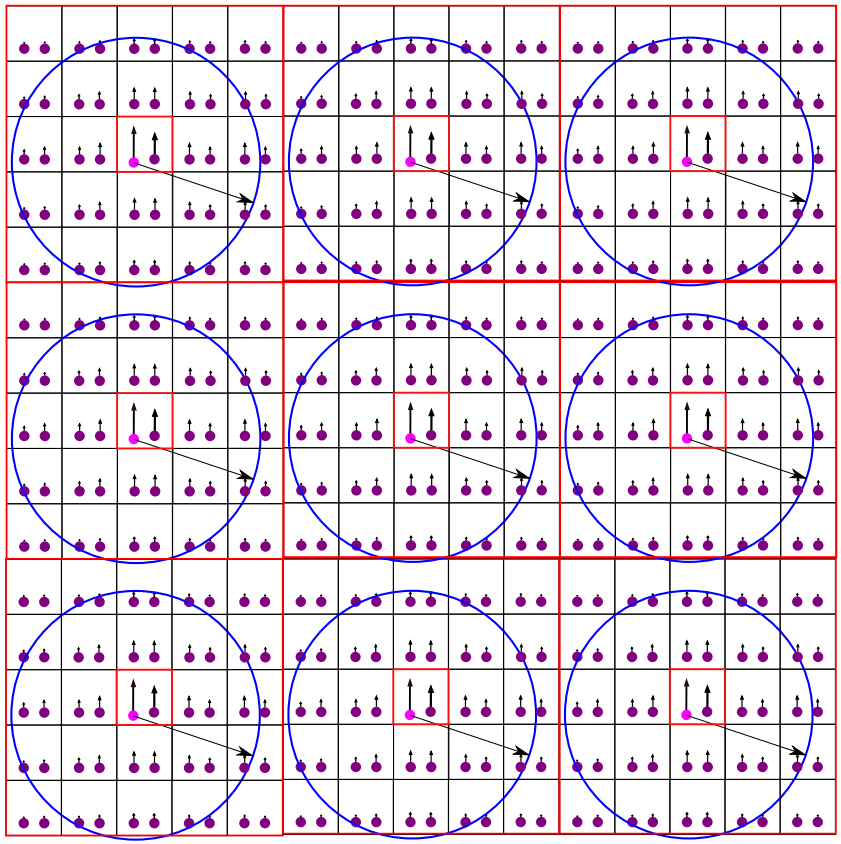
- K. Refson, P. R. Tulip and S. J Clark, Phys. Rev B. **73**, 155114 (2006)
- S. Baroni *et al* (2001), Rev. Mod. Phys **73**, 515-561.
- Variational DFPT (X. Gonze (1997) PRB **55** 10377-10354).
- Richard M. Martin *Electronic Structure: Basic Theory and Practical Methods: Basic Theory and Practical Density Functional Approaches Vol 1* Cambridge University Press, ISBN: 0521782856

The Supercell method

The *supercell method* is an extension of the finite-displacement approach which depends on *short-ranged* nature of FCM: $\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a) \rightarrow 0$ as $\boldsymbol{R}_a \rightarrow \infty$.



In non-polar insulators and most metals $\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a)$ decays as $1/R^5$ or faster.
In polar insulators Coulomb term decays as $1/R^3$
Define radius R_c beyond which $\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a)$ is negligible
For supercell with $L > 2R_c$ then $C^{\kappa,\kappa'}_{\alpha,\alpha'}(\mathrm{sc}) \approx \Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a)$.



The Supercell method

1. Choose sufficiently large supercell and compute $C^{\kappa,\kappa'}_{\alpha,\alpha'}(\mathrm{sc})$ using finite-displacement method.
2. Non-periodic real-space force-constant matrix directly mapped from periodic supercell FCM. $\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a) \equiv C^{\kappa,\kappa'}_{\alpha,\alpha'}(\mathrm{sc})$
3. Fourier transform using definition of D to obtain dynamical matrix of primitive cell at *any* desired $\boldsymbol{q}$.
4. Diagonalise $D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q})$ to obtain eigenvalues and eigenvectors.

This method is often (confusingly) called the “direct” method.

Overlap Errors

Size of supercell limits R_c. Too small a supercell means that $\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a)$ can not be cleanly extracted from $C^{\kappa,\kappa'}_{\alpha,\alpha'}(\mathrm{SC})$ and dispersion curves will contain error.