Imperial College London

Phonon calculations in ONETEP with the finite displacement method

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What are phonons?

Phonons are the quantum mechanical version of *normal modes* found in classical mechanics, in which all parts of a system oscillate with the same frequency

Normal modes are the *elementary vibrations* of the lattice

Robert D. Anderson 2006

Normal mode in a cup of coffee

Vibrational spectroscopy is useful for probing the structure of materials

Different experimental methods: infrared (IR), Raman, inelastic neutron scattering (INS)...

Phonons are closely related to thermodynamic properties such as specific heat, phase transitions and lattice expansion, as well as thermal and electrical conductivity and superconductivity

Ab initio thermodynamics for defect calculations

$$F = U - T\left(S_v + S_c\right) = U - T\left(S_v + k_\mathrm{B} \ln W\right)$$

vibrational entropy

configurational entropy

The equilibrium state of the system minimizes the free energy *F*

$$\Delta F = n\Delta U - nT\Delta S_v - k_\mathrm{B} T \ln \frac{(N+n)!}{N!n!}$$

$$c\left(T\right) = \frac{n}{N+n} \simeq \exp \frac{\Delta S_v}{k_\mathrm{B}} \exp - \frac{\Delta U}{k_\mathrm{B} T}$$

Equilibrium defect concentration *c* for a system of *N* atoms and *n* defects (vacancies/substitutionals)

$$\Delta U = \Delta U_v + E_f$$

difference in vibrational energy

difference in configurational energy (the defect formation energy)

Lattice dynamics in the harmonic approximation

Crystal of repeating unit cells

Unit cell label: a (position R_a)

Ion label: κ (mass M_κ)

Small displacement from equilibrium position: $u_{a,\kappa}$

Cartesian coordinate label: α

Expanding the total energy to quadratic order in the displacement of the ions (the harmonic approximation) gives:

$$E^{\mathrm{tot}} = E^{\mathrm{eq}} + \frac{1}{2} \sum_{a,\kappa,\alpha,a',\kappa',\alpha'} u_{a,\kappa,\alpha} \phi_{\alpha,\alpha'}^{\kappa,\kappa'}(a,a') \, u_{a',\kappa',\alpha'}$$

force constants matrix

(force on ion a,κ by the displacement of ion a',κ')

Solving the classical equation of motion of the ions gives a Bloch-like solution:

$$\mathbf{u}_{a,\kappa} = \boldsymbol{\varepsilon}_{\kappa,\mathbf{q},n} \exp\left(\mathrm{i}\mathbf{q} \cdot \mathbf{R}_{a,\kappa} - \omega_{\mathbf{q},n} t\right)$$

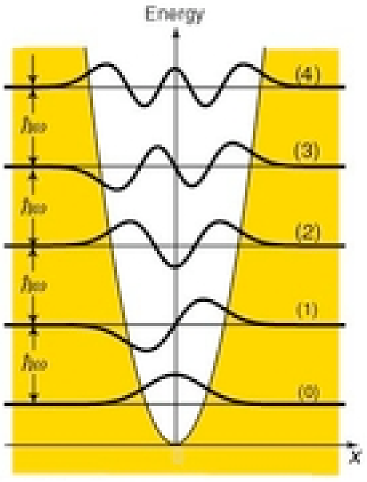
dynamical matrix

(Fourier transform of the force constant matrix/$(M_\kappa M_{\kappa'})^{1/2}$)

$$D_{\alpha,\alpha'}^{\kappa,\kappa'}(\mathbf{q}) \, \boldsymbol{\varepsilon}_{\kappa,\mathbf{q},n} = \omega_{\mathbf{q},n}^2 \boldsymbol{\varepsilon}_{\kappa,\mathbf{q},n}$$

Lattice dynamics in the harmonic approximation

In the QM picture we obtain a separable solution



Each mode *n* satisfies the quantum harmonic oscillator equation with discrete energy levels:

$$E_{\mathbf{q},n,m} = (m + \frac{1}{2})\hbar\omega_{\mathbf{q},n}$$

Therefore, the zero-point energy is:

$$F\left(T=0\right) = \frac{1}{2}\sum_{\mathbf{q},n} \hbar\omega_{\mathbf{q},n}$$

And the T-dependent free energy is:

$$F'\left(T\right) = k_{\mathrm{B}}T\sum_{\mathbf{q},n} \ln\left(1 - \mathrm{e}^{-\hbar\omega_{\mathbf{q},n}/k_{\mathrm{B}}T}\right)$$

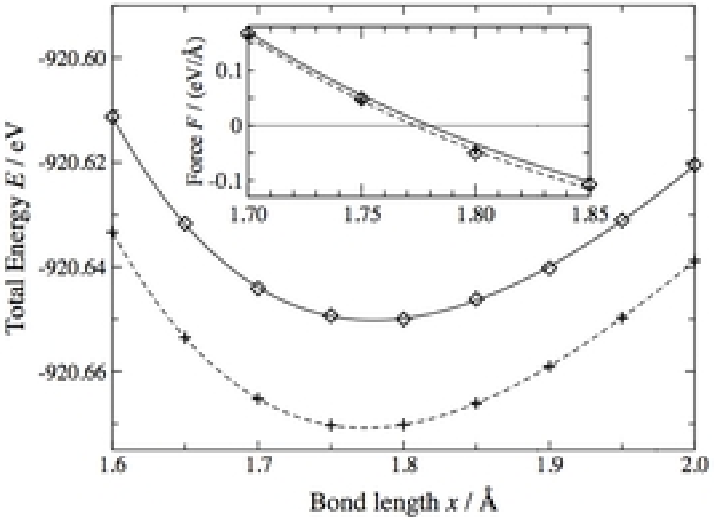
The finite displacement method

Displace ion κ' a small distance ±d in direction α' and evaluate the force on every ion in the system

Use this information to build up the force constants matrix:

$$\phi^{\kappa,\kappa'}_{\alpha,\alpha'} \approx \frac{F^{+}_{\kappa,\alpha} - F^{-}_{\kappa,\alpha}}{2d}$$

$6N$ single point energy calculations needed, although this can usually be reduced by taking advantage of the symmetries of the system



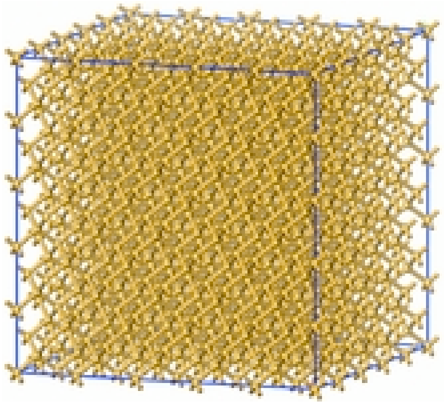
Interaction potential of a water dimer: forces in CASTEP and ONETEP

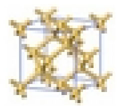
A. A. Mostofi, M. Robinson, N. D. M. Hine, P. D. Haynes, C.-K. Skylaris, and M. C. Payne, *Accurate ionic forces and geometry optimisation in linear scaling density-functional theory with local orbitals*

Use a supercell to obtain the dynamical matrix at different **q**-points:

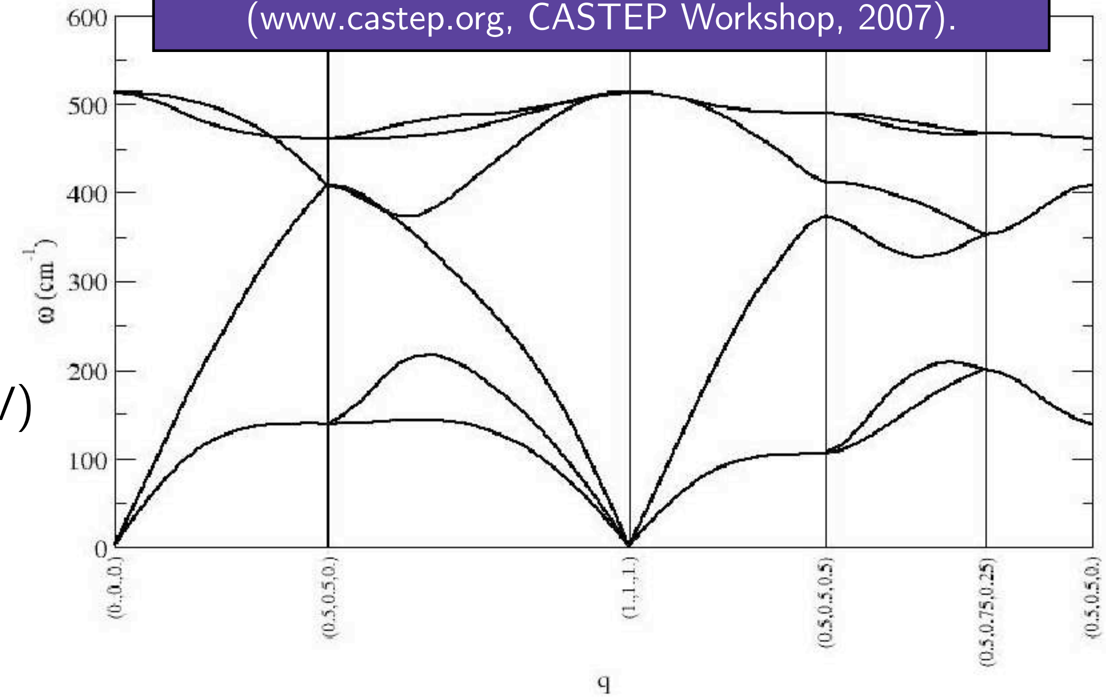
$$D^{\kappa,\kappa'}_{\alpha,\alpha'}(\mathbf{q}) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_a \phi^{\kappa,\kappa'}_{\alpha,\alpha'}(a,0)\, \mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{R}_a}$$

ONETEP calculations: bulk Si



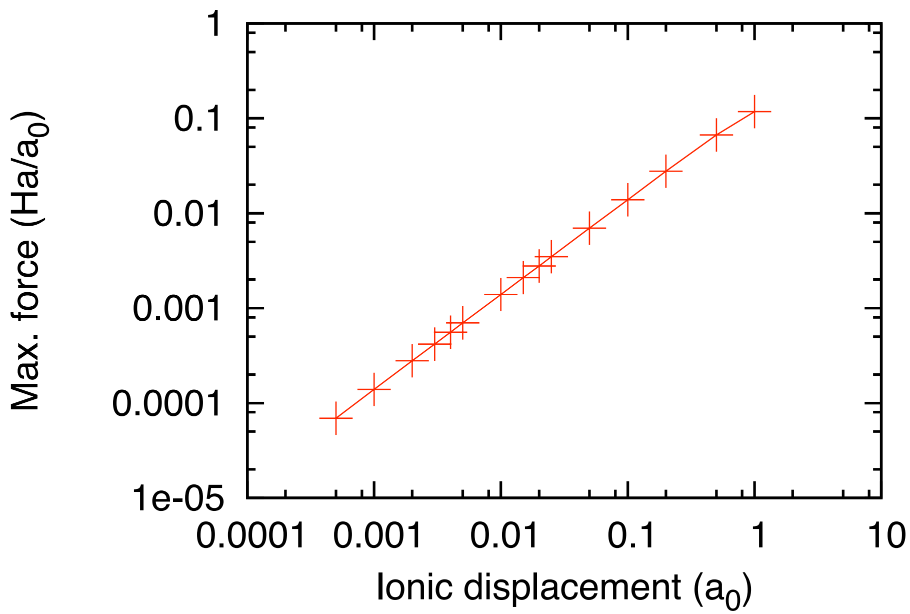


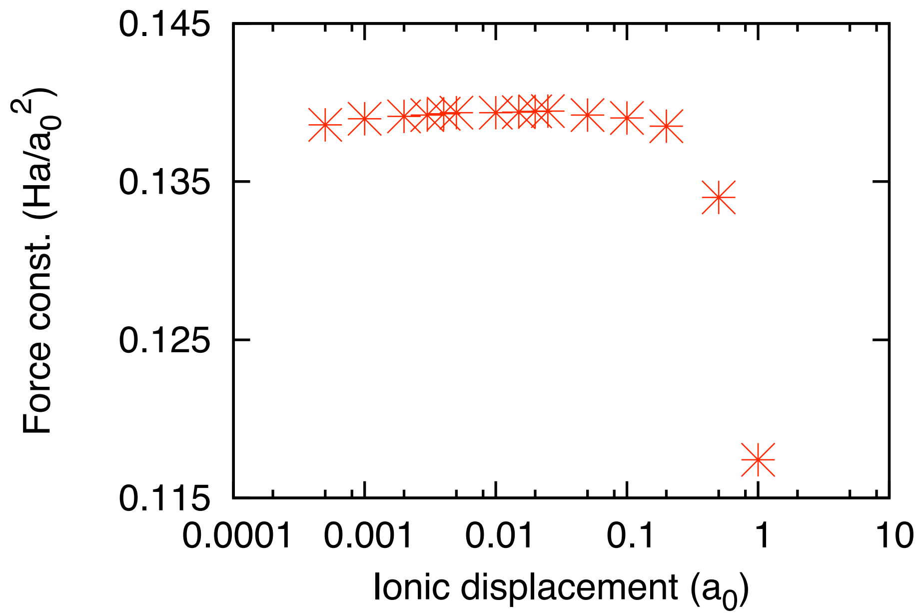
K. Refson, *Phonons and dielectric response calculations* (www.castep.org, CASTEP Workshop, 2007).



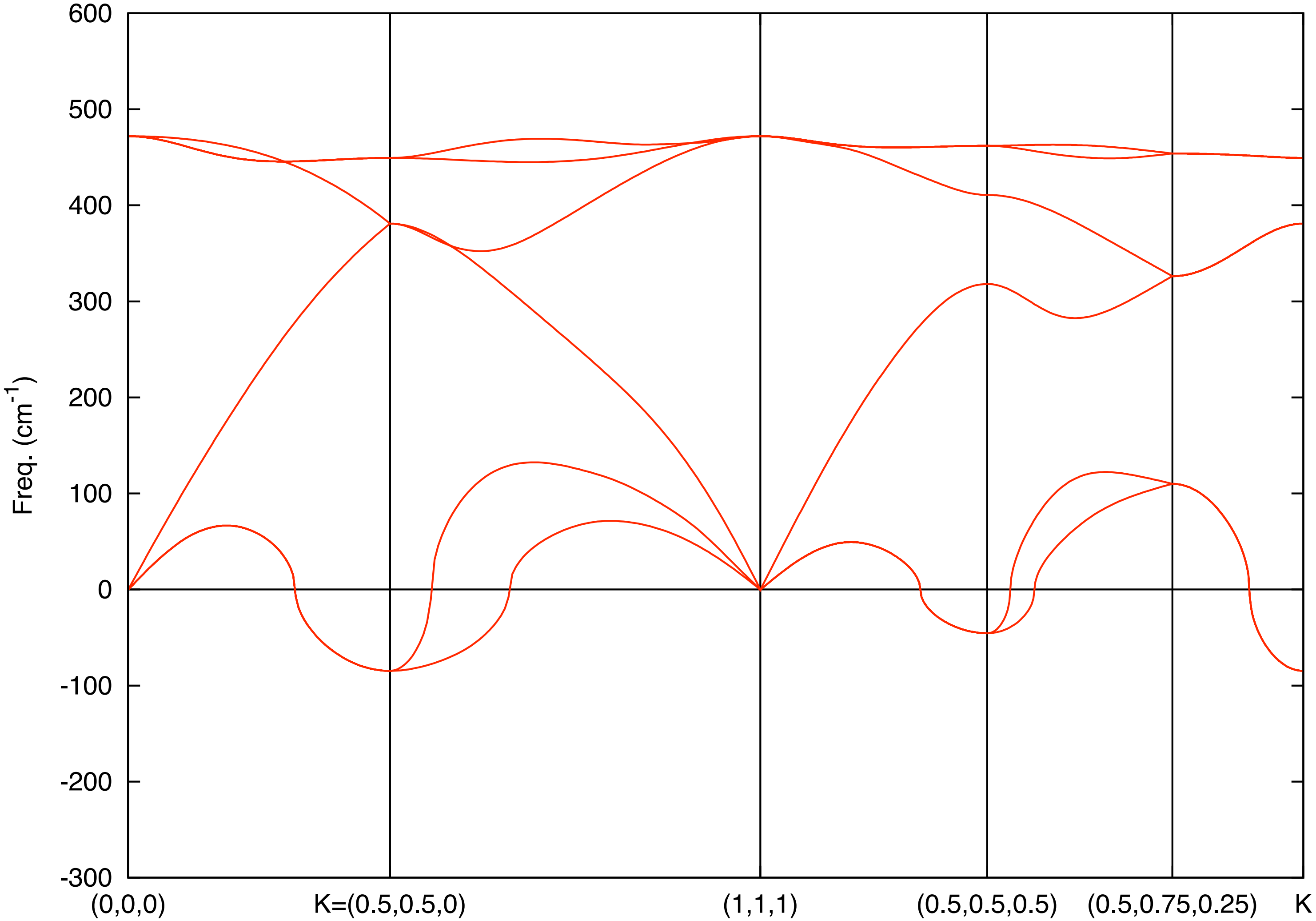
ONETEP:

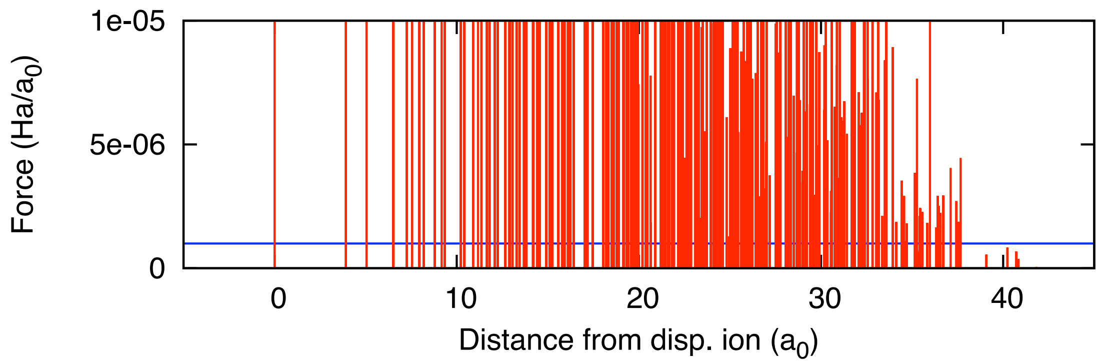
- 1000-atom SC ($L = 50.8\ a_0$)
- Plane wave cut-off energy = 29.4 Ha (800 eV)
- No density kernel truncation
- 9 NGWFs/atom
- NGWF radius = $8.0\ a_0$
- Ionic displacements = $0.0005\ a_0$ - $1.0\ a_0$





When phonons go bad





Ionic displacement (a_0):	
1.0	✗
0.5	
0.2	
0.1	
0.05	
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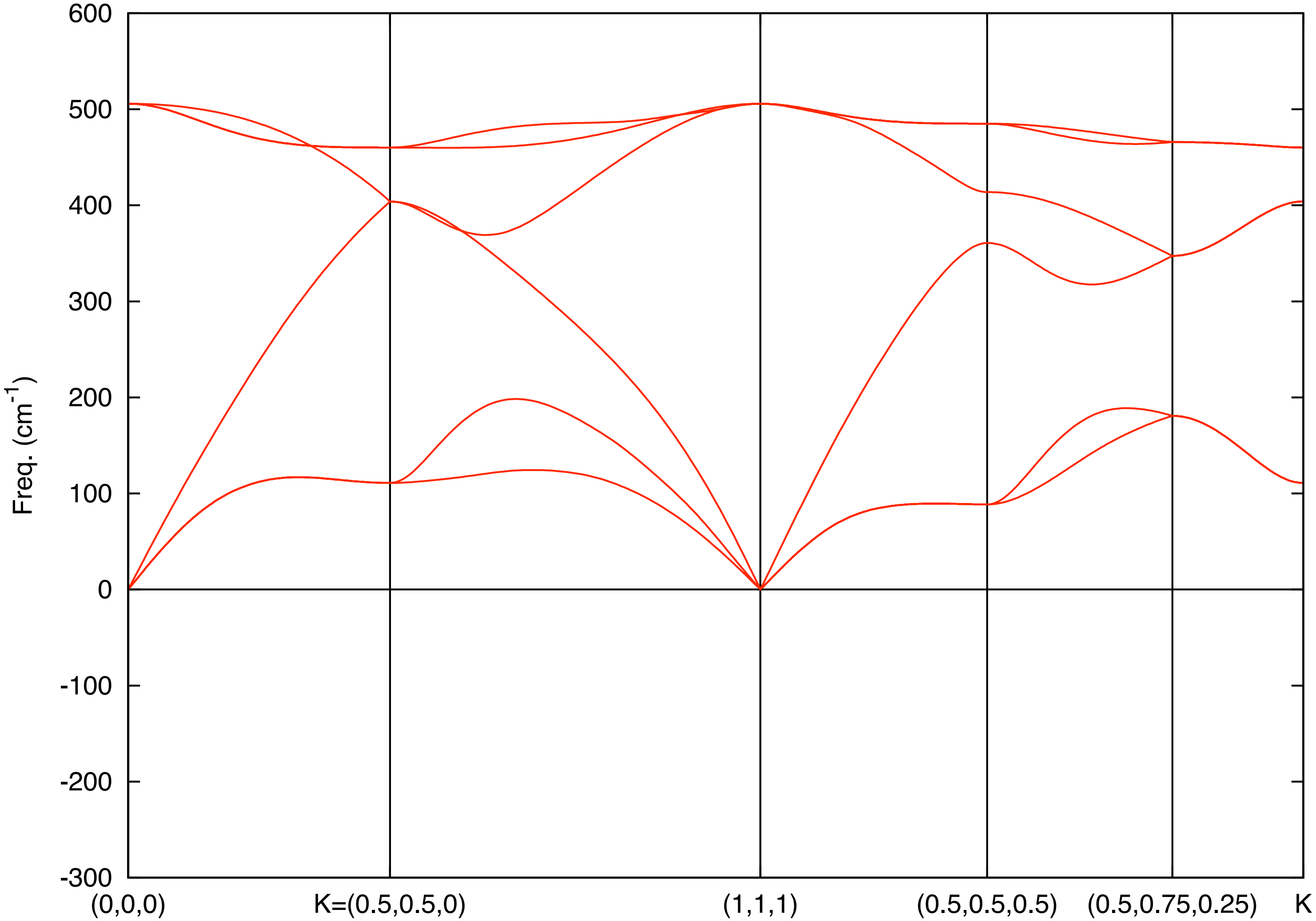

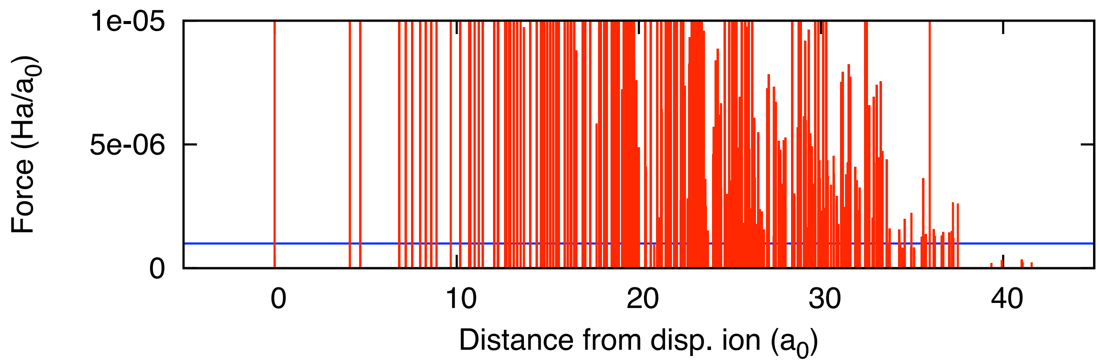

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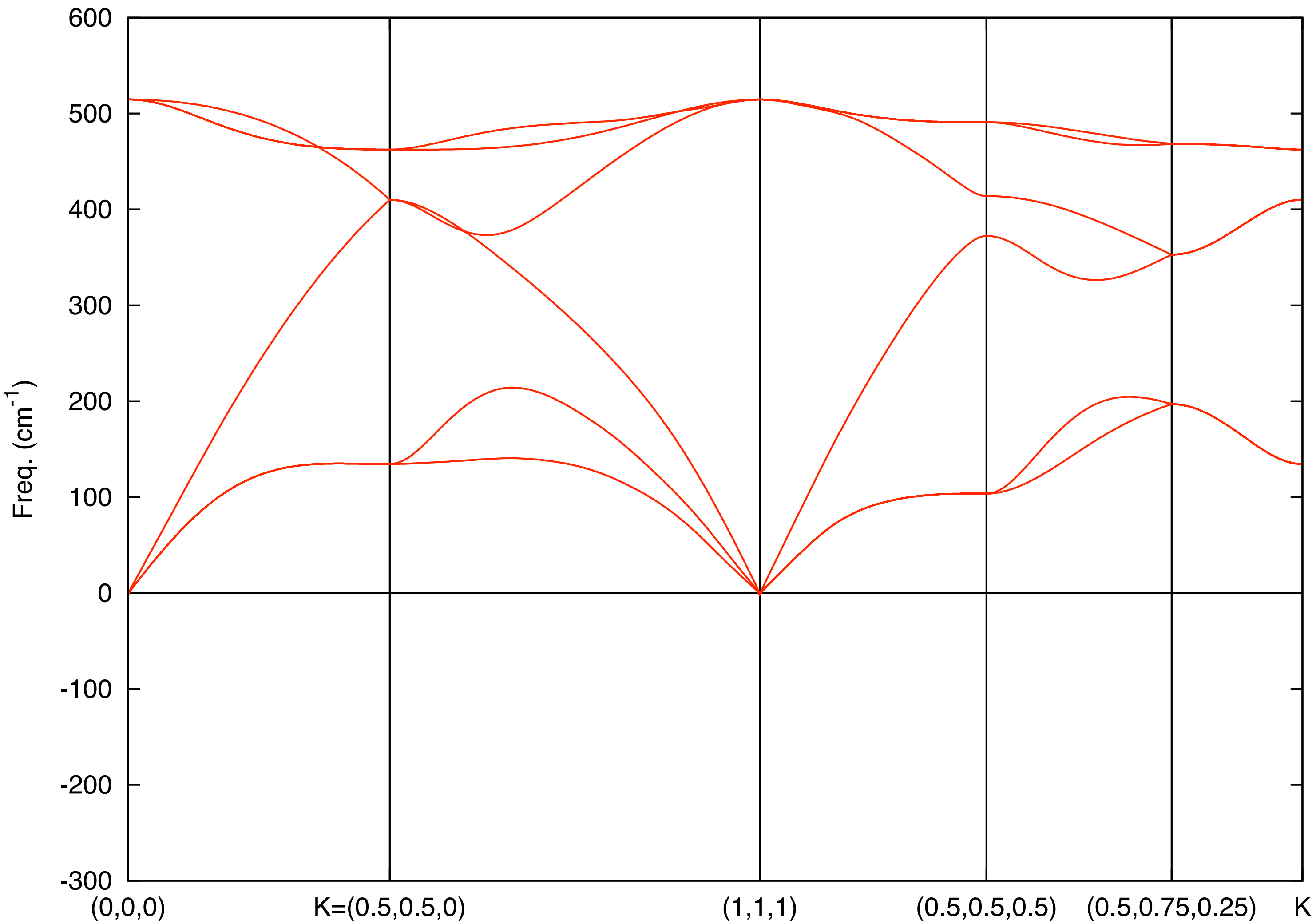

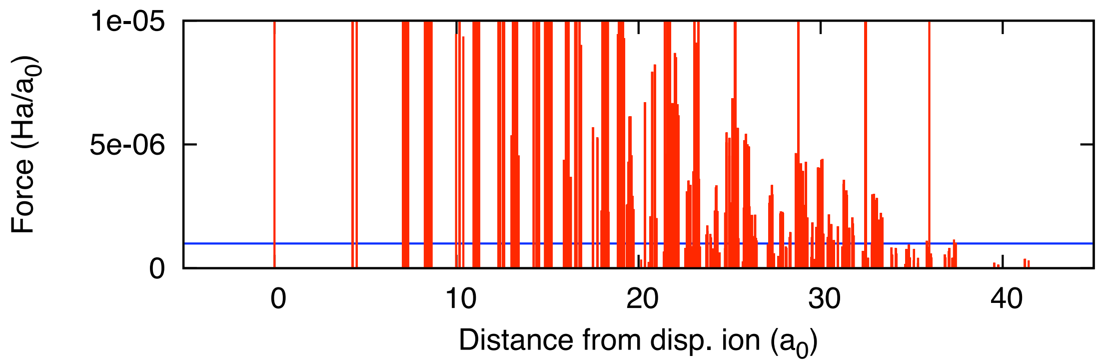

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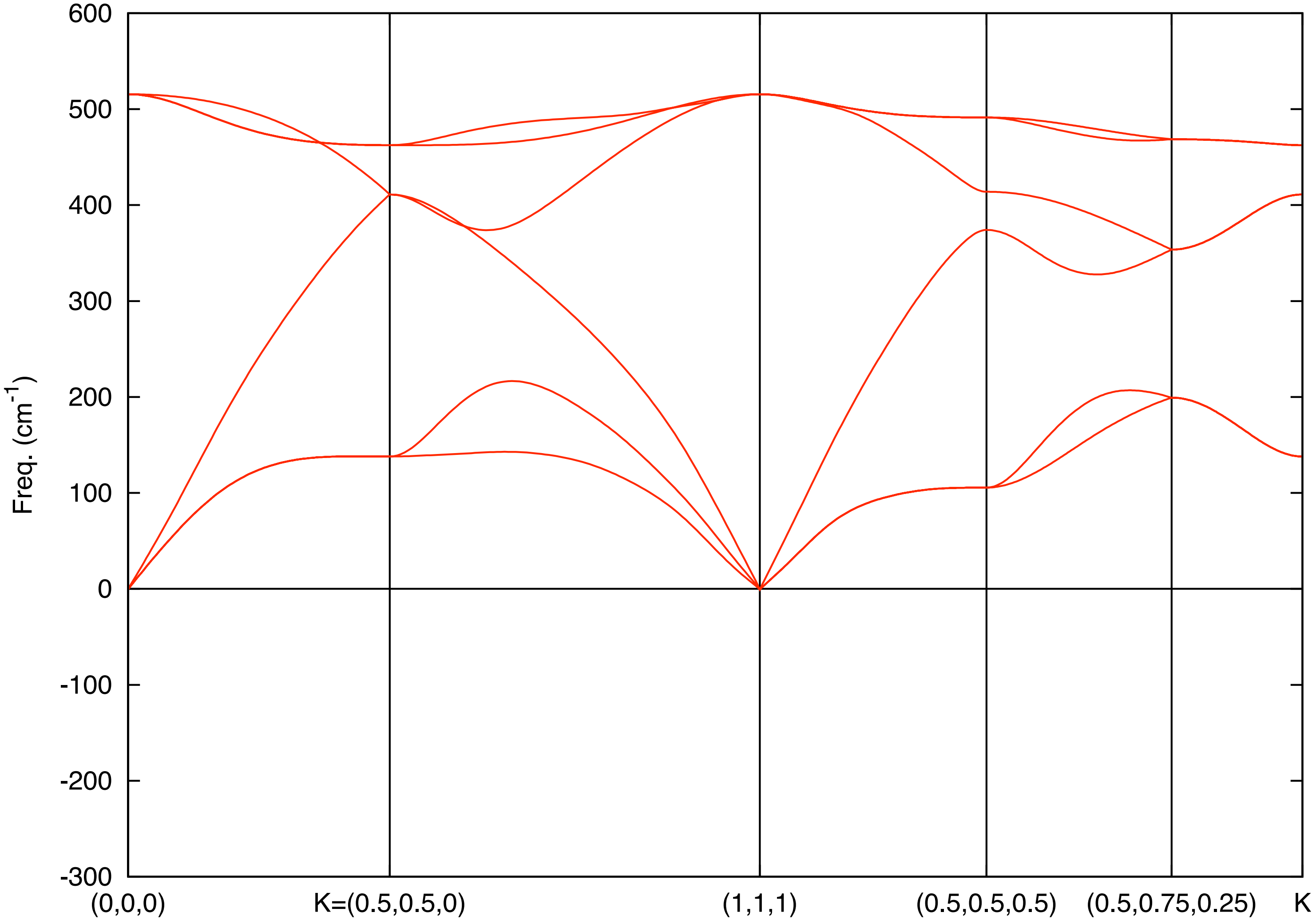

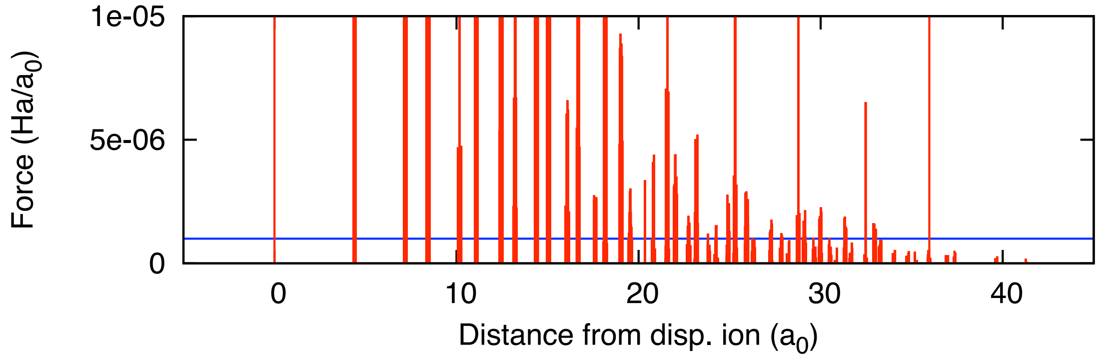

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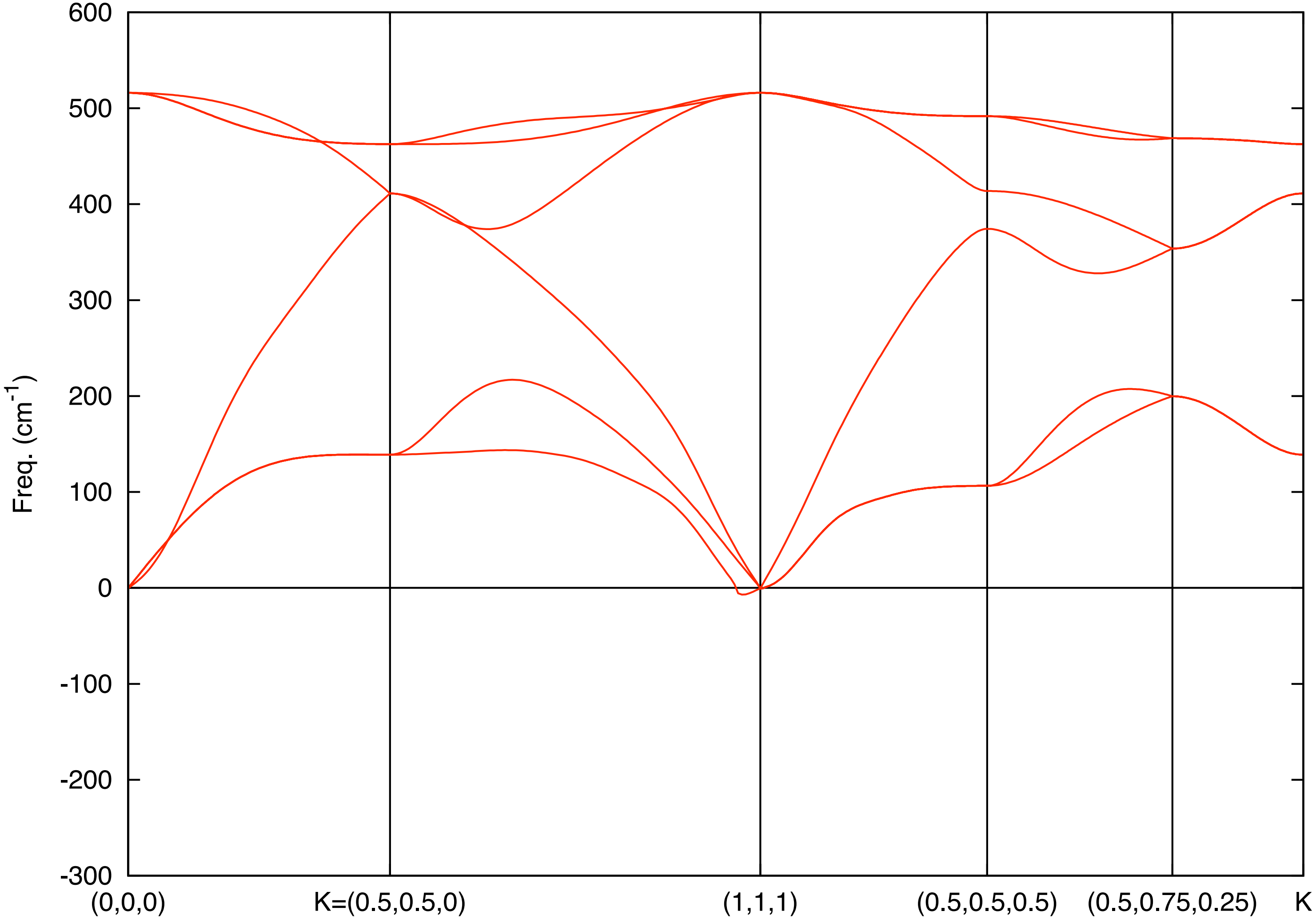

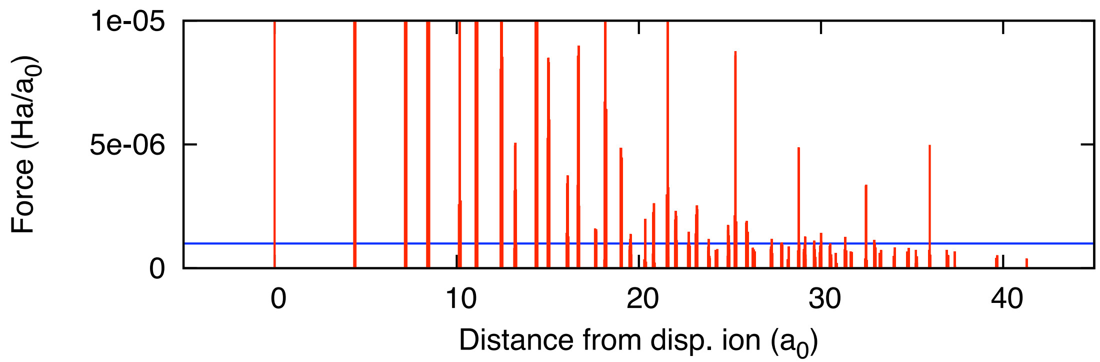

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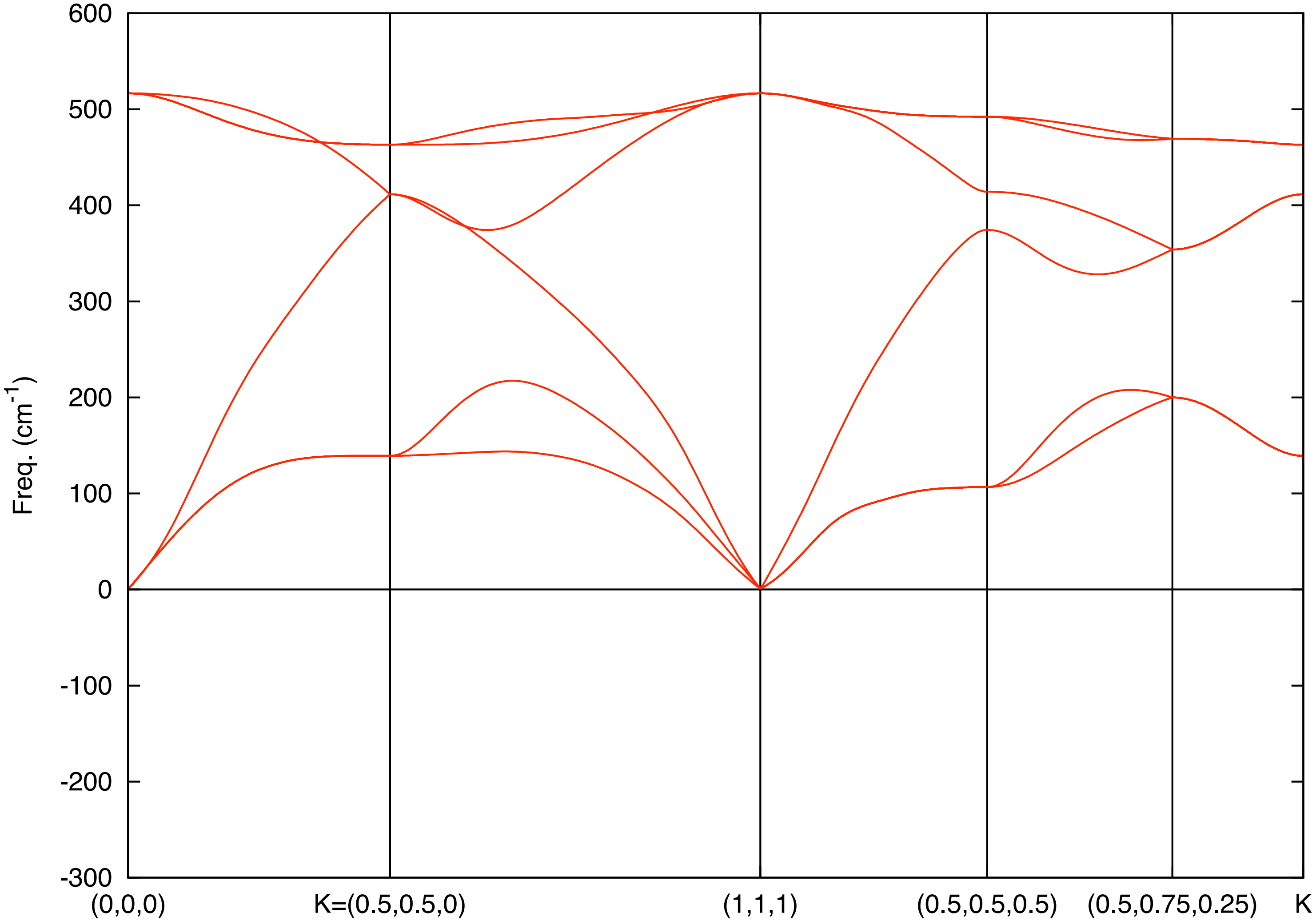

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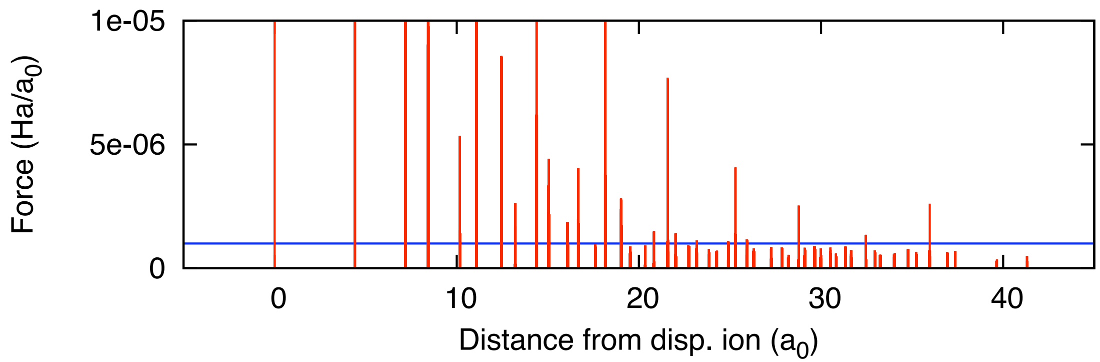

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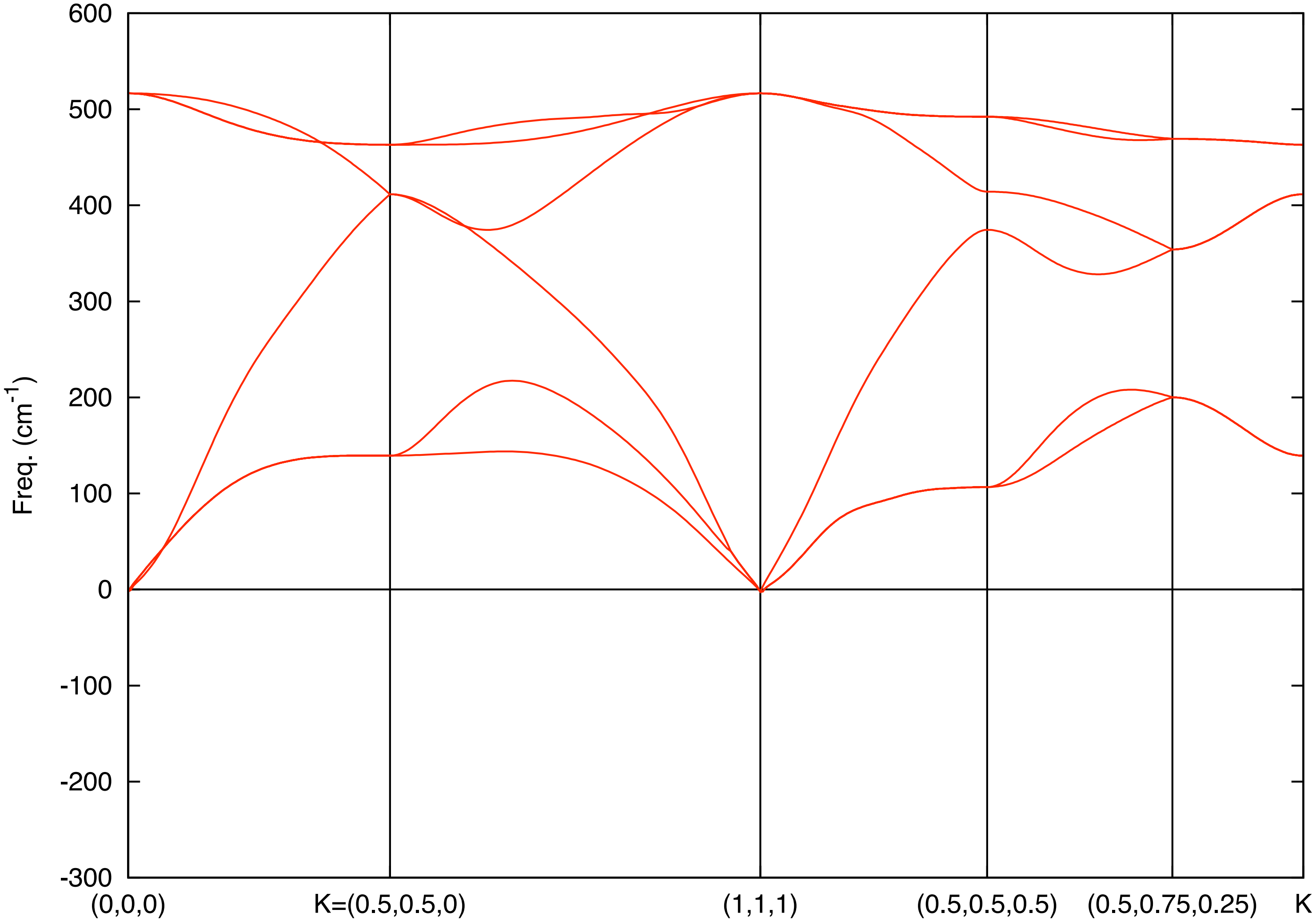

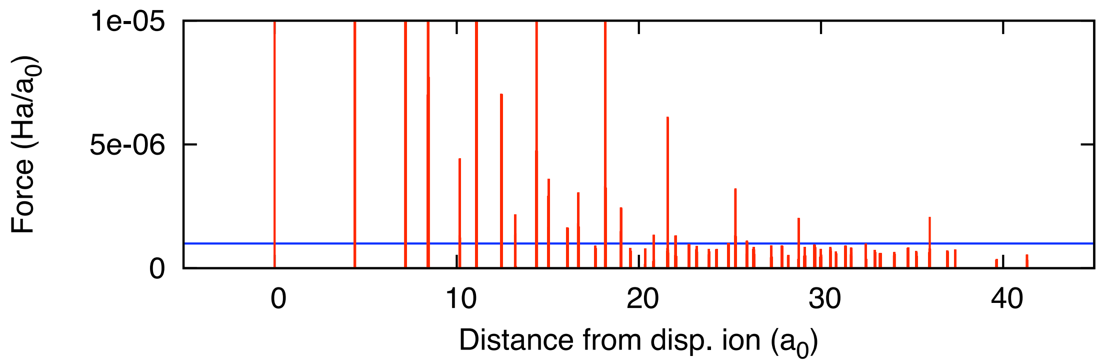

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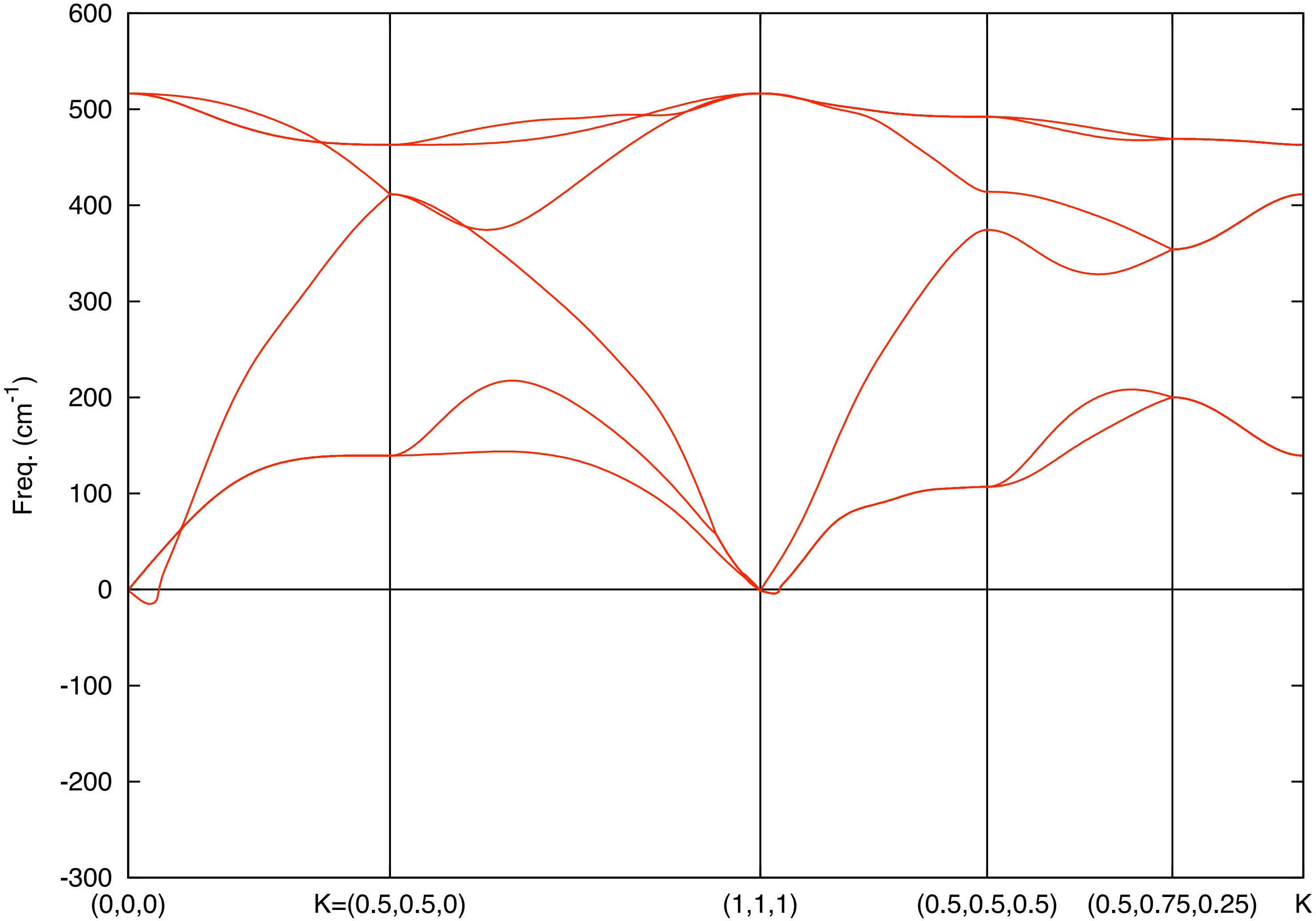

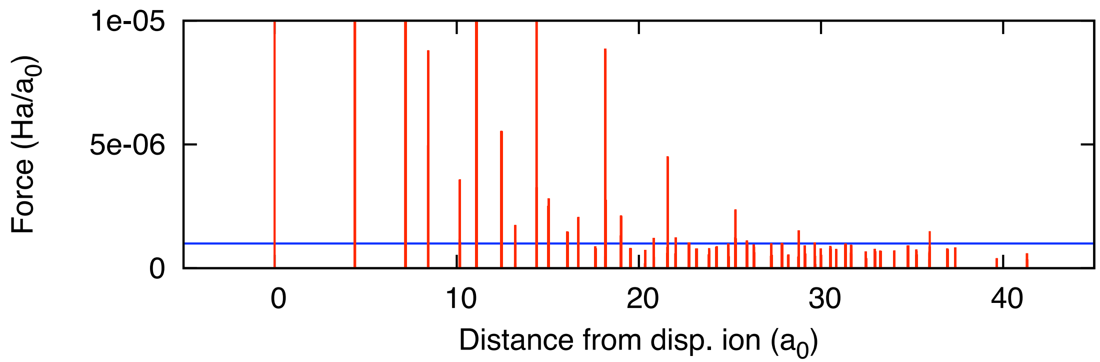

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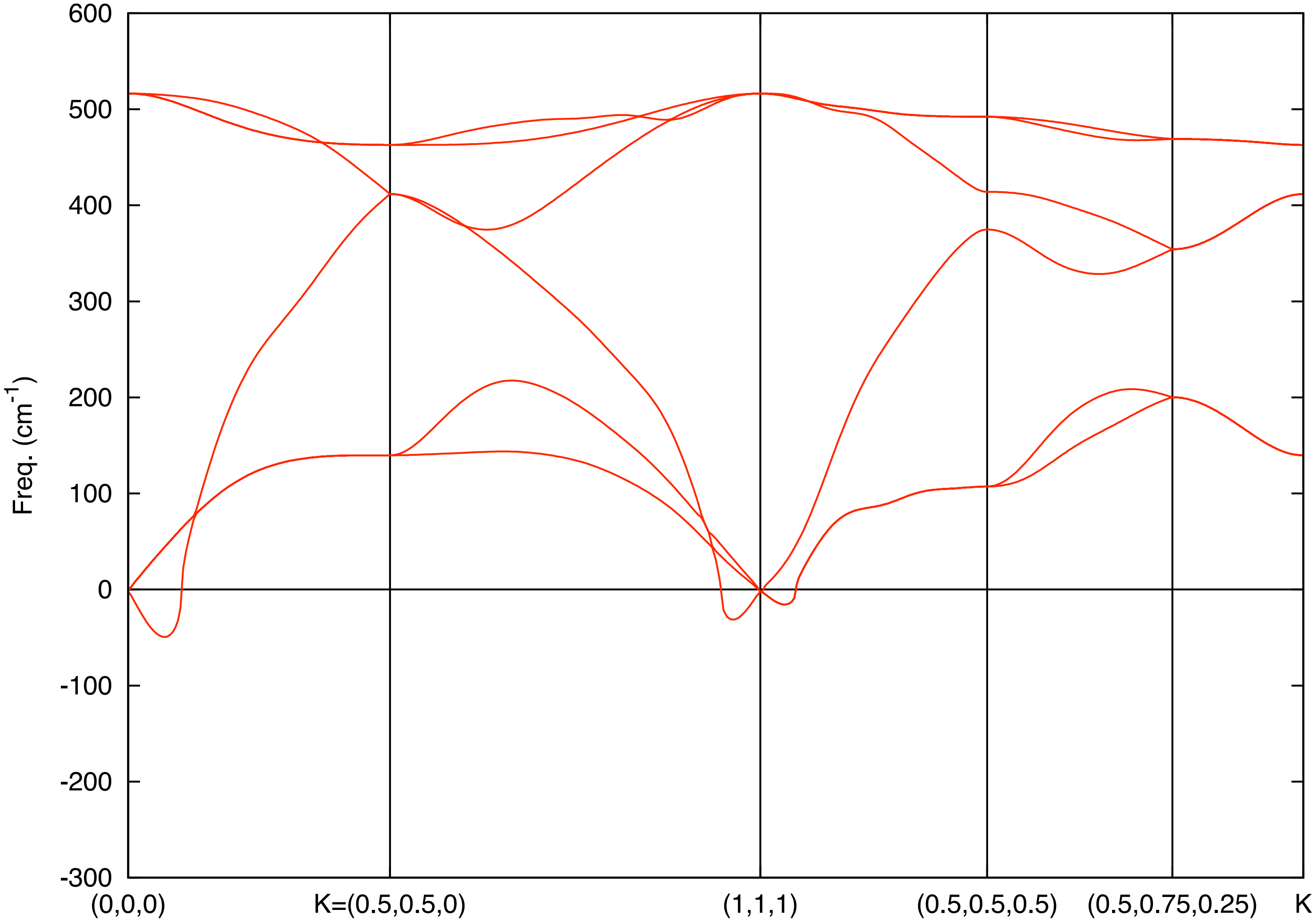

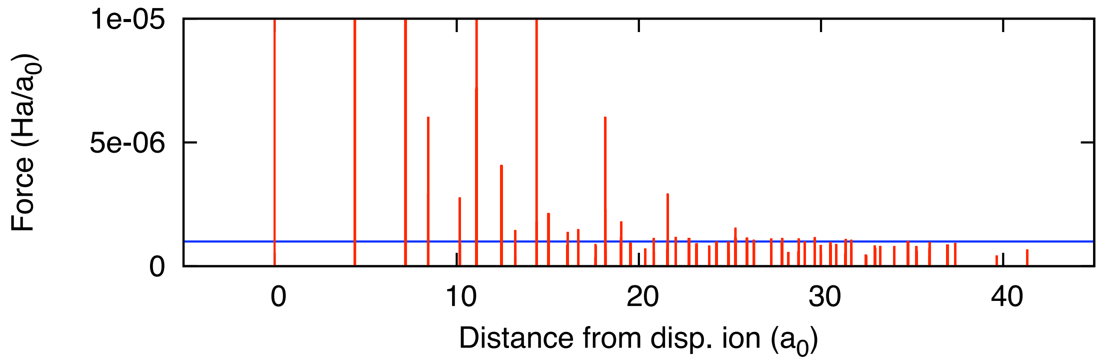

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0.005	
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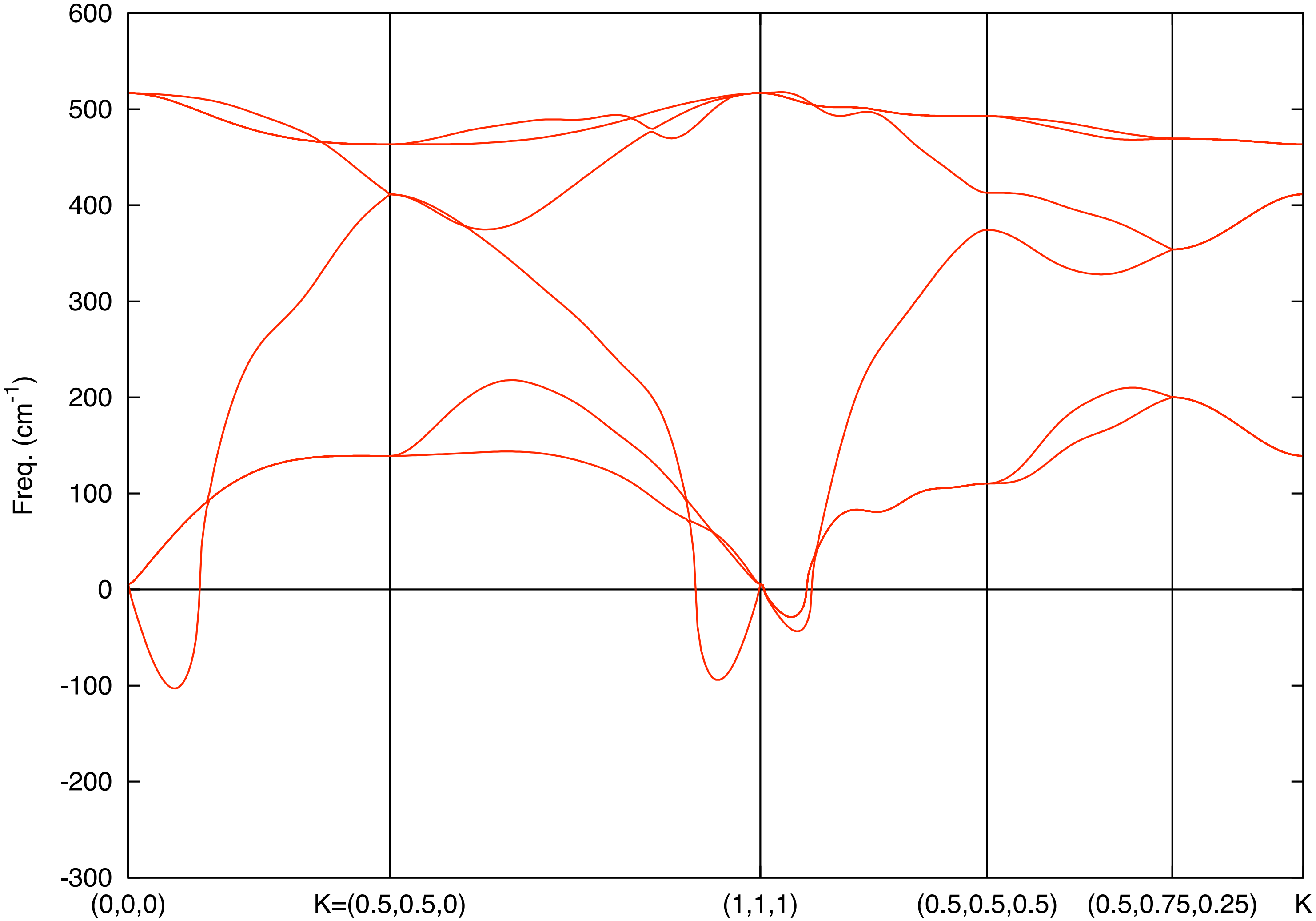
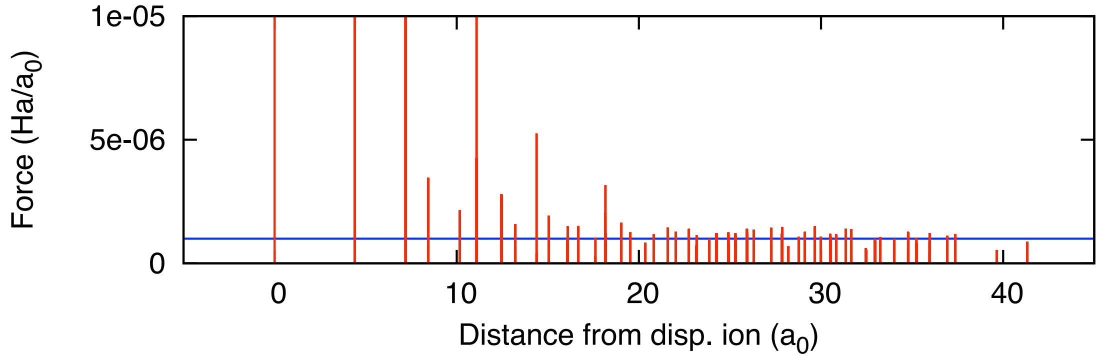
CASTEP default value

When phonons go bad





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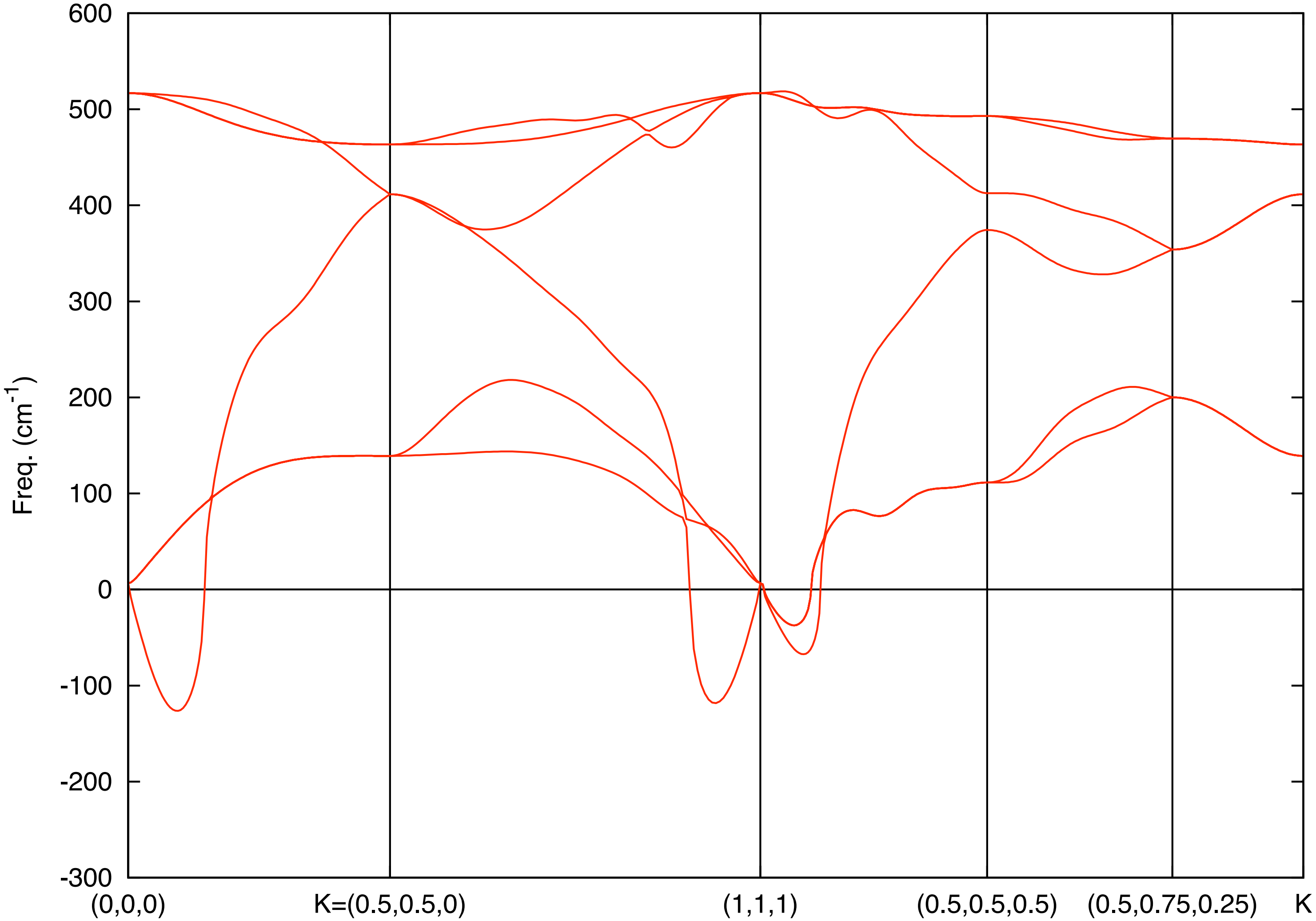

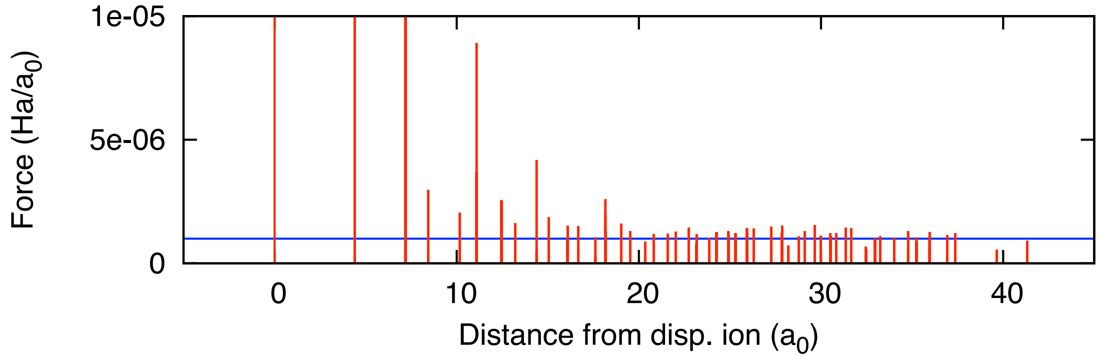

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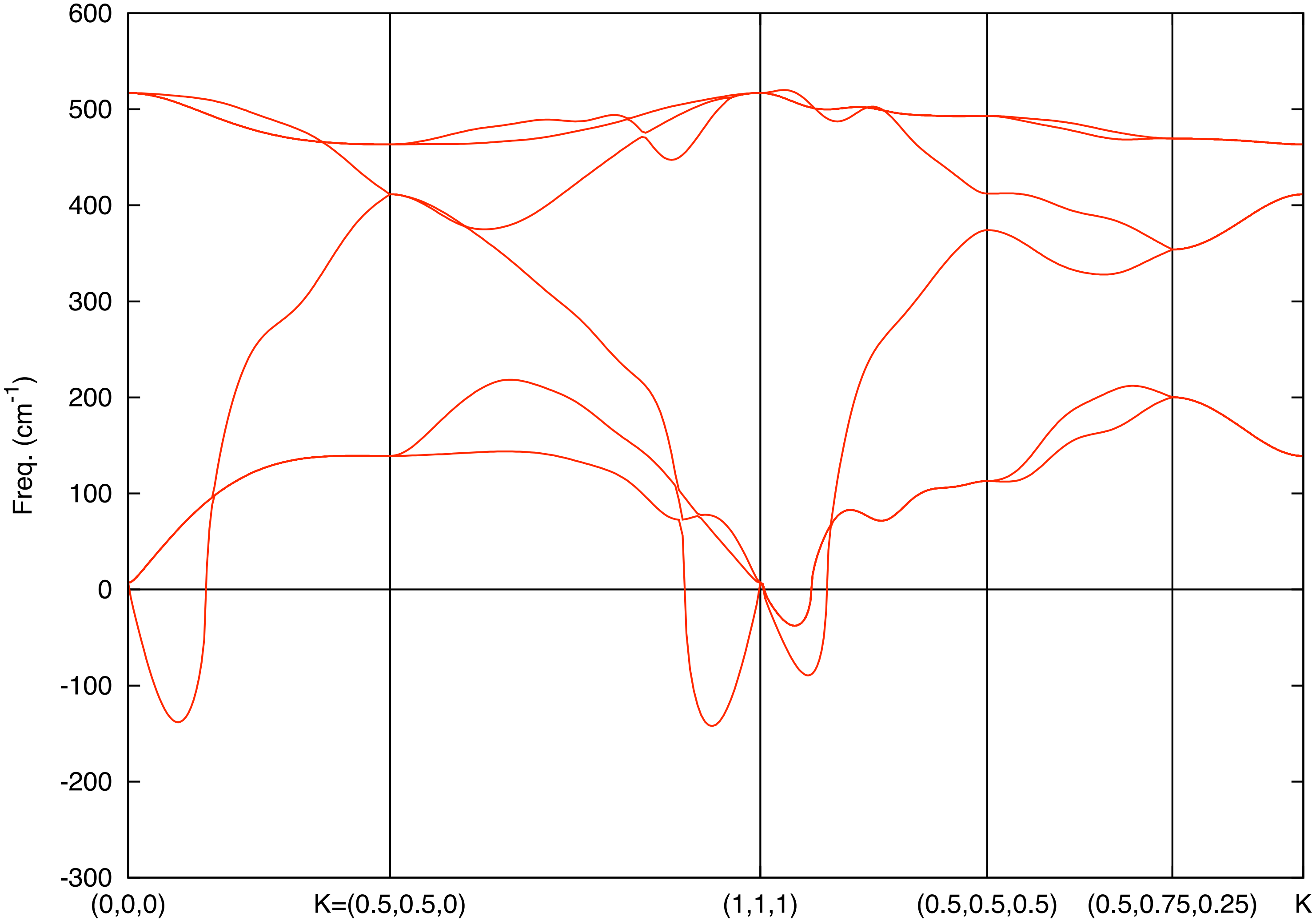

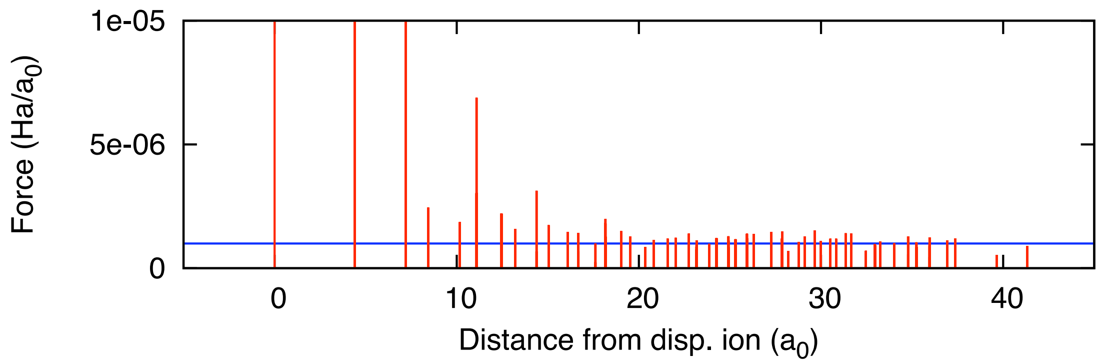

Ionic displacement (a_0):	
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0.5	✗
0.2	✔
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0.05	✔
0.025	✔
0.020	✗
0.015	✗
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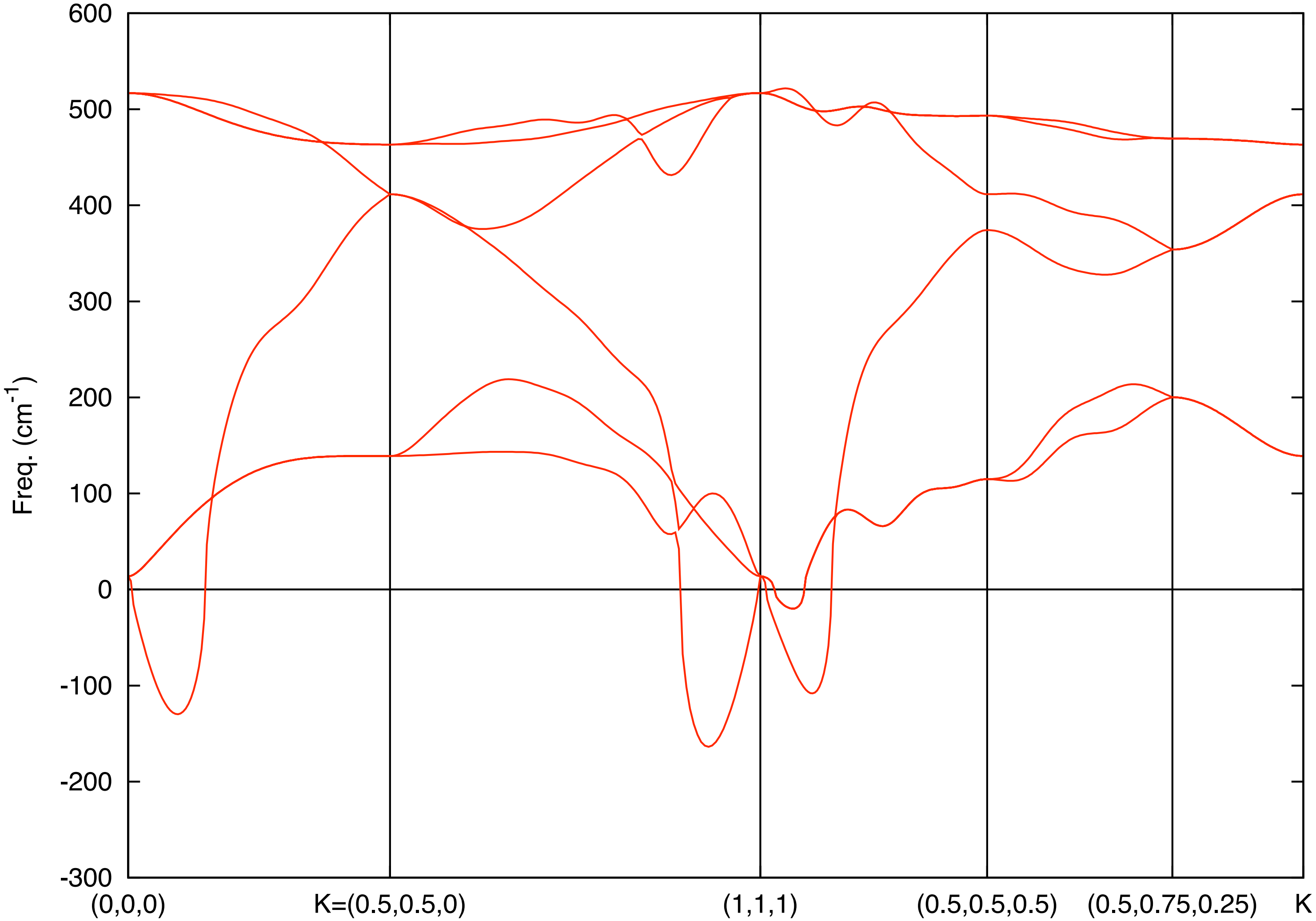

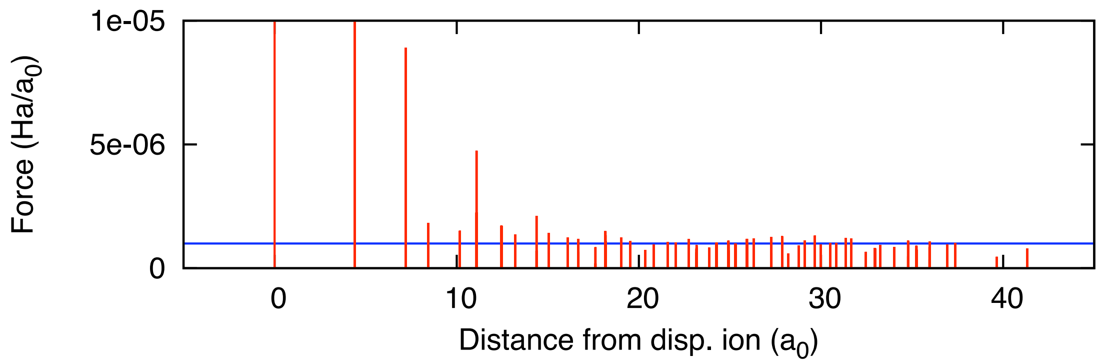

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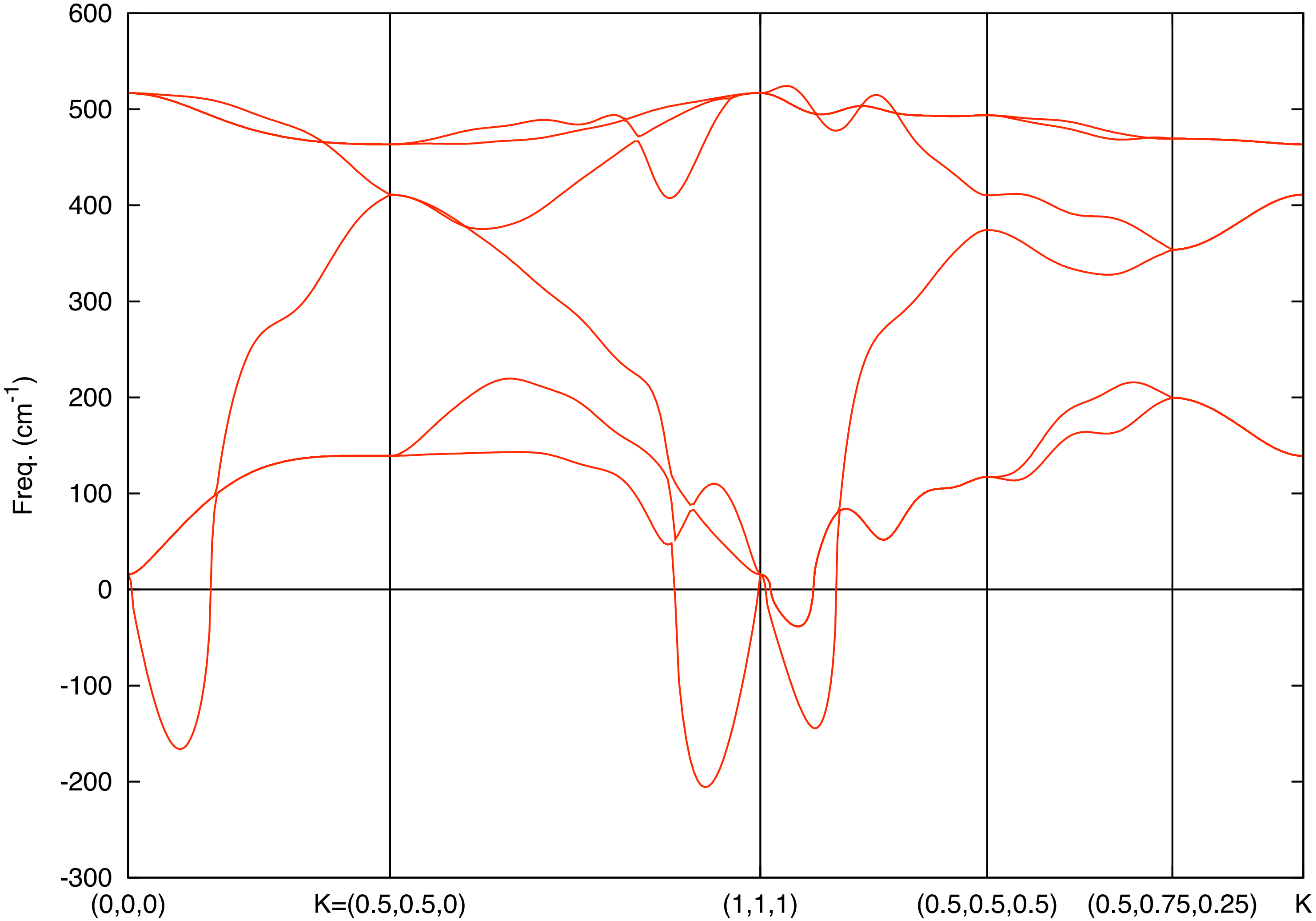

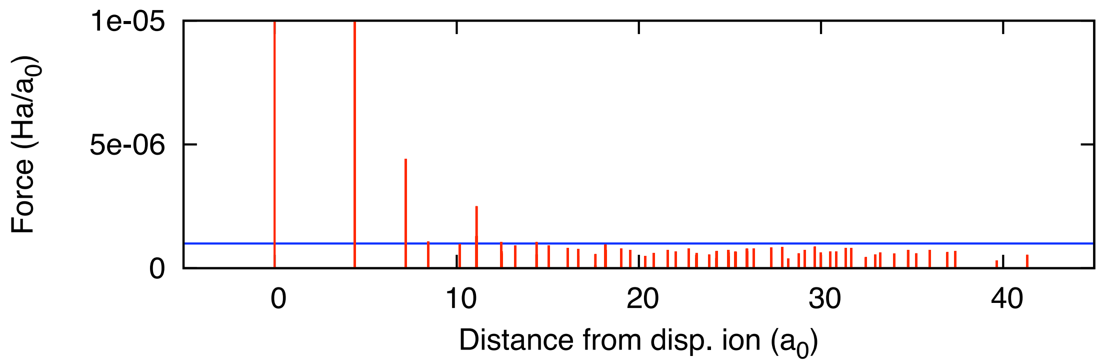

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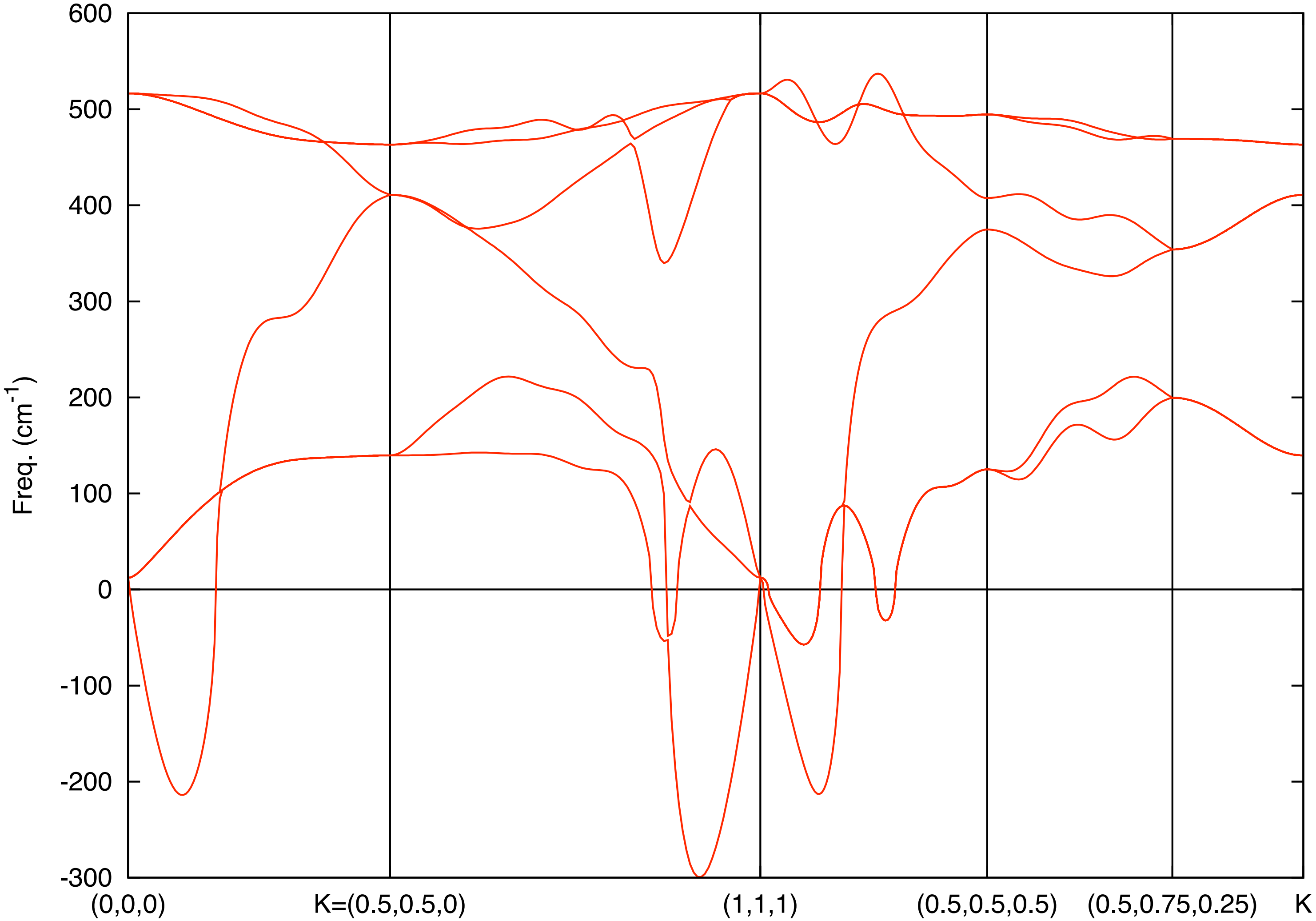

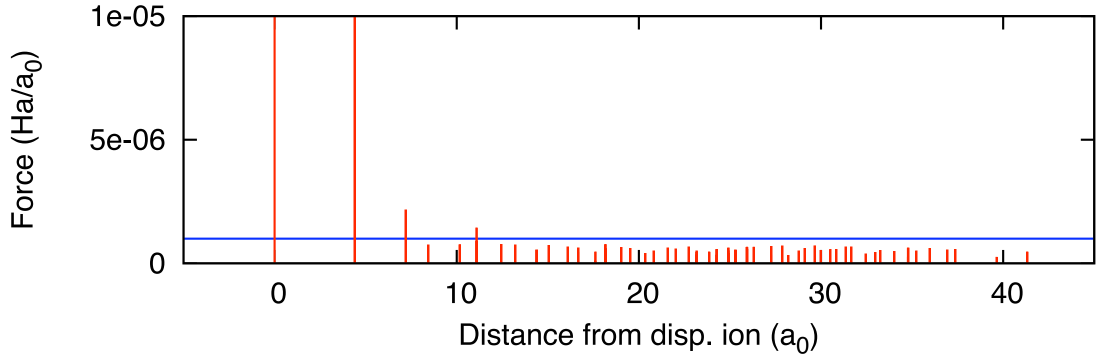

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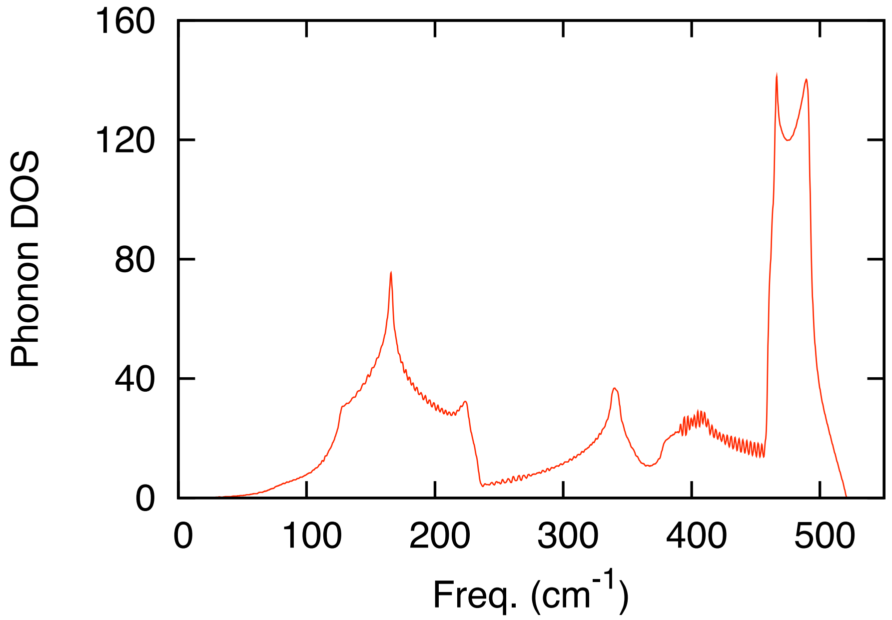
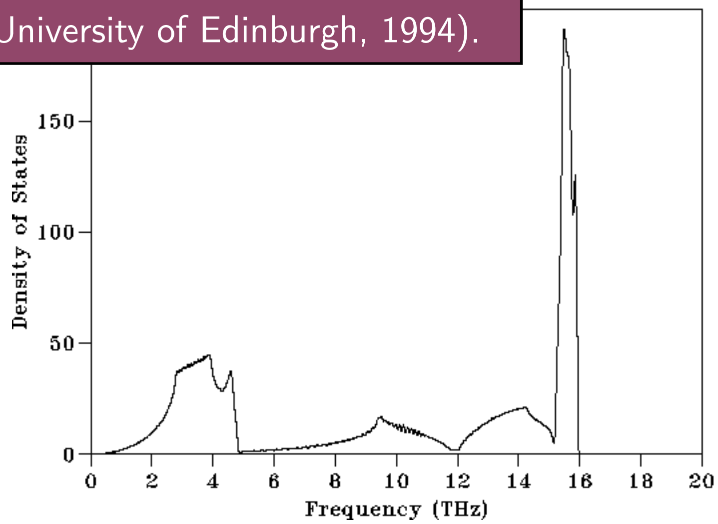
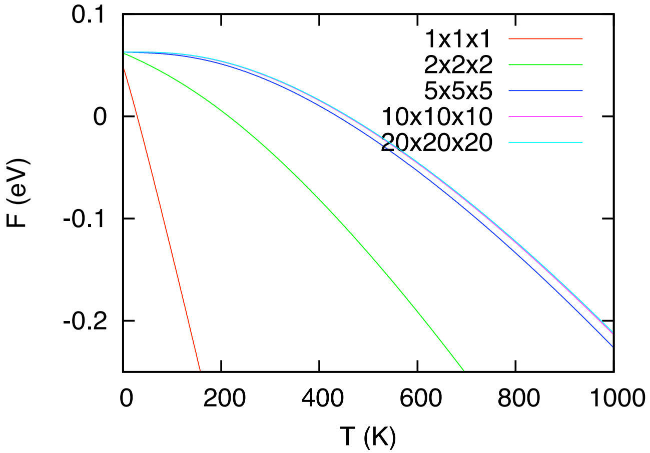
0.001	✘
0.0005	✘

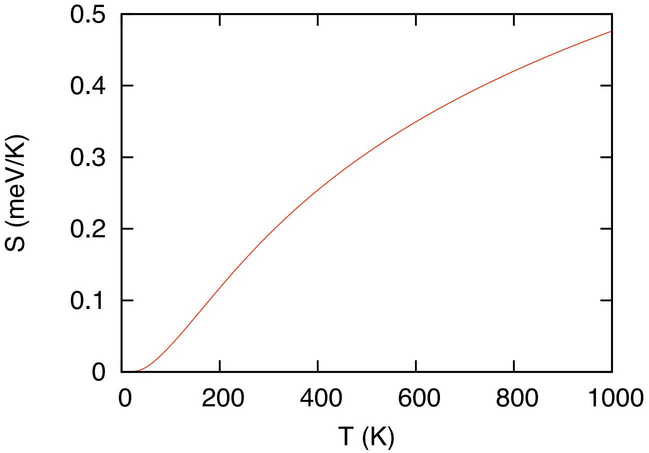
Phonon DOS and vibrational free energy

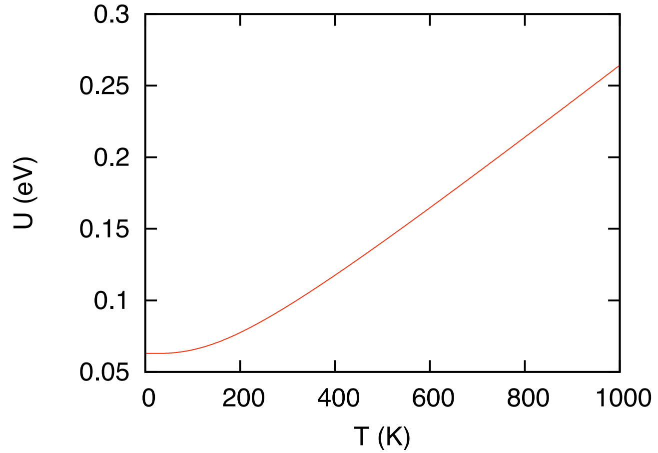


S. J. Clark, *Complex structures in tetrahedrally bonded semiconductors* (PhD Thesis, University of Edinburgh, 1994).







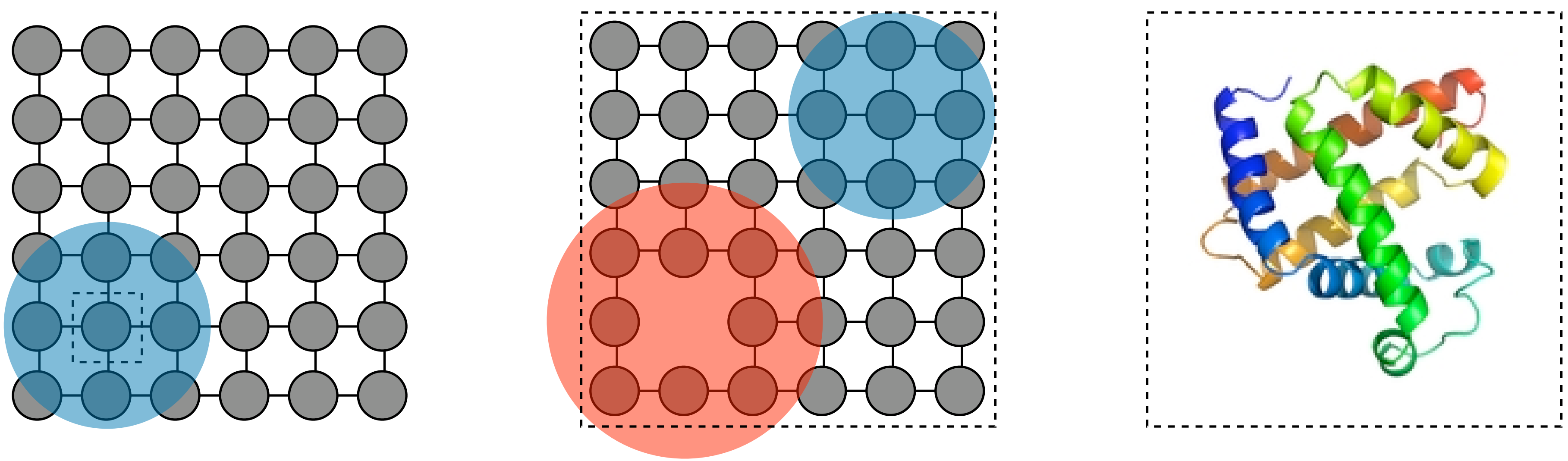


Conclusions

If you are interested in performing phonon calculations in ONETEP...

- Make use of the symmetry of the system
- Converge the forces with respect to the usual ONETEP parameters
- Be aware of rotational/librational modes for molecules
- Use fairly large displacements (~0.1 a_0); if possible try varying the displacement size
- Check that forces are symmetric and obey the acoustic sum rule
- Check that the max. force/noise ratio is $> 3.5\times10^3$

Future work



Defect systems and linear-scaling phonon calculations