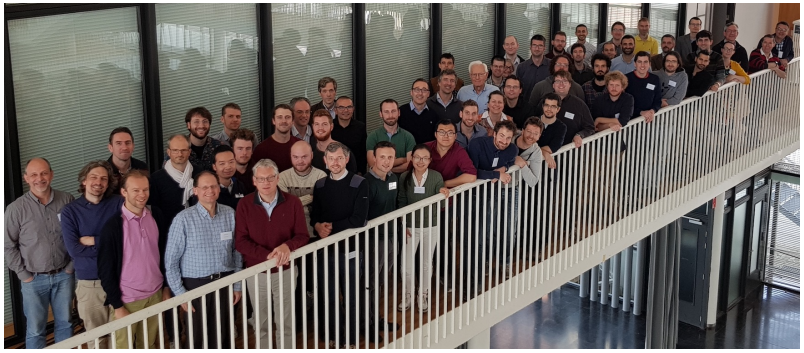
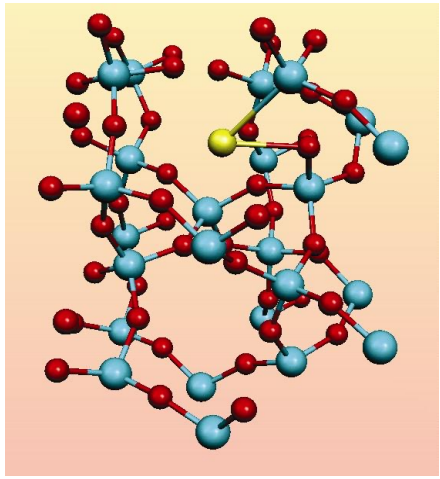
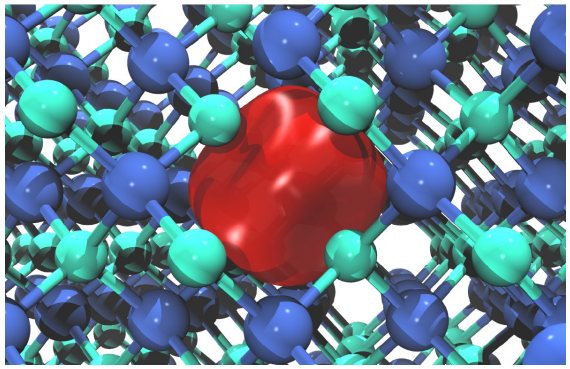
A guided tour of

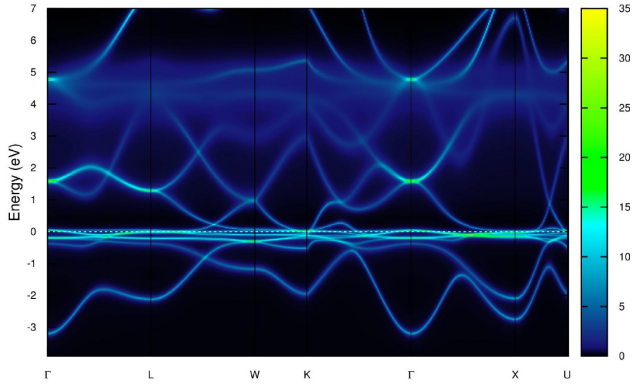
Overview

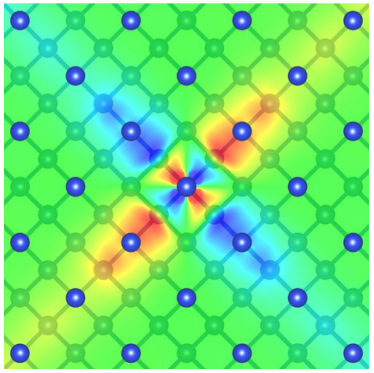


1. The ABINIT software project
2. ABINIT basics
3. Pseudopotentials / PAW
4. Reliability / Portability / Accuracy
5. Materials properties from energy derivatives
6. Density-Functional Perturbation Theory
7. >1500 phonon band structure from ABINIT
8. Effects of the electron-phonon interaction









ABINIT software project

Ideas (1997) :

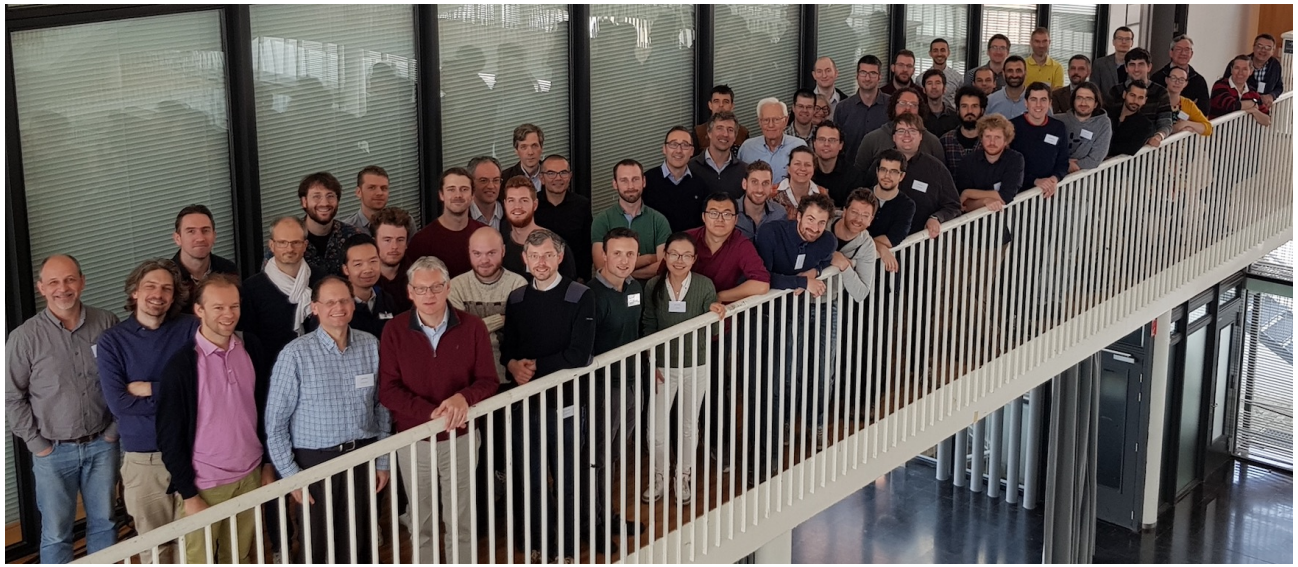
1) Software for first-principles simulations are more and more complex : needs a worldwide collaboration, of specialized, complementary, groups
2) Linux software development : ‘free software’ model

Now (2021) :

>5000 citations
>800 kLines of F90 + many python scripts (abipy)
about 50 contributors to ABINITv8/v9

Last release v9.6.2,
http://www.abinit.org

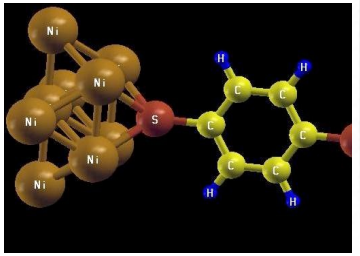
Available freely
(GPL, like Linux).

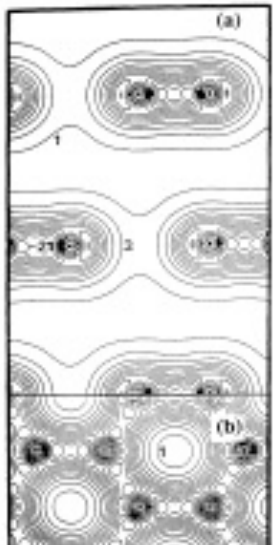


Properties from DFT+MBPT+ ...

Computation of ...

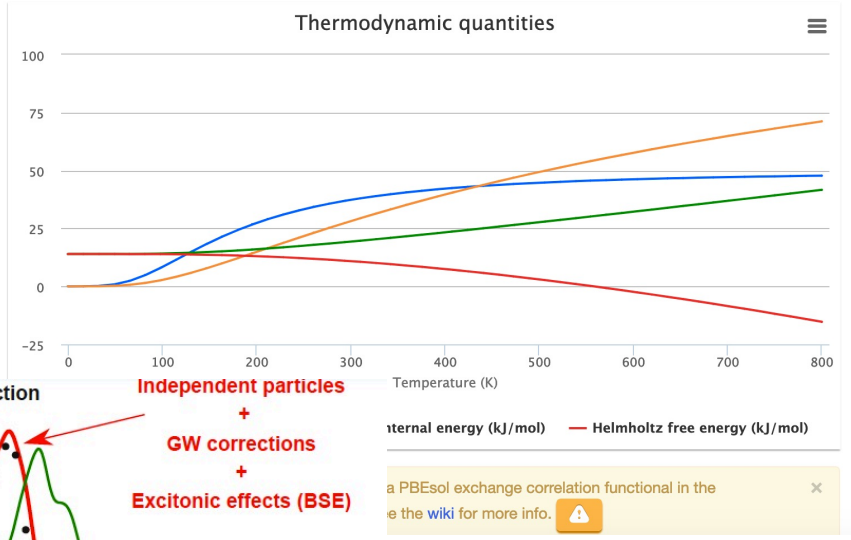
- interatomic distances, angles, total energies
- electronic charge densities, electronic energies

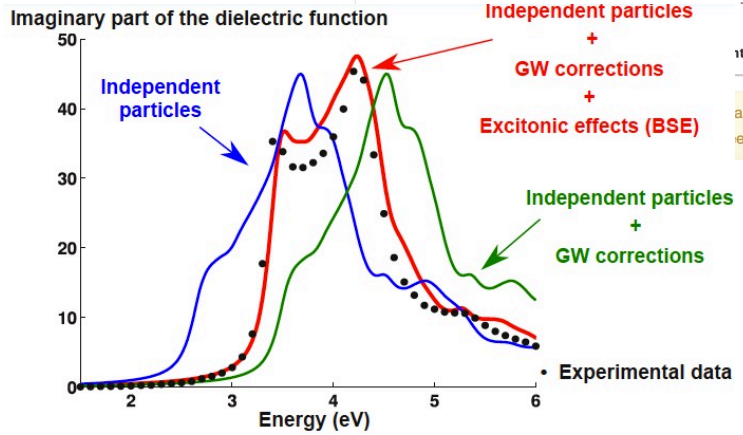




A basis for the computation of ...

- chemical reactions
- electronic transport
- vibrational properties
- thermal capacity
- dielectric behaviour
- optical response
- superconductivity
- surface properties
- spectroscopic responses
- ...





ABINIT v9 capabilities (I)

Methodologies

Pseudopotentials/Plane Waves

+ Projector Augmented Waves (for selected capabilities)

Many pseudopotential types, different PAW generators

(ATOMPAW is shipped with ABINIT)

Density functionals : LDA, GGA (many : PBE and variations, HCTH, ...),

LDA+U (or GGA+U)

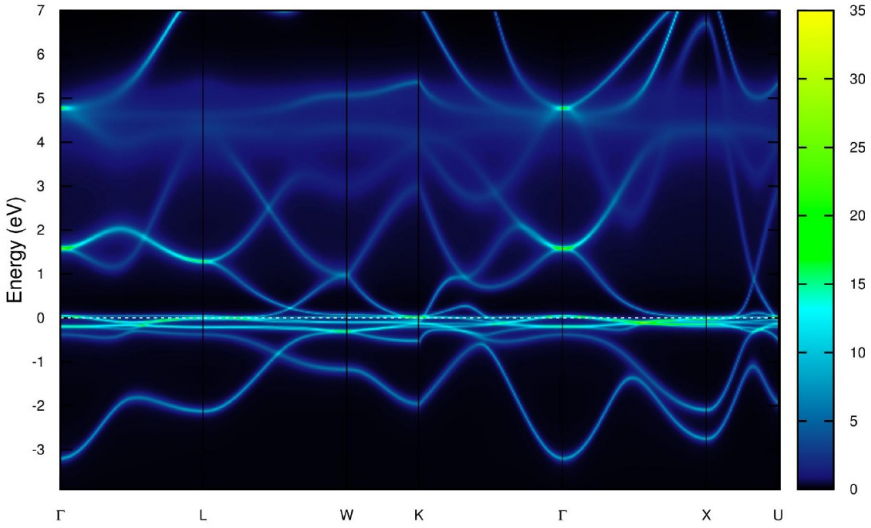
hybrid functionals + …

LR-TDDFT for finite systems excitations

GW for accurate electronic eigenenergies

Bethe-Salpeter for accurate optical properties

Dynamical mean field-theory (DMFT)



alpha-Cerium from DMFT

ABINIT v9 capabilities (II)

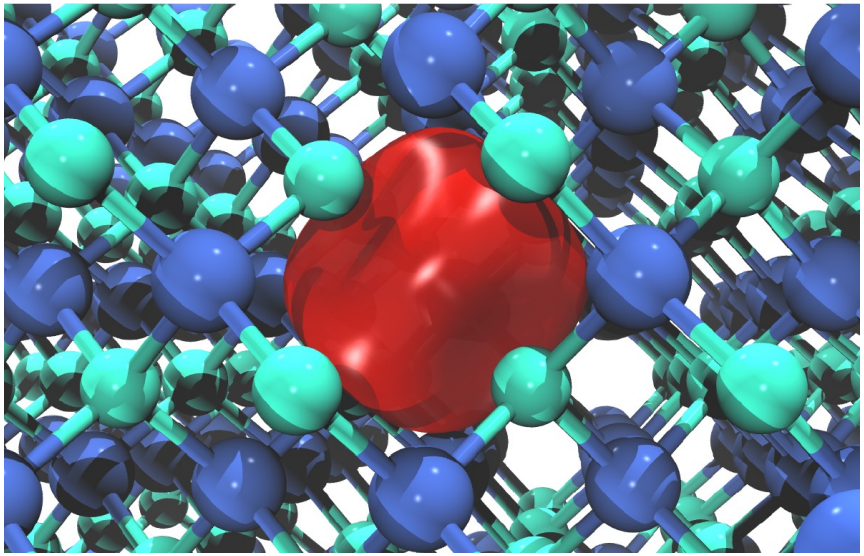
Insulators/metals - smearings : Fermi, Gaussian, Gauss-Hermite ...

Collinear spin / non-collinear spin / spin-orbit coupling

Forces, stresses, automatic optimisation of atomic positions and unit cell parameters (Broyden and Molecular dynamics with damping)

Molecular dynamics, Nosé thermostat, Langevin dynamics

Path-Integral Molecular Dynamics, String / NEB method for saddle points



Susceptibility matrix by sum over states

Optical (linear + non-linear) spectra

Polarization, finite electric field

Electric field gradients

Positron lifetime

Symmetry analyser

(database of 230 spatial groups + 1191 Shubnikov magnetic groups)

ABINIT v9 capabilities (III)

Density-Functional Perturbation Theory :

- Responses to atomic displacements, to static homogeneous electric field, to strain perturbations

- Second-order derivatives of the energy, giving direct access to :
  dynamical matrices at any q, phonon frequencies, force constants ;
  phonon DOS, thermodynamic properties (quasi-harmonic approximation) ;
  dielectric tensor, Born effective charges ;
  elastic constants, internal strain ;
  piezoelectric tensor ...
- Matrix elements, giving direct access to :
  electron-phonon coupling (mobility, Seebeck, superconductivity)
  temperature-dependence of the electronic structure
- Non-linear responses thanks to the 2n+1 theorem - at present :
  non-linear dielectric susceptibility; Raman cross-section ;
  electro-optic tensor

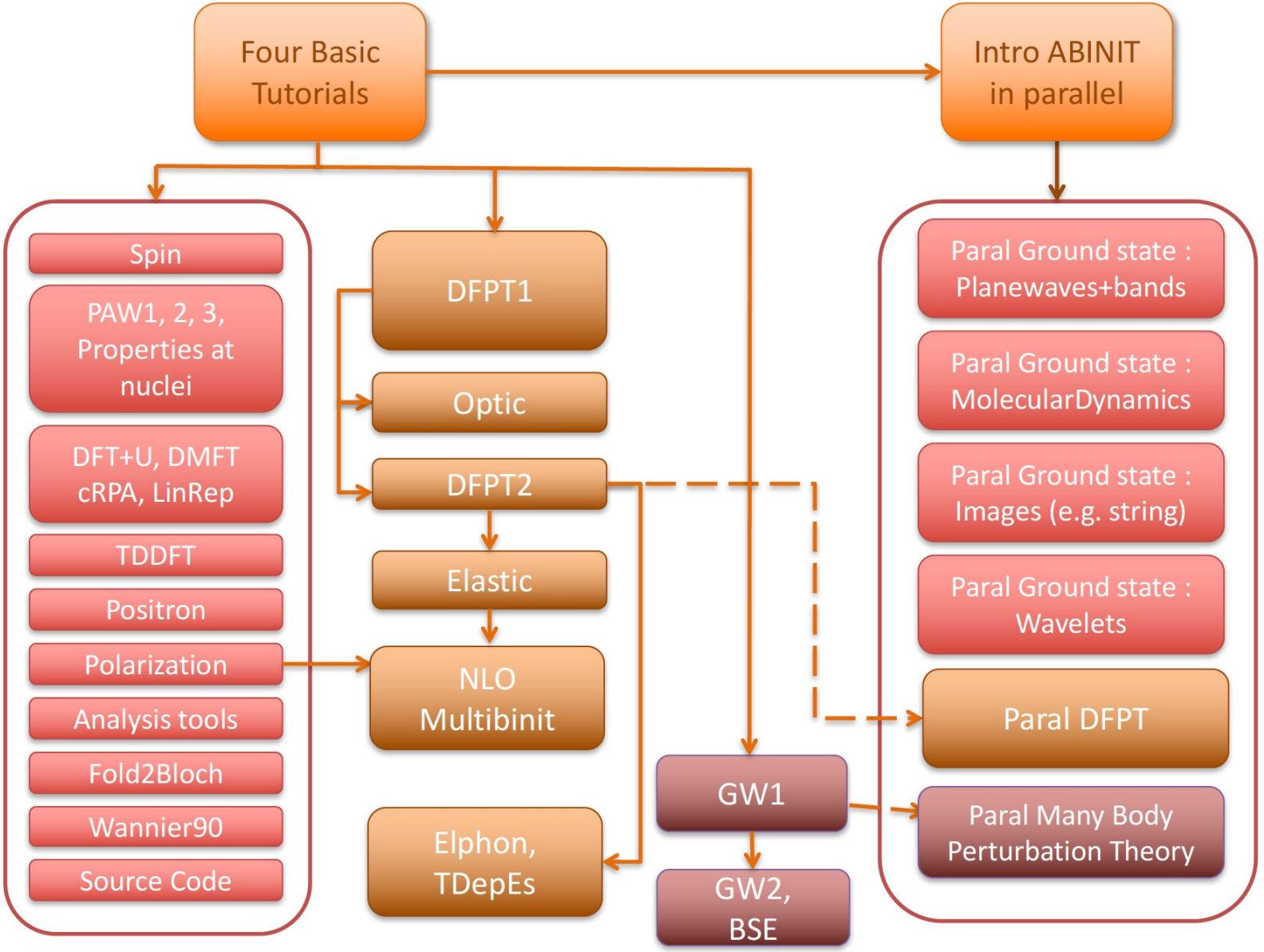
Basic Documentation

Web site http://www.abinit.org ; http://docs.abinit.org

- User's guides
- Installations notes
- List of input variables + description
- List of topics = a hub to input variables, files, tutorial, bibrefs
- over 1000 example input files
- >30 tutorial lessons (each 1-2 hours)
  https://docs.abinit.org/tutorial

+ New Forum Web site https://discourse.abinit.org
(old forum http://forum.abinit.org with more than 2000 registered members)

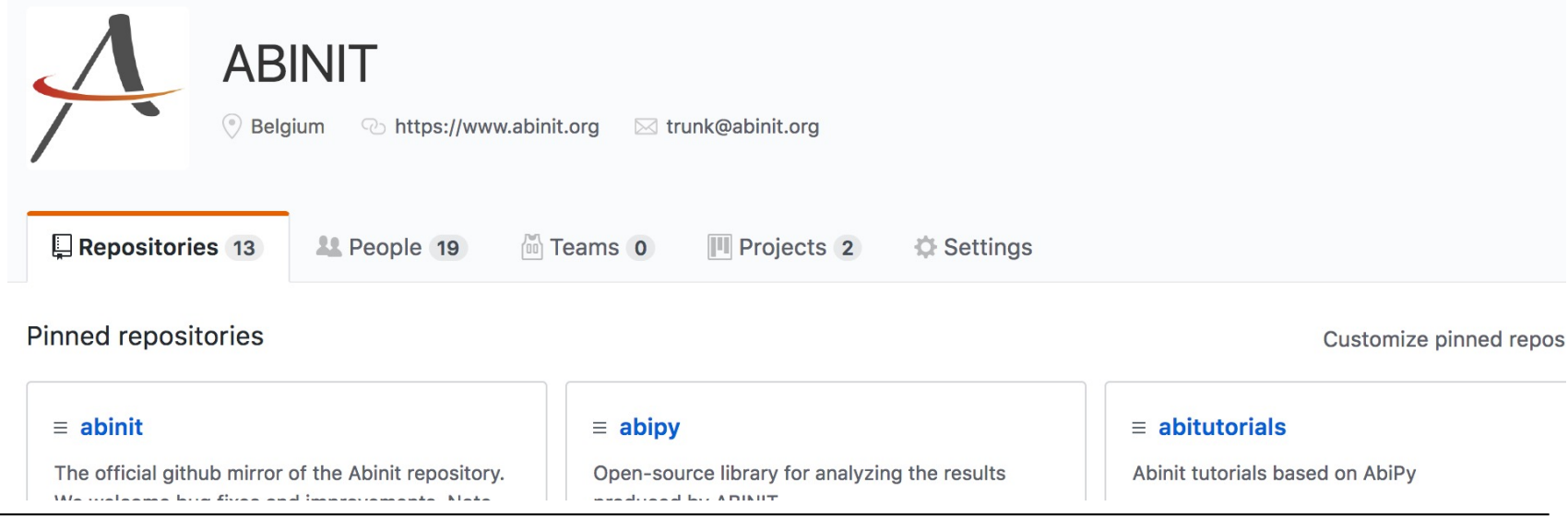
ABINIT tutorial : layout + dependencies



ABINIT + python : Abipy, Abitutorials …

ABINIT organization on GitHUB https://github.com/abinit

Abipy : python library for launching ABINIT jobs,
and analysing/plotting the results http://pythonhosted.org/abipy
=> e.g. connecting ABINIT with tools for high-throughput calculations developed in the Materials Project context (like Pymatgen, Fireworks).
Abitutorials : tutorial based on Jupyter notebooks ABINIT+python



ABINIT : basics

Density Functional Theory calculations

In ABINIT …

Representation of mathematical formalism
with a Plane Wave basis set :

- wavefunctions
- density, potential

Periodic boundary conditions
=> wavefunctions characterized by a wavevector (k-vector)

PseudoPotentials (or Projector Augmented Waves – PAW)

Iterative techniques to solve the equations
(Schrödinger equation ; DFT Self-consistency ; optimisation of atomic positions)

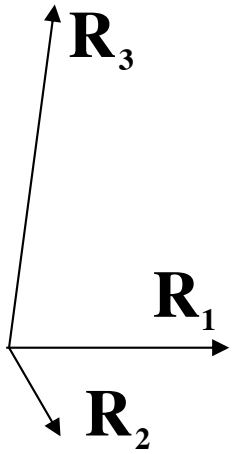
ABINIT : a periodic code

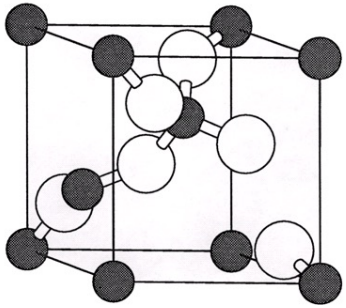
Plane waves e^{iKr} : particularly simple and efficient (when used with pseudopotentials), but infinite spatial extent.

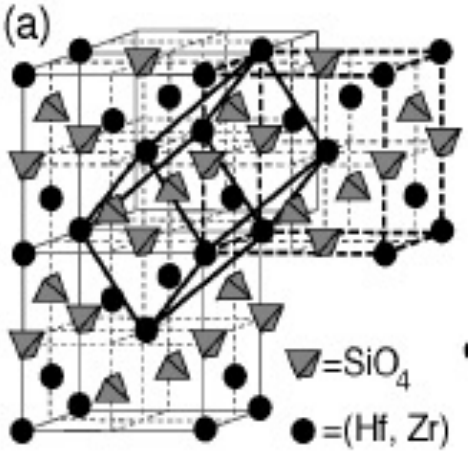
Cannot use a finite set of planewaves for finite systems !

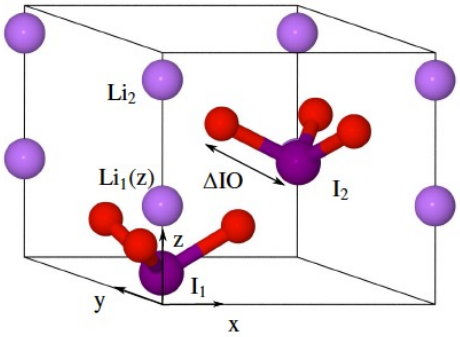
Need periodic boundary conditions.

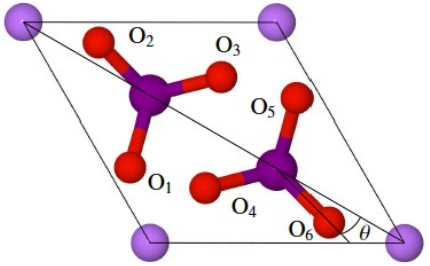
Primitive vectors $\mathbf{R}_j$, primitive cell volume Ω_0







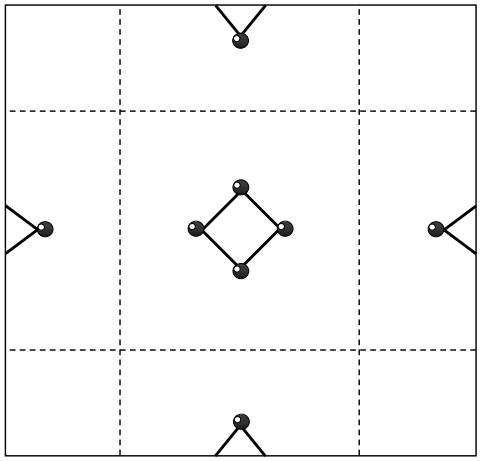




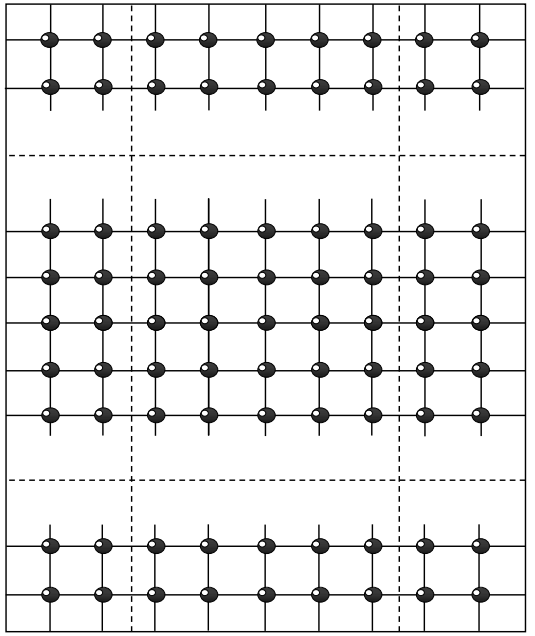
OK for crystalline solids

But : finite systems, surfaces, defects, polymers, nanosystems ... ?

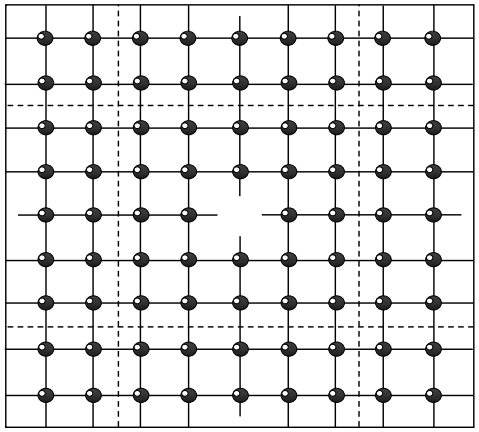
Solution : the supercell technique



Molecule,
cluster



Surface : treatment
of a slab
Interface

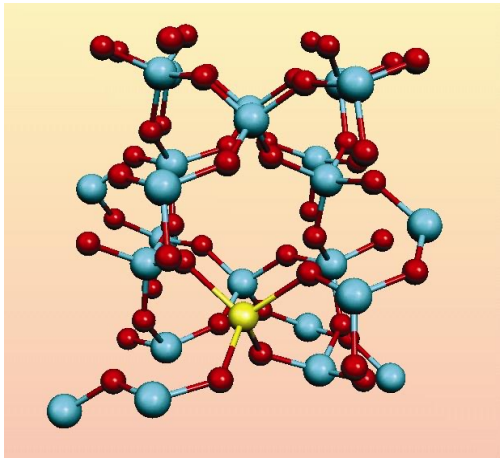


Point defect in a bulk solid

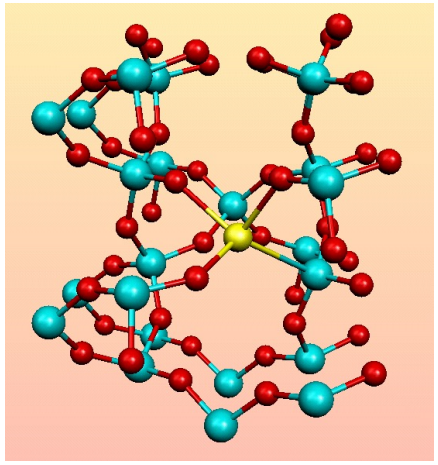
The supercell must be sufficiently big : convergence study

Examples of defects SiO_2-quartz : Pb

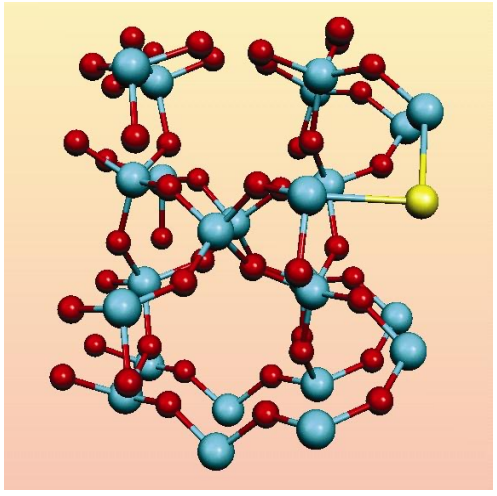
72-atom supercell of quartz



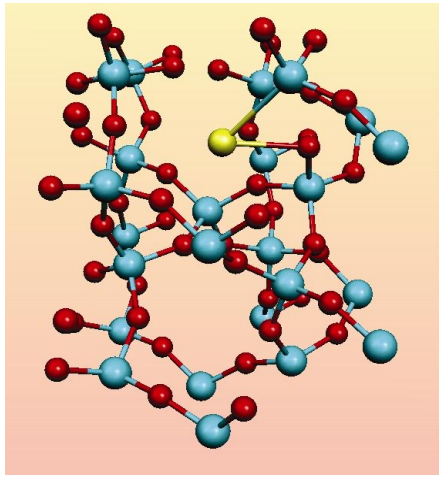
Pb^{Si}



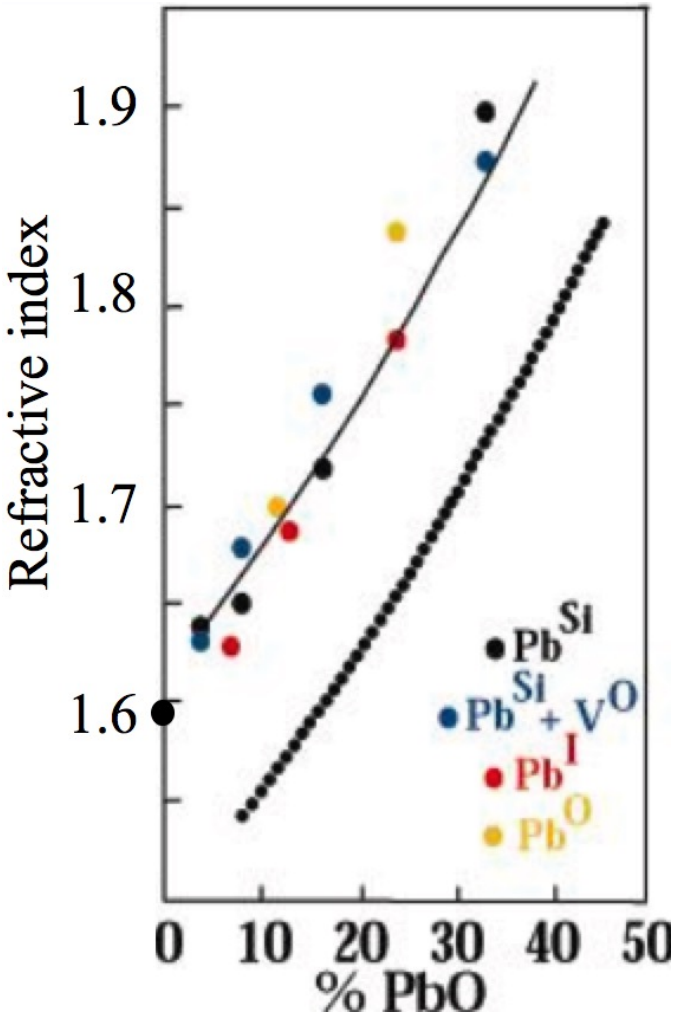
$Pb^{Si} + V^{O}$



Pb^{O}



Pb^{I}



Comparison with amorphous SiO_2

Pseudopotentials

Core and valence electrons (I)

Core electrons occupy orbitals that are « the same » in the atomic environment or in the bonding environment

It depends on the accuracy of the calculation !

Separation between core and valence orbitals : the density...

$$n(\mathbf{r}) = \sum_{i}^{N} \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})$$

$$= \sum_{i \in core}^{N_{core}} \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) + \sum_{i \in val}^{N_{val}} \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) = n_{core}(\mathbf{r}) + n_{val}(\mathbf{r})$$

« Frozen core » $\text{for i} \in \text{core} : \psi_i = \psi_i^{atom}$

Small core / Large core

It depends on the target accuracy of the calculation !

(remark also valid for pseudopotentials, with similar cores)

For some elements, the core/valence partitioning is obvious, for some others, it is not.

F atom : $\boxed{(1s)^2} + (2s)^2(2p)^5$

IP 1keV 10-100 eV

Ti atom : $\boxed{(1s)^2(2s)^2(2p)^6}(3s)^2(3p)^6(4s)^2(3d)^2$ small core

$\boxed{(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6}(4s)^2(3d)^2$ large core

IP 99.2 eV 43.3eV

Gd atom : small core with n=1,2,3 shells , might include 4s, 4p, and 4d in the core. 4f partially filled

Core and valence electrons (II)

Separation between core and valence orbitals : the energy ...

$$E_{\mathrm{KS}}\left[\{\psi_i\}\right] = \sum_i \left\langle \psi_i \right| -\frac{1}{2}\nabla^2 \left| \psi_i \right\rangle + \int V_{ext}(\mathbf{r}) n(\mathbf{r})\,\mathrm{d}\mathbf{r} + \frac{1}{2}\int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 + E_{\mathrm{xc}}\left[n\right]$$

$$\begin{aligned} E_{\mathrm{KS}}\left[\{\psi_i\}\right] = & \sum_{i\in core}^{N_{core}} \left\langle \psi_i \right| -\frac{1}{2}\nabla^2 \left| \psi_i \right\rangle + \int V_{ext}(\mathbf{r}) n_{core}(\mathbf{r})\,\mathrm{d}\mathbf{r} + \frac{1}{2}\int \frac{n_{core}(\mathbf{r}_1)n_{core}(\mathbf{r}_2)}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \\ & + \sum_{i\in val}^{N_{val}} \left\langle \psi_i \right| -\frac{1}{2}\nabla^2 \left| \psi_i \right\rangle + \int V_{ext}(\mathbf{r}) n_{val}(\mathbf{r})\,\mathrm{d}\mathbf{r} + \frac{1}{2}\int \frac{n_{val}(\mathbf{r}_1)n_{val}(\mathbf{r}_2)}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \\ & + \int \frac{n_{val}(\mathbf{r}_1)n_{core}(\mathbf{r}_2)}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 + E_{\mathrm{xc}}\left[n_{core} + n_{val}\right] \end{aligned}$$

Removing core electrons (I)

From the previous construction : valence orbitals must still be orthogonal to core orbitals
(=> oscillations, slope at the nucleus ...)

Pseudopotentials try to remove completely the core orbitals from the simulation

Problem with the number of nodes
This is a strong modification of the system ...

Pseudopotentials confine the strong changes within a « cut-off radius »

Removing core electrons (II)

Going from $\left(-\frac{1}{2}\nabla^2 + v\right) | \psi_i > = \varepsilon_i | \psi_i >$

To $\left(-\frac{1}{2}\nabla^2 + v_{ps}\right) | \psi_{ps,i} > = \varepsilon_{ps,i} | \psi_{ps,i} >$

Possible set of conditions (norm-conserving pseudopotentials)

NCPP - Hamann D.R., Schlüter M., Chiang C, Phys.Rev.Lett. 43, 1494 (1979)

$$\varepsilon_i = \varepsilon_{ps,i}$$

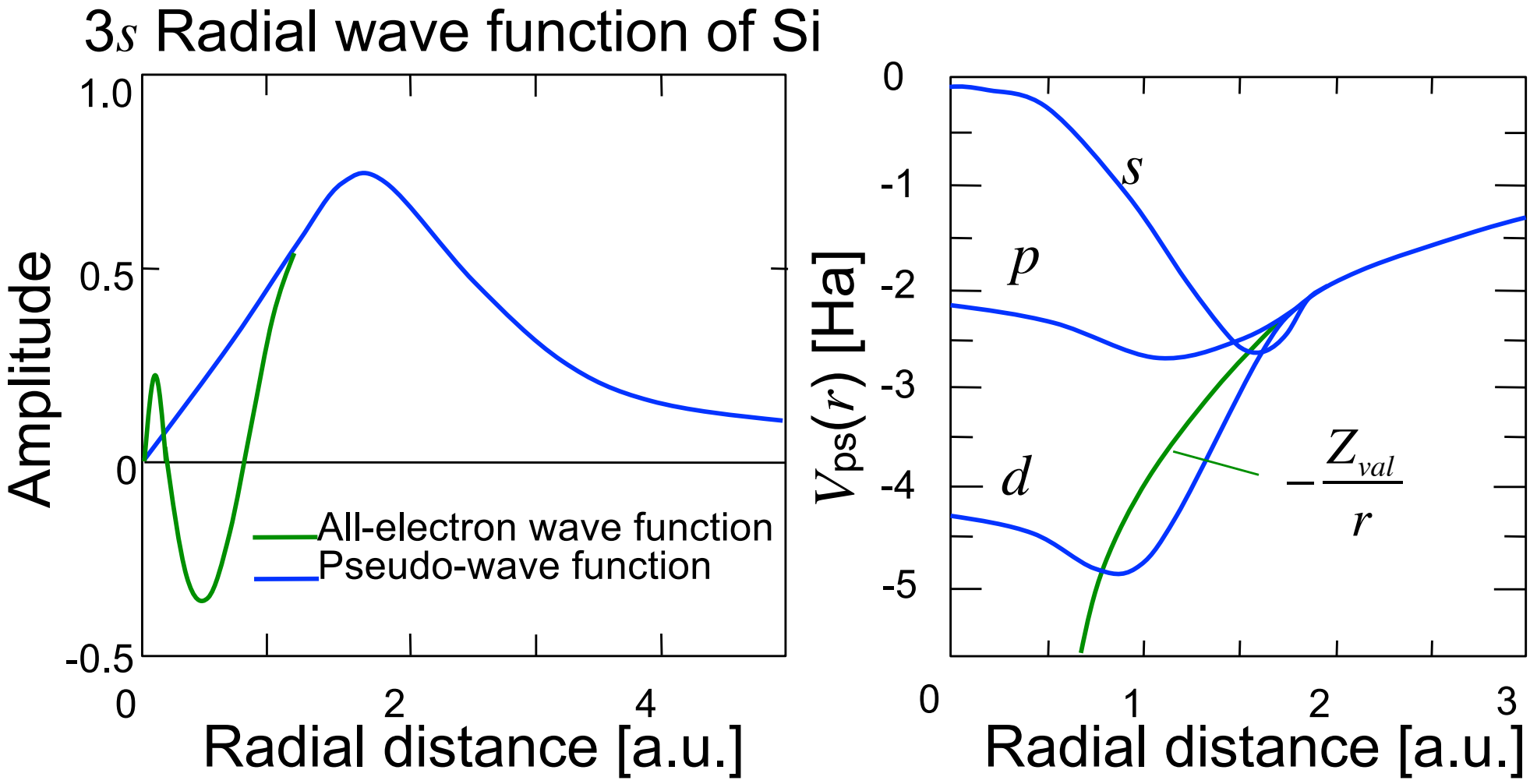
$$\psi_i(\mathbf{r}) = \psi_{ps,i}(\mathbf{r}) \quad \text{for} \quad r > r_c$$

$$\int_{r<r_c} |\psi_i(\mathbf{r})|^2 d\mathbf{r} = \int_{r<r_c} |\psi_{ps,i}(\mathbf{r})|^2 d\mathbf{r}$$

For the lowest angular momentum channels (s + p ... d ...f)

Generalisation : ultra-soft pseudopotentials (USPP), projector-augmented plane waves (PAW)

Example of pseudopotential

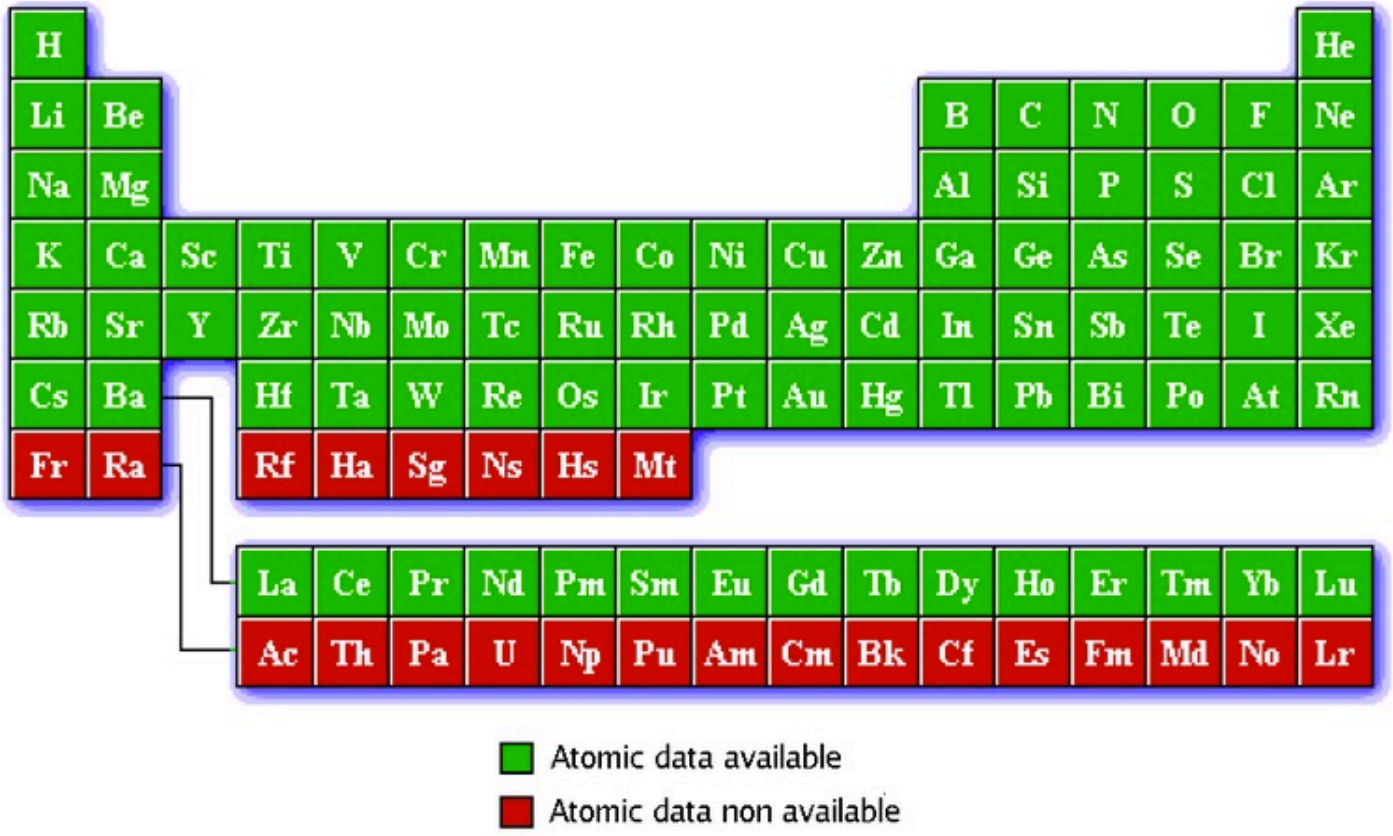


Pseudopotentials/PAW data in ABINIT

- Preferred PAW atomic dataset table : JTH

Jollet, Torrent, Holzwarth, Computer Physics Comm. 185, 1246 (2014)

https://www.abinit.org/psp-tables



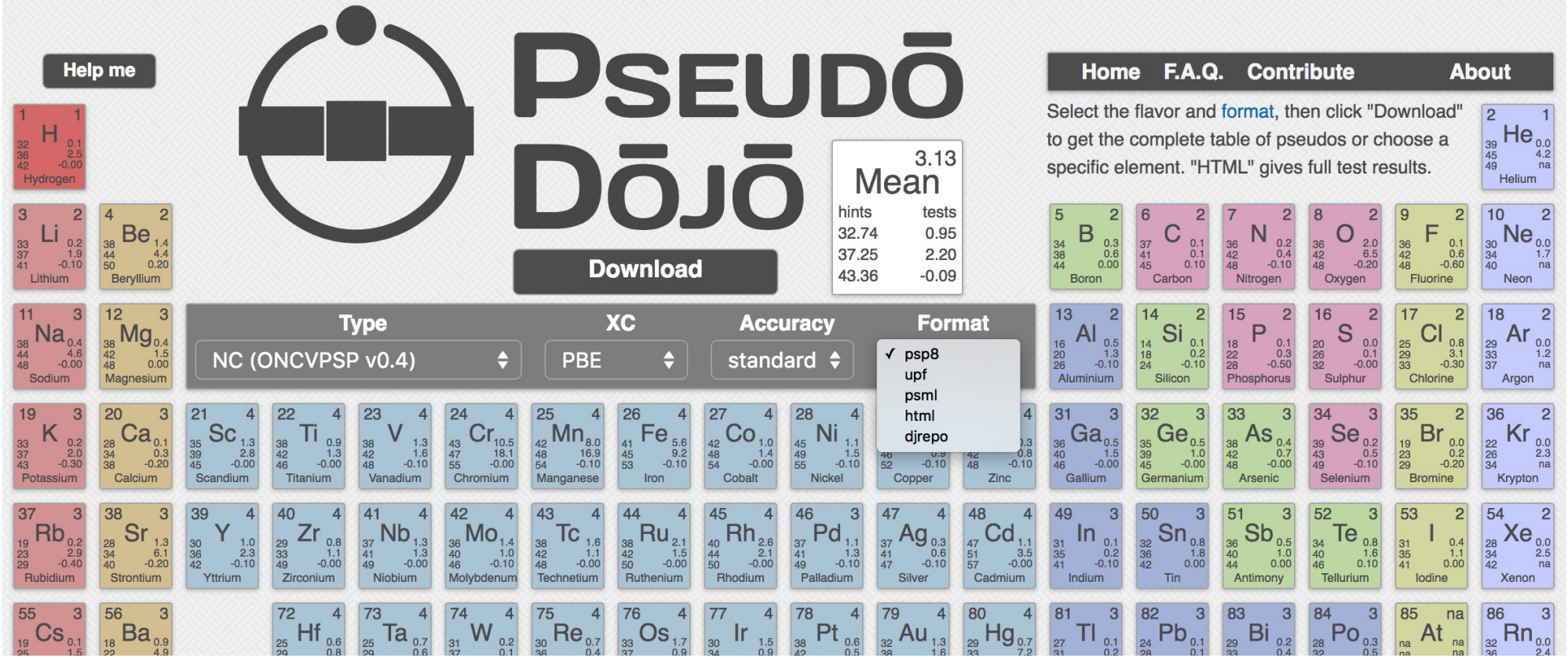
Also, possibility to use : GPAW table, GBRV v1.0 table, or norm-conserving pseudopotentials (e.g. ONCVPSP pseudo generator), or many others

Pseudopotentials/PAW data in ABINIT

- Norm-conserving pseudos : pseudo-dojo approach

  Van Setten et al , Computer Physics Comm. 226, 39 (2018)

  https://www.pseudo-dojo.org



Reliability / portability
Accuracy

Quality control : test suite + test farm

How to secure existing capabilitites despite the development efforts (by diverse groups) and associated bug generation ?

Test suite : >1000 automatic tests (+ new added for each capability)

Test farm : >12 computers (4 to 64 cores)

with 3 compilers (gfort, Intel, NAG) => over 20 'builders'

Name	Brand	CPU / Freq	# cores	RAM	OS	misc
abiref	HP DL360 gen9	Xeon E5-2670v3/ 2.30	2 x 24	32GB	CentOS 7.2	Ref
bob	Dell R430	Xeon E5-2603v3/ 1.60	2 x 6	8GB	Fedora 23	
buda	SuperMicro	Xeon X5570/ 2.7	2 x 4	12GB	CentOS 6.8	2xGPU K40 2xGPU C1060
coba2	HP Z400	Xeon W3520/ 2.7	4	12GB	CentOS 6.5	
cronos	HP DL185 G7	AMD Opteron 6276/ 2.3	2 x 16	16GB	Debian 5.0	
graphene	Apple MacPro	Xeon E5-2697/ 2.7	1 x 12	64GB	MacOS X 10.12	
ibm8	IBM Power S824	Power8/ 3.0	4	8GB	AIX 7.2	
inca	virtual machine	Opteron 6276/ 2.3	12	30GB	CentOS 6.9	
max2	HP DL185	Opteron 6140/ 2.6	2 x 8	12GB	Slinux 6.1	
petrus	Intel	Core i7 3930/ 3.2	6	16GB	openSUSE 12.1	
testf	Bull Novascale	Xeon X5570/ 2.9	2 x 4	12GB	CentOS 5.11	
tikal	Dell T5500	Xeon X5647/ 3.0	8	8GB	Slinux 6.9	
ubu	HP DL360 gen9	Xeon E5-2670v3/ 2.30	2 x 24	32GB	Ubuntu 16.04	

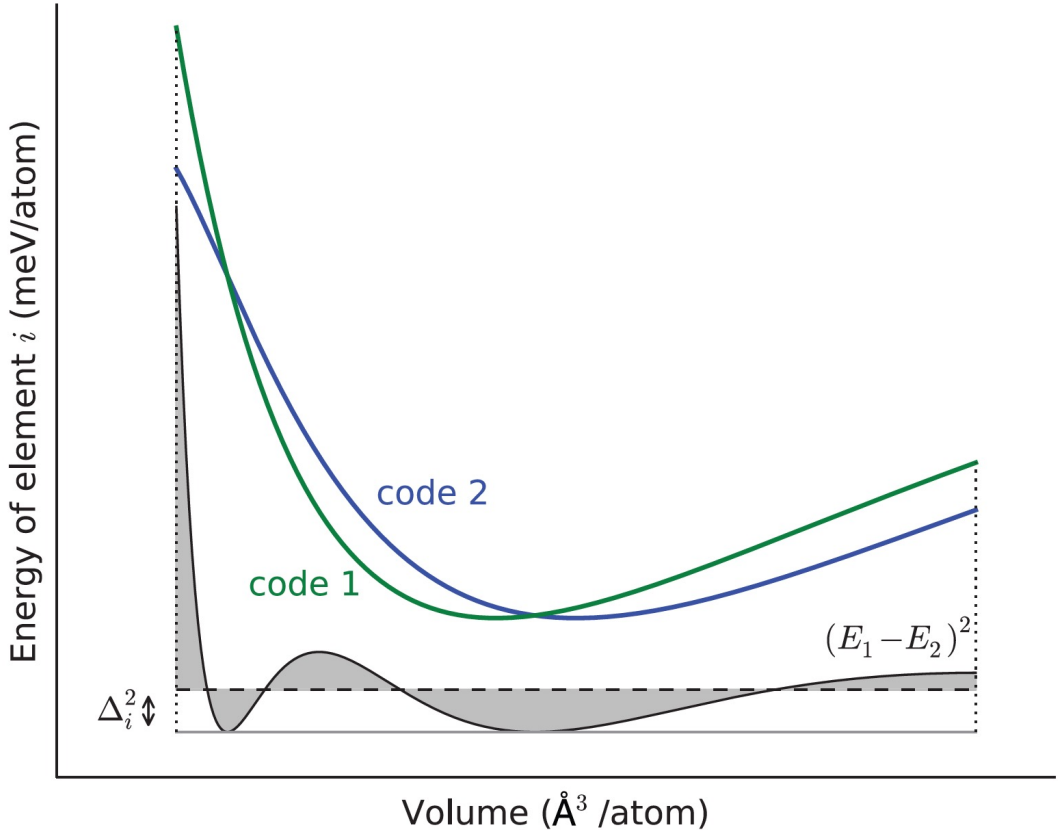
Comparing code/pseudopotential

In 2016, large effort related to the quantification of numerical accuracy/precision:

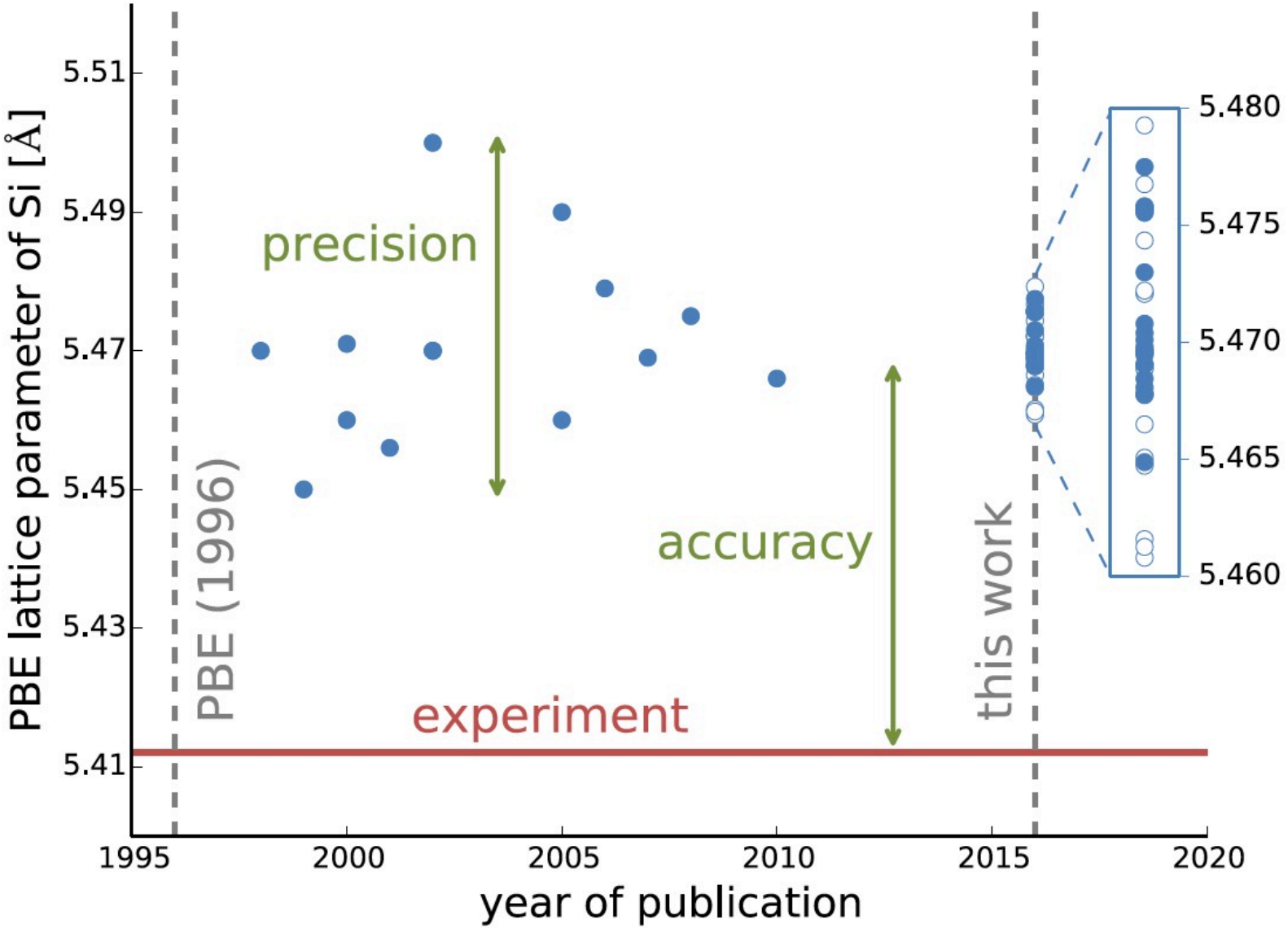
« Delta-factor » collaboration

Lejaeghere ... Cottenier, Science 351, aad3000 (2016)

Specification of **71 elemental solids** for different volumes.



Validation (vs exp.)/ verification (numerics)



All-electron and PAW spread of values

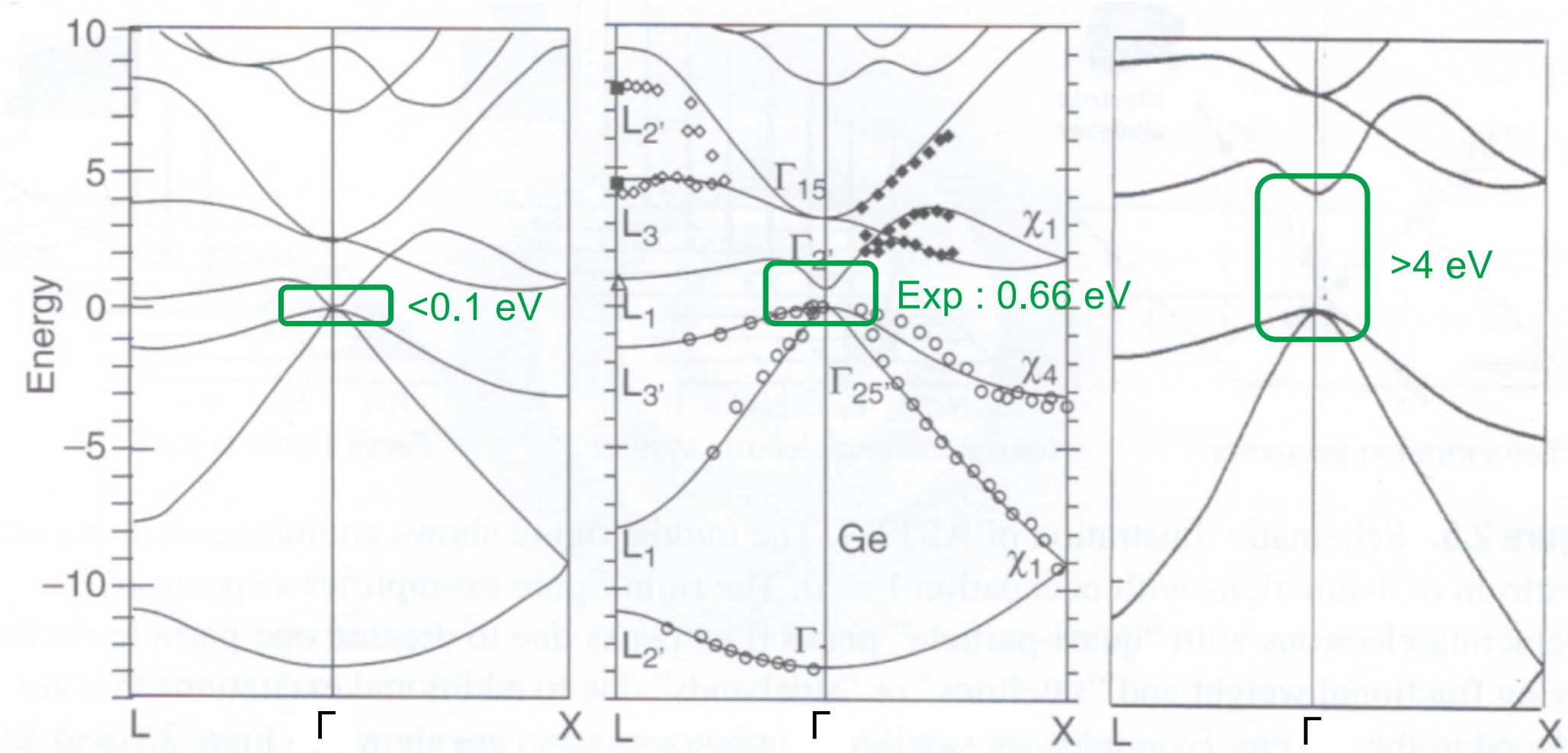
AE = "All-electron" calculations

PAW = "Projector-Augmented Waves"
... a kind of pseudopotential calculation

		average <Δ>	AE: Elk	AE: exciting	AE: FHI-aims/tier2	AE: FLEUR	AE: FPLO/T+F+s	AE: RSPt	AE: WIEN2k/acc
AE	Elk	0.6		0.3	0.3	0.6	1.0	0.9	0.3
	exciting	0.5	0.3		0.1	0.5	0.9	0.8	0.2
	FHI-aims/tier2	0.5	0.3	0.1		0.5	0.9	0.8	0.2
	FLEUR	0.6	0.6	0.5	0.5		0.8	0.6	0.4
	FPLO/T+F+s	0.9	1.0	0.9	0.9	0.8		0.9	0.9
	RSPt	0.8	0.9	0.8	0.8	0.6	0.9		0.8
	WIEN2k/acc	0.5	0.3	0.2	0.2	0.4	0.9	0.8	
PAW	GBRV12/ABINIT	0.9	0.9	0.8	0.8	0.9	1.3	1.1	0.8
	GPAW09/ABINIT	1.4	1.3	1.3	1.3	1.3	1.7	1.5	1.3
	GPAW09/GPAW	1.6	1.5	1.5	1.5	1.5	1.8	1.7	1.5
	JTH02/ABINIT	0.6	0.6	0.6	0.6	0.6	0.9	0.7	0.5
	PSlib100/QE	0.9	0.9	0.8	0.8	0.8	1.3	1.1	0.8
	VASPGW2015/VASP	0.6	0.4	0.4	0.4	0.6	1.0	0.8	0.3

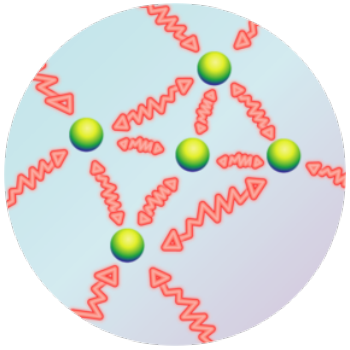
Accurate band gap from GW approximation

Germanium band structure

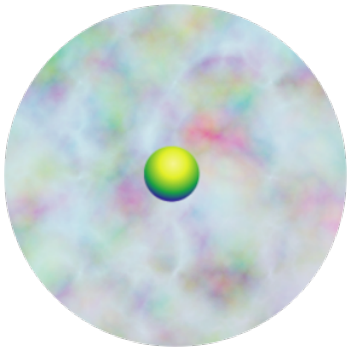


DFT (LDA) GW & experiment (circles) Hartree-Fock

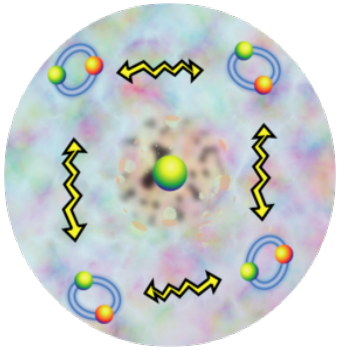
GW approximation



Wavefunctions



DFT



GW

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right)\psi_i(\mathbf{r}) + V_{xc}(\mathbf{r})\psi_i(\mathbf{r}) = \varepsilon_i^{KS}\psi_i(\mathbf{r}) \qquad \text{DFT}$$

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right)\psi_i(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}';\varepsilon_i^{QP})\psi_i(\mathbf{r}')d\mathbf{r}' = \varepsilon_i^{QP}\psi_i(\mathbf{r})$$

$$\Sigma(\mathbf{r},\mathbf{r}';\omega) = \lim_{\delta\to 0+}\frac{i}{2\pi}\int d\omega' e^{i\omega'\delta} G(\mathbf{r},\mathbf{r}';\omega+\omega') W(\mathbf{r},\mathbf{r}';\omega') \qquad \text{GW}$$

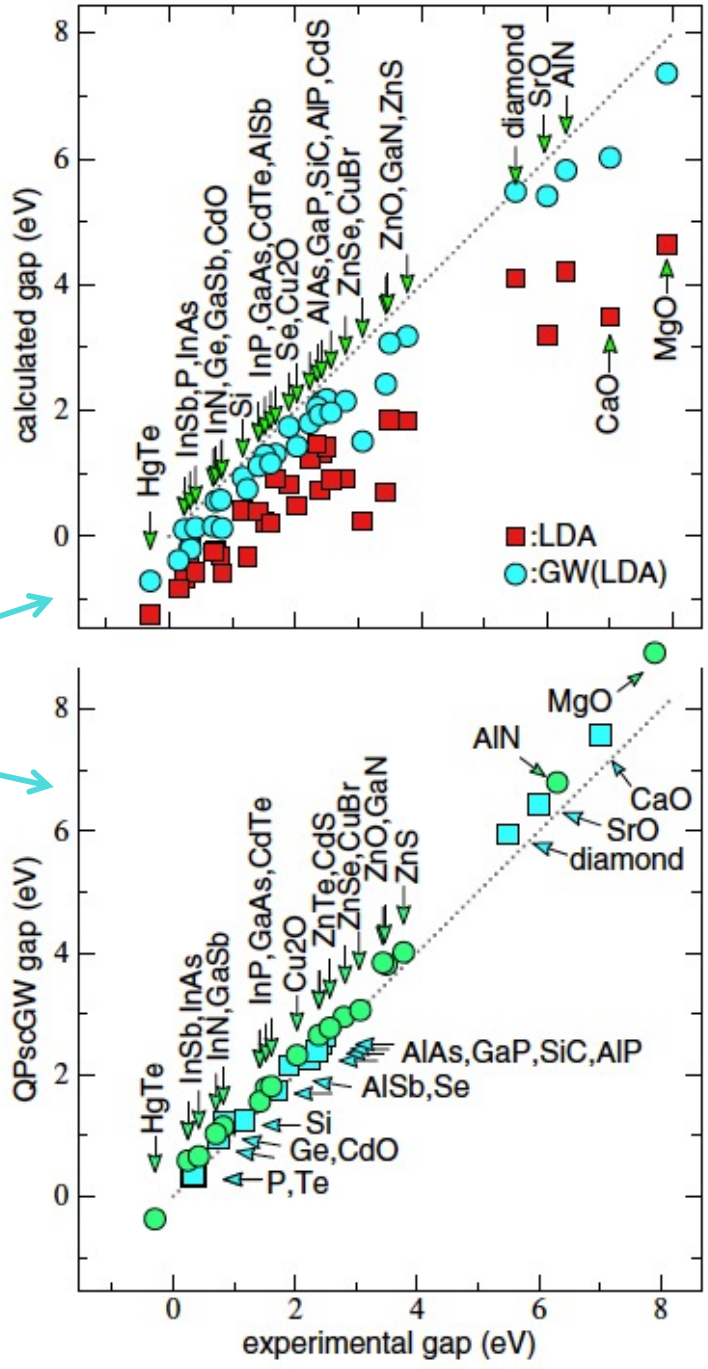
Self energy — Green's function — Screened interaction

GW approximation

- Heavier than DFT/LDA
  (e.g. CPU time x100...x1000)

- Start from DFT calculation,
  then can be one-shot (GW@LDA)
  or self-consistent (SCGW)

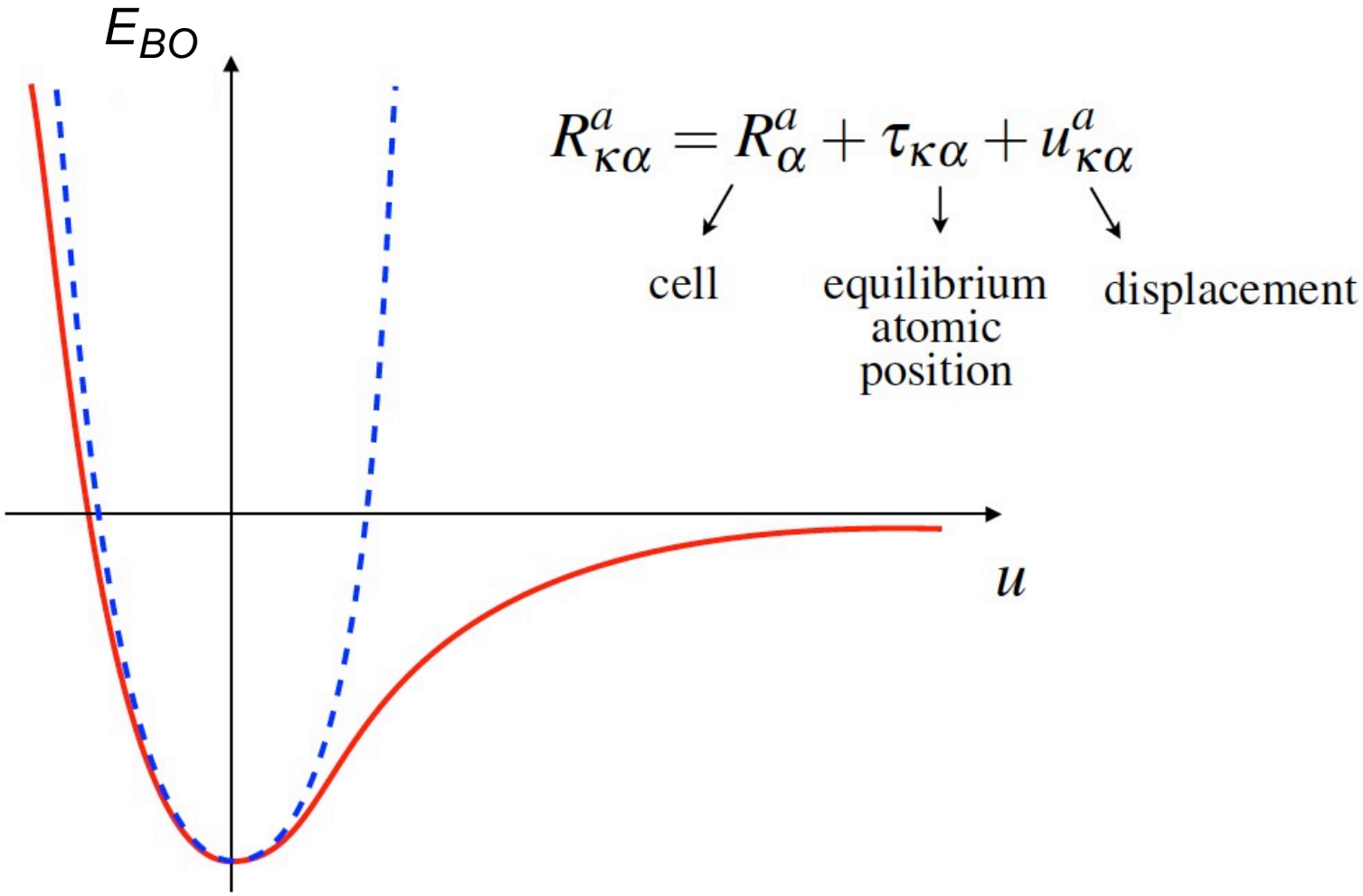
- SCGW "Gold standard"
  (within 0.1...0.3eV),
  but GW@LDA is often fine



Material properties from total energy derivatives : phonons

Changing atomic positions

Born-Oppenheimer approximation …



Phonon frequencies from force constants

Matrix of interatomic force constants :

$$C_{\kappa\alpha,\kappa'\alpha'}(a,a') = \frac{\partial^2 E_{BO}}{\partial R^{a}_{\kappa\alpha} \partial R^{a'}_{\kappa'\alpha'}}$$

Fourier Transform (using translational invariance) :

$$\tilde{C}_{k\alpha,k'\alpha'}(\vec{q}) = \sum_{a'} C_{k\alpha,k'\alpha'}(0,a')\, e^{i\vec{q}.\vec{R}^{a'}}$$

Computation of phonon frequencies and eigenvectors = solution of generalized eigenvalue problem

$$\sum_{k'\alpha'} \tilde{C}_{k\alpha,k'\alpha'}(\vec{q}).u_{m\vec{q}}(k'\alpha') = M_k \,.\, \omega^2_{m\vec{q}} \,.\, u_{m\vec{q}}(k\alpha)$$

phonon displacement pattern

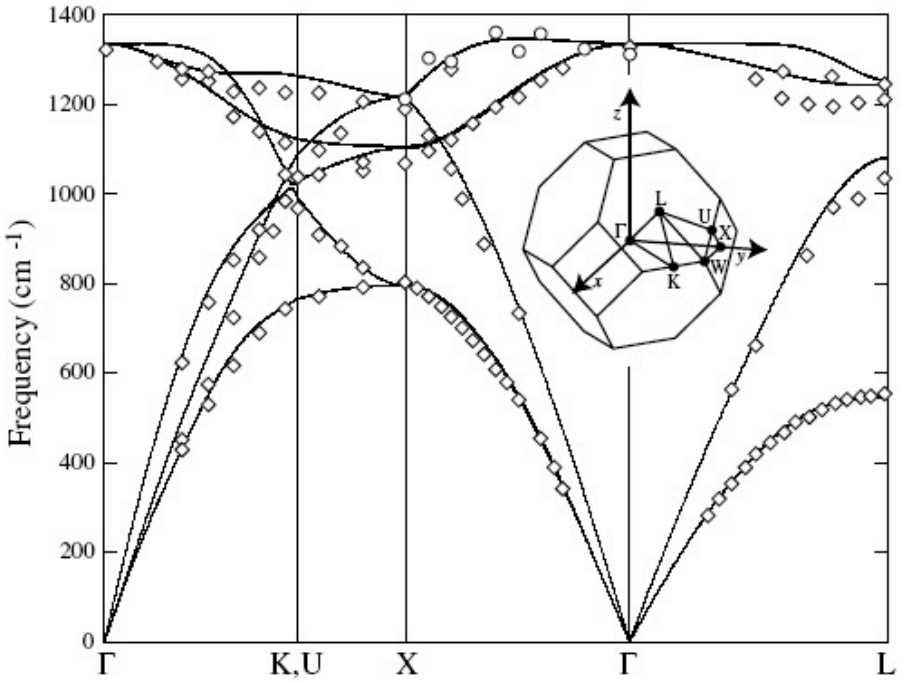
masses

square of phonon frequencies

How to get second derivatives of the energy ?

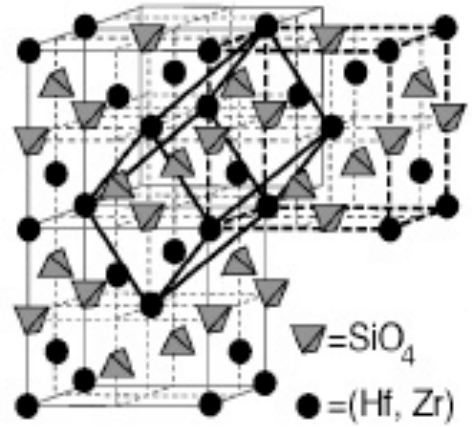
Density Functional Perturbation Theory...

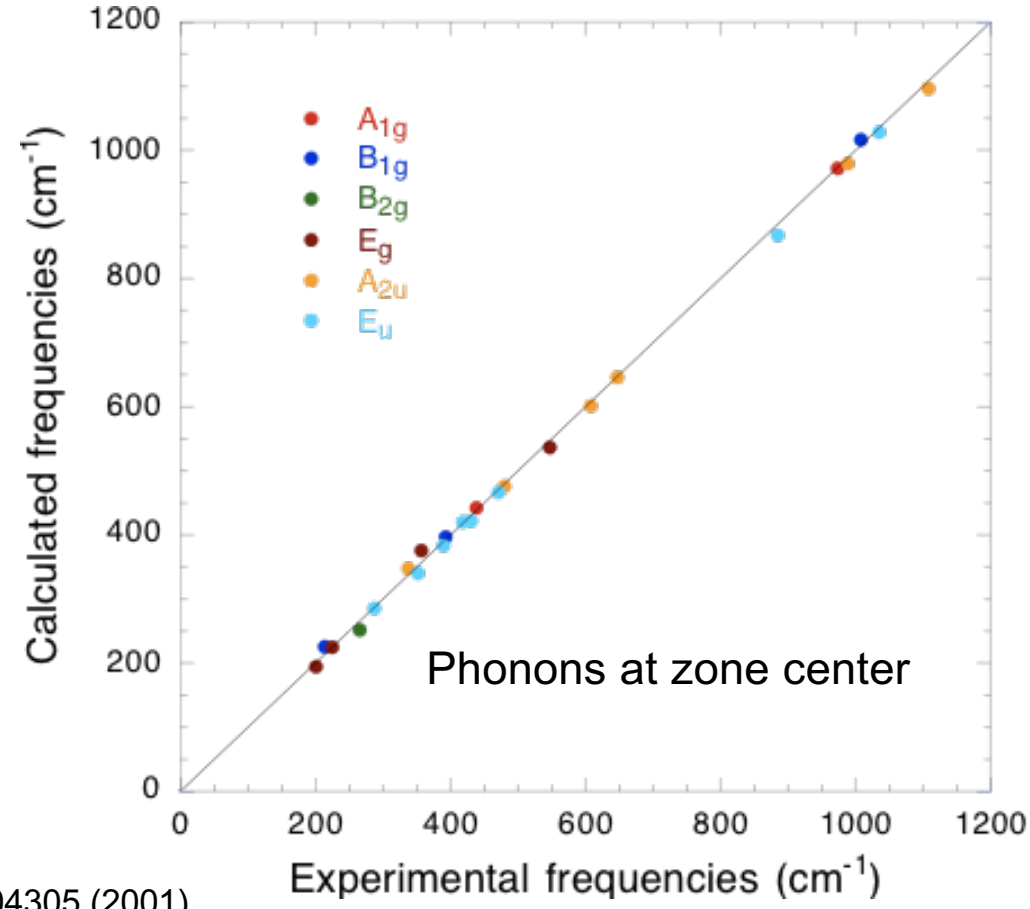
Phonons : exp vs theory



Diamond

Zircon





XG, G.-M. Rignanese and R. Caracas.
Zeit. Kristall. 220, 458-472 (2005)

Rignanese, XG and Pasquarello. *Phys. Rev. B* 63, 104305 (2001)

Challenges for periodic materials ?

In addition of being able to compute derivatives of BO energy :

Treating phonons of different wavelengths ?
(Not only periodic ones)

Treating electric field ?
Electric field => linear potential,
incompatible with periodicity

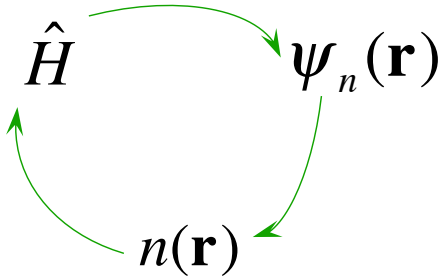
Even for phonons at zero wavevector (Gamma),
treating LO-TO splitting
(longitudinal optic – transverse optic)

Density-functional perturbation theory (DFPT)

Basic equations in DFT

Solve self-consistently Kohn-Sham equation

$$\begin{cases} \hat{H}\left|\psi_n\right\rangle = \varepsilon_n\left|\psi_n\right\rangle \\ \hat{H} = \hat{T} + \hat{V} + \hat{V}_{Hxc}[n] \\ n(\vec{r}) = \sum_n^{occ} \psi_n^*(\vec{r})\psi_n(\vec{r}) \end{cases}$$



$$\delta_{mn} = \left\langle \psi_m \middle| \psi_n \right\rangle \text{for } m,n \in \text{occupied set}$$

or minimize

$$E_{el}\{\psi\} = \sum_n^{occ} \left\langle \psi_n \middle| \hat{T} + \hat{V} \middle| \psi_n \right\rangle + E_{Hxc}[n]$$

What is $\hat{V}$?

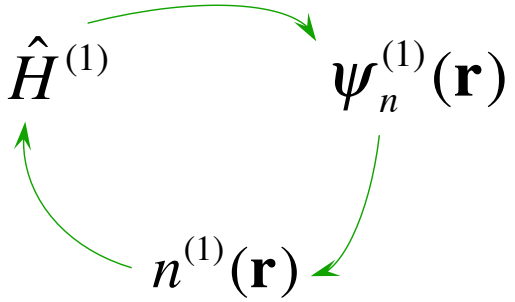
$$\hat{V}(\vec{r}) = \sum_{a\kappa} -\frac{Z_\kappa}{\left|\vec{r} - \vec{R}_\kappa^a\right|}$$

Basic equations in DFPT

Solve self-consistently Sternheimer equation

$$\begin{cases} (\hat{H}^{(0)}-\varepsilon_n^{(0)})\left|\psi_n^{(1)}\right\rangle = -(\hat{H}^{(1)}-\varepsilon_n^{(1)})\left|\psi_n^{(0)}\right\rangle \\ \varepsilon_n^{(1)} = \left\langle\psi_n^{(0)}\right|\hat{H}^{(1)}\left|\psi_n^{(0)}\right\rangle \\ \hat{H}^{(1)} = \hat{V}^{(1)}+\int\frac{\delta^2 E_{Hxc}}{\delta\rho(r)\delta\rho(r')}n^{(1)}(r')dr' \end{cases}$$

$$0 = \left\langle\psi_m^{(0)}\right|\left.\psi_n^{(1)}\right\rangle \text{ for m} \in \text{occupied set}$$



$$n^{(1)}(\vec{r}) = \sum_n^{occ}\psi_n^{(1)*}(\vec{r})\psi_n^{(0)}(\vec{r})+\psi_n^{(0)*}(\vec{r})\psi_n^{(1)}(\vec{r})$$

or minimize

$$E_{el}^{(2)}\left\{\psi^{(1)};\psi^{(0)}\right\} = \sum_n^{occ}\left\langle\psi_n^{(1)}\right|\hat{H}^{(0)}-\varepsilon_n^{(0)}\left|\psi_n^{(1)}\right\rangle+\left\langle\psi_n^{(1)}\right|\hat{V}^{(1)}\left|\psi_n^{(0)}\right\rangle + \left\langle\psi_n^{(0)}\right|\hat{V}^{(1)}\left|\psi_n^{(1)}\right\rangle+\left\langle\psi_n^{(0)}\right|\hat{V}^{(2)}\left|\psi_n^{(0)}\right\rangle + \frac{1}{2}\iint\frac{\delta^2 E_{Hxc}}{\delta\rho(\vec{r})\delta\rho(\vec{r}')}\,n^{(1)}(\vec{r})\,n^{(1)}(\vec{r}')\,d\vec{r}\,d\vec{r}'$$

What is $\hat{V}^{(1)}$, $\hat{V}^{(2)}$?

The potential and its 1st derivative

Derivative with respect to $R^{a}_{\kappa\alpha}$

$$V^{(0)}(\vec{r}) = \sum_{a\kappa} -\frac{Z_\kappa}{\left|\vec{r}-\vec{R}^{a}_{\kappa}\right|}$$

$$V^{(1)}(\vec{r}) = \frac{\partial V(\vec{r})}{\partial R^{a}_{\kappa,\alpha}} = \frac{Z_\kappa}{\left|\vec{r}-\vec{R}^{a}_{\kappa}\right|^2} \cdot \frac{\partial\left|\vec{r}-\vec{R}^{a}_{\kappa}\right|}{\partial u^{a}_{\kappa,\alpha}} = -\frac{Z_\kappa}{\left|\vec{r}-\vec{R}^{a}_{\kappa}\right|^3} \cdot \left(\vec{r}-\vec{R}^{a}_{\kappa}\right)_\alpha$$

Generalisation to pseudopotentials can be worked out ...

Collective displacement with wavevector $\vec{q}$

$$V^{(1)}_{\vec{q},\kappa,\alpha}(\vec{r}) = \sum_{a} e^{i\vec{q}\vec{R}_a} \frac{\partial V(\vec{r})}{\partial R^{a}_{\kappa,\alpha}}$$

Factorization of the phase

Suppose unperturbed system periodic $V^{(0)}(\vec{r}+\vec{R}_a) = V^{(0)}(\vec{r})$

If perturbation characterized by a wavevector : $V^{(1)}(\vec{r}+\vec{R}_a) = e^{i\vec{q}.\vec{R}_a}\ V^{(1)}(\vec{r})$

all responses, at linear order, will be characterized by a wavevector :

$$\mathrm{n}^{(1)}(\vec{r}+\vec{R}_a) = e^{i\vec{q}.\vec{R}_a}\ \mathrm{n}^{(1)}(\vec{r}) \qquad \psi^{(1)}_{m,\vec{k},\vec{q}}(\vec{r}+\vec{R}_a) = e^{i(\vec{\mathrm{k}}+\vec{q})\vec{R}_a}\ \psi^{(1)}_{m,\vec{k},\vec{q}}(\vec{r})$$

Now, define related periodic quantities

$$\overline{\mathrm{n}}^{(1)}(\vec{r}) = e^{-i\vec{q}\,\vec{r}}\ \mathrm{n}^{(1)}(\vec{r}) \qquad u^{(1)}_{m,\vec{k},\vec{q}}(\vec{r}) = (N\Omega_0)^{1/2}\ e^{-i(\vec{\mathrm{k}}+\vec{q})\vec{r}}\ \psi^{(1)}_{m,\vec{k},\vec{q}}(\vec{r})$$

In equations of DFPT, only these periodic quantities appear:

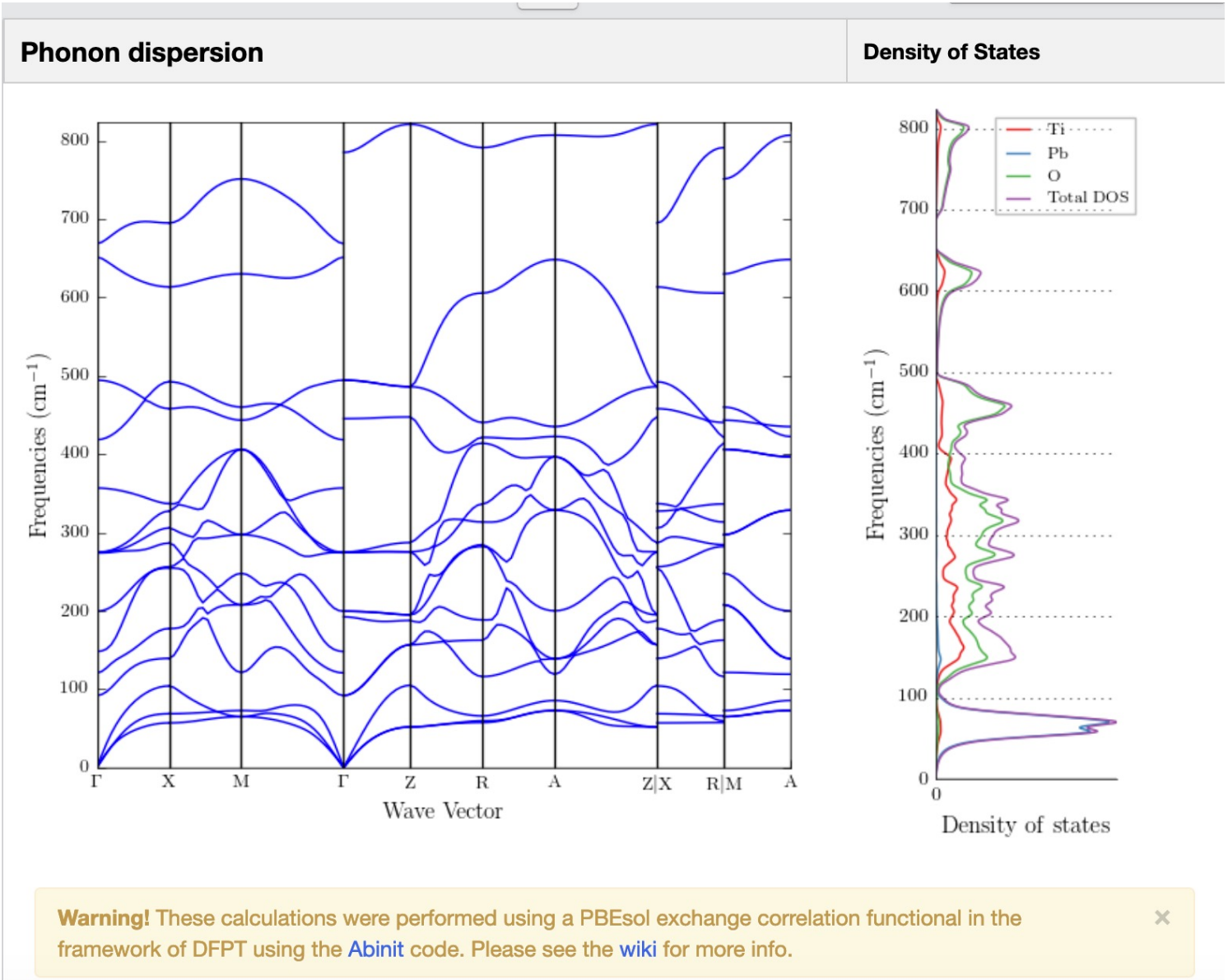
phases $e^{-i\vec{q}.\vec{r}}$ and $e^{-i(\vec{k}+\vec{q})\vec{r}}$ can be factorized

Treatment of perturbations incommensurate with unperturbed system periodicity is thus mapped onto the original periodic system.

The materials project: >1500 ABINIT phonon band structures

Materials Project >1500 ABINIT phonon band structures

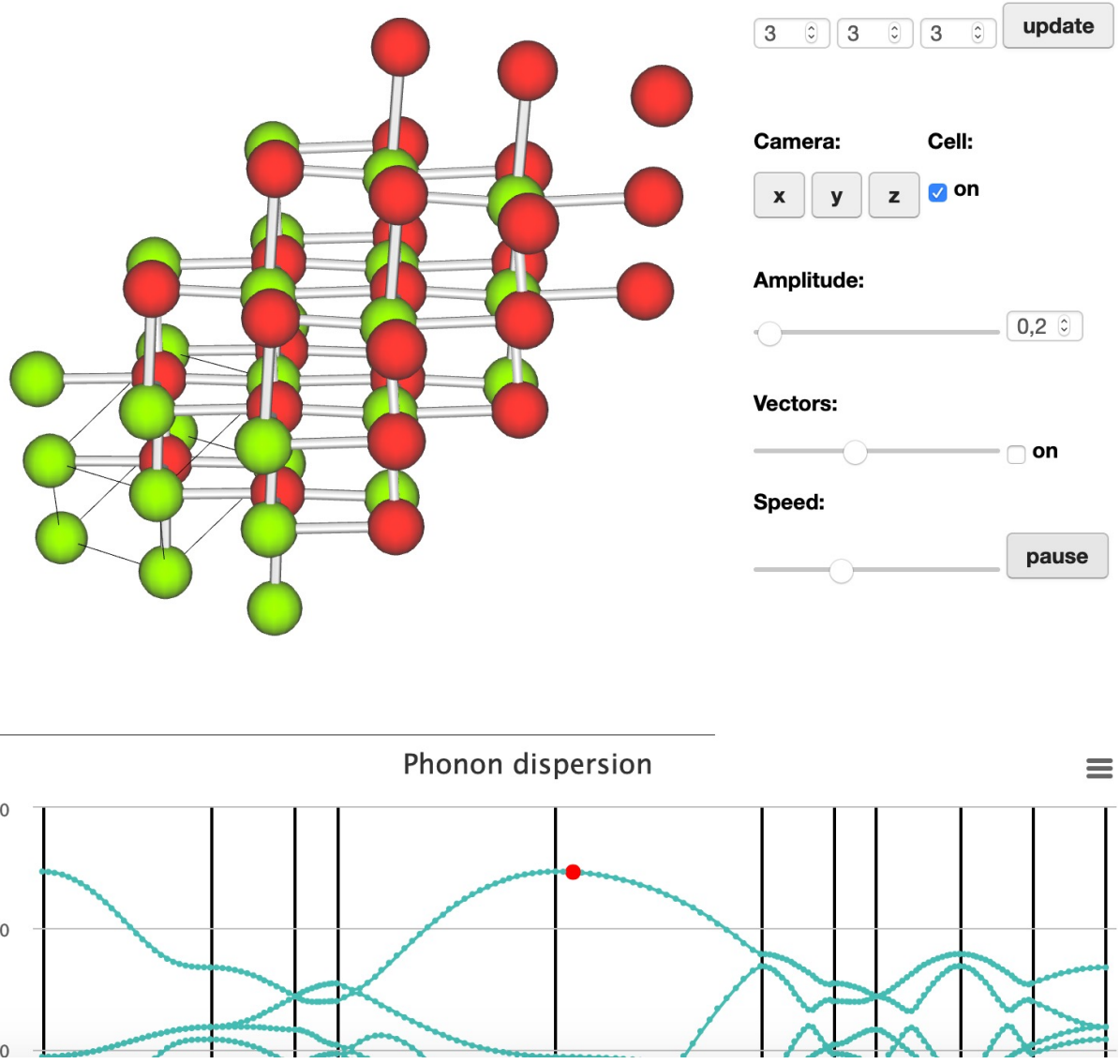
G. Petretto, *et al*, *Scientific Data.* 5, 180065 (2018)



$PbTiO_3$

Materials Project >1500 ABINIT phonon band structures

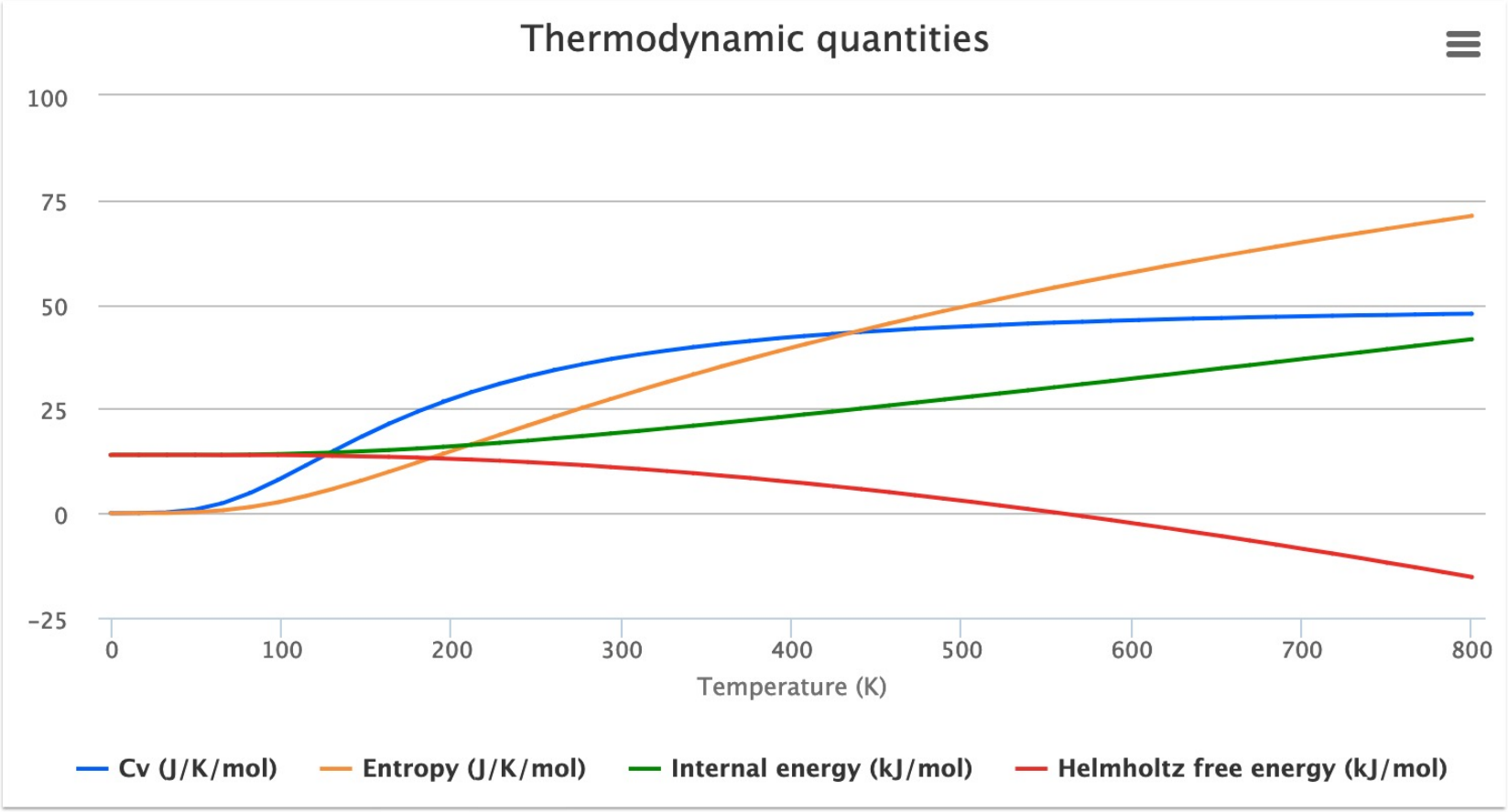
http://materialsproject.org



GaN

Materials Project >1500 ABINIT phonon band structures

http://materialsproject.org

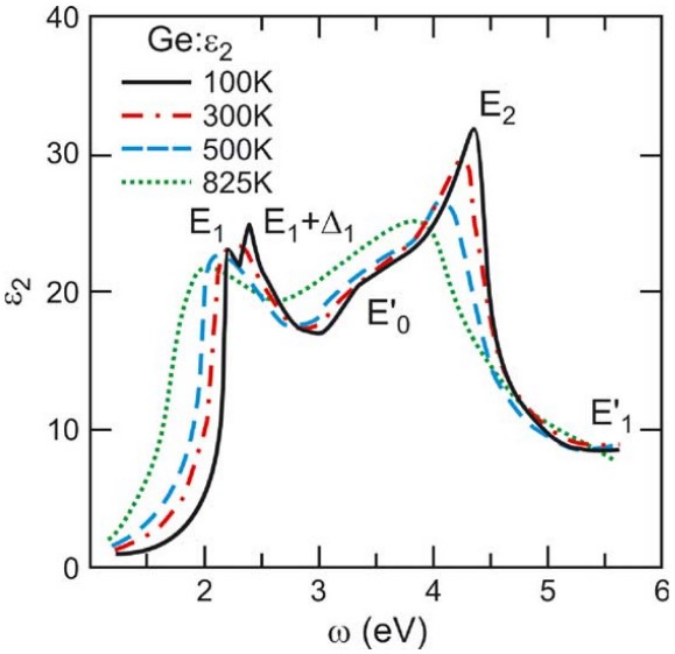


MgO

Warning! These calculations were performed using a PBEsol exchange correlation functional in the framework of DFPT using the Abinit code. Please see the wiki for more info.

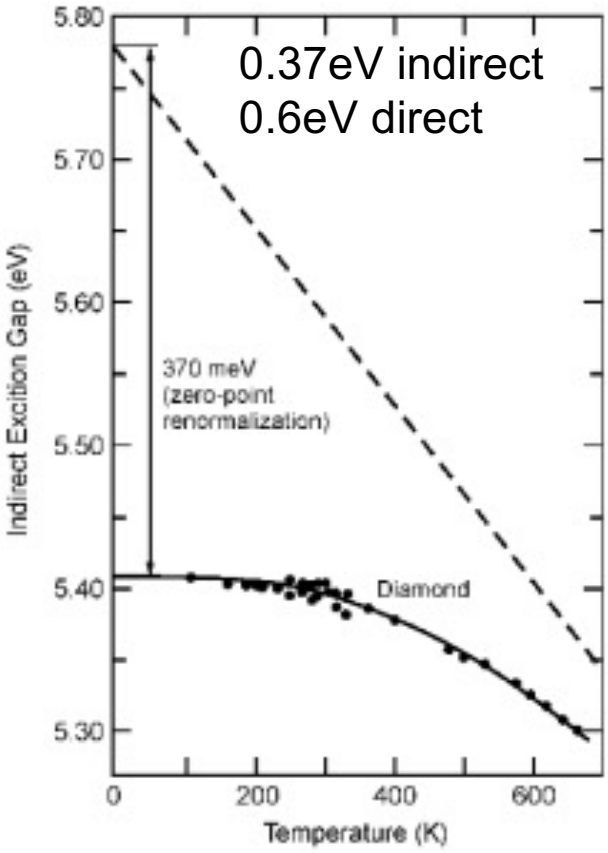
Effects of the electron-phonon interaction

T-dependence of electronic/optical properties



L. Viña, S. Logothetidis and M. Cardona,
Phys. Rev. B **30**, 1979 (1984)

- peaks shift in energy
- peaks broaden with increasing temperature : decreased electron lifetime

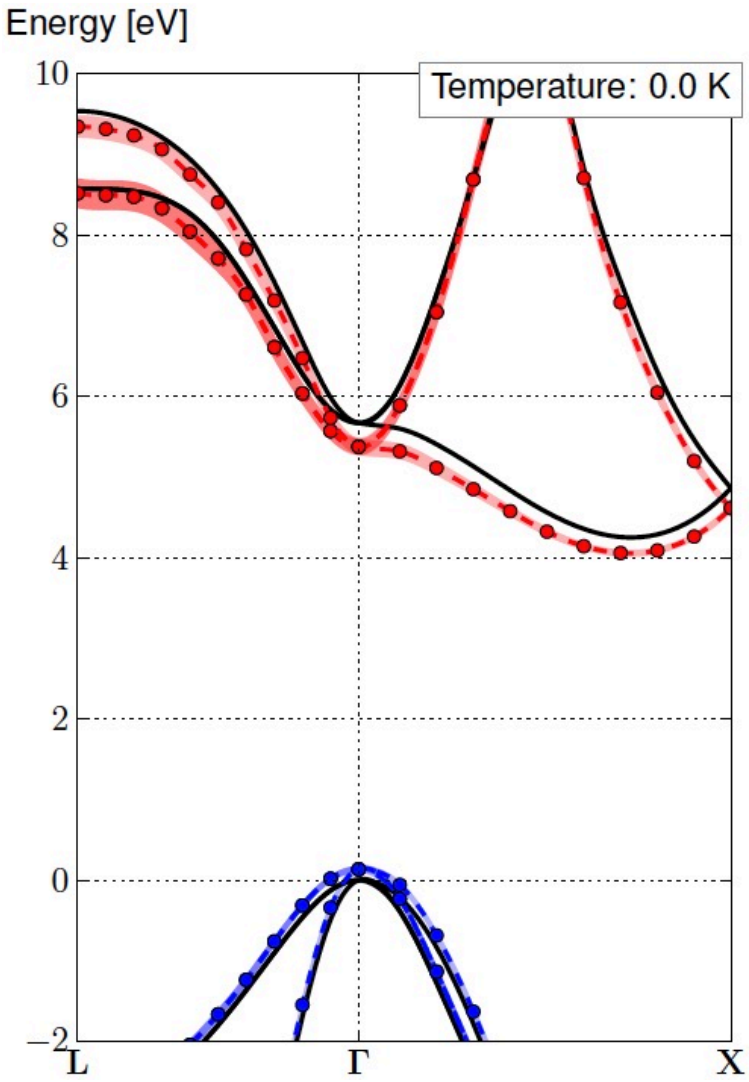


- even at 0K, vibrational effects are important, due to Zero-Point Motion

Usually, not included in first-principles (DFT or beyond) calculations !

M. Cardona, *Solid State Comm.* **133**, 3 (2005)

DFT T-dependent band structure

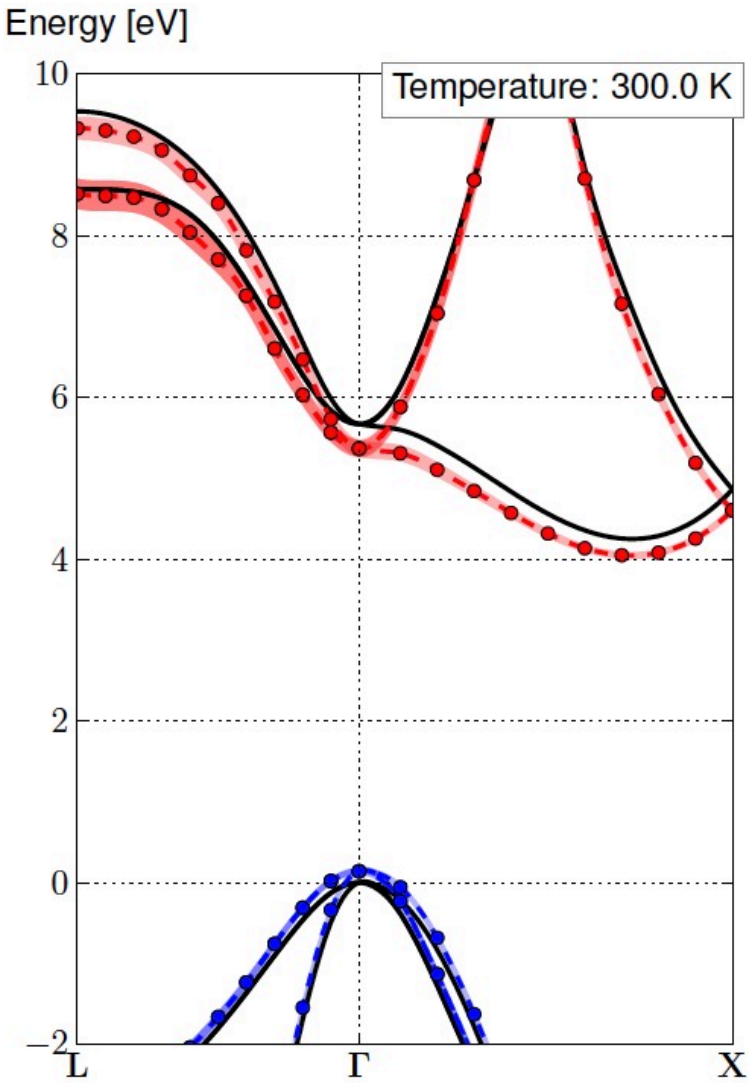


Diamond 0 Kelvin
(incl. Zero-point motion)

Note the widening of
the bands = lifetime

S. Poncé, Y. Gillet, J. Laflamme Janssen, A. Marini, M. Verstraete & XG, J. Chem. Phys. 143, 102813 (2015)

DFT T-dependent band structure

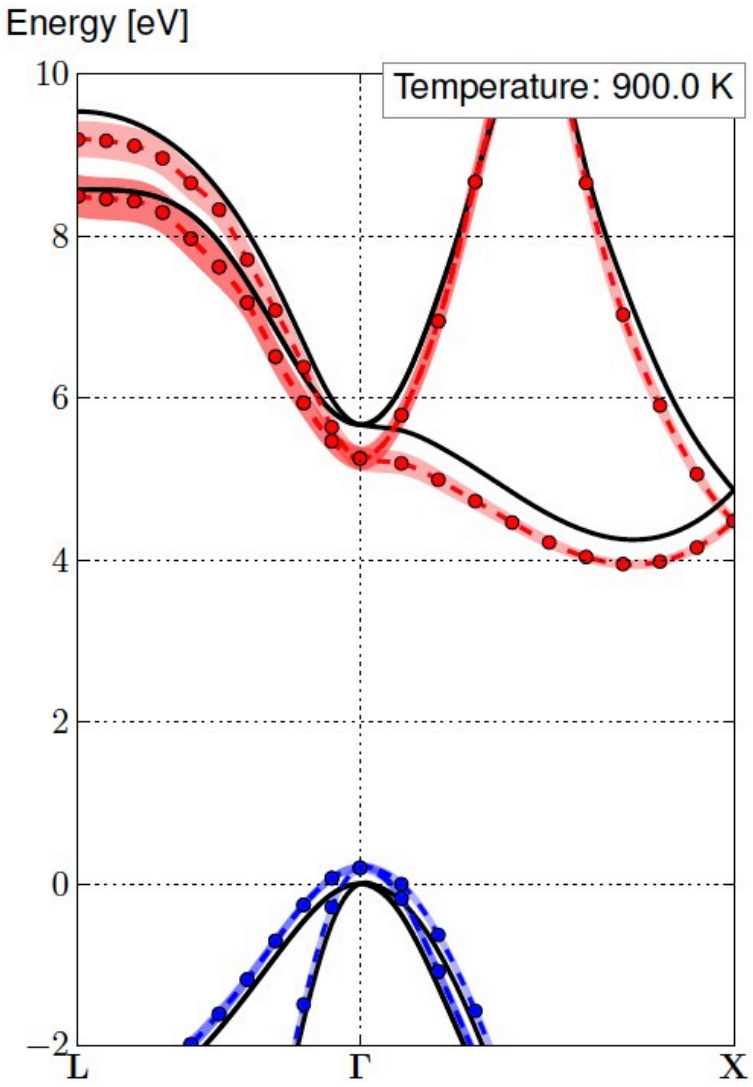


Diamond 300 Kelvin

Note the widening of the bands = lifetime

S. Poncé, Y. Gillet, J. Laflamme Janssen, A. Marini, M. Verstraete & XG, J. Chem. Phys. 143, 102813 (2015)

DFT T-dependent band structure

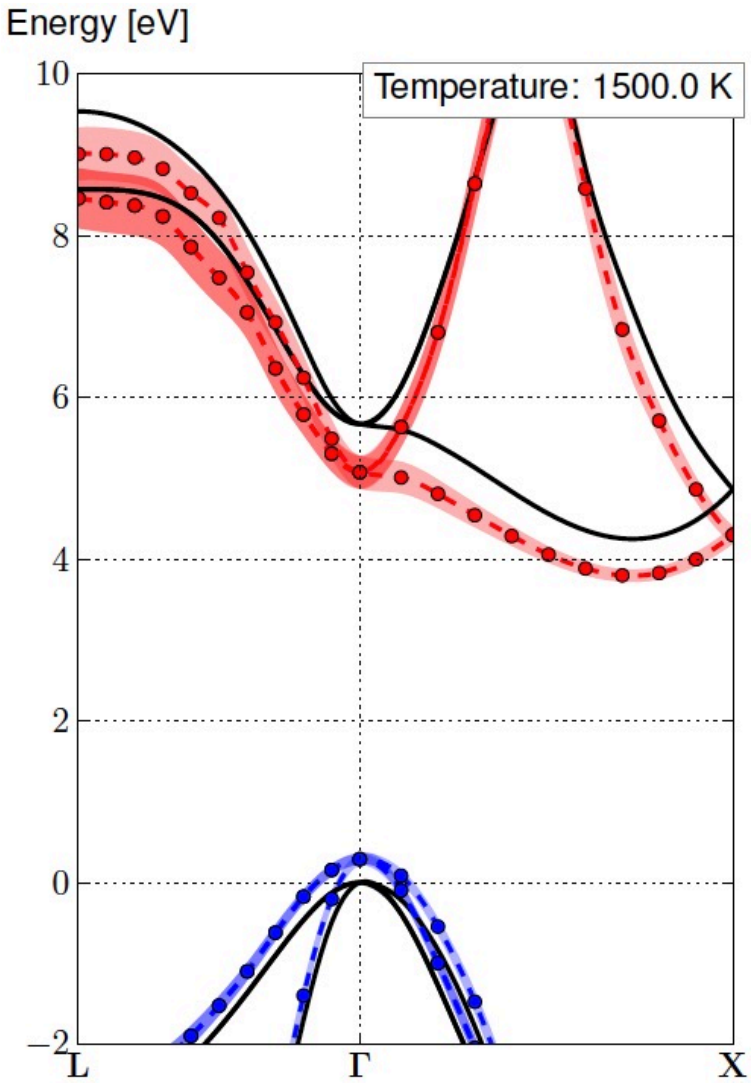


Diamond 900 Kelvin

Note the widening of the bands = lifetime

S. Poncé, Y. Gillet, J. Laflamme Janssen, A. Marini, M. Verstraete & XG, J. Chem. Phys. 143, 102813 (2015)

DFT T-dependent band structure



Diamond 1500 Kelvin

Note the widening of the bands = lifetime

S. Poncé, Y. Gillet, J. Laflamme Janssen, A. Marini, M. Verstraete & XG, J. Chem. Phys. 143, 102813 (2015)

G_0W_0 + self-consistency + vertex (+e-h)...?

	scGW RPA	scGW e-h	EXP
Ge	0.95	0.81	0.74
Si	1.41	1.24	1.17
GaAs	1.85	1.62	1.52
SiC	2.88	2.53	2.40
CdS	2.87	2.39	2.42
AlP	2.90	2.57	2.45
GaN	3.82	3.27	3.20
ZnO	3.8	3.2	3.44
ZnS	4.15	3.60	3.91
C	6.18	5.79	5.48
BN	7.14	6.59	≈6.25
MgO	9.16	8.12	7.83
LiF	15.9	14.5	14.20
Ar	14.9	13.9	14.20
Ne	22.1	21.4	21.70

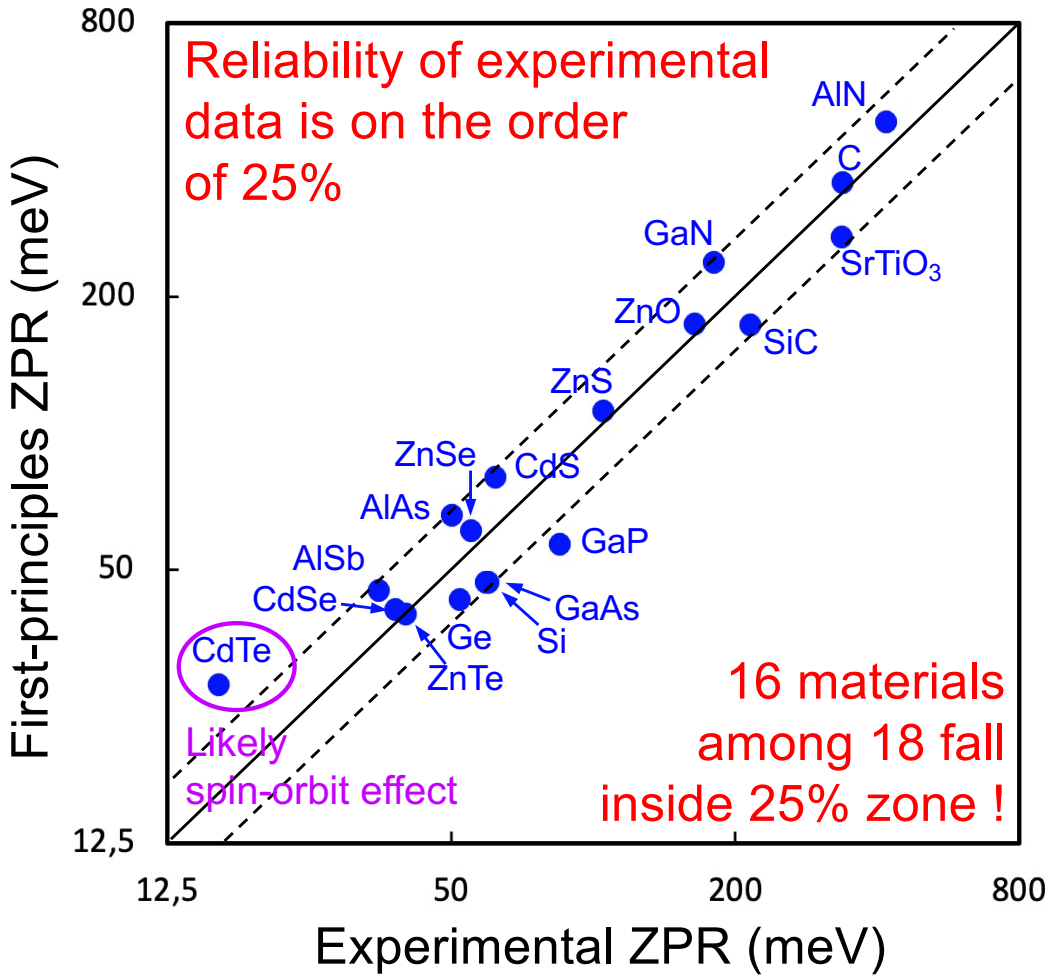
From Shishkin, Marsman, Kresse, PRL 99, 246403 (2007)

scGW RPA vs EXP
Diff. 0.1eV ... 1.4 eV

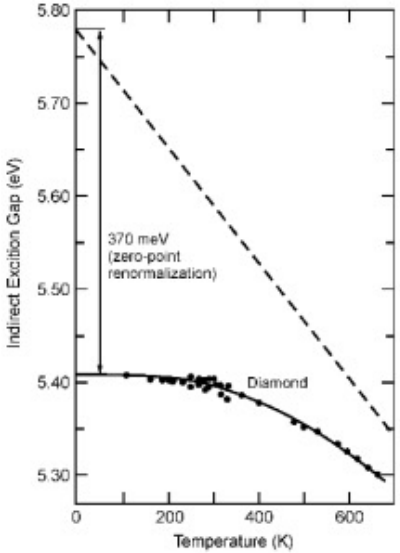
scGW + e-h is even better …
Remaining discrepancy
0.1 eV ... 0.4 eV

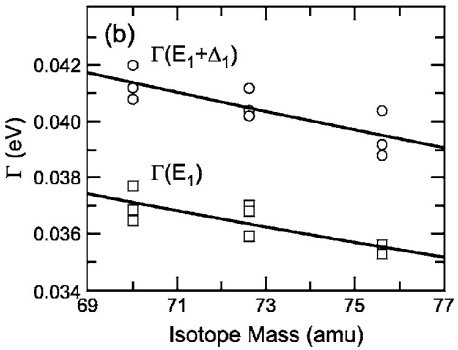
Due to phonons, at least partly !

Non-adiabatic AHC theory vs experiment



ZPR of the band gap
Two different exp techniques





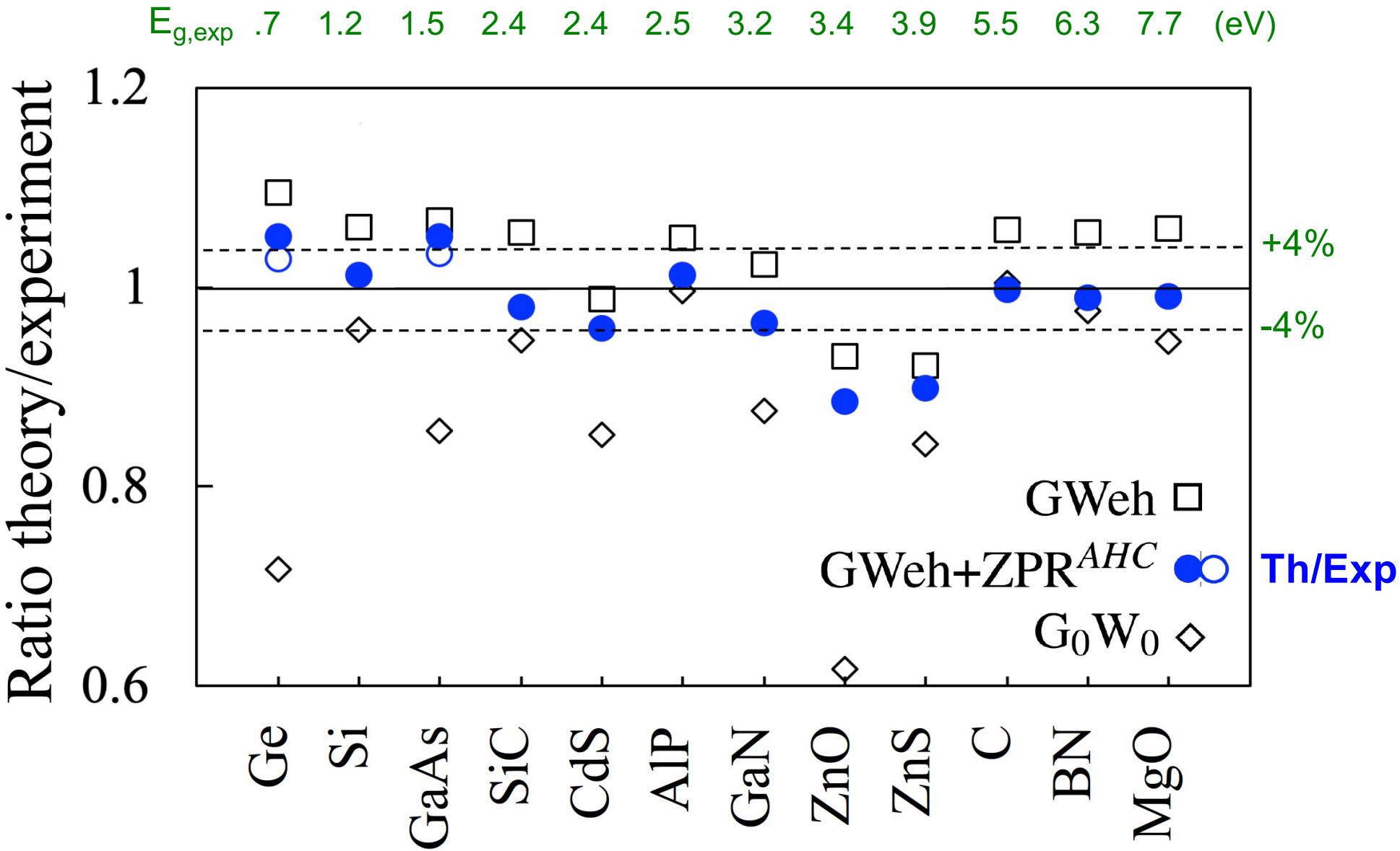
$$E_M = E_\infty + B M^{-1/2}$$

Miglio, Brousseau, Godbout, Côté, Antonius, Chan, Louie, Giantomassi and XG, *npj Comput Materials 6, 167,2020*

Cardona & Thewalt, *Rev. Mod. Phys.*, **77**, 1173 (2005)

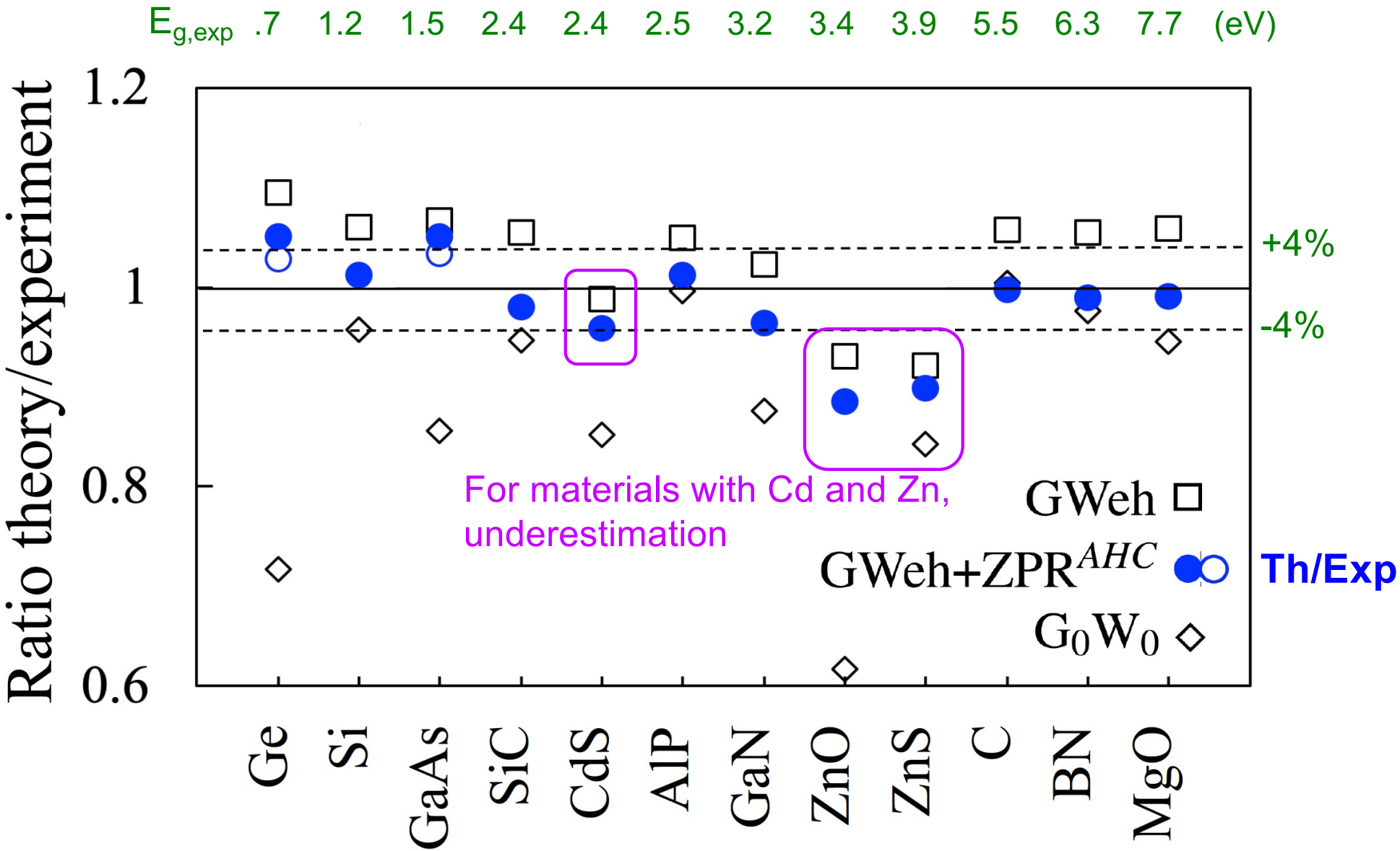
Band gap : theory vs experiment

Miglio et al, *npj Computational Materials 6:167 (2020)*



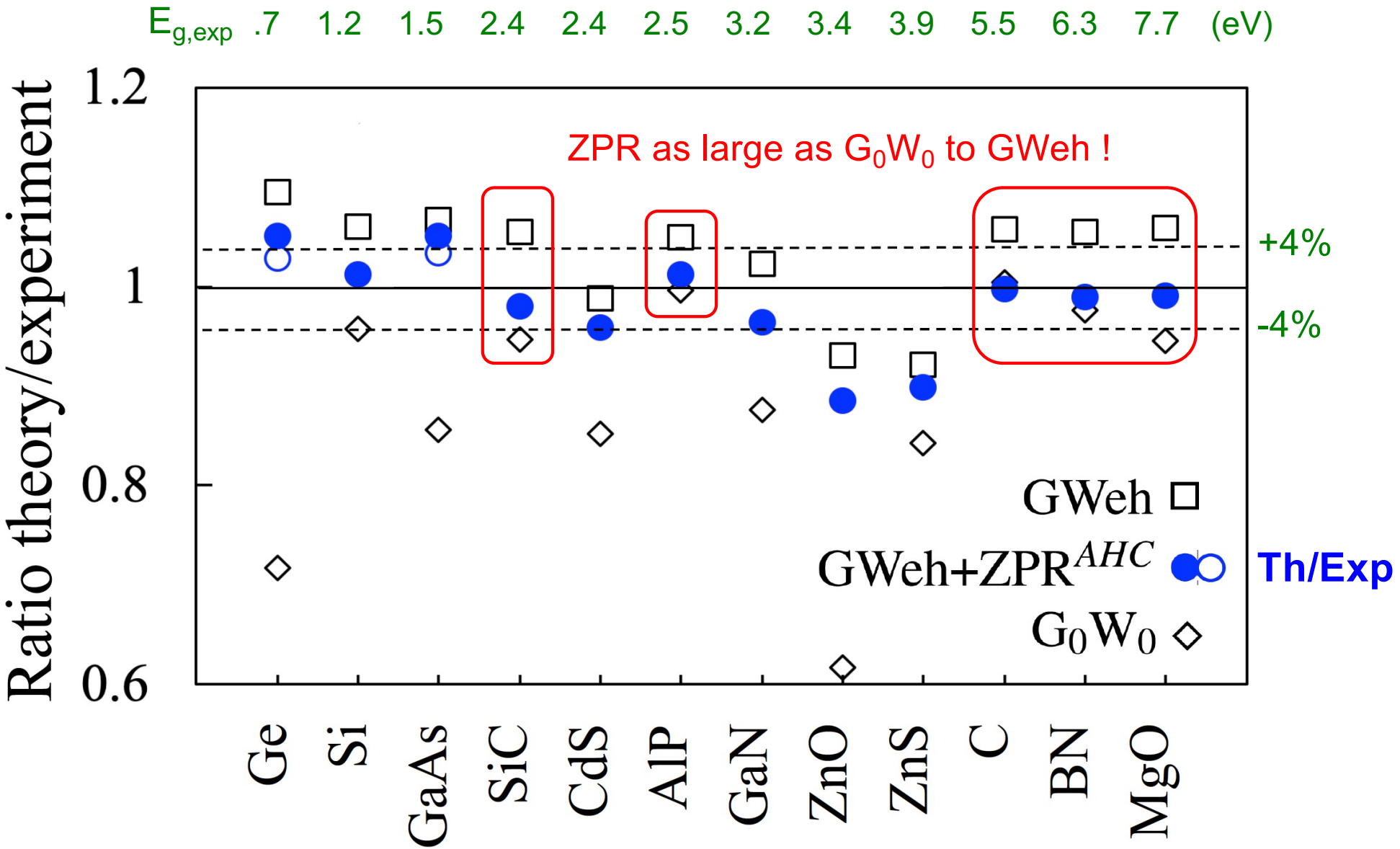
Band gap : theory vs experiment

Miglio et al, *npj Computational Materials 6:167 (2020)*



Band gap : theory vs experiment

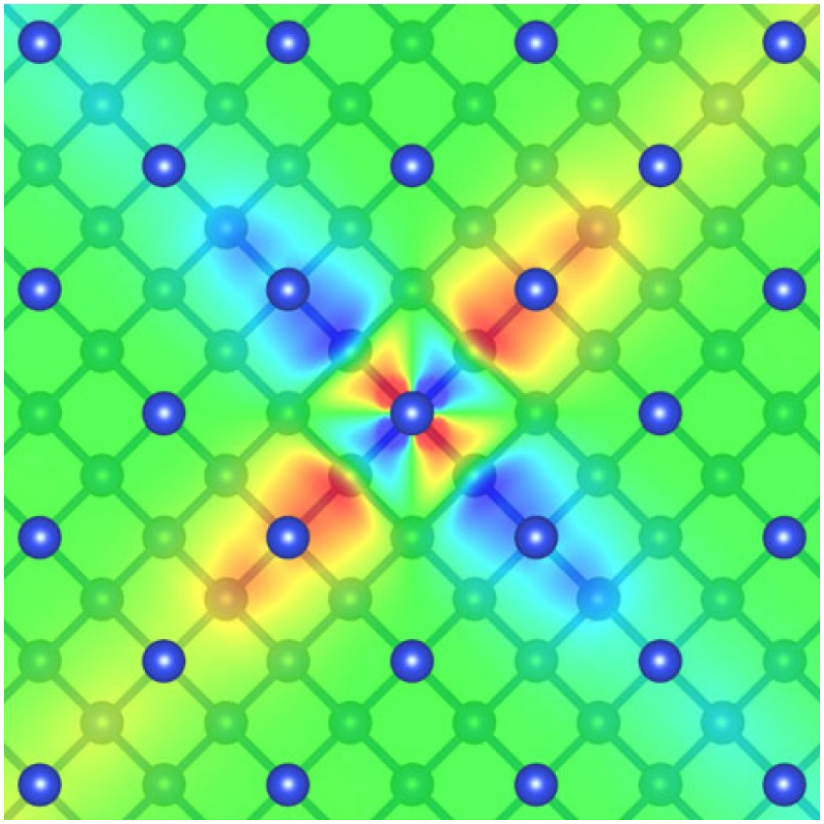
Miglio et al, *npj Computational Materials 6:167 (2020)*



Electron mobility

Electron-phonon beyond Fröhlich: dynamical quadrupoles in polar and covalent solids
Brunin et al, Phys. Rev. Lett. 125, 136601 (2020).

Silicon



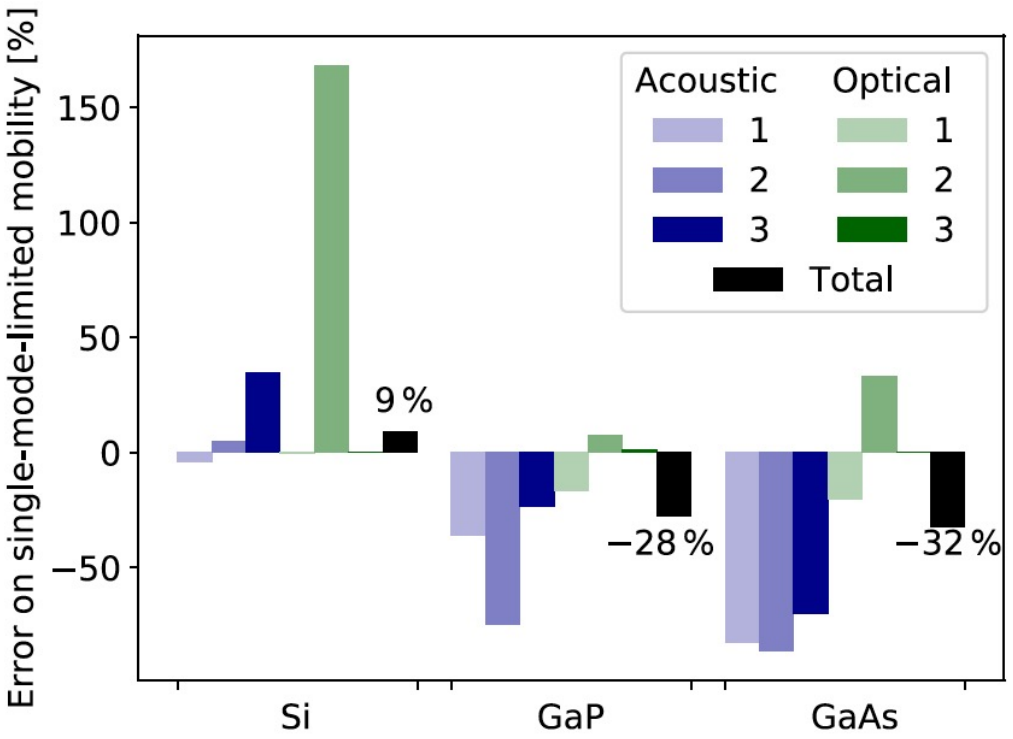


FIG. 3. Error on the single-phonon-mode limited mobility when the quadrupole interaction is not correctly treated in Si, GaP, and GaAs, for acoustic (blue) and optical (green) modes. The error on the total mobility is given in black.

ABINIT Impact

ABINIT bibliometry (as of Nov 2021)

Comput. Mat. Science 25, 478 (2002) – 16 authors. 2649 citations

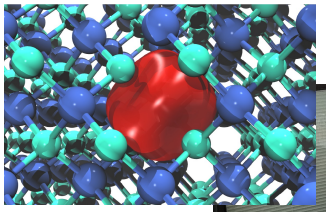
Z. Kristallogr. 220, 558 (2005) – 20 authors. 1111 citations

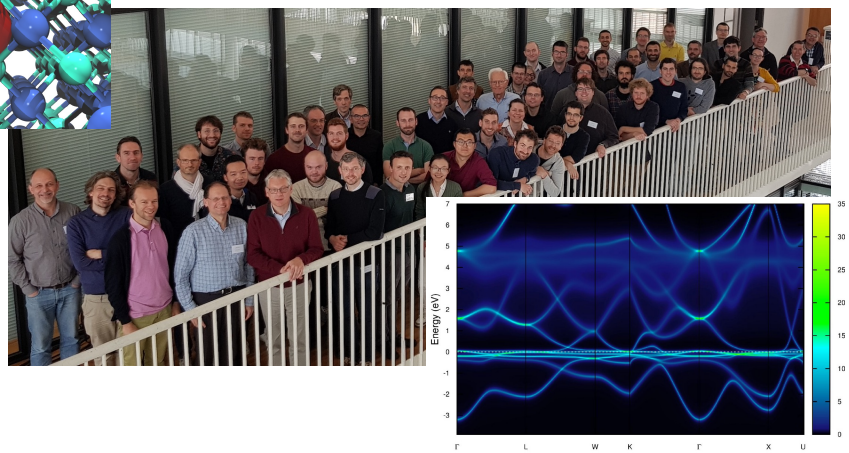
Comp. Phys. Comm. 180, 2582 (2009) – 33 authors. 2005 citations

1. Comp. Phys. Comm. 205, 106 (2016) – 55 authors. 434 citations

+ Recent publication about ABINIT :
Comp. Phys. Comm. 248, 107042 (2020) – 53 authors
J. Chem. Phys. 152, 124102 (2020) – 43 authors

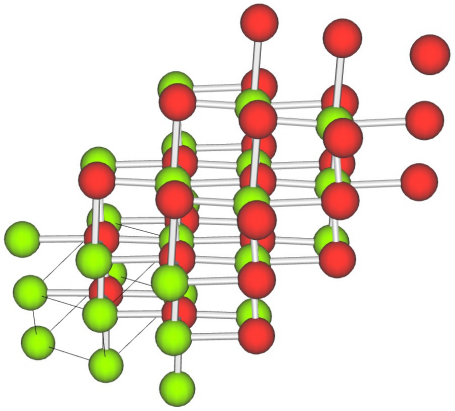
Wrap-up

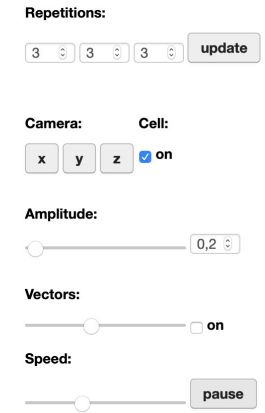




+ ABINIT : open source, many capabilities, well documented, well tested, strong on phonon and electron-phonon properties

+ >1500 phonon band structures available on the Materials project





+ Temperature-dependent electronic structure. Zero-point correction needed for high-quality computations.