Vibrational Spectroscopy Methods

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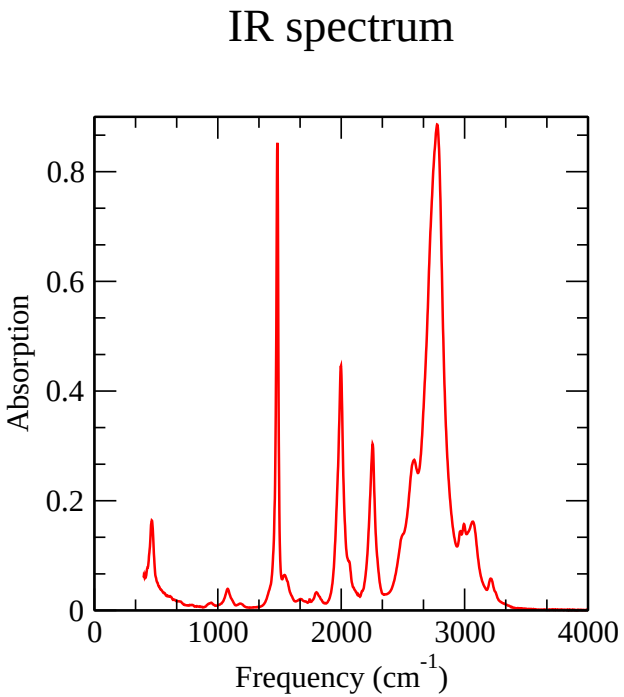
Motivations for ab-initio lattice dynamics I

Motivations from experimental spectroscopy:

- Vibrational spectroscopy is sensitive probe of structure and dynamics of materials.
- All experimental methods (IR, raman, INS, IXS) provide *incomplete* information.
  - IR and raman have inactive modes
  - Hard to distinguish fundamental and overtone (multi-phonon) processes in spectra
  - No experimental technique provides complete eigenvector information $\Rightarrow$ mode assignment based on similar materials, chemical intuition, guesswork.
- Hard to find accurate model potentials to describe many systems
- Fitted force-constant models only feasible for small, high symmetry systems.



Motivations for ab-initio lattice dynamics II

Motivations from predictive modelling

- Lattice dynamics calculation can establish stability or otherwise of putative structure.
- LD gives direct information on interatomic forces.
- LD can be used to study phase transitions via soft modes.
- Quasi-harmonic lattice dynamics can include temperature and calculate ZPE and Free energy of wide range of systems.
- Electron - phonon coupling is origin of (BCS) superconductivity.

Lattice Dynamics of Crystals

References

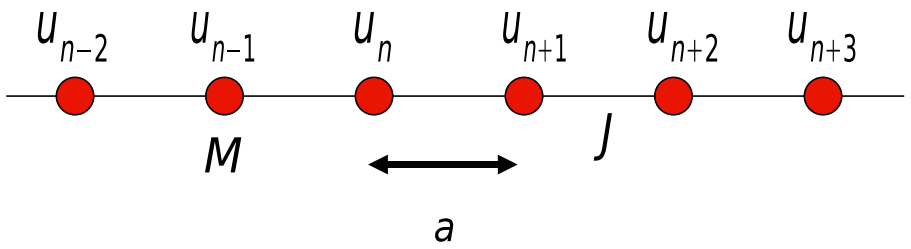
Books on Lattice Dynamics

- 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

Monatomic Crystal in 1d (I)



Born-Von Karman boundary conditions

If only nearest neighbours interact:

$$E^{harm} = \frac{1}{2} J \sum_n (u_n - u_{n+1})^2$$

where $J = \Phi_{nn'}$ force constant

Equation of motion of n-th atom:

$$M \frac{\partial^2 u_n}{\partial t^2} = -\frac{\partial E^{harm}}{\partial u_n} = -J(2u_n - u_{n+1} - u_{n-1})$$

Monatomic Crystal (II)

Solution is known to be the equation of a travelling wave

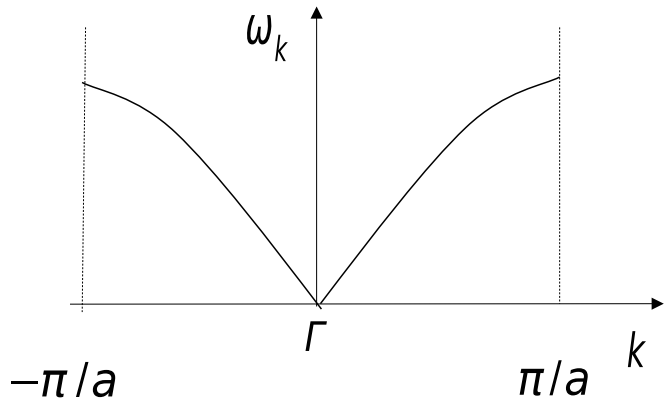
$$u_n(t) = \sum_k \tilde{u}_k \exp\left[i(kx - \omega_k t)\right] \qquad \forall k \in \mathrm{BZ}$$

When this expression is inserted in the equation of motion one obtains:

$$M\omega_k^2 = 2\mathrm{J}\left[1 - \cos(ka)\right]$$

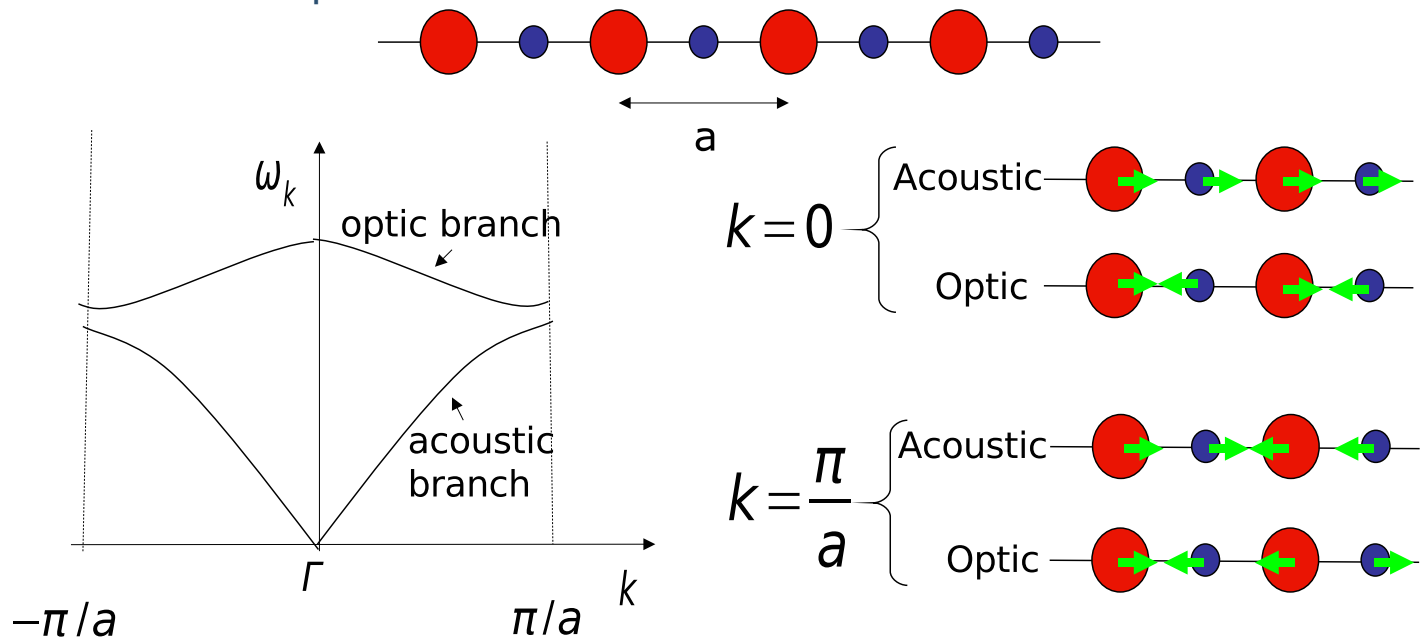
which leads to the following dispersion curve:

$$\omega_k = \sqrt{\frac{4\mathrm{J}}{M}}\left|\sin(ka/2)\right| \qquad \forall k \in \mathrm{BZ}$$



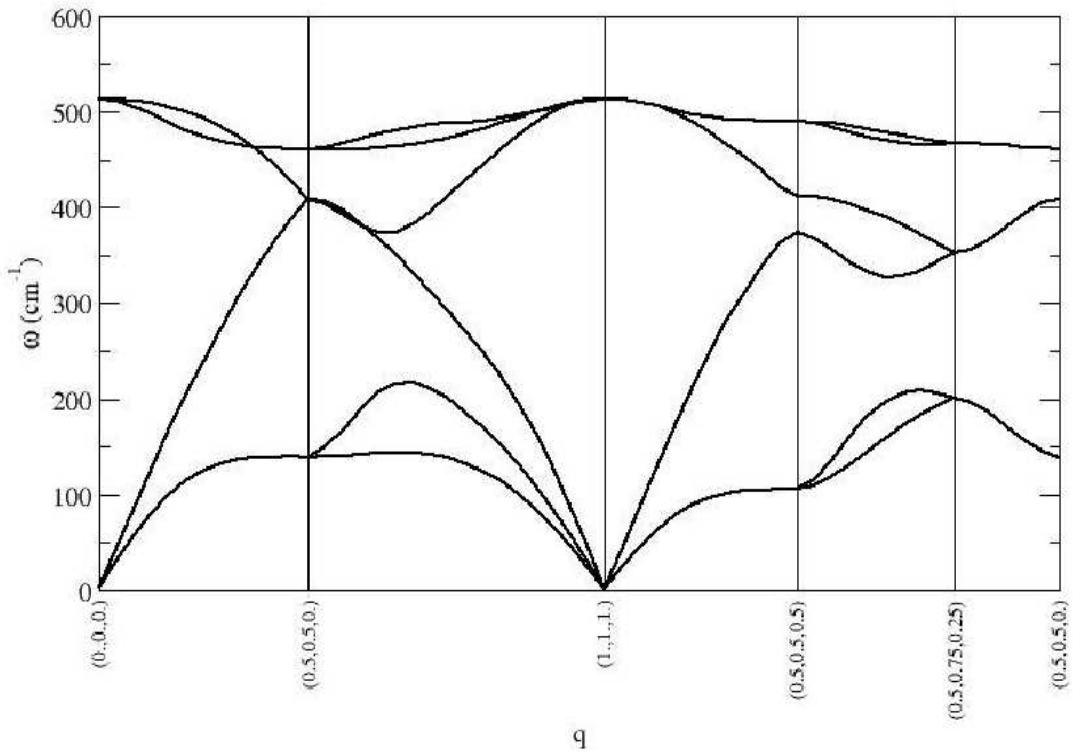
Diatomic Crystal - Optic modes

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



Characterization of Vibrations in 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 $\boldsymbol{q} \rightarrow 0$ and $3N-3$ *optic* branches.



Formal Theory of Lattice Dynamics

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

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

  where $\boldsymbol{u}_{\kappa,\alpha}$ is the vector of atomic displacements from equilibrium and $\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a)$ is the matrix of *force constants* $\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a) = \frac{\partial^2 E}{\partial \boldsymbol{u}_{\kappa,\alpha} \partial \boldsymbol{u}_{\kappa',\alpha'}}$
- At equilibrium the forces $-\frac{\partial E}{\partial \boldsymbol{u}_{\kappa,\alpha}}$ are all zero so 1^{st} term vanishes.
- In the *Harmonic Approximation* the 3^{rd} and higher order terms are assumed to be negligible
- Assume *Born von Karman* periodic boundary conditions and substituting *plane-wave* $\boldsymbol{u}_{\kappa,\alpha} = \boldsymbol{\varepsilon}_{m\kappa,\alpha\boldsymbol{q}} exp(i\boldsymbol{q}.\boldsymbol{R}_{\kappa,\alpha} - \omega t)$ yields eigenvalue equation:

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

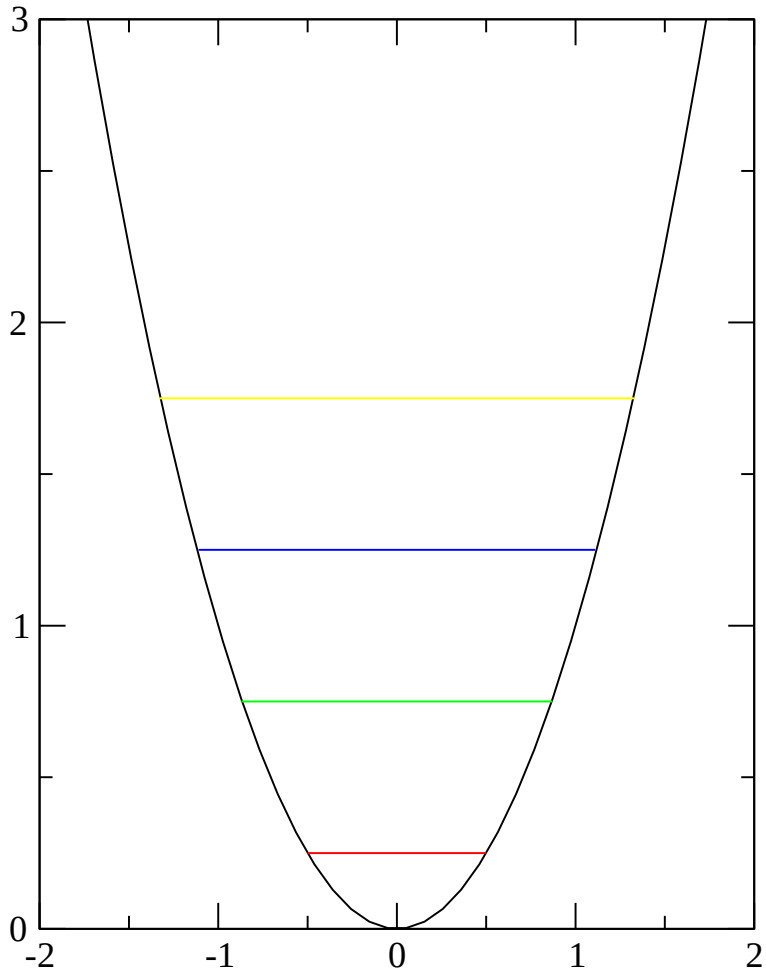
  where frequencies are square roos of eigenvalues. The **dynamical matrix**

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

  is the Fourier transform of the force constant matrix.

Quantum Theory of Lattice Modes

- The classical energy expression can be transformed into a quantum-mechanical Hamiltonian for nuclei.
- In harmonic approximation nuclear wavefunction is *separable* into product by mode transformation.
- Each *mode* satisfies harmonic oscillator Schroedinger eqn with energy levels $E_{m,n} = \left(n + \frac{1}{2}\right) \hbar\omega_m$ for mode m.
- Quantum excitations of modes known as *phonons* in crystal
- Transitions between levels n_1 and n_2 interact with photons of energy $(n_2 - n_1)\,\hbar\omega_m$, ie multiples of *fundamental* frequency ω_m.
- In *anharmonic* case where 3$^{\text{rd}}$-order term not negligible, *overtone* frequencies are not multiples of fundamental.



Formal Theory of Lattice Dynamics II

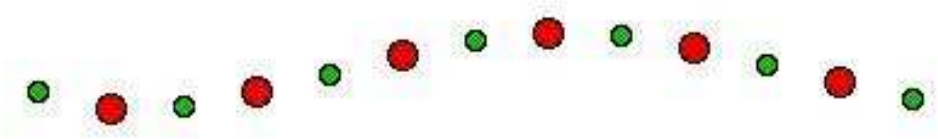
- The dynamical matrix is a $3N \times 3N$ matrix at each wavevector $\boldsymbol{q}$.
- $D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q})$ is a hermitian matrix $\Rightarrow$ eigenvalues $\omega^2_{m,\boldsymbol{q}}$ are real.
- $3N$ eigenvalues $\Rightarrow$ modes at each $\boldsymbol{q}$ leading to $3N$ branches in dispersion curve.
- The mode eigenvector $\boldsymbol{\varepsilon}_{m\kappa,\alpha}$ 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.
- In 1970s force constants fitted to experiment using simple models.
- 1980s - force constants calculated from empirical potential interaction models (now available in codes such as GULP)
- mid-1990s - development of *ab-initio* electronic structure methods made possible calculation of force constants with no arbitrary parameters.

ab-initio Lattice Dynamics

The Frozen-phonon method

The **frozen phonon** method:

- Create a structure perturbed by guessed eigenvector
- evaluate *ground-state energy* as function of *amplitude* λ with series of single-point energy calculations on perturbed configurations.
- Use $E_0(\lambda)$ to evaluate $k = \frac{d^2 E_0}{d\lambda^2}$
- Frequency given by $\sqrt{k/\mu}$. (μ is reduced mass)
- Need to use supercell commensurate with $\boldsymbol{q}$.
- Need to identify eigenvector in advance (perhaps by symmetry).
- Not a general method: useful only for small, high symmetry systems or limited circumstances otherwise.
- Need to set this up "by hand" customised for each case.



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

$$\frac{dF_{\kappa,\alpha}}{du} \approx \frac{F^+_{\kappa,\alpha} - F^-_{\kappa,\alpha}}{2u} = \frac{d^2E_0}{du_{\kappa,\alpha}du_{\kappa',\alpha'}}$$

- 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.
- Like frozen-phonon method, works only at $\boldsymbol{q}=0$.

The Supercell method

The *supercell method* is an extension of the finite-displacement approach.

- Relies on *short-ranged* nature of FCM; $\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a) \rightarrow 0$ as $\boldsymbol{R}_a \rightarrow \infty$.
- For non-polar insulators and most metals $\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a)$ decays as $1/R^5$ or faster.
- For polar insulators Coulomb term decays as $1/R^3$
- Can define "cut off" radius R_c beyond which $\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a)$ can be treated as zero.
- In supercell with $L > 2R_c$ then $C^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q}=0) = \Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a)$.
- Method:
  1. choose sufficiently large supercell and compute $C^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q}_{\text{supercell}}=0)$ using finite-displacement method.
  2. This object is just the real-space force-constant matrix $\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a)$.
  3. Fourier transform using

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

     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.

First and second derivatives

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 $\hat{H} = \nabla^2 + V_{\mathrm{SCF}}$
- Force $F = -\frac{dE}{d\lambda} = -\left\langle \frac{d\psi}{d\lambda}\right| \hat{H}\,|\psi\rangle - \langle\psi|\,\hat{H}\left|\frac{d\psi}{d\lambda}\right\rangle - \langle\psi|\,\frac{dV}{d\lambda}\,|\psi\rangle$
  where λ represents an atomic displacement perturbation.
- If $\langle\psi|$represents the ground state of $\hat{H}$ then the first two terms vanish because $\langle\psi|\,\hat{H}\left|\frac{d\psi}{d\lambda}\right\rangle = \epsilon_n\,\langle\psi|\left|\frac{d\psi}{d\lambda}\right\rangle = 0$. This is the *Hellman-Feynmann Theorem*.
- Force constants are the *second* derivatives of energy
  $k = \frac{d^2E}{d\lambda^2} = -\frac{dF}{d\lambda} = \left\langle \frac{d\psi}{d\lambda}\right|\frac{dV}{d\lambda}\,|\psi\rangle + \langle\psi|\,\frac{dV}{d\lambda}\left|\frac{d\psi}{d\lambda}\right\rangle - \langle\psi|\,\frac{d^2V}{d\lambda^2}\,|\psi\rangle$
- None of the above terms vanishes.
- Second derivatives need **linear response** of wavefunctions *wrt* perturbation ($\left\langle \frac{d\psi}{d\lambda}\right|$).
- 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 representation:
  $\phi^{(1)}_{\boldsymbol{k},\boldsymbol{q}}(\boldsymbol{r}) = e^{-i(\boldsymbol{k}+\boldsymbol{q}).\boldsymbol{r}} u^{(1)}(\boldsymbol{r})$ where $u^{(1)}(\boldsymbol{r})$ has periodicity of unit cell.
  $\Rightarrow$ can store $u^{(1)}(\boldsymbol{r})$ in computer rep'n using basis of *primitive* cell.
- First-order response orbitals are solutions of **Sternheimer equation**

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

  P_c is projection operator onto unoccupied states. 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.
- Two major approaches to finding $\phi^{(1)}$ are suited to plane-wave basis sets:
  - Green's function (S. Baroni *et al* (2001), Rev. Mod. Phys **73**, 515-561).
  - Variational DFPT (X. Gonze (1997) PRB **55** 10377-10354).

  CASTEP uses Gonze's variational DFPT method.
- DFPT has huge advantage - can calculate response to *incommensurate* $\boldsymbol{q}$ from a calculation on primitive cell.
- Disadvantage of DFPT - lots of programming required.

Scary Maths

Second-derivatives in dynamical matrix given by (norm-conserving V_{PS}):

$$E^{(2)}_{el,-\mathbf{q},\mathbf{q}}\{u^{(0)};u^{(1)}\} = \frac{\Omega_0}{(2\pi)^3}\int_{BZ}\sum_{m}^{occ} s\left[\left\langle u^{(1)}_{m\mathbf{k},\mathbf{q}}|H^{(0)}_{\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}} - \epsilon^{(0)}_{m\mathbf{k}}|u^{(1)}_{m\mathbf{k},\mathbf{q}}\right\rangle + \left\langle u^{(1)}_{m\mathbf{k},\mathbf{q}}|v^{(1)}_{sep,\mathbf{k}+\mathbf{q},\mathbf{k}}|u^{(0)}_{m\mathbf{k}}\right\rangle + \left\langle u^{(0)}_{m\mathbf{k}}|v^{(1)}_{sep,\mathbf{k},\mathbf{k}+\mathbf{q}}|u^{(1)}_{m\mathbf{k},\mathbf{q}}\right\rangle + \left\langle u^{(0)}_{m\mathbf{k}}|v^{(2)}_{sep,\mathbf{k},\mathbf{k}}|u^{(0)}_{m\mathbf{k}}\right\rangle d\mathbf{k}\right] +$$

$$\frac{1}{2}\int_{\Omega_0}\left\{\left[\overline{n}^{(1)}_{\mathbf{q}}(\mathbf{r})\right]^*\left[\overline{v}^{(1)}_{loc,\mathbf{q}}(\mathbf{r}) + \overline{\mathbf{v}}^{(\mathbf{1})}_{\mathbf{xc0},\mathbf{q}}(\mathbf{r})\right] + \left[\overline{n}^{(1)}_{\mathbf{q}}(\mathbf{r})\right]\left[\overline{v}^{(1)}_{loc,\mathbf{q}}(\mathbf{r}) + \overline{\mathbf{v}}^{(\mathbf{1})}_{\mathbf{xc0},\mathbf{q}}(\mathbf{r})\right]^*\right\} d\mathbf{r} +$$

$$\frac{1}{2}\int_{\Omega_0}\left.\frac{dv_{xc}}{dn}\right|_{n^{(0)}(\mathbf{r})}\left|\overline{n}^{(1)}_{\mathbf{q}}(\mathbf{r})+\right|^2 d\mathbf{r} + \mathbf{2\pi\Omega_0}\sum_{\mathbf{G}}\frac{\left|\overline{\mathbf{n}}^{(\mathbf{1})}_{\mathbf{q}}(\mathbf{G})\right|^{\mathbf{2}}}{|\mathbf{q}+\mathbf{G}|^{\mathbf{2}}} +$$

$$\int_{\Omega_0} n^{(0)}(\mathbf{r})\mathbf{v}^{(\mathbf{2})}_{\mathbf{loc}}\mathbf{dr} + \frac{\mathbf{1}}{\mathbf{2}}\left.\frac{\mathbf{d^2E_{xc}}}{\mathbf{d\lambda d\lambda^*}}\right|_{\mathbf{n^{(0)}}}$$

Expression for ultrasoft potentials is considerably more complicated.

Fourier Interpolation of dynamical Matrices

- DFPT formalism requires self-consistent iterative solution for *every* separate $\boldsymbol{q}$.
- Hundreds of $\boldsymbol{q}$'s needed for good dispersion curves, thousands for good Phonon DOS.
- Can take advantage of short-range nature of real-space FCM $\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a)$.
- Compute $D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q})$ on a Monkhorst-Pack grid of $\boldsymbol{q}$ vectors.
- Approximation to FCM in $p \times q \times r$ supercell given by Fourier transform of dynamical matrices on $p \times q \times r$ grid.

$$\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a) = \sum_{\boldsymbol{q}} C^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q}) e^{i\boldsymbol{q}.\boldsymbol{R}_a}$$

- Fourier transform using to obtain dynamical matrix of primitive cell at *any* desired $\boldsymbol{q}$, Exactly as with Finite-displacement-supercell method
- Diagonalise mass-weighted $D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q})$ to obtain eigenvalues and eigenvectors.
- Longer-ranged coulombic contribution varies as $1/R^3$ but can be handled analytically.
- Need only DFPT calculations on a few tens of $\boldsymbol{q}$ points on grid to calculate $D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q})$ on arbitrarily dense grid (for DOS) or fine (for dispersion) path.

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 M-P grid of $\boldsymbol{q}$ with Fourier interpolation to arbitrary fine set of $\boldsymbol{q}$.

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.

Limitations: DFPT currently implemented only for norm-conserving pseudopotentials and insulators. (Need `fix_occupancy = T`, not just band gap.)

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 $1e-5$ 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`
- N.B. Defaults are not very good in CASTEP 4.0. Fixed in 4.1.
- $D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q})$ calculated at $\boldsymbol{q}$-points specified in *cell* file by one of
  - `%BLOCK phonon_kpoint_list` for the explicitly named points
  - `%BLOCK phonon_kpoint_path` to construct a path joining the nodal points given. Spacing along path is `phonon_kpoint_path_spacing`
  - `phonon_kpoint_mp_grid` *p q r* and possibly `phonon_kpoint_mp_offset` *0.125 0.125 0.125* to explicitly specify a M-P grid for a DOS.
  - `phonon_kpoint_mp_spacing` $\delta\boldsymbol{q}$ 1/ang to generate a M-P grid of a specified linear spacing

Example output


```
+                        Vibrational Frequencies                        +
+                        -----------------------                        +
+                                                                       +
+   Performing frequency calculation at     10 wavevectors (q-pts)      +
+                                                                       +
+   Branch number Frequency (cm-1)                                      +
+ ===================================================================== +
+                                                                       +
+ --------------------------------------------------------------------- +
+  q-pt=    1 (  0.000000  0.000000  0.000000)     0.022727             +
+  q->0 along (  0.050000  0.050000  0.000000)                          +
+ --------------------------------------------------------------------- +
+                                                                       +
+     1       -4.041829                0.0000000                      +
+     2       -4.041829                0.0000000                      +
+     3       -3.927913                0.0000000                      +
+     4      122.609217                7.6345830                      +
+     5      122.609217                7.6345830                      +
+     6      165.446374                0.0000000                      +
+     7      165.446374                0.0000000                      +
+     8      165.446374                0.0000000                      +
+     9      214.139992                7.6742825                      +
+ --------------------------------------------------------------------- +
```

N.B. 3 Acoustic phonon frequencies should be zero by Acoustic Sum Rule. Post-hoc correction if `phonon_sum_rule = T`.

CASTEP phonon calculations II - Fourier Interpolation

To select set `phonon_fine_method = interpolate`
Specify grid of $\boldsymbol{q}$-points using `phonon_kpoint_mp_grid` *p q r*.
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` *0.125 0.125 0.125* to shift one point to Γ
$D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q})$ interpolated to $\boldsymbol{q}$-points specified in *cell* file by one of

- `%BLOCK phonon_fine_kpoint_list` for the explicitly named points
- `%BLOCK phonon_fine_kpoint_path` to construct a path joining the nodal points given. Spacing along path is `phonon_fine_kpoint_path_spacing`
- `phonon_fine_kpoint_mp_grid` *p q r* and possibly `phonon_fine_kpoint_mp_offset` *0.125 0.125 0.125* to explicitly specify a M-P grid for a DOS.
- `phonon_fine_kpoint_mp_spacing` $\delta\boldsymbol{q}$ 1/ang to generate a M-P grid of a specified linear spacing

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. $\Rightarrow$ can calculate fine dispersion plot and DOS on a grid rapidly from one DFPT calculation.
Parameter `phonon_force_constant_cutoff` applies real-space cutoff to $\Phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a)$.
Default is chosen according to MP grid.

CASTEP phonon calculations III - Supercell

- To select set `phonon_fine_method = supercell`
- Set supercell in `.cell` file, eg $2 \times 2 \times 2$ using

```
%BLOCK phonon_supercell_matrix
2 0 0
0 2 0
0 0 2
%ENDBLOCK phonon_supercell_matrix
```

- $D^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q})$ interpolated to $\boldsymbol{q}$-points specified in *cell* file by one of same `phonon_fine_kpoint` keywords as for interpolation.
- Kpoints for supercell set using block or grid keywords `supercell_kpoint...`
- `phonon_force_constant_cutoff` applies as for Interpolation calculation.
- Real-space force-constant matrix is stored in `.check` file.
- As with interpolation, all `fine_kpoint` parameters can be changed on a continuation run. Interpolation is very fast. $\Rightarrow$ can calculate fine dispersion plot and DOS on a grid rapidly from one DFPT calculation.
- Tip. For *fcc* primitive cells use non-diagonal matrix to make cubic supercell.

```
%BLOCK phonon_supercell_matrix
 1  1 -1
 1 -1  1
-1  1  1
%ENDBLOCK phonon_supercell_matrix
```

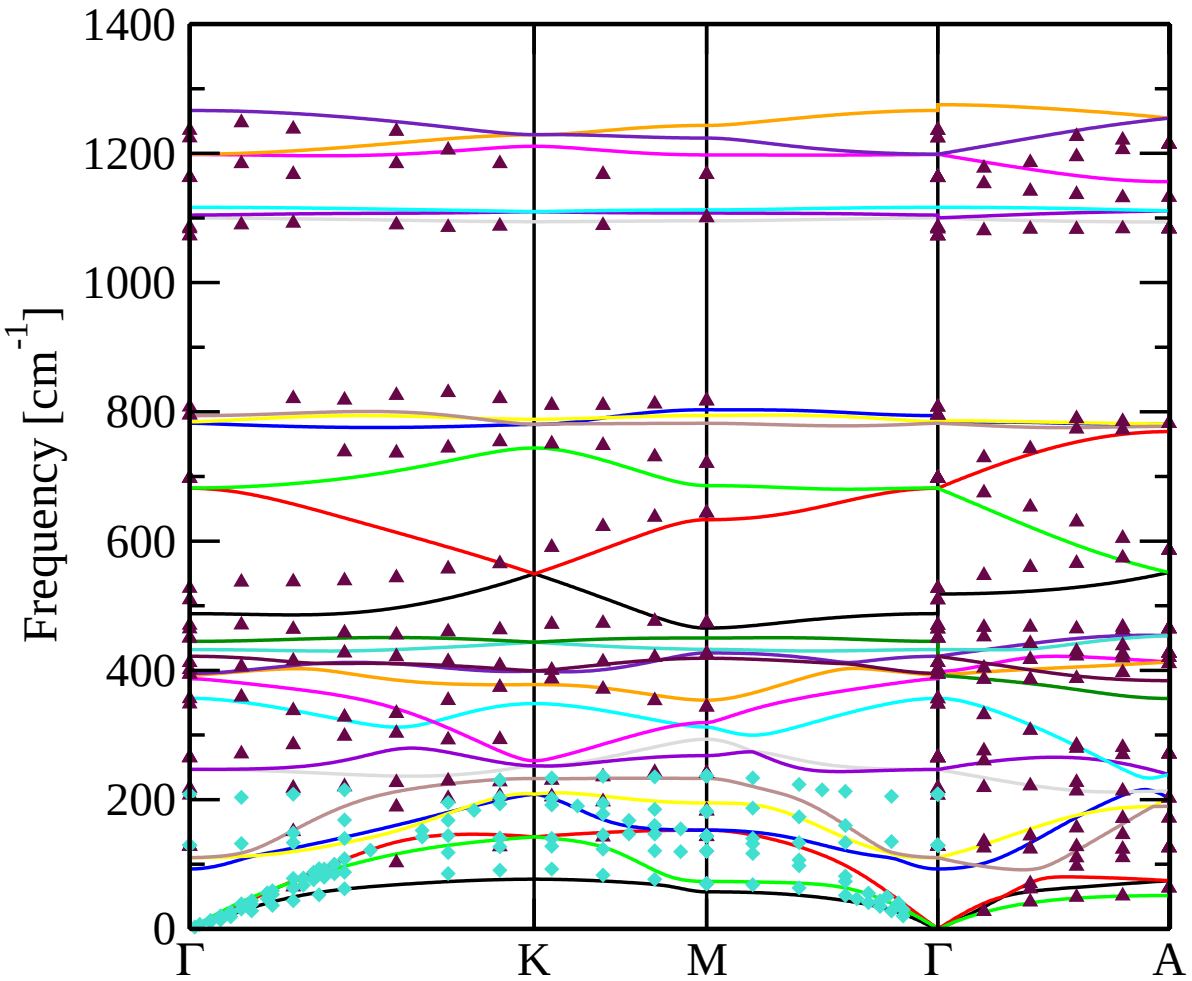
- Convergence: Need very accurate forces to take their derivative.
- Need good representation of any pseudo-core charge density and augmentation charge for ultrasoft potentials on fine FFT grid. Usually need larger `fine_gmax` (or `fine_grid_scale`) than for geom opt/MD to get good results.

Running a phonon calculation

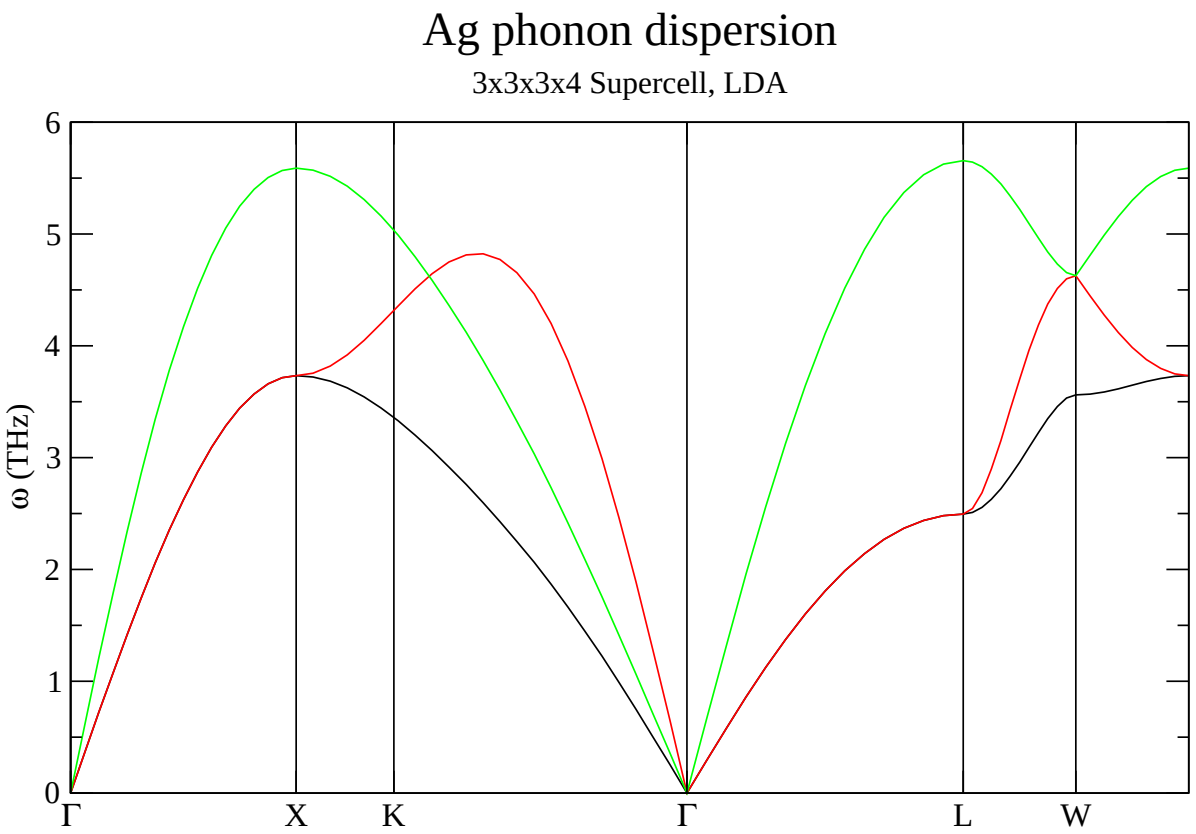
- Phonon calculations can be lengthy. CASTEP saves partial calculation periodically in `.check` file if keywords `num_backup_iter` *n* or `backup_interval` *t*. Backup is every n q-vectors or every t seconds.
- Phonon calculations have high inherent parallelism. Because perturbation breaks symmetry relatively 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!

Examples

DFPT with interpolation - α-quartz

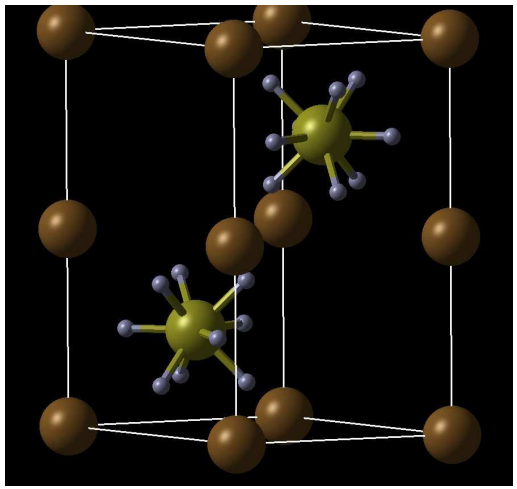


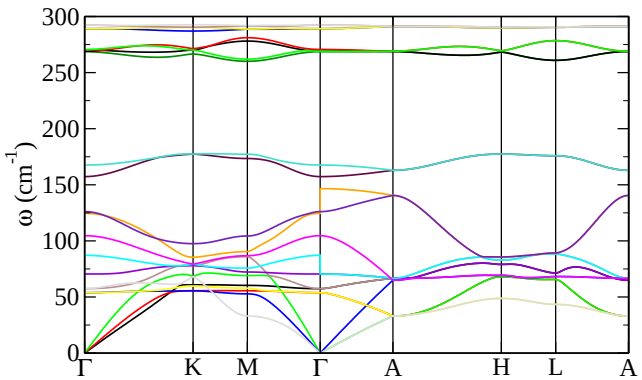
Supercell method - Silver

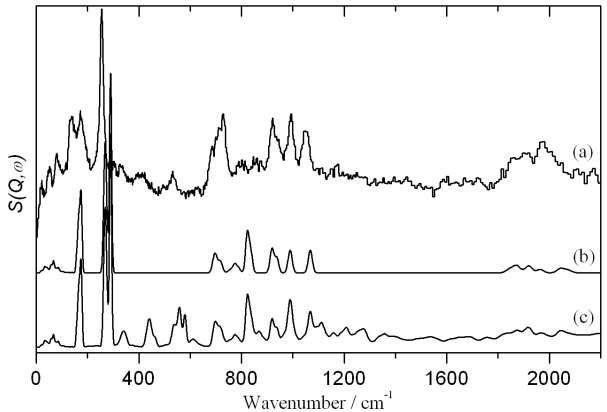


Barium Rhenium Hydride

- with S. F. Parker, ISIS facility, RAL., Inorg. Chem. **45**, 19051 (2006)
- $BaReH_9$ with unusual ReH_9^{2+} ion has very high molar hydrogen content.
- INS spectrum modelled using A-CLIMAX software (A. J. Ramirez Cuesta, ISIS)
- Predicted INS spectrum in mostly excellent agreement with experiment
- LO/TO splitting essential to model INS.
- Librational modes in error (c.f NH_4F)
- Complete mode assignment achieved.

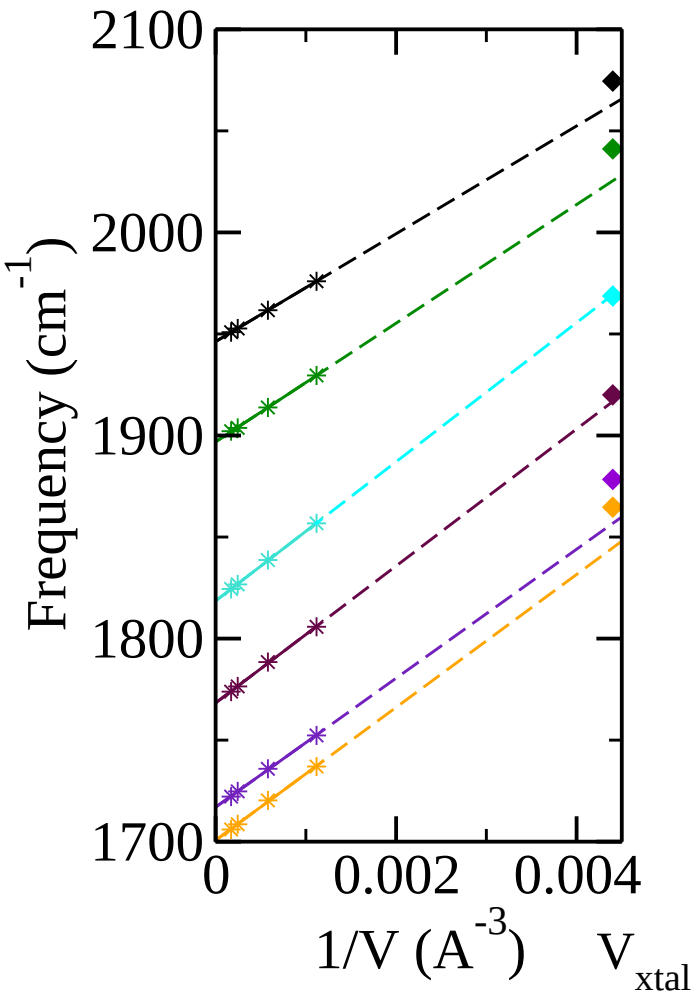






Isolated ReH_9^{2+} ion

- Previous *ab-initio* calculations on isolated ReH_9^{2+} ion gave poor fit to INS.
- Repeat isolated ion using CASTEP.
- CASTEP model: periodic array of ions in charged cell. Exp $1/V$ scaling and take $V \rightarrow \infty$ limit.
- $V \rightarrow \infty$ frequencies in agreement with isolated ion calcs.
- $\Rightarrow$ large ($\approx$ 150 cm^{-1}) crystal field shift
- Can also extrapolate *down* to V_{xtal}.
- Extrapolated ion freqs are very close to A-point crystal freqs.
- Crystal field shift is almost entirely a periodic volume effect.
- Anion modes completely insensitive to presence of cation!



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/slab calculation.
6. Fine FFT grid for finite-displacement calculations.

- Accuracies 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*.
- Less obviously *agreement* may also be due to anharmonicity. There is a "lucky" cancellation of anharmonic shift by PBE GGA error in OH stretch modes!

"Scaling" and other cheats

- DFT usually gives frequencies within a few percent of experiment. Exceptions are usually strongly-correlated systems, *e.g.* some transition-metal Oxides where DFT description of bonding is poor.
- Discrepancies can also be due to anharmonicity. A frozen-phonon calculation can test this.
- In case of OH-bonds, DFT errors and anharmonic shift cancel each other!
- In solid frquencies may be strongly pressure-dependent. DFT error can resemble *effective pressure*. In that case, best comparison with expt. may not be at experimental pressure.
- Hartree-Fock approximation *systematically* overestimates vibrational frequencies by 5-15%. Commpn practice is to multiply by "scaling factor" ≈ 0.9.
- Scaling not recommended for DFT where error is not systematic. Over- and under-estimation equally common.
- For purposes of mode assignment, or modelling experimental spectra to compare intensity it can sometimes be useful to apply a small empirical shift on a per-peak basis. This does not generate an "ab-initio frequency".