

# **First-principles thermodynamic calculations in the harmonic and quasi-harmonic approximations using Quantum Espresso**

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# Outline

- Introduction
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    - Examples and limitations
  - The Quasi Harmonic Approximation (QHA)
    - Basic principles
    - Examples
  - The Quantum-Espresso code



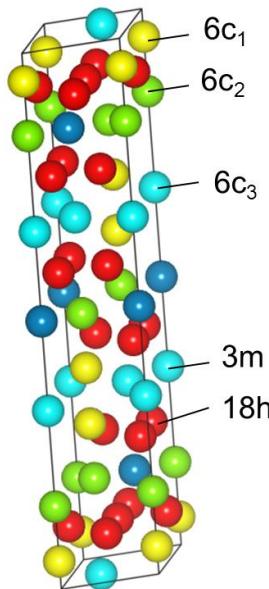
# Introduction

We will consider **solids**...

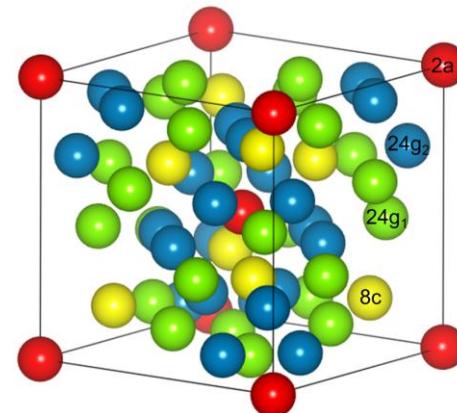
Most solids are **crystalline** (but not all! amorphous solids...)

Atoms are periodically distributed in a crystalline solid:

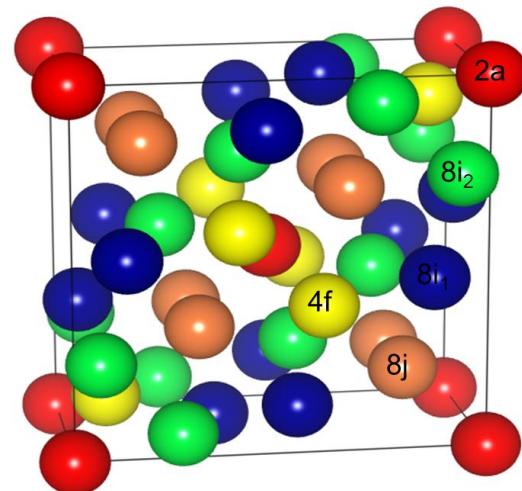
- Unit cell (type, lattice parameters)
  - Basis (number of atoms, atomic type, positions in the unit cell)



## $\mu$ phase



## $\chi$ phase

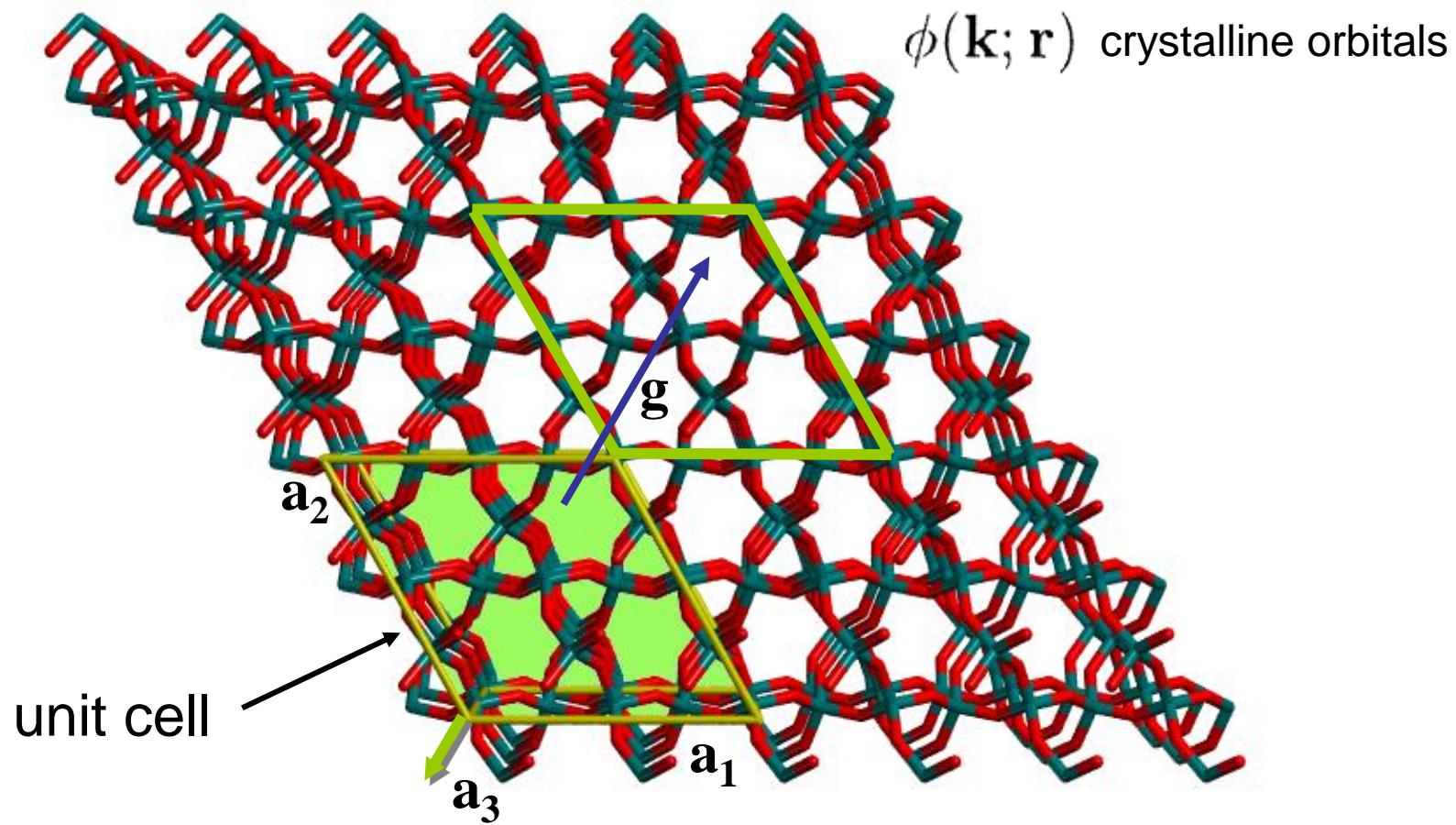


## $\sigma$ phase

# Periodic treatment for crystals

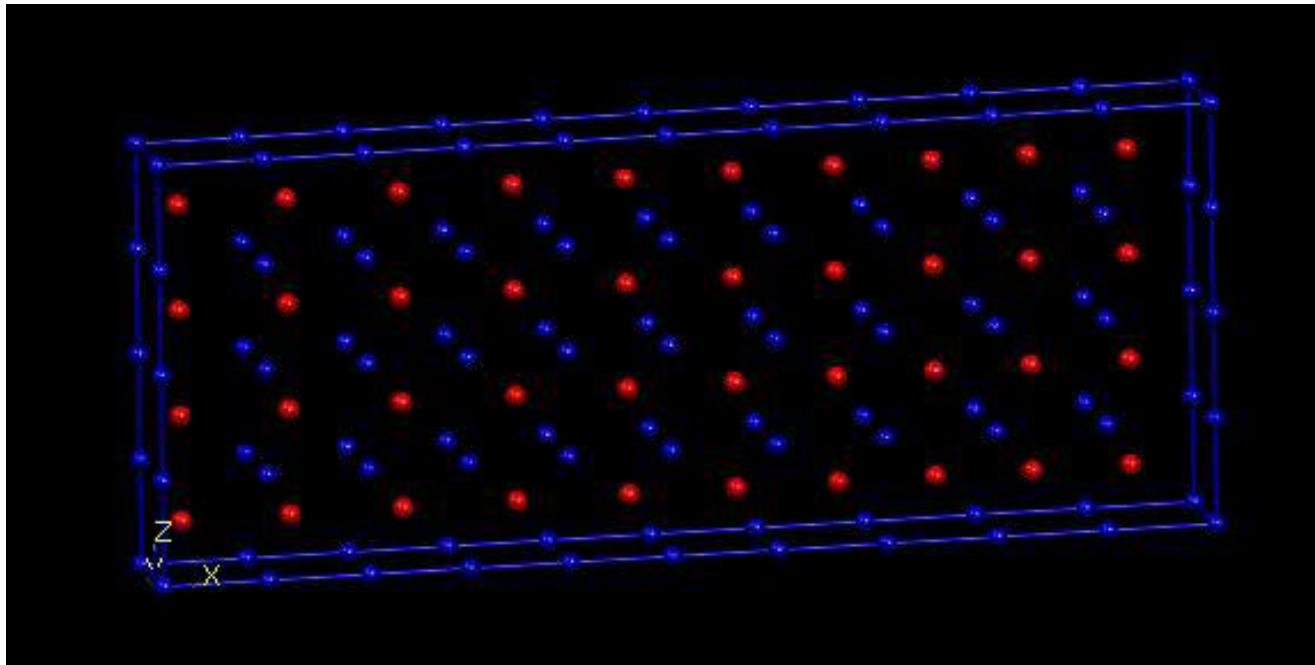
$$\text{Born Von-Karm}\ddot{\text{a}}\text{m rule: } \Psi(\mathbf{r} + N_i \mathbf{a}_i) = \Psi(\mathbf{r}) \quad i = 1, 2, 3$$

Bloch theorem:  $\phi(\mathbf{k}; \mathbf{r} + \mathbf{g}) = \phi(\mathbf{k}; \mathbf{r})e^{i\mathbf{k}\cdot\mathbf{g}}$ ,  $\mathbf{g} = l \mathbf{a}_1 + m \mathbf{a}_2 + n \mathbf{a}_3$



# Introduction

# Atoms move!

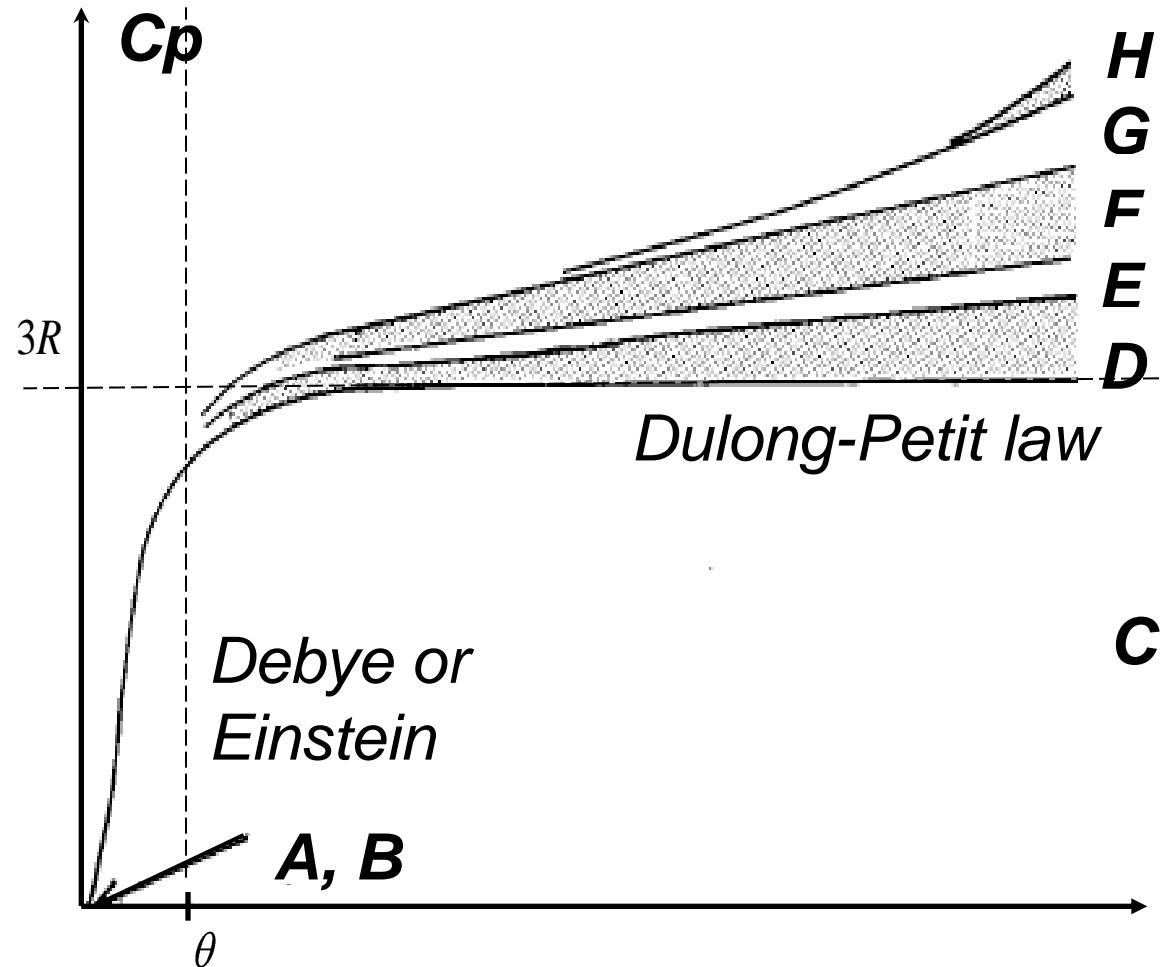


Animation by K. Parlinski (Phonon Software Package)  
primitive cubic crystal AB

# Is it samba? Tango? Or maybe salsa?



# Temperature dependence of heat capacity in real metals



**From G. Grimvall, Thermophysical properties of materials, North-Holland 1986**

(H) contribution to heat capacity because of vacancies formation, varies exponentially with  $T_m/T$ . Usually low for metals, but significant close to  $T_m$

(G) **correction factor to  $C_{el}$  because of non constant  $N(E_F)$**  at high T. For some metals, can be 50% or more of  $C_{el}$  at  $T_m$

(F) **electronic contribution**, linear in T. No enhancement factor ( $\lambda=0$ , no phonons-electrons coupling). Low T data cannot be extrapolated at high T

(E) *explicit anharmonic contributions to  $C_v$ , linear in T to leading order.*

**(D)  $C_P - C_V$  contribution.** Usually dominated by vibrational part, linear in T. Higher order contributions come from higher order anharmonicity and electronic high T excitations.

(C) main contribution from **harmonic vibrational heat capacity**. Asymptotic value  $3R$  at high T.

**(B) phonons contribution** (Debye or Einstein model, Debye approximation for low T)

(A) **electronic heat capacity** (linear in T, enhancement factor for phonon coupling)



# The harmonic approximation

## Two fundamental assumptions:

1. *atoms oscillates around a mean equilibrium position which is a Bravais lattice site*
  2. *typical excursions of each atom from its equilibrium position is small compared to the interatomic spacing* (how much small?)

Let's consider a periodic solid. We indicate with

$$\mathbf{R}_I = \mathbf{R}_\mu + \mathbf{d}_s$$

the equilibrium positions of the atoms.  $\mathbf{R}_\mu$  indicate the Bravais lattice vectors and  $\mathbf{d}_s$  the positions of the atoms in one unit cell ( $s = 1, \dots, N_{at}$ ).

We take  $N$  unit cells with Born-von Karman periodic boundary conditions.  $\Omega$  is the volume of one cell and  $V = N\Omega$  the volume of the solid.

At time  $t$ , each atom is displaced from its equilibrium position.  $\mathbf{u}_l(t)$  is the displacement of the atom  $l$ .



# The harmonic approximation

Within the *Born-Oppenheimer adiabatic approximation* the nuclei move in a potential energy given by the total energy of the electron system calculated (for instance within DFT) at fixed nuclei. We call

$$E_{tot}(\mathbf{R}_I + \mathbf{u}_I)$$

this energy. The electrons are assumed to be in the ground state for each nuclear configuration.

If  $|\mathbf{u}_i|$  is small, we can expand  $E_{tot}$  in a Taylor series with respect to  $\mathbf{u}_i$ . Within the *harmonic approximation*:

$$E_{tot}(\mathbf{R}_I + \mathbf{u}_I) = E_{tot}(\mathbf{R}_I) + \sum_{I\alpha} \cancel{\frac{\partial E_{tot}}{\partial \mathbf{u}_{I\alpha}} \mathbf{u}_{I\alpha}} + \frac{1}{2} \sum_{I\alpha, J\beta} \boxed{\frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}}} \mathbf{u}_{I\alpha} \mathbf{u}_{J\beta} + \dots$$

where the derivatives are calculated at  $\mathbf{u}_I = 0$  and  $\alpha$  and  $\beta$  indicate the three Cartesian coordinates.



# The equations of motion

$$H = \sum_{I\alpha} \frac{\mathbf{P}_{I\alpha}^2}{2M_I} + \frac{1}{2} \sum_{I\alpha, J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{I\alpha} \mathbf{u}_{J\beta}$$

where  $\mathbf{P}_I$  are the momenta of the nuclei and  $M_I$  their masses. The classical motion of the nuclei is given by the  $N \times 3 \times N_{at}$  functions  $\mathbf{u}_{I\alpha}(t)$ . These functions are the solutions of the Hamilton equations:

$$\begin{aligned}\dot{\mathbf{u}}_{l\alpha} &= \frac{\partial H}{\partial \mathbf{P}_{l\alpha}} = \frac{\mathbf{P}_{l\alpha}}{M_l} \\ \dot{\mathbf{P}}_{l\alpha} &= -\frac{\partial H}{\partial \mathbf{u}_{l\alpha}} = -\sum_{J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{l\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{J\beta}\end{aligned}$$

or:

$$M_I \ddot{\mathbf{u}}_{I\alpha} = - \sum_{J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{J\beta} = F_{J\beta}$$

Linear system of  $3N$  2<sup>nd</sup> order differential equations of motion



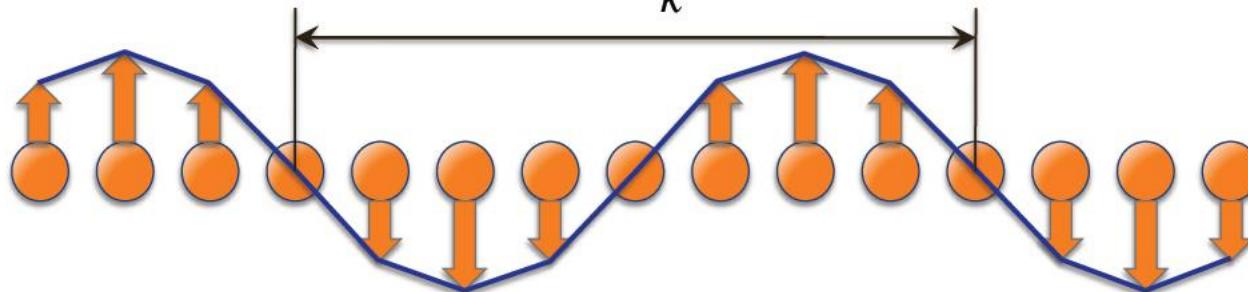
# Phonons solutions

We can search the solution in the form of a phonon. Let's introduce a vector  $\mathbf{q}$  in the first Brillouin zone. For each  $\mathbf{q}$  we can write:

$$\mathbf{u}_{\mu s\alpha}(t) = \frac{1}{\sqrt{M_s}} \mathbf{u}_{s\alpha}(\mathbf{q}) e^{i(\mathbf{q}\mathbf{R}_\mu - \omega_\mathbf{q} t)}$$

where the time dependence is given by a simple exponential  $e^{i\omega_q t}$  and the displacement of the atoms in each cell identified by the Bravais lattice  $\mathbf{R}_\mu$  can be obtained from the displacements of the atoms in one unit cell, for instance the one that corresponds to  $\mathbf{R}_\mu = 0$ :  $\frac{1}{\sqrt{M_s}} \mathbf{u}_{sa}(\mathbf{q})$ .

$$\lambda = \frac{2\pi}{k}$$



# The dynamical matrix

Inserting this solution in the equations of motion and writing  $I = (\mu, s)$ ,  $J = (\nu, s')$  we obtain an eigenvalue problem for the  $3 \times N_{at}$  variables  $\mathbf{u}_{s\alpha}(\mathbf{q})$ :

$$\omega_{\mathbf{q}}^2 \mathbf{u}_{s\alpha}(\mathbf{q}) = \sum_{s'\beta} D_{s\alpha s'\beta}(\mathbf{q}) \mathbf{u}_{s'\beta}(\mathbf{q})$$

where:

$$D_{s\alpha s' \beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\nu} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s \alpha} \partial \mathbf{u}_{\nu s' \beta}} e^{i \mathbf{q} (\mathbf{R}_\nu - \mathbf{R}_\mu)}$$

is the dynamical matrix of the solid.

The dynamical matrix elements can be calculated by first principles calculations with 2 methods:

- ✓ *Supercell method* (or Small Displacement Method)
  - ✓ *Linear Response Method* (Density Function Perturbation Theory, DFPT)



# Properties of the dynamical matrix

- The dynamic matrix is a  $3N_{at} \times 3N_{at}$  Hermitean matrix
  - Symmetrical with respect to  $\mathbf{q} \rightarrow -\mathbf{q}$  change:

$$D_{s\alpha s'\beta}(-\mathbf{q}) = D_{s\alpha s'\beta}(\mathbf{q})$$

- If all atoms are moved by the same displacement  $\mathbf{d}$  from equilibrium, the dynamical matrix is zero:

$$\sum_q D_{s\alpha s'\beta}(\mathbf{q}) = 0$$

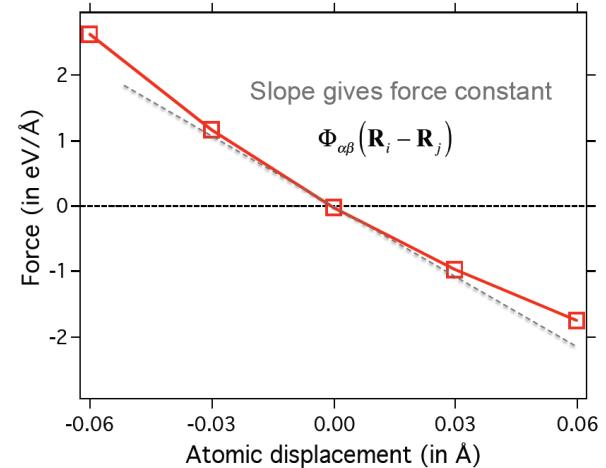


# The supercell method

- Set up a “large” supercell
  - Displace atoms by a “small” amount
  - Linearize and fit atom forces
  - Assemble the dynamical matrix
  - Diagonalize the dynamical matrix (solve the equations of motion)

$$M_I \ddot{\mathbf{u}}_{I\alpha} = - \sum_{J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{J\beta} = - \sum_{J\beta} \Phi_{J\beta} u_{J\beta} = F_{I\alpha}$$

- Works with any DFT total energy code
  - Needs to check supercell is large enough, atomic displacements are small enough, ...
  - Code available: PHON (Dario Alfe')
    - PHONONS (K. Parliski)



# Density Functional Perturbation Theory (DFPT)

Within DFT the ground state total energy of the solid, calculated at fixed nuclei, is:

$$E_{tot} = \sum_i \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{loc}(\mathbf{r}) \rho(\mathbf{r}) d^3 r + E_H[\rho] + E_{xc}[\rho] + U_{II}$$

where  $\rho(\mathbf{r})$  is the density of the electron gas:

$$\rho(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

and  $|\psi_i\rangle$  are the solution of the Kohn and Sham equations.  $E_H$  is the Hartree energy,  $E_{xc}$  is the exchange and correlation energy and  $U_{II}$  is the ion-ion interaction. According to the Hellmann-Feynman theorem, the first order derivative of the ground state energy with respect to an external parameter is:

$$\frac{\partial E_{tot}}{\partial \lambda} = \int \frac{\partial V_{loc}(\mathbf{r})}{\partial \lambda} \rho(\mathbf{r}) d^3 r + \frac{\partial U_{ll}}{\partial \lambda}$$



# Density Functional Perturbation Theory (DFPT)

Deriving with respect to a second parameter  $\mu$ :

$$\frac{\partial^2 E_{tot}}{\partial \mu \partial \lambda} = \int \frac{\partial^2 V_{loc}(\mathbf{r})}{\partial \mu \partial \lambda} \rho(\mathbf{r}) d^3 r + \frac{\partial^2 U_{ll}}{\partial \mu \partial \lambda}$$

$$+ \int \frac{\partial V_{loc}(\mathbf{r})}{\partial \lambda} \frac{\partial \rho(\mathbf{r})}{\partial \mu} d^3 r$$

So the new quantity that we need to calculate is the charge density induced, at first order, by the perturbation:

$$\frac{\partial \rho(\mathbf{r})}{\partial \mu} = \sum_i \frac{\partial \psi_i^*(\mathbf{r})}{\partial \mu} \psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) \frac{\partial \psi_i(\mathbf{r})}{\partial \mu}$$

To fix the ideas we can think that  $\lambda = \mathbf{u}_{\mu s \alpha}$  and  $\mu = \mathbf{u}_{\nu s' \beta}$



# Density Functional Perturbation Theory (DFPT)

The wavefunctions obey the following equation:

$$\left[ -\frac{1}{2} \nabla^2 + V_{KS}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

where  $V_{KS} = V_{loc}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})$ .  $V_{KS}(\mathbf{r}, \mu)$  depends on  $\mu$  so that also  $\psi_i(\mathbf{r}, \mu)$ , and  $\varepsilon_i(\mu)$  depend on  $\mu$ . We can expand these quantities in a Taylor series:

$$V_{KS}(\mathbf{r}, \mu) = V_{KS}(\mathbf{r}, \mu = 0) + \mu \frac{\partial V_{KS}(\mathbf{r})}{\partial \mu} + \dots$$

$$\psi_i(\mathbf{r}, \mu) = \psi_i(\mathbf{r}, \mu=0) + \mu \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} + \dots$$

$$\varepsilon_i(\mu) = \varepsilon_i(\mu=0) + \mu \frac{\partial \varepsilon_i}{\partial \mu} + \dots$$



# Density Functional Perturbation Theory (DFPT)

Inserting these equations and keeping only the first order in  $\mu$  we obtain:

$$\left[ -\frac{1}{2} \nabla^2 + V_{KS}(\mathbf{r}) - \varepsilon_i \right] \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} = - \frac{\partial V_{KS}}{\partial \mu} \psi_i(\mathbf{r}) + \frac{\partial \varepsilon_i}{\partial \mu} \psi_i(\mathbf{r})$$

where:  $\frac{\partial V_{KS}}{\partial \mu} = \frac{\partial V_{loc}}{\partial \mu} + \frac{\partial V_H}{\partial \mu} + \frac{\partial V_{xc}}{\partial \mu}$  and

$$\frac{\partial V_H}{\partial \mu} = \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial \rho(\mathbf{r}')}{\partial \mu} d^3 r'$$

$$\frac{\partial V_{xc}}{\partial \mu} = \frac{dV_{xc}}{d\rho} \frac{\partial \rho(\mathbf{r})}{\partial \mu}$$

depend self-consistently on the charge density induced by the perturbation.



# The DFPT self-consistent cycle

DFT

$$V_0(\mathbf{r}) \leftrightarrows n(\mathbf{r})$$

$$\begin{aligned}
 V_{SCF}(\mathbf{r}) &= V_0(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mu_{xc}(\mathbf{r}) \\
 &\downarrow \\
 n(\mathbf{r}) &= \sum_{\epsilon_v < E_F} |\phi_v(\mathbf{r})|^2 \\
 &\downarrow \\
 (-\Delta + V_{SCF}(\mathbf{r}))\phi_v(\mathbf{r}) &= \epsilon_v \phi_v(\mathbf{r})
 \end{aligned}$$

DFPT

$$V'(\mathbf{r}) \rightleftharpoons n'(\mathbf{r})$$

$$\begin{array}{c}
 \xrightarrow{\hspace{1cm}} V'_{SCF}(\mathbf{r}) = V'(\mathbf{r}) + \int \frac{n'(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mu'_{xc}(\mathbf{r}) \xleftarrow{\hspace{1cm}} \\
 \downarrow \\
 \xrightarrow{\hspace{1cm}} n'(\mathbf{r}) = 2 \operatorname{Re} \sum_{\epsilon_v < E_F} \phi_v^*(\mathbf{r}) \phi_v'(\mathbf{r}) \\
 \downarrow \\
 \xrightarrow{\hspace{1cm}} (-\Delta + V_{SCF}(\mathbf{r}) - \epsilon_v) \phi_v'(\mathbf{r}) = P_c V'_{SCF}(\mathbf{r}) \phi_v(\mathbf{r})
 \end{array}$$

SB, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987)



# The ph.x code

The program `ph.x` solves this self-consistent linear system for  $3 \times N_{at}$  perturbations at a fixed vector  $\mathbf{q}$ . With  $\frac{\partial \rho(\mathbf{r})}{\partial \mu}$  for all the perturbations it calculates the dynamical matrix

$$D_{s\alpha s' \beta}(\mathbf{q})$$

at the given  $\mathbf{q}$ . Diagonalizing this matrix we obtain  $3 \times N_{at}$  frequencies  $\omega_{\mathbf{q}}$ . By repeating this procedure for several  $\mathbf{q}$  we could plot  $\omega_{\mathbf{q}}$  as a function of  $\mathbf{q}$  and display the phonon dispersions. However, it is more convenient to adopt a different approach that requires the calculation of the dynamical matrix in a small set of points  $\mathbf{q}$ .

# The ph.x code

## The dynamical matrix of the solid:

$$D_{s\alpha s'\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\nu} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s\alpha} \partial \mathbf{u}_{\nu s'\beta}} e^{i\mathbf{q}(\mathbf{R}_\nu - \mathbf{R}_\mu)} \quad (26)$$

is a periodic function of  $\mathbf{q}$  with  $D_{s\alpha s' \beta}(\mathbf{q} + \mathbf{G}) = D_{s\alpha s' \beta}(\mathbf{q})$  for any reciprocal lattice vector  $\mathbf{G}$ . Moreover, since in a solid all Bravais lattice points are equivalent, it does not depend on  $\mu$ . Eq.26 is a Fourier expansion of a three dimensional periodic function. We have Fourier components only at the discrete values  $\mathbf{R}_\nu$  of the Bravais lattice and we can write:

$$\frac{1}{\sqrt{M_s M_{s'}}} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s \alpha} \partial \mathbf{u}_{\nu s' \beta}} = \frac{\Omega}{(2\pi)^3} \int d^3 \mathbf{q} D_{s \alpha s' \beta}(\mathbf{q}) e^{-i \mathbf{q} (\mathbf{R}_\nu - \mathbf{R}_\mu)} \quad (27)$$



# The ph.x code

We can use the properties of the discrete Fourier transform and sample the integral in a uniform mesh of points  $\mathbf{q}$ . This will give the interatomic force constants only for a set of  $\mathbf{R}_\nu$  neighbors of  $\mathbf{R}_\mu$ . The code `q2r.x` reads a set of dynamical matrices calculated in a uniform mesh of  $\mathbf{q}$  points and calculates, using Eq. 27, the interatomic force constants for a few neighbors of the point  $\mathbf{R}_\mu = 0$ .

# The ph.x code

Let us consider a one dimensional periodic function  $f(x + a) = f(x)$  with period  $a$ . This function can be expanded in a Fourier series and will have a discrete set of Fourier components at the point  $k_n = \frac{2\pi}{a} n$ , where  $n$  is an integer (positive, negative or zero).

$$f(x) = \sum_n c_n e^{ik_n x} \quad (28)$$

where the coefficients of the expansion are:

$$c_n = \frac{1}{a} \int_0^a f(x) e^{-ik_n x} dx \quad (29)$$

In general, if  $f(x)$  is a sufficiently smooth function,  $c_n \rightarrow 0$  at large  $n$ . Now suppose that we know  $f(x)$  only in a uniform set of  $N$  points  $x_j = j\Delta x$  where  $\Delta x = a/N$  and  $j = 0, \dots, N - 1$ ,



# The ph.x code

then we can calculate:

$$\tilde{c}_n = \frac{1}{N} \sum_{j=0}^{N-1} f(x_j) e^{-i \frac{2\pi}{N} nj} \quad (30)$$

$\tilde{c}_n$  is a periodic function of  $n$  and  $\tilde{c}_{n+N} = \tilde{c}_n$ . So, if  $N$  is sufficiently large that  $c_n = 0$  when  $|n| \geq N/2$  then  $\tilde{c}_n$  is a good approximation of  $c_n$  for  $|n| < N/2$  and the function

$$f(x) = \sum_{n=-N/2}^{n=N/2} \tilde{c}_n e^{ik_n x} \quad (31)$$

is a good approximation of the function  $f(x)$  also on the points  $x$  different from  $x_j$ .



# The ph.x code

Therefore, if the dynamical matrix is a sufficiently smooth function of  $\mathbf{q}$  and the interatomic force constants decay sufficiently rapidly in real space, we can use Eq. 26 to calculate the dynamical matrix at arbitrary  $\mathbf{q}$ , limiting the sum to a few  $\mathbf{R}_\nu$  neighbors of  $\mathbf{R}_\mu = 0$ . The program `matdyn.x` reads the interatomic force constants calculated by `q2r.x` and calculates the dynamical matrices at an arbitrary  $\mathbf{q}$  using Eq. 26.



# Thermodynamic functions in the harmonic approximation

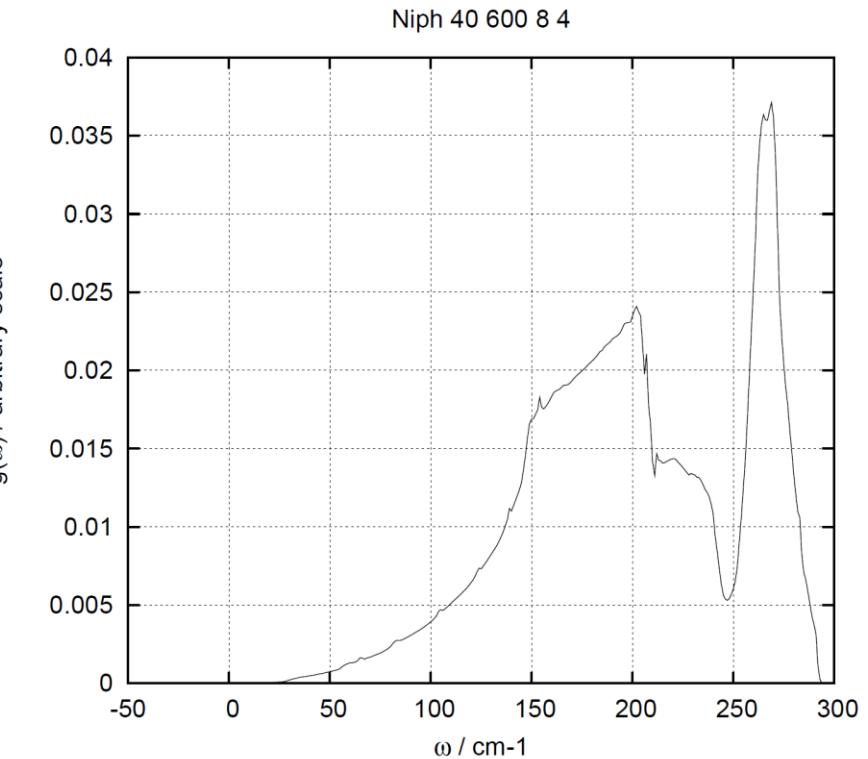
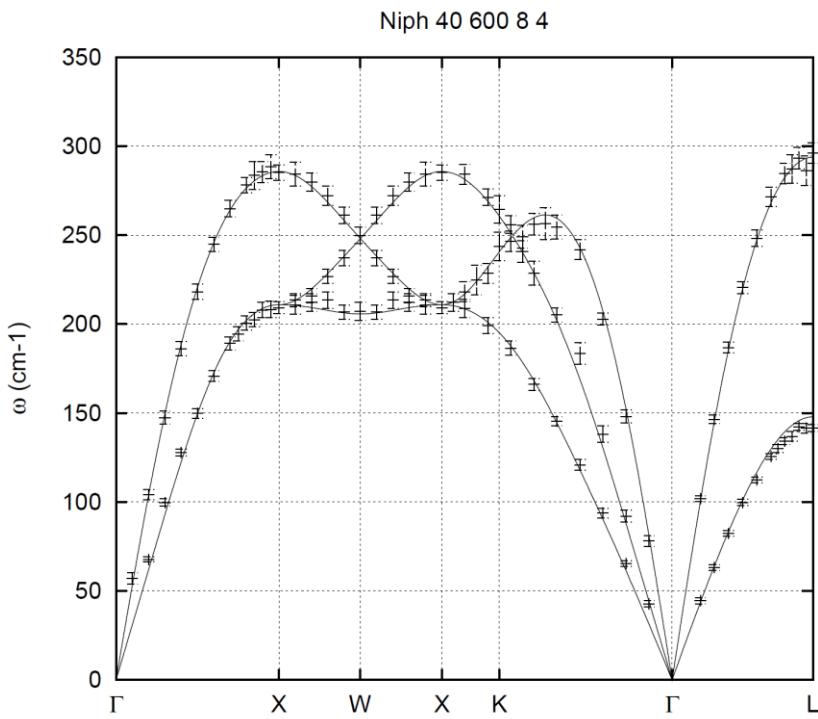
$$F(V_0, T) = U_0(V_0) + \frac{1}{2} \sum_{\vec{q}, \nu} \hbar \omega(\vec{q}, \nu) + k_B T \sum_{\vec{q}, \nu} \log(1 - e^{-\frac{\hbar \omega(\vec{q}, \nu)}{k_B T}})$$

$$C_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_V$$

- The vibrational free energy and all other thermodynamic properties in the harmonic approximation can be determined from the phonon frequencies calculated at the equilibrium volume  $V_0$
  - These frequencies, phonon dispersion curves in the BZ and phonon DOS can be calculated by first principles by:
    - ✓ *Supercell method (or Small Displacement Method)*
    - ✓ *Linear Response Method (Density Functional Perturbation)*



# First principles phonons for Ni: harmonic

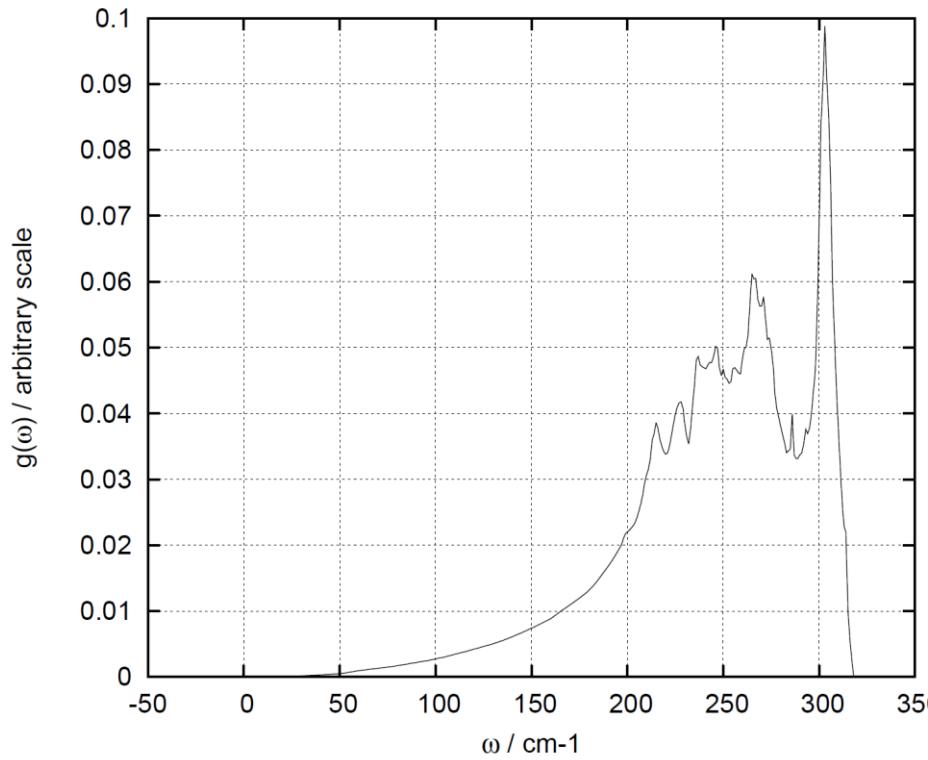
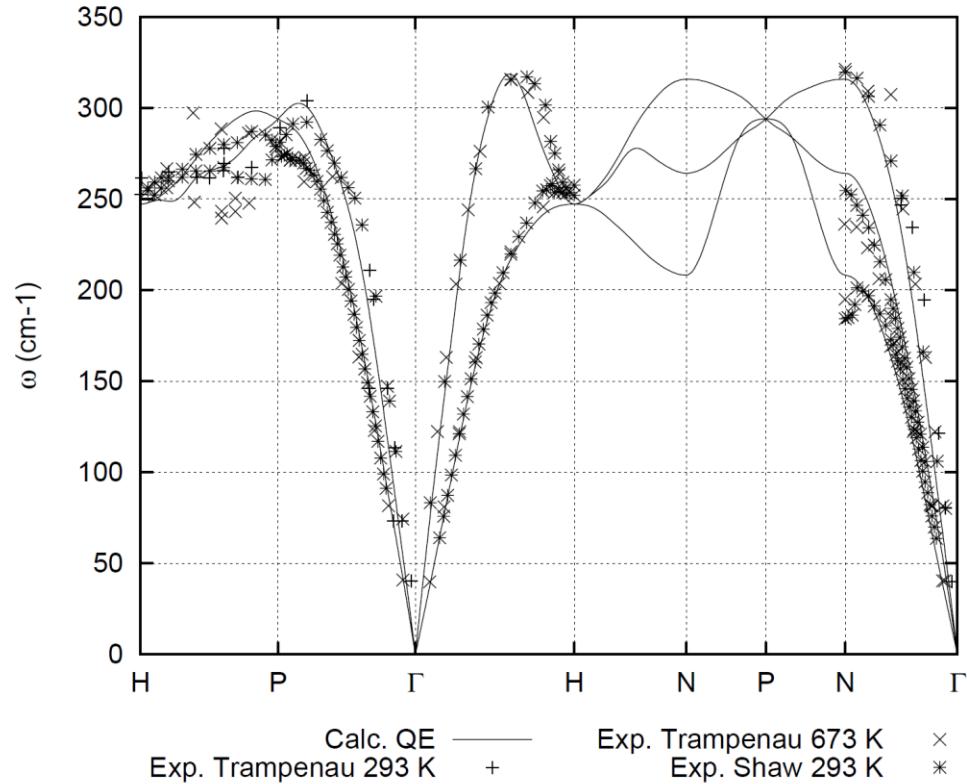


Exp. Data from R. J. Birgenau et al., Phys Rev 136 (1964) 1359

Phonons dispersion and DOS calculated by first principles with Quantum-Espresso and the Linear Response Method

PBE potential, ultrasoft pseudopotentials, Ecut=40 Ry, k-points mesh 8\*8\*8, q-points mesh (4\*4\*4)

# First principles phonons for Cr: harmonic



Exp. data from Trampenau et al. Phys Rev B 47 (1993) 3132 and Shaw et al., Phys Rev B 4 (1971) 969

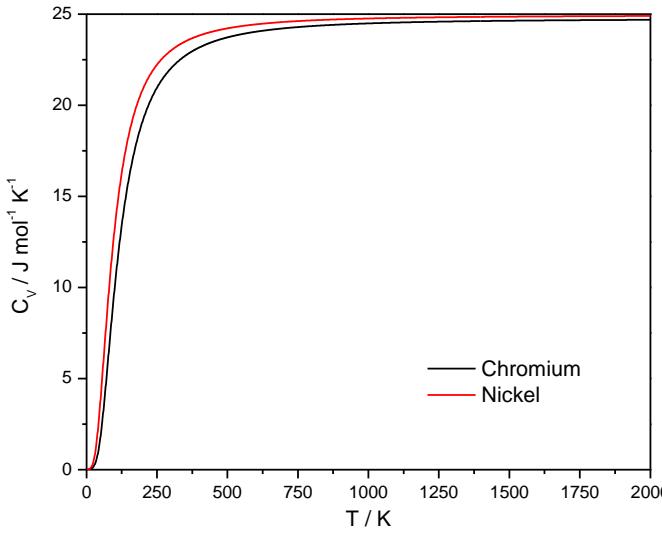
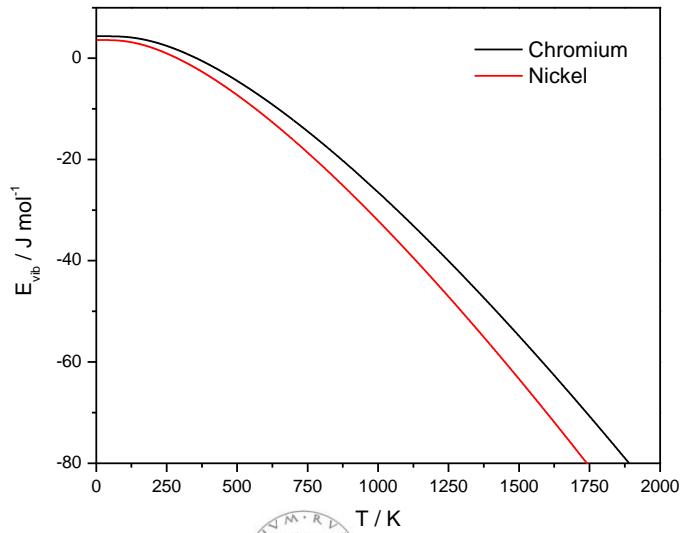
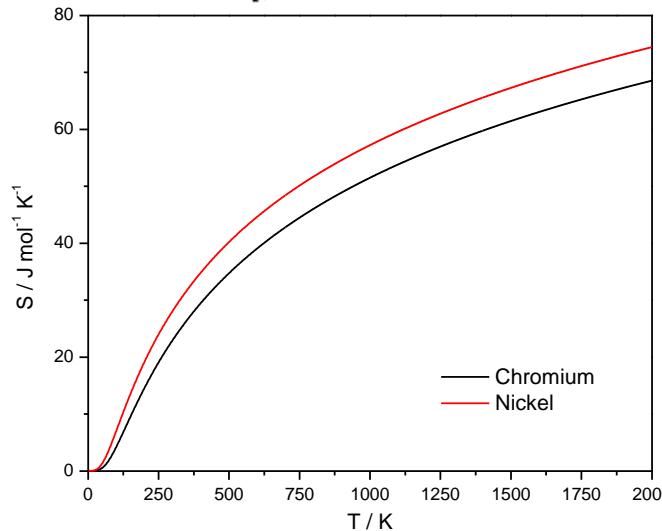
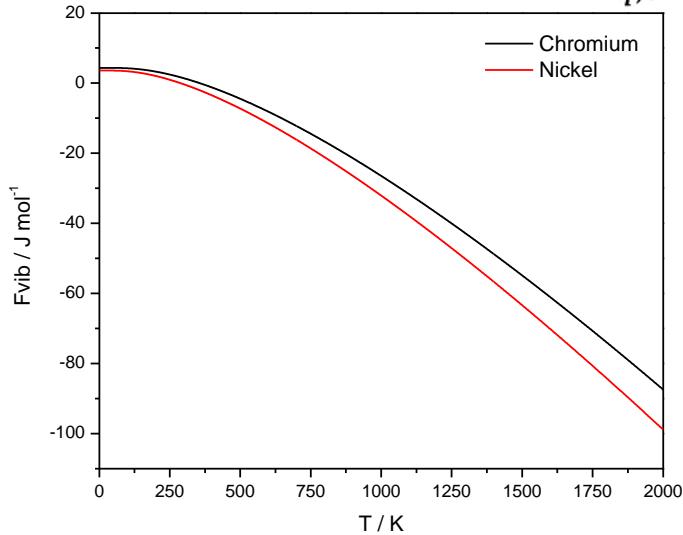
## Phonons dispersion and DOS calculated by first principles with Quantum-Espresso and the Linear Response Method

PBE potential, ultrasoft pseudopotentials, Ecut=100 Ry, k-points mesh 16\*16\*16, q-points mesh 8\*8\*8

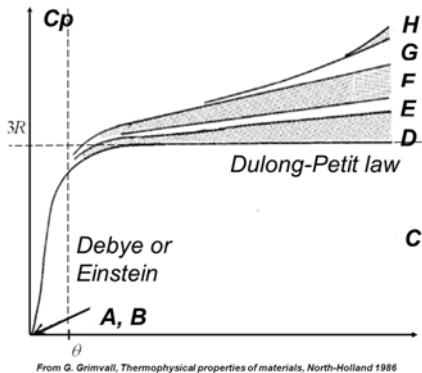


# Thermodynamics of Cr and Ni: harmonic approximation

$$F(V_0, T) = U_0(V_0) + \frac{1}{2} \sum_{\vec{q}, \nu} \hbar \omega(\vec{q}, \nu) + k_B T \sum_{\vec{q}, \nu} \log(1 - e^{-\frac{\hbar \omega(\vec{q}, \nu)}{k_B T}})$$

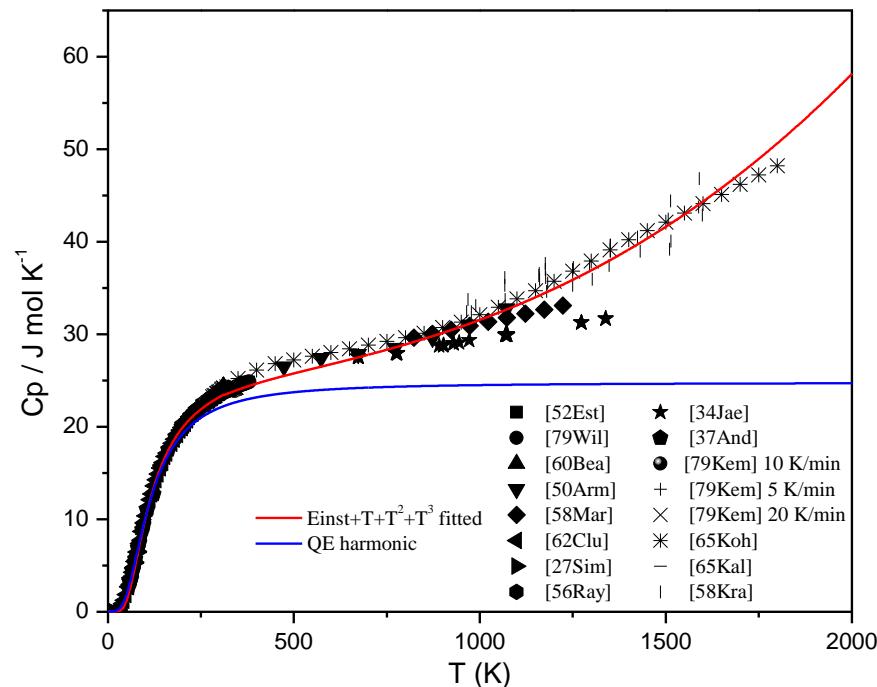
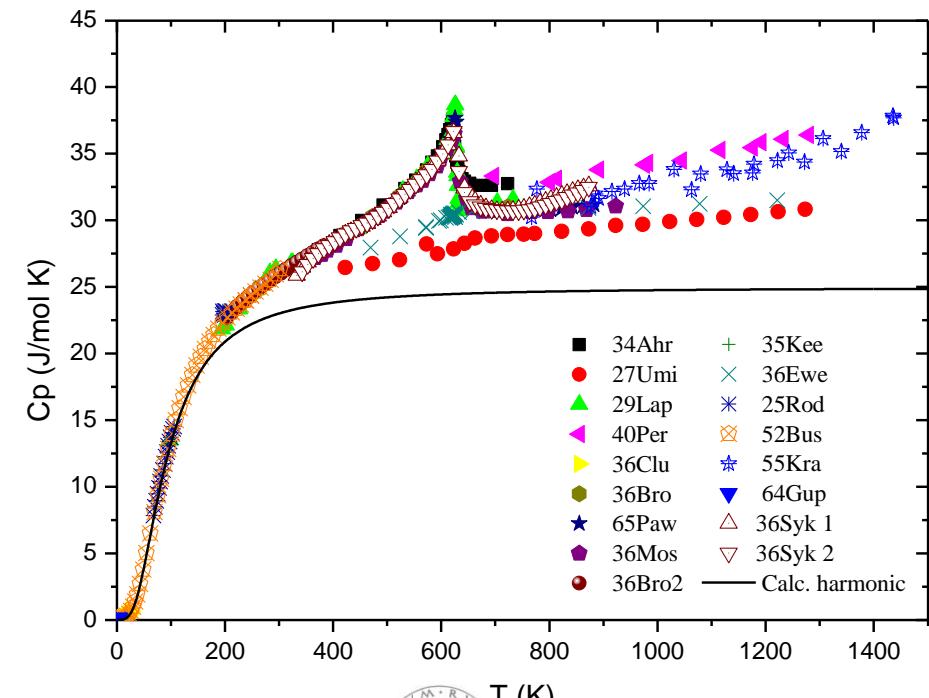


# Limitations of the harmonic approximation



The harmonic crystal is quite different from a real crystal:

- Phonons are independent (no phonon-phonon interactions)
- Infinite phonon lifetime
- Infinite thermal conductivity
- No thermal expansion ( $V=$ constant)



# The quasi-harmonic approximation (QHA)

$$F(V, T) = U_0(\textcolor{red}{V}) + \frac{1}{2} \sum_{\vec{q}, \nu} \hbar \omega(\vec{q}, \nu, \textcolor{red}{V}) + k_B T \sum_{\vec{q}, \nu} \log(1 - e^{-\frac{\hbar \omega(\vec{q}, \nu, \textcolor{red}{V})}{k_B T}})$$

*Phonons calculations are performed at different volumes, then F is minimized*

$$U(S, V) = F + TS$$

$$G(T, p) = F + pV$$

## *Bulk modulus*

$$B_T = V \left( \frac{\partial^2 F}{\partial V^2} \right)_T$$

$$F(V_0, T) = U_0(V_0) + \frac{1}{2} \sum_{\vec{q}, \nu} \hbar \omega(\vec{q}, \nu) + k_B T \sum_{\vec{q}, \nu} \log(1 - e^{-\frac{\hbar \omega(\vec{q}, \nu)}{k_B T}})$$

## *Thermal expansion*

$$\beta = V^{-1} \left( \frac{\partial V}{\partial T} \right)_P$$

$$C_p - C_V = TV\beta^2 B_T$$

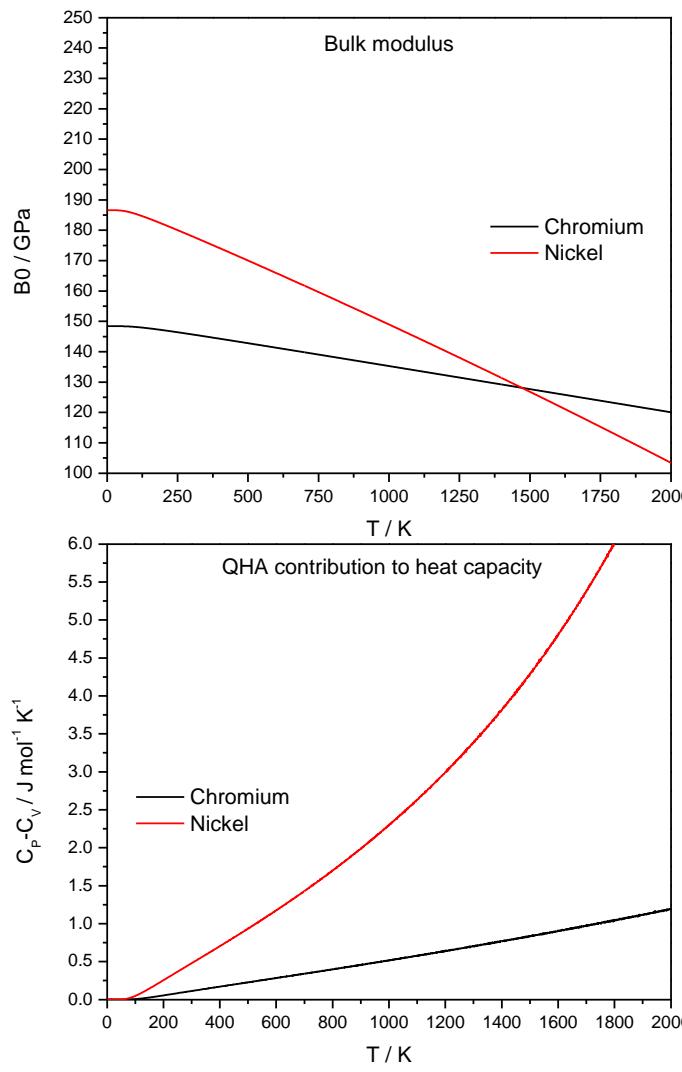
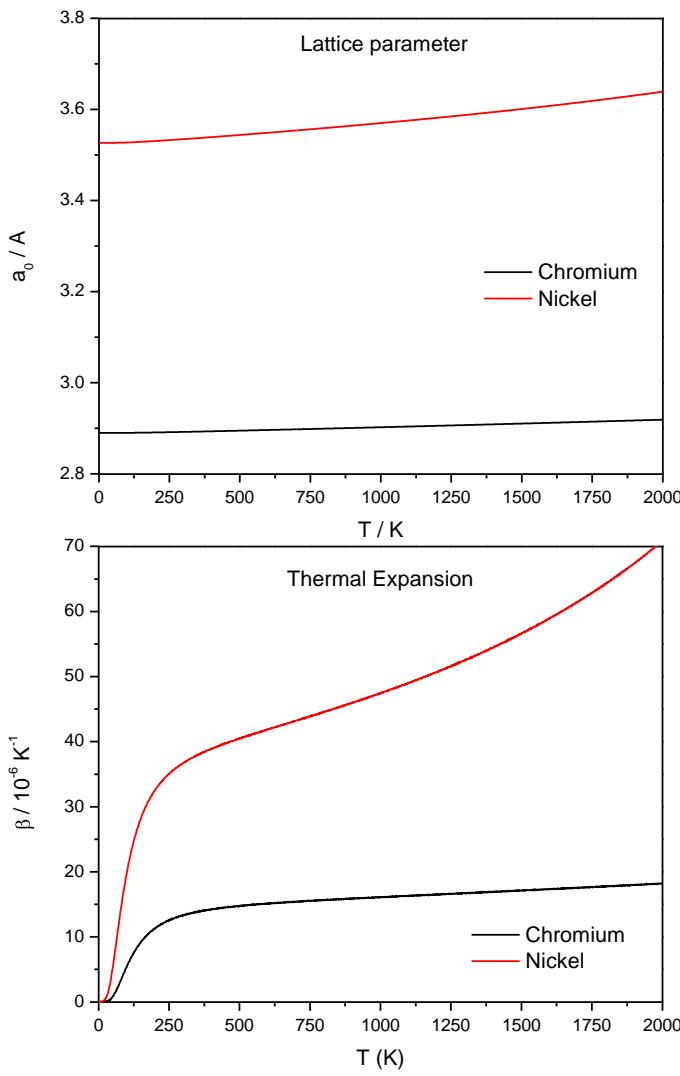
## *Heat capacity*

$$C_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_V$$

$$C_p = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_p$$



# Thermophysical properties for Cr and Ni in the QHA

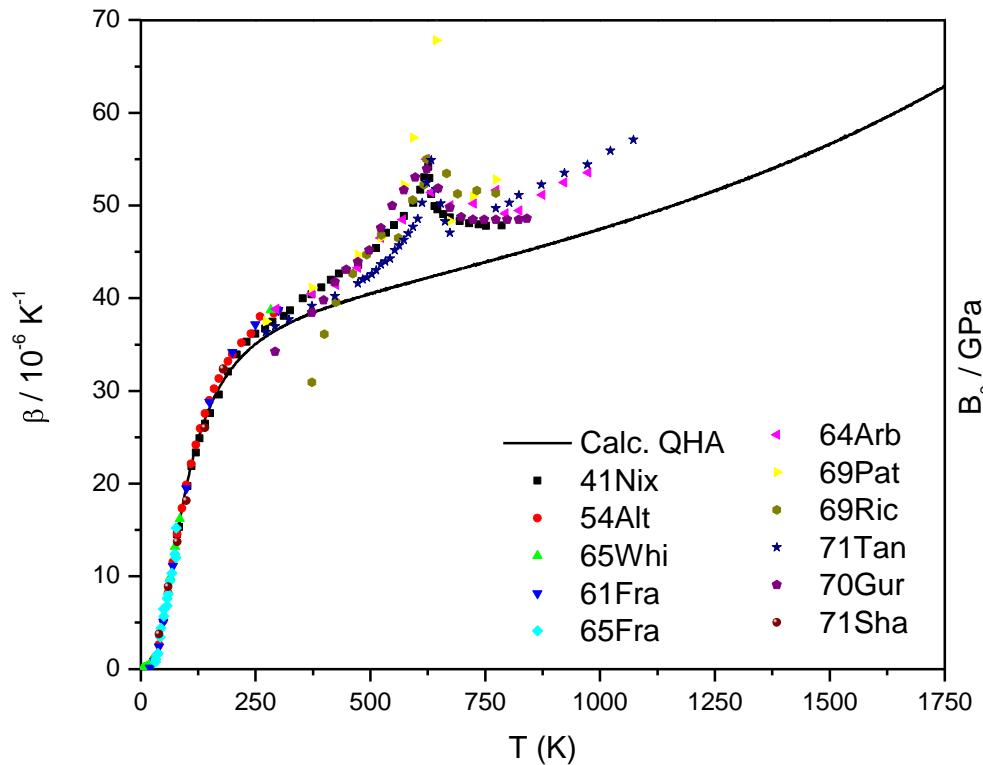


Thermophysical functions calculated by first principles with Quantum-Espresso and the Linear Response Method in the quasi-harmonic approximation

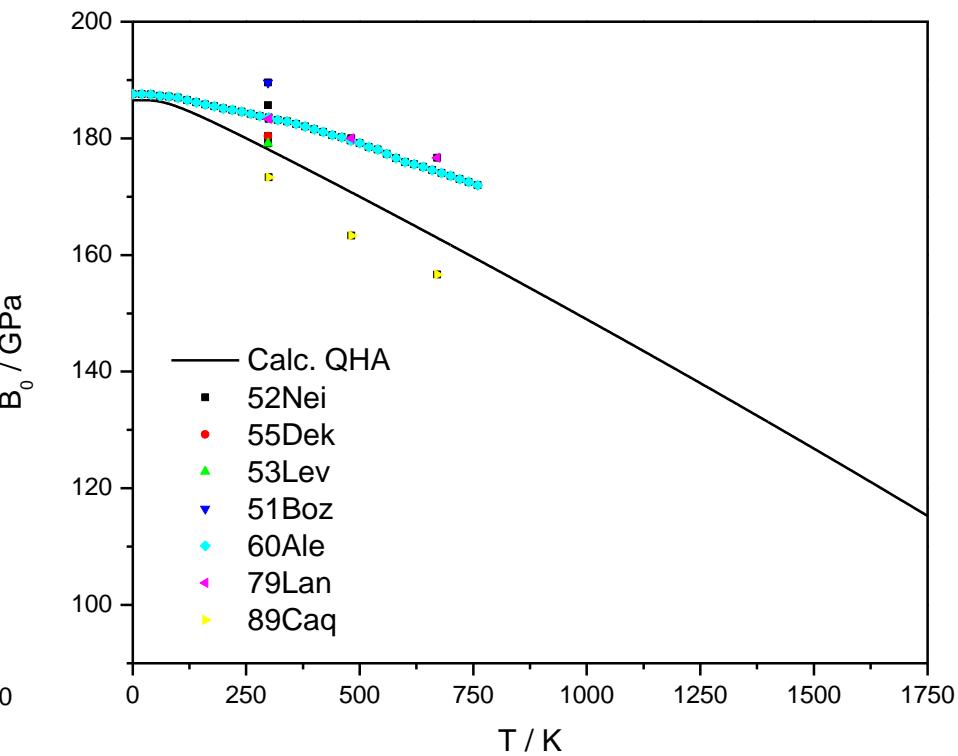


# Quasi Harmonic Approximation: comparison with experimental data for Ni

## *Thermal expansion*



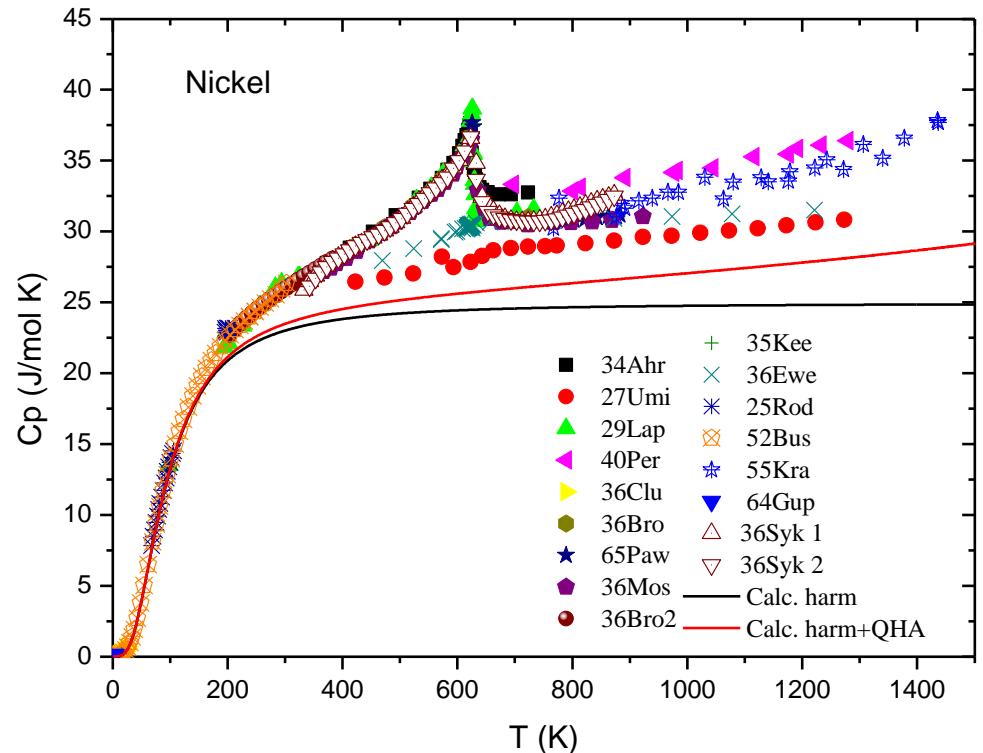
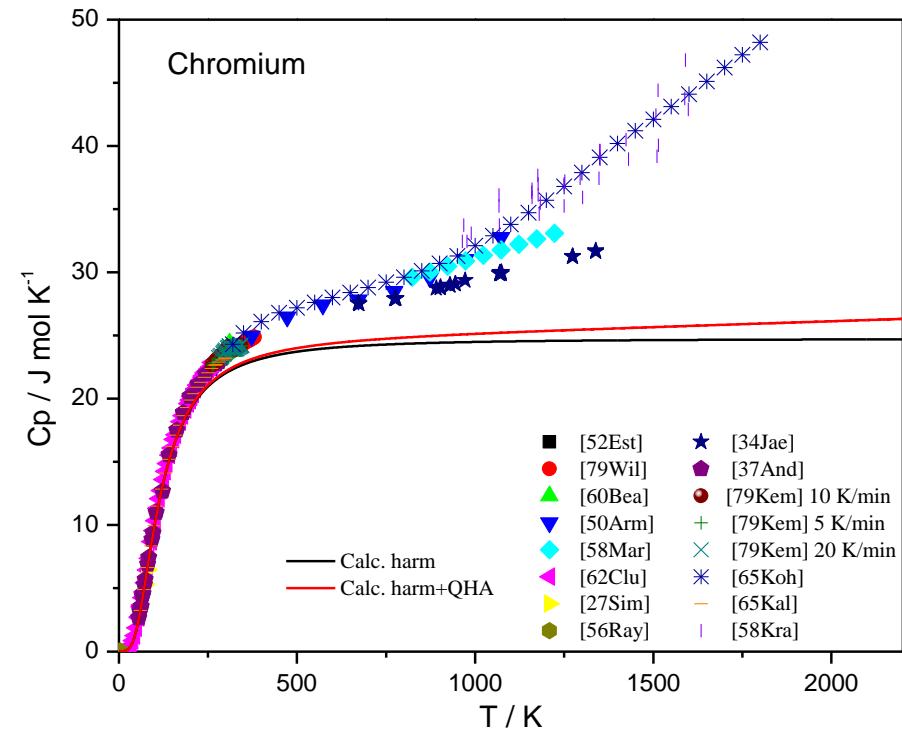
## *Bulk modulus*



# Thermophysical functions calculated by first principles with Quantum-Espresso and the Linear Response Method in the quasi-harmonic approximation



# First principles heat capacity for Cr and Ni (Quasi Harmonic Approximation)



# Thermodynamic functions calculated by first principles with Quantum-Espresso and the Linear Response Method in the quasi-harmonic approximation



# Electronic contribution

The electronic contribution to the heat capacity can be obtained by integrating the first principles calculated DOS (at constant equilibrium volume).

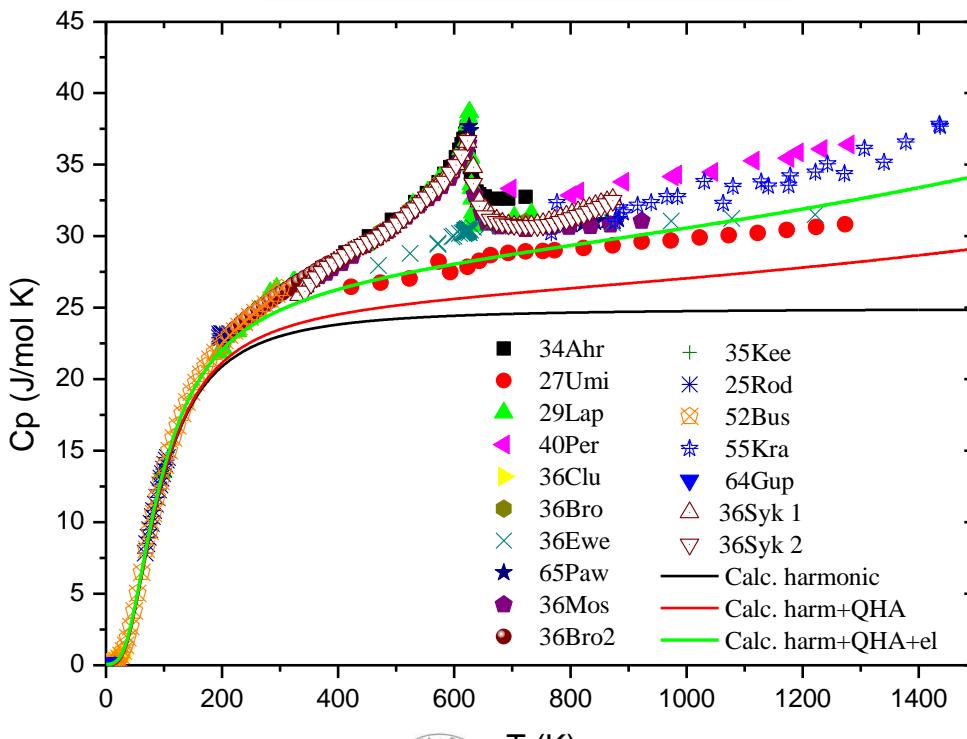
Computational details:

- Quantum Espresso code
- PBE potential
- Cut off Energy= 100 Ry (Cr), 40 Ry (Ni)
- K points mesh 24\*24\*24 (Cr), 32\*32\*32 (Ni)

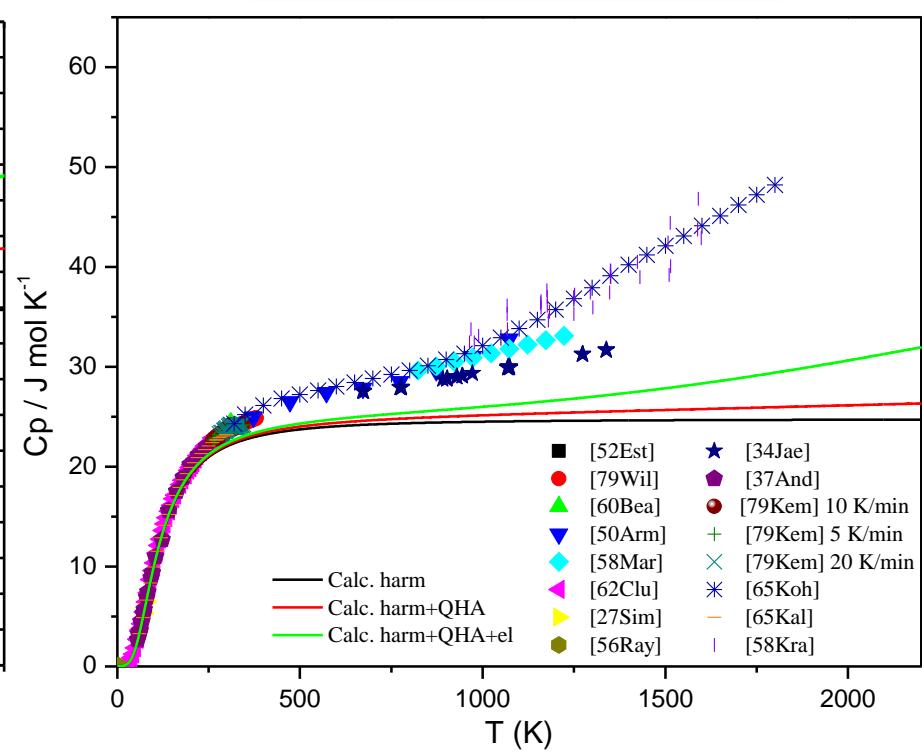
$$E_{el} = 2 \int EN(E)f(E) dE$$

$$C_{el} = \frac{\partial E_{el}}{\partial T} = 2 \int (E - E_F)N(E) \frac{\partial f}{\partial T} dE$$

*Nickel*



*Chromium*



# The Quantum Espresso open source code



QUANTUM ESPRESSO

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[QE WIKI](#) ::[CONTACTS](#) ::[QUOTE](#) ::[LOGOS](#) ::

**1 April 2011 The new release, v.4.3, of the Quantum ESPRESSO distribution is available for download.**

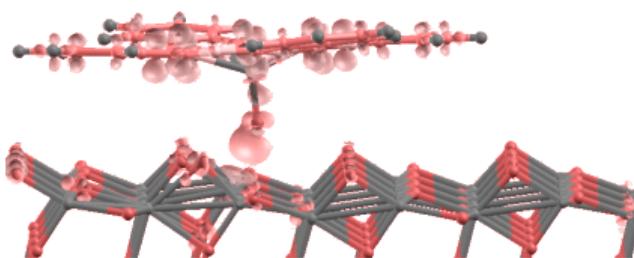
**13 July 2010**  
Bugfix release v.4.2.1 of the  
Quantum ESPRESSO distribution is  
available for download.

**10 May 2010**  
A new version, v.4.2, of the  
Quantum ESPRESSO distribution is  
available for download.

**12 April 2010**  
The final bugfix release, v.4.1.3, of  
the Quantum ESPRESSO distribution  
is available for download. This  
supersedes all previous 4.1.x  
releases.

**20 July 2009**  
The new release of the Quantum  
ESPRESSO distribution is available  
for download (version 4.1)

Quantum ESPRESSO is an integrated suite of computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials (both norm-conserving and ultrasoft).



What I cannot compute, I do not understand [adapted from Richard P. Feynman]

<http://www.quantum-espresso.org/>



# The Quantum Espresso open source code

Many modules and tools are available:

**pwscf.x**

ph.x

# matdyn.x

q2r

# plotdos

10 / 10

# GUI (Graphical User Interface)



# References

IOP PUBLISHING

J. Phys.: Condens. Matter **21** (2009) 395502 (19pp)

JOURNAL OF PHYSICS: CONDENSED MATTER

doi:10.1088/0953-8984/21/39/395502

# QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials

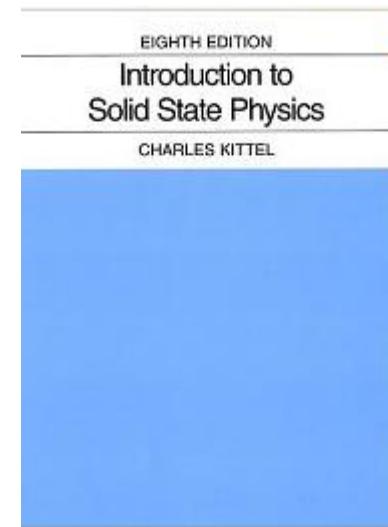
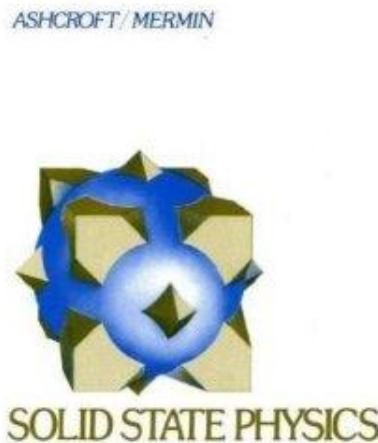
Paolo Giannozzi<sup>1,2</sup>, Stefano Baroni<sup>1,3</sup>, Nicola Bonini<sup>4</sup>,  
Matteo Calandra<sup>5</sup>, Roberto Car<sup>6</sup>, Carlo Cavazzoni<sup>7,8</sup>,  
Davide Ceresoli<sup>4</sup>, Guido L Chiarotti<sup>9</sup>, Matteo Cococcioni<sup>10</sup>,  
Ismaila Dabo<sup>11</sup>, Andrea Dal Corso<sup>1,3</sup>, Stefano de Gironcoli<sup>1,3</sup>,  
Stefano Fabris<sup>1,3</sup>, Guido Fratesi<sup>12</sup>, Ralph Gebauer<sup>1,13</sup>,  
Uwe Gerstmann<sup>14</sup>, Christos Gouguassis<sup>5</sup>, Anton Kokalj<sup>1,15</sup>,  
Michele Lazzeri<sup>5</sup>, Layla Martin-Samos<sup>1</sup>, Nicola Marzari<sup>4</sup>,  
Francesco Mauri<sup>5</sup>, Riccardo Mazzarello<sup>16</sup>, Stefano Paolini<sup>3,9</sup>,  
Alfredo Pasquarello<sup>17,18</sup>, Lorenzo Paulatto<sup>1,3</sup>, Carlo Sbraccia<sup>1,†</sup>,  
Sandro Scandolo<sup>1,13</sup>, Gabriele Sclauzero<sup>1,3</sup>, Ari P Seitsonen<sup>5</sup>,  
Alexander Smogunov<sup>13</sup>, Paolo Umari<sup>1</sup> and  
Renata M Wentzcovitch<sup>10,19</sup>



## Other useful references

## Introductory tests:

- N. W. Ashcroft, N. D. Mermin, *Solid State Physics*, Holt, Reinhart and Winston, 1976
  - C. Kittel, *Introduction to Solid State Physics*, Wiley; 8 edition (November 11, 2004)



- S. Baroni, S. De Gironcoli, A. Dal Corso, P. Giannozzi, Rev. Mod. Phys. 73 (2001) 515
  - S. Baroni, P. Giannozzi, E. Isaev, in Theoretical & Computational Methods in Mineral Physics: Geophysical Applications (2009)

# Other software codes for phonons calculations

- PHON, Dario Alfe', <http://www.homepages.ucl.ac.uk/~ucfbdx/phon/>
  - PHONONS (K. Parlinski) <http://wolf.ifj.edu.pl/phonon/>
  - VASP 5.2, <http://cms.mpi.univie.ac.at/vasp/>
  - ABINIT, <http://www.abinit.org/>



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*Andrea Dal Corso, SISSA, Trieste, Italy*

*Suzana G. Fries, ICAMS, Bochum, Germany*



DISCIPLINARY CENTRE FOR  
CED MATERIALS SIMULATION

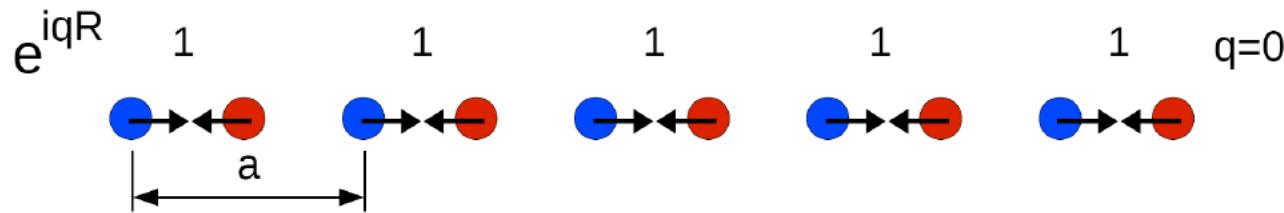


# You for listening...

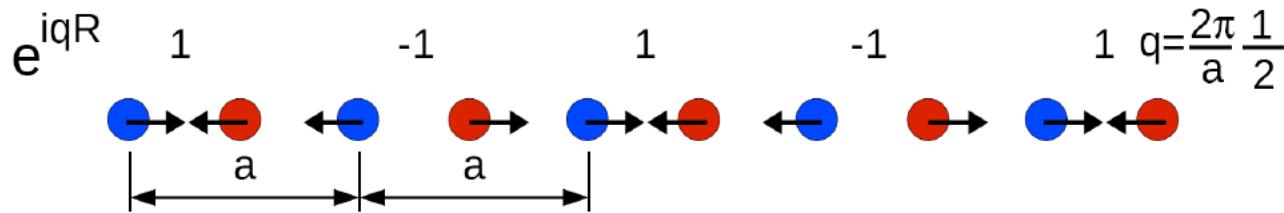
*Many thanks to Andrea Dal Corso for providing some of these slides*

# Characteristic of phonons

A  $\Gamma$ -point phonon has the same displacements in all unit cells ( $\mathbf{q} = 0$ ):

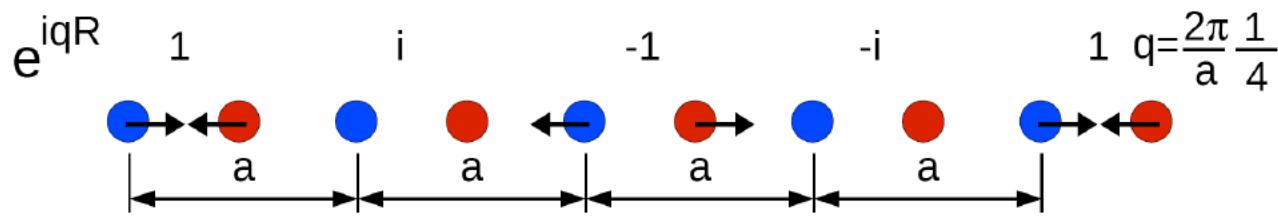


A zone border phonon with  $\mathbf{q}_{ZB} = \mathbf{G}/2$ , where  $\mathbf{G}$  is a reciprocal lattice vector, has displacements which repeat periodically every two unit cells:



# Characteristic of phonons

A phonon with  $\mathbf{q} = \mathbf{q}_{ZB}/2$  has displacements which repeat every four unit cells:



A phonon at a general wavevector  $\mathbf{q}$  could be incommensurate with the underlying lattice:

