

# Density-functional theory, density-functional perturbation theory, and the QUANTUM ESPRESSO software distribution

*Paolo Giannozzi*

Università di Udine and CNR IOM-Democritos, Italy

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# Density-Functional Theory

Transforms the many-electron problem into an equivalent problem of (fictitious) non-interacting electrons, the *Kohn-Sham equations*:

$$H_{KS}\psi_v \equiv \left( -\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\mathbf{r}) \right) \psi_v(\mathbf{r}) = \epsilon_v\psi_v(\mathbf{r})$$

The effective potential is a *functional* of the charge density:

$$V_{KS}(\mathbf{r}) = V(\mathbf{r}) + v[n(\mathbf{r})], \quad n(\mathbf{r}) = \sum_v |\psi_v(\mathbf{r})|^2$$

(Hohenberg-Kohn 1964, Kohn-Sham 1965). The sum is over occupied states only.  $V(\mathbf{r})$  is the external potential on the system (the bare potential of the nuclei).

The exact form of  $v[n(\mathbf{r})]$  is unknown, but approximate functionals yielding good results for the ground state of many materials are known. Less simple “advanced” functionals allow to deal with difficult cases and to obtain even better results.

# Density-Functional Theory II

The electronic energy is a functional of the charge density and is written as:

$$E[\{\psi\}] = -\frac{\hbar^2}{2m} \sum_v \int \psi_v^*(\mathbf{r}) \nabla^2 \psi_v(\mathbf{r}) d\mathbf{r} + \int V(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{e^2}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[n(\mathbf{r})]$$

Kohn-Sham equations arise from the minimization of the energy functional:

$$E = \min_{\psi} E[\{\psi\}], \quad \int \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} = \delta_{ij}$$

The functional  $v[n(\mathbf{r})]$  can thus be written as

$$v(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \equiv V_H(\mathbf{r}) + V_{xc}(\mathbf{r}).$$

The second term above is called *exchange-correlation potential*.

# Density-Functional Theory in practice

- Expanding the Kohn-Sham orbitals into a suitable *basis* set turns Density-Functional Theory into a multi-variate minimization problem, and the Kohn-Sham equations into a *non-linear matrix eigenvalue problem*
- The use of *pseudopotentials* allows one to ignore chemically inert core states and to use *plane waves*
- Plane waves are *orthogonal* and the *matrix elements* of the Hamiltonian are usually easy to calculate; the *completeness* of the basis is easy to check
- Plane waves allow to efficiently solve the diagonalization problem and to solve the Poisson equation using iterative techniques, *matrix-vector products*, *Fast Fourier Transforms* (FFTs)

(NB: Other approaches based on different basis sets and all-electron atoms exist)

# Density-Functional Perturbation Theory

Let us assume that the external potential depends on some parameter  $\lambda$

$$V_\lambda(\mathbf{r}) \simeq V(\mathbf{r}) + \lambda \frac{\partial V(\mathbf{r})}{\partial \lambda} + \frac{1}{2} \lambda^2 \frac{\partial^2 V(\mathbf{r})}{\partial \lambda^2} + \dots$$

(all derivatives calculated at  $\lambda = 0$ ) and expand the charge density

$$n_\lambda(\mathbf{r}) \simeq n(\mathbf{r}) + \lambda \frac{\partial n(\mathbf{r})}{\partial \lambda} + \frac{1}{2} \lambda^2 \frac{\partial^2 n(\mathbf{r})}{\partial \lambda^2} + \dots$$

and the energy functional into powers of  $\lambda$ :

$$E_\lambda \simeq E + \lambda \frac{\partial E}{\partial \lambda} + \frac{1}{2} \lambda^2 \frac{\partial^2 E}{\partial \lambda^2} + \dots$$

The first-order derivative  $\partial E / \partial \lambda$  does not depend on any derivative of  $n(\mathbf{r})$  (*Hellmann-Feynman theorem*):

$$\frac{\partial E}{\partial \lambda} = \int n(\mathbf{r}) \frac{\partial V(\mathbf{r})}{\partial \lambda} d\mathbf{r}$$

## Energy functional expansion terms

The second-order derivative  $\partial^2 E / \partial \lambda^2$  depends on the first-order derivative of the charge density,  $\partial n(\mathbf{r}) / \partial \lambda$ :

$$\frac{\partial^2 E}{\partial \lambda^2} = \int \frac{\partial V(\mathbf{r})}{\partial \lambda} \frac{\partial n(\mathbf{r})}{\partial \lambda} d\mathbf{r} + \int n(\mathbf{r}) \frac{\partial^2 V(\mathbf{r})}{\partial \lambda^2} d\mathbf{r}$$

The result can be generalized to mixed derivatives:

$$\frac{\partial^2 E}{\partial \lambda \partial \mu} = \int \frac{\partial V(\mathbf{r})}{\partial \lambda} \frac{\partial n(\mathbf{r})}{\partial \mu} d\mathbf{r} + \int n(\mathbf{r}) \frac{\partial^2 V(\mathbf{r})}{\partial \lambda \partial \mu} d\mathbf{r}$$

(the order of derivatives can be exchanged)

In general, the  $(2n + 1)$ -th derivative of energy depends only on derivatives up to order  $n$  of the charge density ( $(2n + 1)$  *theorem*) due to its variational character.

$\partial n / \partial \lambda$  can be calculated either by the self-consistent procedure shown below, or by direct minimization of the 2nd-order energy, written as a functional of  $\partial n / \partial \lambda$ .

# Self-consistent Linear Response

The basic DFT equations for the linear response to a perturbation  $\delta V$  are:

$$\delta V_{KS}(\mathbf{r}) = \delta V(\mathbf{r}) + e^2 \int \frac{\delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \int \frac{\delta V_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')} \delta n(\mathbf{r}') d\mathbf{r}'$$

$$\delta n(\mathbf{r}) = 4\text{Re} \sum_v \psi_v^*(\mathbf{r}) P_c \frac{1}{\epsilon_v - H_{KS}} P_c \delta V_{KS} \psi_v,$$

where  $P_c$  is the projector over the empty-state manifold.

The variation of the charge density can be recast into the form

$$\delta n(\mathbf{r}) = 4\text{Re} \sum_v \psi_v^*(\mathbf{r}) \Delta\psi_v(\mathbf{r}), \quad \text{where} \quad \Delta\psi_v = P_c \frac{1}{\epsilon_v - H_{KS}} P_c \delta V_{KS} \psi_v$$

$\Delta\psi_v$  can be obtained from the solution of a linear equation:

$$(\epsilon_v - H_{KS}) P_c \Delta\psi_v = P_c \delta V_{KS} \psi_v.$$

The above equations define a self-consistent procedure that can be solved by iteration, much in the same way as in the solution of KS equations.

# Normal vibrational modes in crystals and molecules

Harmonic approximation: the interatomic potential energy is expanded to 2nd order. The resulting Hamiltonian transforms into a sum of independent oscillators.

*Normal mode* frequencies,  $\omega$ , and displacement patterns,  $U_I^\alpha$  for cartesian component  $\alpha$  of atom  $I$ , at atomic position  $\mathbf{R}_I$ , are determined by the secular equation:

$$\sum_{J,\beta} \left( C_{IJ}^{\alpha\beta} - M_I \omega^2 \delta_{IJ} \delta_{\alpha\beta} \right) U_J^\beta = 0,$$

where  $C_{IJ}^{\alpha\beta}$  is the matrix of *inter-atomic force constants* (IFC), i.e. second derivatives of the (*total*) energy with respect to atomic positions:

$$C_{IJ}^{\alpha\beta} \equiv \frac{\partial^2 E(\{\mathbf{R}\})}{\partial R_I^\alpha \partial R_J^\beta}.$$

In crystals, normal modes are classified by a wave-vector  $\mathbf{q}$ . Phonon frequencies,  $\omega(\mathbf{q})$ , and displacement patterns,  $U_s^\alpha(\mathbf{q})$ , are determined by the secular equation:

$$\sum_{t,\beta} \left( \tilde{C}_{st}^{\alpha\beta}(\mathbf{q}) - M_s \omega^2(\mathbf{q}) \delta_{st} \delta_{\alpha\beta} \right) U_t^\beta(\mathbf{q}) = 0$$



## Calculation of phonon spectra

Introduce monochromatic perturbation  $\mathbf{u}$  to atomic positions  $\mathbf{R}_I = \mathbf{R}_l + \boldsymbol{\tau}_s$  as

$$\mathbf{R}_I[\mathbf{u}_s(\mathbf{q})] = \mathbf{R}_l + \boldsymbol{\tau}_s + \mathbf{u}_s(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{R}_l}.$$

( $\mathbf{R}_l$  =lattice vector,  $\boldsymbol{\tau}_s$  =equilibrium position of the  $s$ -th atom in the unit cell).

Fourier transforms of force constants at  $\mathbf{q}$  are second derivatives of the energy with respect to such monochromatic perturbations:

$$\tilde{C}_{st}^{\alpha\beta}(\mathbf{q}) \equiv \sum_{\mathbf{R}} e^{-i\mathbf{q}\cdot\mathbf{R}} C_{st}^{\alpha\beta}(\mathbf{R}) = \frac{1}{N_c} \frac{\partial^2 E}{\partial u_s^{*\alpha}(\mathbf{q}) \partial u_t^\beta(\mathbf{q})}$$

( $N_c$  number of cells in crystal). These can be computed knowing the linear response  $\partial n(\mathbf{r})/\partial u_s^\alpha(\mathbf{q})$  and diagonalized to get phonon modes at  $\mathbf{q}$ . Note that:

- the linear response has the same wave vector  $\mathbf{q}$  of the perturbation: this algorithm will work for *any*  $\mathbf{q}$  without any supercell involved
- in the spirit of adiabatic approximation, one can use *static* response.

## Phonons and macroscopic electric fields

Polar materials in the  $\mathbf{q}=0$  (long-wavelength) limit: a macroscopic (finite and constant) electric field is present. Gives rise to observable *TO-LO splitting*. Macroscopic electric field incompatible with Periodic Boundary Conditions! Must be separately treated.

Phenomenological expression for the energy as a function of atomic displacements,  $\mathbf{u}_s$ , and of macroscopic electric field,  $\mathbf{E}$  (Born and Huang long-wavelength limit):

$$E(\{\mathbf{u}\}, \mathbf{E}) = \frac{1}{2} \sum_{st} \sum_{\alpha\beta} \mathbf{u}_s \cdot {}^{an}\tilde{\mathbf{C}}_{st} \cdot \mathbf{u}_t - \frac{\Omega}{8\pi} \mathbf{E} \cdot \boldsymbol{\epsilon}_\infty \cdot \mathbf{E} - e \sum_s \mathbf{u}_s \cdot \mathbf{Z}^*_s \cdot \mathbf{E},$$

( ${}^{an}\tilde{\mathbf{C}}_{st}$  force constants,  $\boldsymbol{\epsilon}_\infty$  dielectric tensor,  $\mathbf{Z}^*_s$  Born effective charge tensor).

Under which circumstances is an electric field  $\mathbf{E}$  generated by atomic displacements  $\mathbf{u}$ ? Which consequences does it have? The answer comes from electrostatics.

## Phonons and macroscopic electric fields (2)

Let us consider *electric induction*  $D = E + 4\pi P$  (where  $P$  is the polarization):

$$D = E + P_{el} + P_{ion} = \epsilon_{\infty} \cdot E + \frac{4\pi}{\Omega} e \sum_s \mathbf{u}_s \cdot \mathbf{Z}_s^*$$

Maxwell equations tell us  $\mathbf{q} \cdot D = 0$  and  $\mathbf{q} \times E = 0 \implies E = \mathbf{q}(\mathbf{q} \cdot E)$ , hence

$$E = -\frac{4\pi e}{\Omega} \sum_t \frac{\mathbf{q}(\mathbf{q} \cdot \mathbf{Z}_t^* \mathbf{u}_t)}{\mathbf{q} \cdot \epsilon_{\infty} \cdot \mathbf{q}}$$

and

$$E(\{\mathbf{u}\}) = \frac{1}{2} \sum_{st} \sum_{\alpha\beta} \mathbf{u}_s \cdot \tilde{\mathbf{C}}_{st} \cdot \mathbf{u}_t, \quad \tilde{\mathbf{C}}_{st} = {}^{an}\tilde{\mathbf{C}}_{st} + {}^{na}\tilde{\mathbf{C}}_{st}$$

where

$${}^{na}\tilde{\mathbf{C}}_{st} = \frac{4\pi}{\Omega} \frac{(\mathbf{q} \cdot \mathbf{Z}_s^*)_{\alpha} (\mathbf{q} \cdot \mathbf{Z}_t^*)_{\beta}}{\mathbf{q} \cdot \epsilon_{\infty} \cdot \mathbf{q}}$$

A "non-analytical" term has appeared in the force constants!

## Effective charges and dielectric tensor

Effective charges  $Z^*$  are related to polarization  $P$  induced by a lattice distortion:

$$Z_s^{*\alpha\beta} = \frac{\Omega}{e} \frac{\partial P_\alpha}{\partial u_s^\beta(\mathbf{q} = 0)}.$$

Dielectric tensor  $\epsilon_\infty^{\alpha\beta}$  are related to polarization induced by an electric field  $E$ :

$$\epsilon_\infty^{\alpha\beta} = \delta_{\alpha\beta} + 4\pi \left. \frac{\partial P_\alpha}{\partial E_\beta} \right|_{\mathbf{u}_s(\mathbf{q}=0)=0}.$$

One can observe that such quantities are second derivatives of the energy as well:

$$Z_s^{*\alpha\beta} = Z_s \delta_{\alpha\beta} - \frac{1}{N_c} \frac{\partial^2 E}{\partial E_\alpha \partial u_s^\beta(\mathbf{q} = 0)},$$

$$\epsilon_\infty^{\alpha\beta} = \delta_{\alpha\beta} + \frac{1}{N_c} \frac{\partial^2 E}{\partial E_\alpha \partial E_\beta}.$$

# Linear Response to an Electric Field

If the perturbing potential represents a macroscopic electric field  $\delta E$ :

$$\delta V = -e\delta E_0 \cdot \mathbf{r}$$

it is ill-defined in a crystal, because  $\mathbf{r}$  is not a lattice-periodic operator! it can however be recast into a well-defined expression using the following trick:

$$\langle \psi_c | \mathbf{r} | \psi_v \rangle = \frac{\langle \psi_c | [H_{KS}, \mathbf{r}] | \psi_v \rangle}{\epsilon_c - \epsilon_v} \quad \text{for } c \neq v$$

We can rewrite  $|\bar{\psi}_v^\alpha\rangle = P_c r_\alpha |\psi_v\rangle$  as the solution of a linear system:

$$(H_{KS} - \epsilon_v) |\bar{\psi}_v^\alpha\rangle = P_c [H_{KS}, \mathbf{r}_\alpha] |\psi_v\rangle,$$

where the commutator is well defined and can be easily computed:

$$[H_{KS}, \mathbf{r}] = -\frac{\hbar^2}{m} \frac{\partial}{\partial \mathbf{r}} + [\hat{V}_{NL}, \mathbf{r}] = -\frac{i\hbar \mathbf{p}}{m} + [\hat{V}_{NL}, \mathbf{r}].$$

Here  $\hat{V}_{NL}$  is the nonlocal part of the pseudopotential.

## Calculation of effective charges

Polarization induced by an atomic displacement:

$$\frac{\partial P_\alpha}{\partial u_s^\beta(\mathbf{q} = 0)} = -\frac{e}{N_c \Omega} \int \mathbf{r} \frac{\partial n(\mathbf{r})}{\partial u_s(\mathbf{q} = 0)} d\mathbf{r} + \frac{e}{\Omega} Z_s \delta_{\alpha\beta}.$$

The integral is ill-defined for a crystal with Periodic Boundary Conditions, but we can use the trick just introduced. The effective charges can be written as:

$$Z_s^{*\alpha\beta} = Z_s + \frac{4}{N_c} \sum_{n=1}^{N/2} \left\langle \bar{\psi}_n^\alpha \left| \frac{\partial \psi_n}{\partial u_\beta(\mathbf{q} = 0)} \right. \right\rangle.$$

using the linear response to an atomic perturbation.

Remembering that the  $Z^*$  are mixed second derivatives of the energy, effective charges are alternatively computed as the force linearly induced on an atom by an electric field, using the linear response to an electric field:

$$Z_s^{*\alpha\beta} = Z_s + \frac{4}{N_c} \sum_{n=1}^{N/2} \left\langle \psi_n \left| \frac{\partial V}{\partial u_\beta(\mathbf{q} = 0)} \right| \frac{\partial \psi_n}{\partial E_\alpha} \right\rangle$$

## Calculation of dielectric tensor

The linear response to a macroscopic electric field can be calculated using the same trick as above. In fact,  $V(\mathbf{r}) = e\mathbf{E} \cdot \mathbf{r}$  is ill-defined but we need only non-diagonal matrix elements. The convenient way to solve the linear-response equations is to iterate over  $V_{KS}(\mathbf{r})$  while keeping  $\mathbf{E}$  fixed:

$$\frac{\partial V_{KS}(\mathbf{r})}{\partial \mathbf{E}} = \frac{\partial V(\mathbf{r})}{\partial \mathbf{E}} + \int \left( \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta v_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')} \right) \frac{\partial n(\mathbf{r}')}{\partial \mathbf{E}} d\mathbf{r}'.$$

Finally:

$$\epsilon_{\infty}^{\alpha\beta} = \delta_{\alpha\beta} - \frac{16\pi e}{N_c \Omega} \sum_{n=1}^{N/2} \left\langle \bar{\psi}_n^{\alpha} \left| \frac{\partial \psi_n}{\partial E_{\beta}} \right. \right\rangle.$$

In the end, all we need to properly deal with LO-TO splitting in phonons are three additional linear-response calculations to an electric field

Final note: alternative techniques based on the *modern theory of polarizability* (Berry's phase) exist for the calculation of effective charges.

# Inter-atomic force constants in real space

Inter-atomic force constants in real space,  $C_{st}^{\alpha\beta}(\mathbf{R})$ , are obtained by

- calculating  $\tilde{C}_{st}^{\alpha\beta}(\mathbf{q})$  on a discrete  $(n_1, n_2, n_3)$  grid of  $\mathbf{q}$ -vectors:

$$\mathbf{q}_{ijk} = \frac{i-1}{n_1}\mathbf{G}_1 + \frac{j-1}{n_2}\mathbf{G}_2 + \frac{k-1}{n_3}\mathbf{G}_3, \quad i = 1, \dots, n_1, \text{ and the like for } j, k;$$

- Fourier-transforming to the corresponding real-space grid:

$$C(\mathbf{q}_{ijk}) \iff C(\mathbf{R}_{lmn}), \quad \mathbf{R}_{lmn} = l\mathbf{R}_1 + m\mathbf{R}_2 + n\mathbf{R}_3$$

$$l = -n_1/2, \dots, n_1/2 \text{ and the like for } m, n.$$

The denser the grid of  $\mathbf{q}$ -vectors, the larger the vectors  $\mathbf{R}_{lmn}$  for which the inter-atomic force constants are calculated.

For non polar system, inter-atomic force constants are short-ranged and require a moderate number of calculations at different  $\mathbf{q}$ .



## Inter-atomic force constants in real space (2)

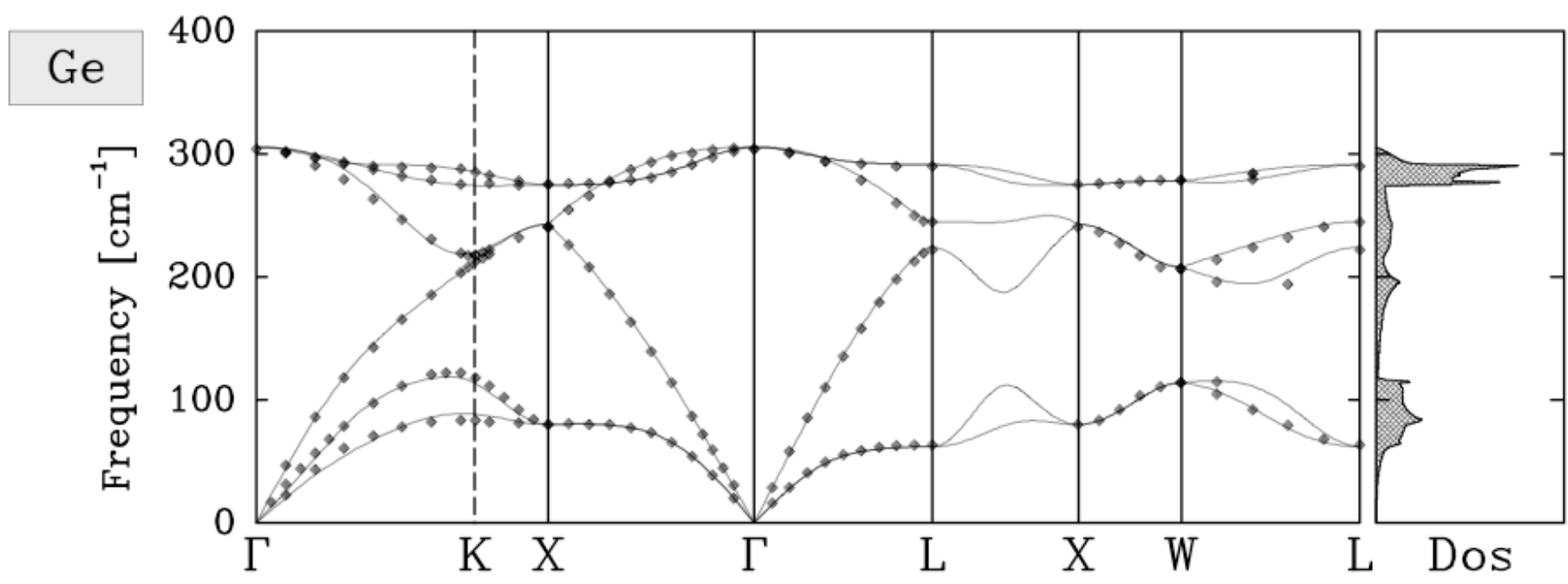
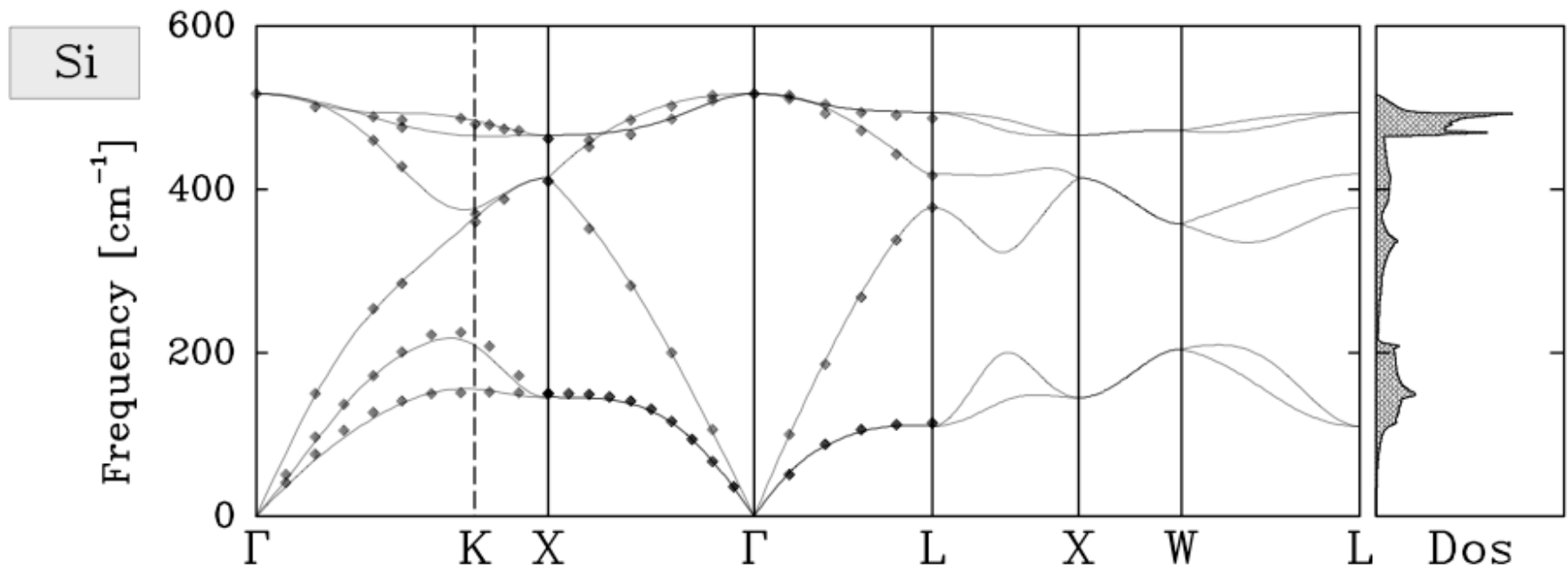
In simple semiconductors like Si and Ge,  $\mathbf{q}$ -point grids like  $4 \times 4 \times 4$  already yield rather converged force constants in real space. Symmetry is used to reduce the number of needed linear-response calculations.

Once inter-atomic force constants are known, the entire phonon dispersion at any  $\mathbf{q}$  can be straightforwardly calculated.

References: *Phonons and related crystal properties from density-functional perturbation theory*, S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515-562 (2001).

*Density-Functional Perturbation Theory*, P. Giannozzi and S. Baroni, in *Handbook of Materials Modeling*, Vol.1: “Methods and Models”, Editor S. Yip, Volume Editors: E. Kaxiras, N. Marzari, and B. Trout (Springer, 2005), p.195-214

*Thermal Properties of Materials from ab-initio Quasi-Harmonic Phonons*, S. Baroni, P. Giannozzi, and E. Isaev, Rev. Mineral. Geochem. **71**, 39-57 (2010)



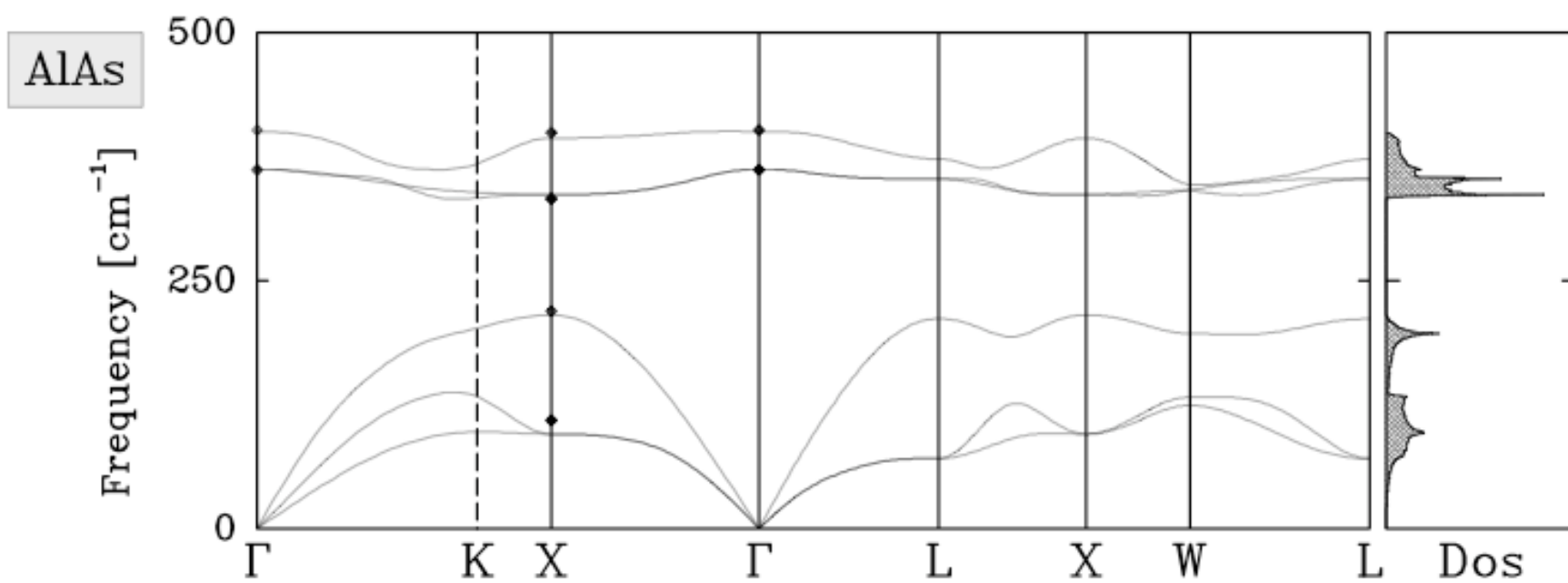
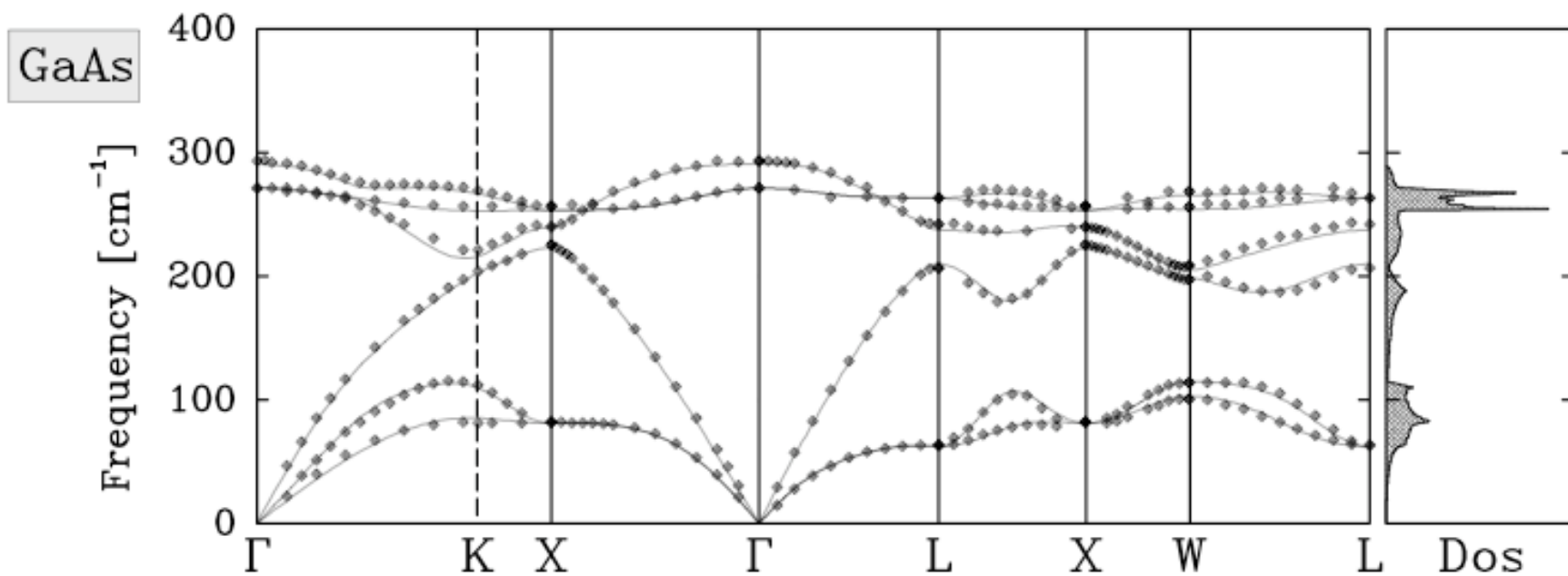
## Interatomic force constants in polar materials

For materials having a TO-LO splitting (e.g.: polar semiconductors), the non-analytic term in the force constants makes inter-atomic force constants in real space *no longer short-ranged*. Fourier-interpolation is no longer possible. Solution:

- Subtract from  $\tilde{C}_{st}^{\alpha\beta}(\mathbf{q}_{ijk})$  a term that has the same  $\mathbf{q} \rightarrow 0$  limit of the non-analytic term  ${}^{na}\tilde{C}_{st}^{\alpha\beta}(\mathbf{q})$  (and that is easy to calculate)
- Fourier-transform from reciprocal to real space as for the non-polar case: force constants in real space are now short-ranged.
- When force constants at a general  $\mathbf{q}$  are re-calculated from those in real space, re-add the term removed before the Fourier transform.

A suitable form for the term to be subtracted is the one described in:

X. Gonze *et al.*, Phys. Rev **B** 50, 13035 (1994)



## Electron-phonon interaction

With the change of potential induced by a phonon mode, one can compute the electron-phonon interaction coefficient  $\lambda$ :

$$\lambda = \sum_{\mathbf{q}\nu} \lambda_{\mathbf{q}\nu} = \sum_{\mathbf{q}\nu} \frac{\gamma_{\mathbf{q}\nu}}{\pi \hbar N(\epsilon_F) \omega_{\mathbf{q}\nu}^2}$$

where  $N(\epsilon_F)$  is the DOS at the Fermi level, and for phonon mode  $\nu$  at wavevector  $\mathbf{q}$ :

$$\gamma_{\mathbf{q}\nu} = 2\pi\omega_{\mathbf{q}\nu} \sum_{ij} \int \frac{d^3k}{\Omega_{BZ}} |g_{\mathbf{q}\nu}(\mathbf{k}, i, j)|^2 \delta(\epsilon_{\mathbf{q},i} - \epsilon_F) \delta(\epsilon_{\mathbf{k}+\mathbf{q},j} - \epsilon_F),$$

$$g_{\mathbf{q}\nu}(\mathbf{k}, i, j) = \left( \frac{\hbar}{2M\omega_{\mathbf{q}\nu}} \right)^{1/2} \langle \psi_{i,\mathbf{k}} | \frac{\partial V_{KS}}{\partial U^{(\nu)}(\mathbf{q})} | \psi_{j,\mathbf{k}+\mathbf{q}} \rangle.$$

$U^{(\nu)}$  is a displacement along phonon  $\nu$ . This quantity can be easily calculated using DFPT.

McMillan formula for the superconducting  $T_c$ :

$$T_c = \frac{\Theta_D}{1.45} \exp \left[ \frac{-1.04(1 + \lambda)}{\lambda(1 - 0.62\mu^*) - \mu^*} \right]$$

# Practical phonon calculation in QUANTUM ESPRESSO

First step: scf calculation *at equilibrium positions* (performed by `pw.x`)

- Single phonon calculation at finite wave-vector  $\mathbf{q}$ 
  - Generate  $\psi_{\mathbf{k},v}$  and  $\psi_{\mathbf{k}+\mathbf{q},v}$  in the Irreducible Brillouin Zone relative to the small group of  $\mathbf{q}$ ; Calculate  $C(\mathbf{q})$ , diagonalize, produce  $\omega(\mathbf{q})$  and  $U(\mathbf{q})$  (code `ph.x`)
- Single phonon calculation at  $\Gamma$  wave-vector ( $\mathbf{q}=0$ )
  - Calculate  $C(\mathbf{q} = 0)$ , diagonalize, produce  $\omega(\mathbf{q} = 0)$  and  $U(\mathbf{q} = 0)$  (code `ph.x`)  
For polar materials: calculate non-analytical terms that are missing from  $C(\mathbf{q} = 0)$  (LO-TO splitting are absent from  $\omega(\mathbf{q} = 0)$ ): specify option `epsil=.true.` to `ph.x` (will calculate and store in output file  $Z^*$  and  $\epsilon^\infty$ ).
  - Impose Acoustic Sum Rule (ASR), add the nonanalytic LO-TO splitting, calculate cross sections (code `dynmat.x`)

# Practical phonon dispersions calculation

First step as before: scf calculation *at equilibrium positions* (performed by `pw.x`)

- Perform many single-phonon calculations on a uniform grid of wave-vectors  $\mathbf{q}_i$ , including  $\mathbf{q} = 0$  (if system is polar, calculate in the latter case  $Z^*$  and  $\epsilon^\infty$ ); save all  $C(\mathbf{q}_i)$  (and  $Z^*$ ,  $\epsilon^\infty$ ) (code `ph.x` with option `ldisp=.true.`)
- Perform inverse FFT of the  $C(\mathbf{q}_i)$ , obtain interatomic force constants in real space  $C(\mathbf{R})$ . For polar materials: a term having the same behaviour for  $\mathbf{q} \rightarrow 0$  as the non-analytic term is subtracted from  $C(\mathbf{q}_i)$  before the Fourier Transform and re-added to  $C(\mathbf{R})$ , so that no problem related to non-analytic behaviour and related long-rangeness arises in the Fourier Transform (code `q2r.x`)
- Calculate phonons at any wave-vector, diagonalizing the dynamical matrix:

$$D_{st}^{\alpha\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_{\mathbf{R}} C_{st}^{\alpha\beta}(\mathbf{R}) \exp(i\mathbf{q} \cdot \mathbf{R})$$

using code `matdyn.x`

# The QUANTUM ESPRESSO distribution

QUANTUM ESPRESSO (QE) stands for *Quantum opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization*

QE is a distribution (an integrated suite) of software for *first-principle simulations*, i.e., atomistic calculations based on electronic structure, using density-functional theory, a plane-wave basis set, pseudopotentials. Main goals of QE are

- *innovation* in theoretical methods and numerical algorithms
- *efficiency* on modern computer architectures

A great effort is also devoted to *user friendliness* and to the formation of a *users' and developers' community*

QE exists since almost 20 years, resulting from the merge of pre-existing packages; some core components have been under development for  $\sim 30$  years

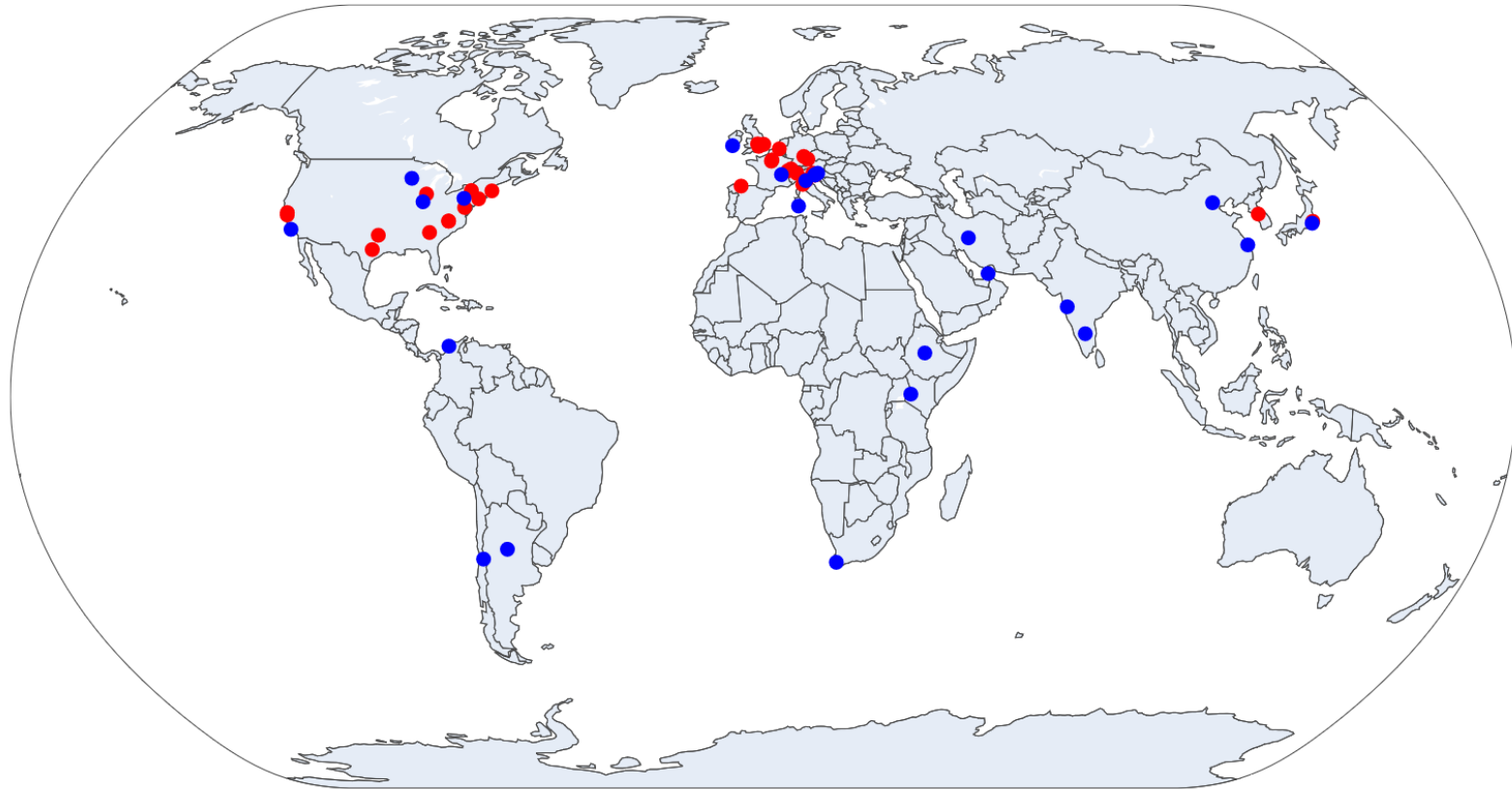
*QE is freely available under the terms of the GNU General Public License*



# QUANTUM ESPRESSO contributors

QE receives contributions from individuals and institutions worldwide (red dots)

QE Developers



QE is one of the community codes of H2020 project  
MaX – *Materials at the Exascale*



# QUANTUM ESPRESSO Foundation

So: who “owns” QE ... ?



... the QUANTUM ESPRESSO Foundation: a non-profit (“limited by guarantee”) company, based in the UK, soon moving to Slovenia, that

- coordinates and supports research, education, and outreach within the QE community
- owns the trademarks and protects the open-source character of QE
- raises funds to foster the QE project and its development

Current members of the Foundation:

SISSA, EPFL, ICTP, Cineca, Texas University at Austin

## Developers' and users' community: factoids

- Slack developers' channel:  $\sim 30$  active members, 38000+ messages since April 2020 (when the channel was opened)
- 20000 commits since the first release under revision control software (first CVS, then SVN, now `git`)
- 1330 “merge requests” accepted on GitLab (<https://gitlab.com/QEF/q-e>) since Dec. 2017
- Almost 40 Schools or tutorials since 2002 (blue dots in the map two slides behind this), attended by  $\sim 1400$  users before the pandemic
- 1100+ applications for the recent (17-28 May 2021) MaX “e-School”
- Almost 15000 citations of the papers documenting QE

# 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 Gougoussis<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 Scaluzero<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>**

This is the main documenting paper (2009). After 8 years and ~ 6000 citations ...

# Advanced capabilities for materials modelling with QUANTUM ESPRESSO

P Giannozzi<sup>1</sup>, O Andreussi<sup>2,9</sup>, T Brumme<sup>3</sup>, O Bunau<sup>4</sup>, M Buongiorno Nardelli<sup>5</sup>, M Calandra<sup>4</sup>, R Car<sup>6</sup>, C Cavazzoni<sup>7</sup>, D Ceresoli<sup>8</sup>, M Cococcioni<sup>9</sup>, N Colonna<sup>9</sup>, I Carnimeo<sup>1</sup>, A Dal Corso<sup>10,32</sup>, S de Gironcoli<sup>10,32</sup>, P Delugas<sup>10</sup>, R A DiStasio Jr<sup>11</sup>, A Ferretti<sup>12</sup>, A Floris<sup>13</sup>, G Fratesi<sup>14</sup>, G Fugallo<sup>15</sup>, R Gebauer<sup>16</sup>, U Gerstmann<sup>17</sup>, F Giustino<sup>18</sup>, T Gorni<sup>4,10</sup>, J Jia<sup>11</sup>, M Kawamura<sup>19</sup>, H-Y Ko<sup>6</sup>, A Kokalj<sup>20</sup>, E Küçükbenli<sup>10</sup>, M Lazzeri<sup>4</sup>, M Marsili<sup>21</sup>, N Marzari<sup>9</sup>, F Mauri<sup>22</sup>, N L Nguyen<sup>9</sup>, H-V Nguyen<sup>23</sup>, A Otero-de-la-Roza<sup>24</sup>, L Paulatto<sup>4</sup>, S Poncé<sup>18</sup>, D Rocca<sup>25,26</sup>, R Sabatini<sup>27</sup>, B Santra<sup>6</sup>, M Schlipf<sup>18</sup>, A P Seitsonen<sup>28,29</sup>, A Smogunov<sup>30</sup>, I Timrov<sup>9</sup>, T Thonhauser<sup>31</sup>, P Umari<sup>21,32</sup>, N Vast<sup>33</sup>, X Wu<sup>34</sup> and S Baroni<sup>10</sup>

... an updated paper was published in 2017. The latest paper ...

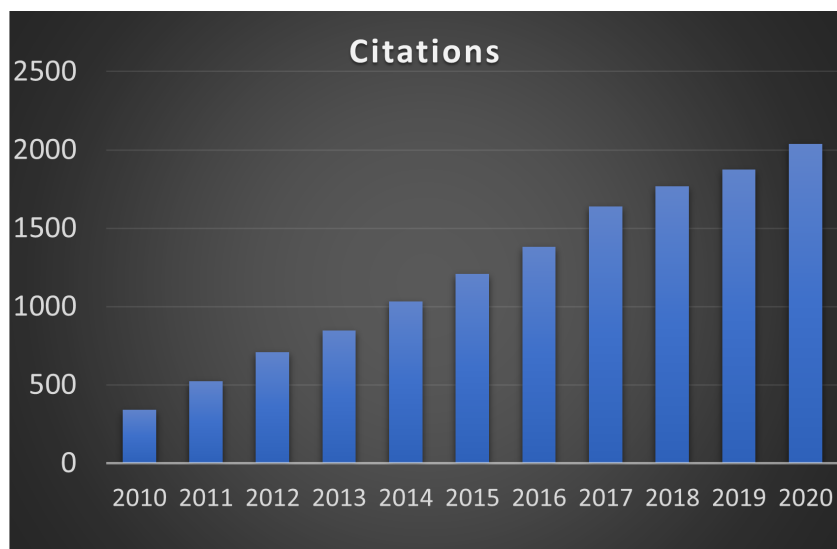
# QUANTUM ESPRESSO toward the exascale

J. Chem. Phys. **152**, 154105 (2020); <https://doi.org/10.1063/5.0005082>

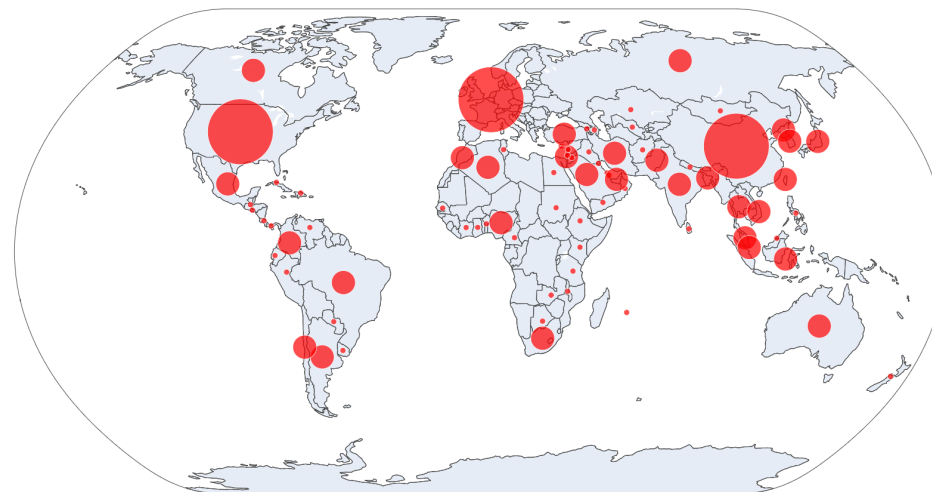
 Paolo Giannozzi<sup>1,2,3,a</sup>,  Oscar Baseggio<sup>4</sup>,  Pietro Bonfà<sup>5,6</sup>, Davide Brunato<sup>4</sup>,  Roberto Car<sup>7</sup>, Ivan Carnimeo<sup>4</sup>,  Carlo Cavazzoni<sup>3,8</sup>,  Stefano de Gironcoli<sup>2,4</sup>,  Pietro Delugas<sup>3,4</sup>,  Fabrizio Ferrari Ruffino<sup>2</sup>,  Andrea Ferretti<sup>6</sup>,  Nicola Marzari<sup>3,9</sup>,  Iurii Timrov<sup>9</sup>,  Andrea Urru<sup>4</sup>, and  Stefano Baroni<sup>2,3,4</sup>

... deals with the results of the MaX project.

Time evolution and geographic distribution of citations:



QE Impact



# Requirements on effective software for quantum simulations at the nanoscale

- Diffusion of first-principle techniques among non-specialists requires software that is **easy to use** and (reasonably) **bug-free** and **error-proof**
- Scientific ethics requires that **results should be reproducible** and **algorithms susceptible of validation**
- Complex problems require a mix of solutions coming from different approaches and methods: software should be **interoperable with other software**
- Introducing innovation requires new ideas to materialize into new algorithms through codes: software should be **easy to extend and to improve**
- Challenging calculations stress the limits of available computer power: software should be **fast and efficient**
- Finally, software must be **maintainable!**

# On usability and reliability

- *Usability*:  
simple text input along with graphical interfaces, provided by multiple sources; a large and ever-increasing number of checks on input and on results.
- *Reproducibility*:  
text input is very stable in the years; all past QE versions are available to everybody; automated tests (see next) are run on different hardware and run-time conditions.
- *Verification* (correctness of results):  
large number of tests, automatically executed every night after changes have been made. See: <http://bionano2.dimi.uniud.it:8010/#/console>
- *Validation* (precision and accuracy of the physical model):  
See e.g. *Reproducibility in density-functional theory calculations of solids*, K. Lejaeghere *et multis aliis*, Science **351** (6280), aad3000 (2016)  
Tests *precision* of the algorithm (pseudopotentials vs all-electron DFT), not physical *accuracy* of results. Much more work is available, also on accuracy.



# Requirements on effective software for quantum simulations at the nanoscale

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## Solutions for interoperability

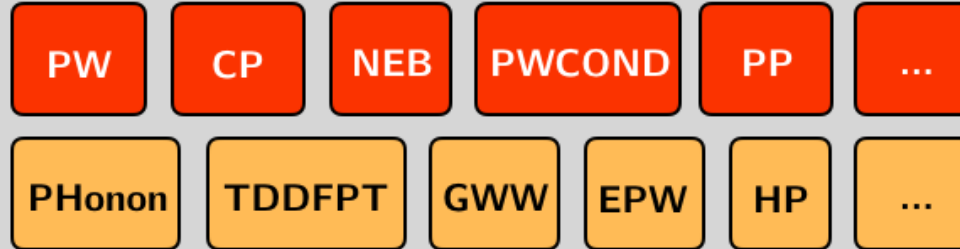
- I/O with schema-based, standard-compliant XML file, plus binary files (optionally in portable HDF5 format) for large records (e.g. wavefunctions, charge density). Allows easy parsing and transferral of data both inside QE and between QE and external software.
- More modular code and parallelization logic. Allows to call QE code as a library and to execute it inside a MPI communicator provided by the external software

An incomplete list of interoperable applications:

- QM-MM, with LAMMPS for the MM part (Comput. Phys. Commun. *195*, 191 (2015)), also available with MPI communications
- Advanced minimization algorithms (under development)
- Path-Integral Molecular Dynamics with i-Pi (CPC *185*, 1019 (2014))
- High-throughput computing with AiiDA (Comput. Mater. Sci. *111* 218 (2016))



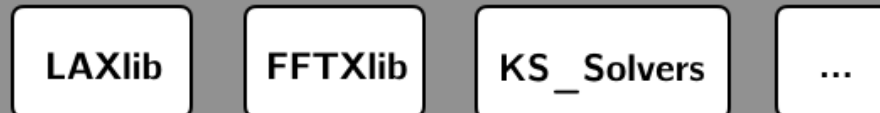
### PROPERTY CALCULATORS



### QUANTUM-ENGINE MODULES



### DOMAIN-SPECIFIC MATHEMATICAL LIBRARIES



### LOW-LEVEL SYSTEM LIBRARIES



# Requirements on effective software for quantum simulations at the nanoscale

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# Major recent or notable QE improvements and extensions

Mostly in the field of “advanced functionals”:

- New methods for van-der-Waals-bonded systems:
  - non-local functionals (“vdw-DF”)
  - semi-empirical corrections: Grimme’s DFT+D2, DFT+D3
  - non-so-empirical corrections; Tkatchenko-Scheffler, exchange-hole dipole moment model (XDM), many-body dispersions
- Improved functionals:
  - Adaptively Compressed Exchange and Selected Columns of Density Matrix localization for hybrid functionals (I. Carnimeo, S. Baroni, P. Giannozzi, Electron. Struct. **1**, 015009 (2019))
  - Molecular dynamics with hybrid functionals using localized Wannier functions
  - Usable meta-GGA (SCAN) functionals
  - Extended Hubbard functionals with intersite terms: DFT+U+V

Note that all functionals from `libxc` can now be used in QE

# Major recent or notable QE improvements and extensions II

Mostly in the field of “linear response”:

- EPW, of course!
- Phonons with Ultrasoft pseudopotentials and for noncolinear magnetism
- Phonons with DFT+U and with van der Waals (vdW-DF) functionals
- Time-dependent extension to DFT: TD-DFPT, for calculation of
  - Electronic excitations
  - Electron energy-loss spectroscopy (EELS)
  - Magnetic excitations (magnons)
- Linear-response calculation of Hubbard U parameters
- Phonon-induced electron self-energy (contributed by Jae-Mo Lihm)

# Requirements on effective software for quantum simulations at the nanoscale

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# Parallelization towards the exascale

Scalability of realistic calculations on up to tens of thousands cores, using all available OpenMP and MPI parallelization levels, was demonstrated in the past.

Careful optimization of nonscalable RAM and computations required!

Scalability *strongly depends upon the kind and size of system!*

However: Accelerated hybrid architectures such as NVidia GPU's are the current "big thing" in high-performance computing. Problems:

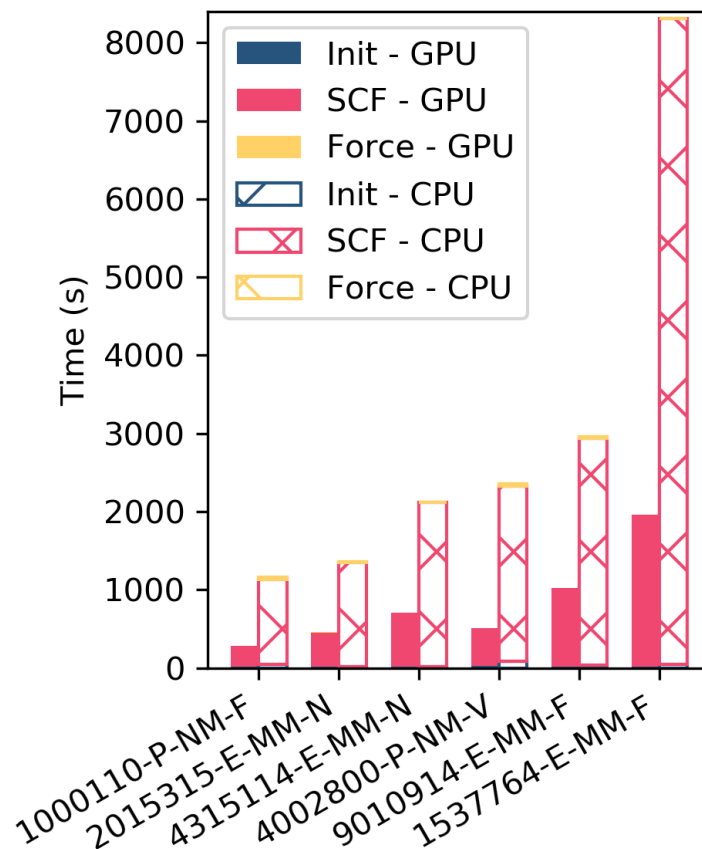
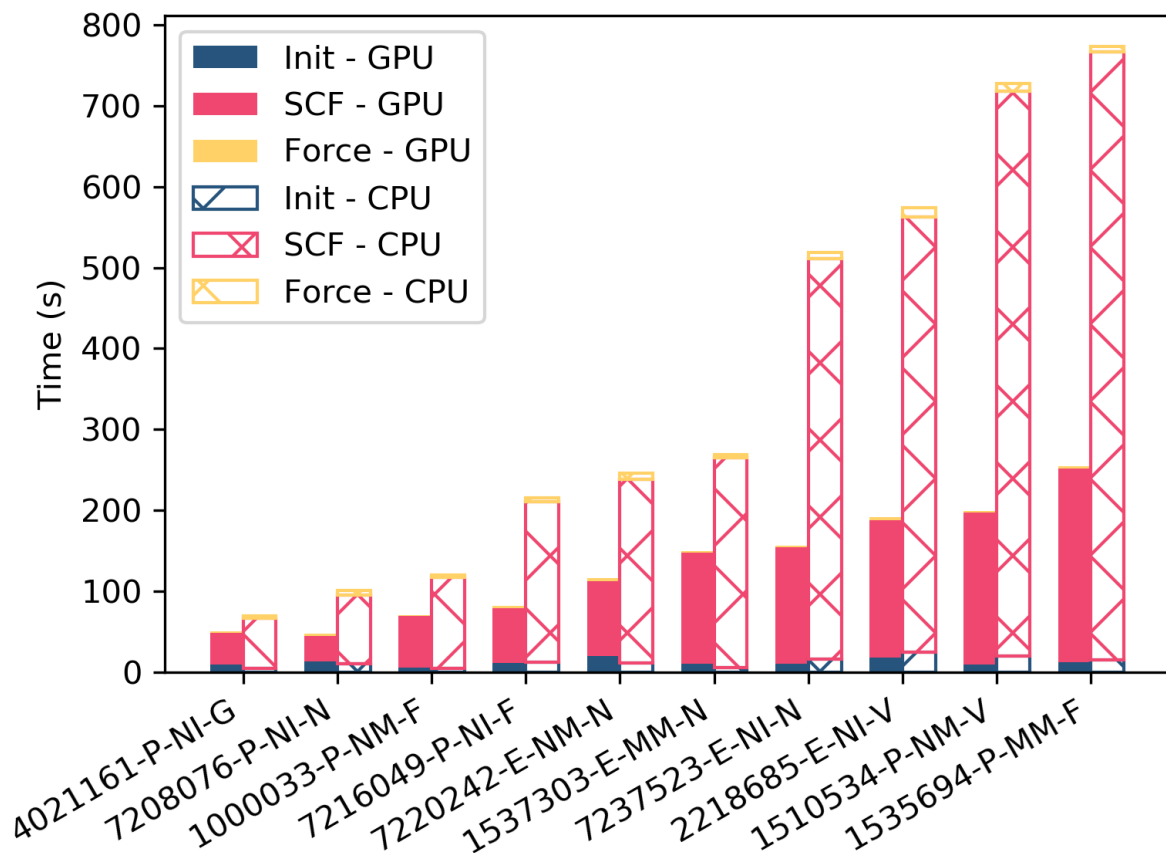
- Large code rewriting needed to obtain interesting performances
- Maintainability of the code becomes problematic

Solutions:

- Current: rewrite selected computational kernels using CUDA Fortran. Integrates much better into the Fortran-based code of QE.
- Future: portable code with OpenMP v.5 or OpenACC



# Current performances on Nvidia GPUs



# Credits

- Thanks to the organizers of the EPW Virtual meeting ...
- ... to all people whose slides and pictures I borrowed ....
- ... to all people who contributed to QE in a way or another ...
- ...and thanks to you all