DFPT in FHI-aims

Nathaniel Raimbault, Danilo Brambila

Coffee talk, Berlin, Common room, 11/06/18

People

Mariana Rossi

Nathaniel Raimbault

Reinhard Maurer

Volker Blum

Honghui Shang

Simone Koecher

Christian Carbogno

Danilo Brambila

Raul Laasner

Motivation

We want to evaluate:

- Phonon-limited carrier lifetimes
- Hot electron relaxation
- Renormalization of the electronic structure
- Born effective charges
- Raman spectra
- Sum-frequency generation

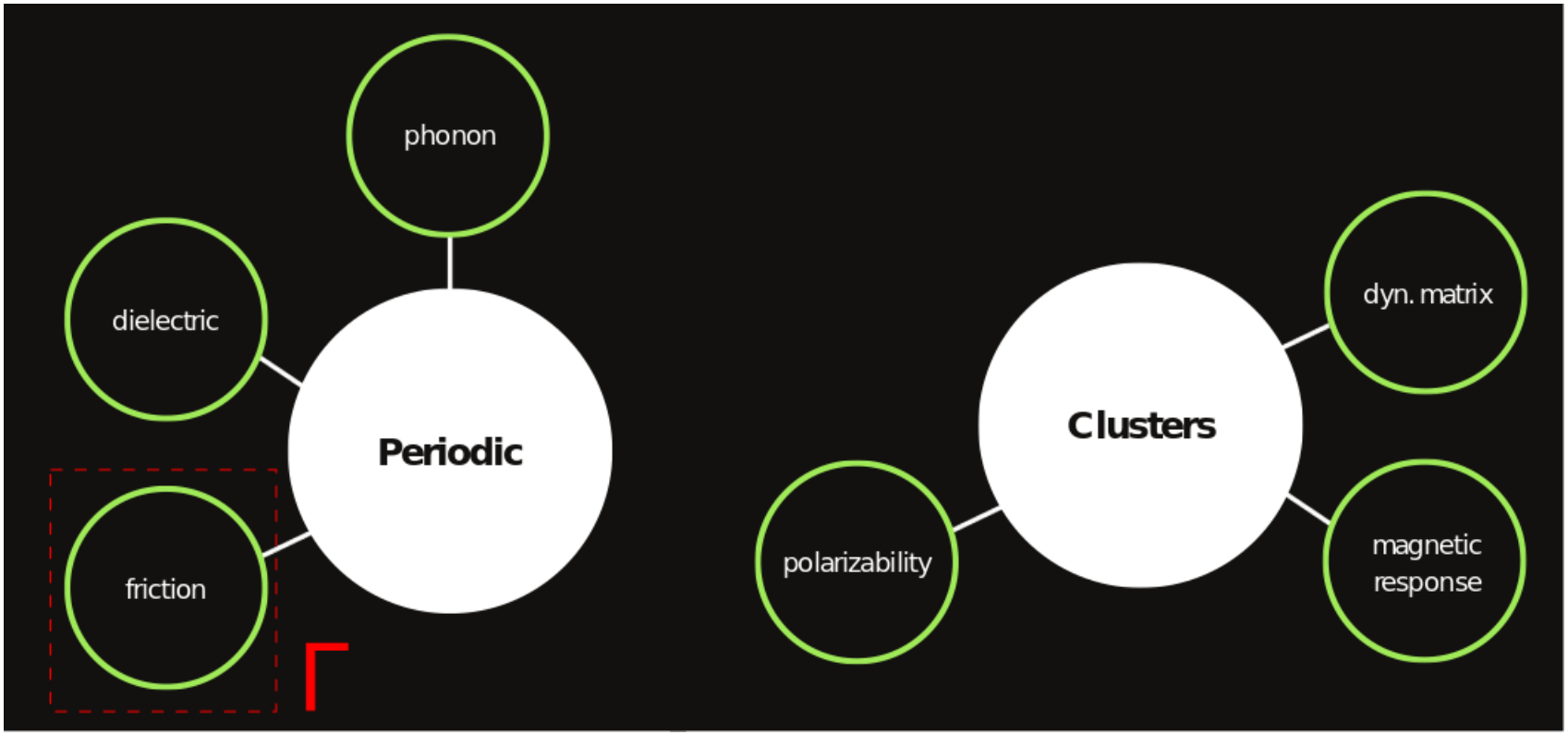
All of these properties require the $\partial^2\mathbf{E}$

$$\partial^2 E = E_{min}[n, \partial n] \qquad \text{(2n+1 theorem)}$$

But derivatives w.r.t. what??

$$\frac{\partial^2 E}{\partial R_I \partial R_J} \text{ for phonons;} \quad \frac{\partial^2 E}{\partial e_\gamma \partial e_\delta} \text{ for dielectrics;}$$

DFPT branches



Main ideas and equations - comparison

$$\hat{h}\psi = E\psi, \qquad \text{with} \qquad \psi = \sum_k C_{\mu k}\xi_\mu$$

where ξ is the basis set.
Now the second order derivatives, e.g. for phonons:

$$E^{(2)} = \frac{\partial^2 E}{\partial R_I \partial R_J} = -\frac{\partial F_I}{\partial R_j} - \sum_\mu \frac{\partial F_I}{\partial \xi_\mu}\frac{\partial \xi_\mu}{\partial R_J} - \sum_{\mu I} \frac{\partial F_I}{\partial C_{\mu I}}\frac{\partial C_{\mu I}}{\partial R_J}$$

Main ideas and equations - comparison

$$E^{(2)} = \frac{\partial^2 E}{\partial R_I \partial R_J} = -\frac{\partial F_I}{\partial R_j} - \sum_{\mu} \frac{\partial F_I}{\partial \xi_\mu} \frac{\partial \xi_\mu}{\partial R_J} - \sum_{\mu I} \frac{\partial F_I}{\partial C_{\mu I}} \frac{\partial C_{\mu I}}{\partial R_J}$$

From perturbation theory:

$$A[\Delta X, X_0] = A^{(0)}[X_0] + A^{(1)}[X_0]\Delta X$$

Expanding $\hat{h}$, ψ and the eigenvalues E up to first order:

$$(\hat{h}^{(0)} - E^{(0)})\psi^{(1)} = (\hat{h}^{(1)} - E^{(1)})\psi^{(0)}$$

Main ideas and equations - comparison

The Sternheimer equation

$$(\hat{h}^{(0)} - \lambda^{(0)})\psi^{(1)} = (\hat{h}^{(1)} - \lambda^{(1)})\psi^{(0)}$$

writing $\psi^{(1)}$ in terms of the basis set ξ we finally obtain

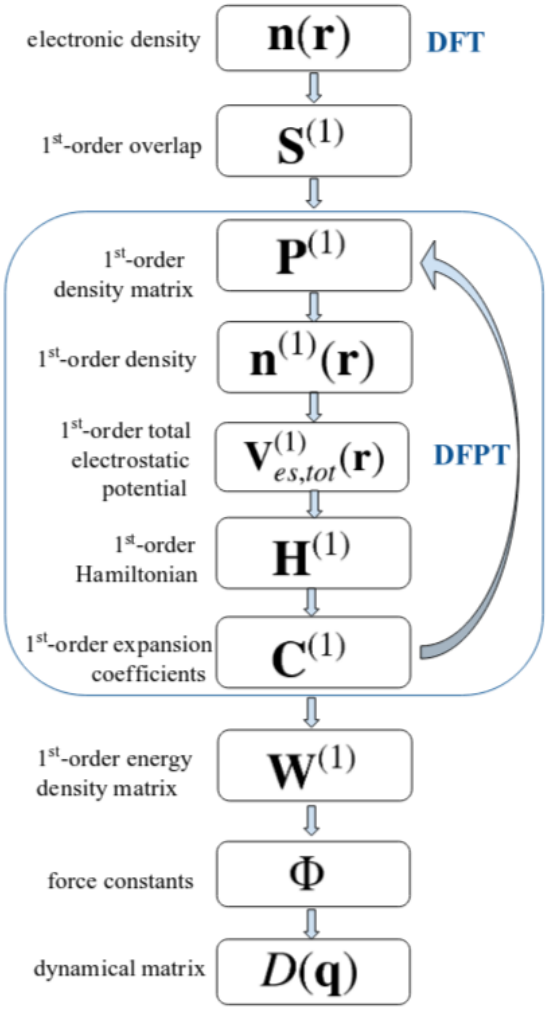
$$\sum_{\nu}(H^{(0)}_{\mu\nu} - \lambda^{(0)}_{i} S^{(0)}_{\mu\nu})C^{(1)}_{\nu i} - \sum_{\nu}\lambda^{(0)}_{i} S^{(1)}_{\mu\nu} C^{(0)}_{\nu i} = \sum_{\nu}(H^{(1)}_{\mu\nu} - \lambda^{(1)}_{i} S^{(0)}_{\mu\nu})C^{(0)}_{\nu i}$$

The equation above is then solved with the **C**oupled **P**erturbed **S**elf-**C**onsistent **F**ield (**CPSCF**) cycle.

Main ideas and equations - comparison

Solution via the CPSCF cycle

$$(H^{(0)}_{\mu\nu} - \lambda^{(0)}_i S^{(0)}_{\mu\nu}) C^{(1)}_{\nu i} - \lambda^{(0)}_i S^{(1)}_{\mu\nu} C^{(0)}_{\nu i} = (H^{(1)}_{\mu\nu} - \lambda^{(1)}_i S^{(0)}_{\mu\nu}) C^{(0)}_{\nu i}$$



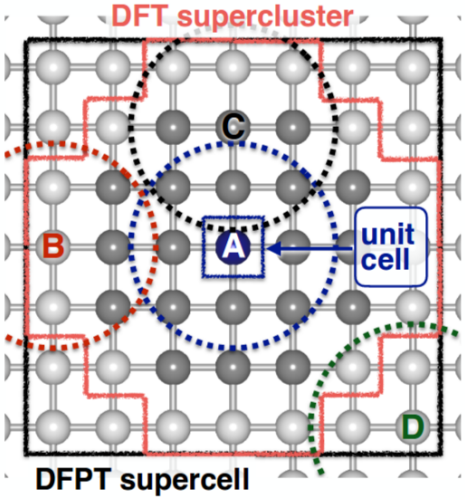
How is DFPT in FHI-aims different from other codes?

PROS:

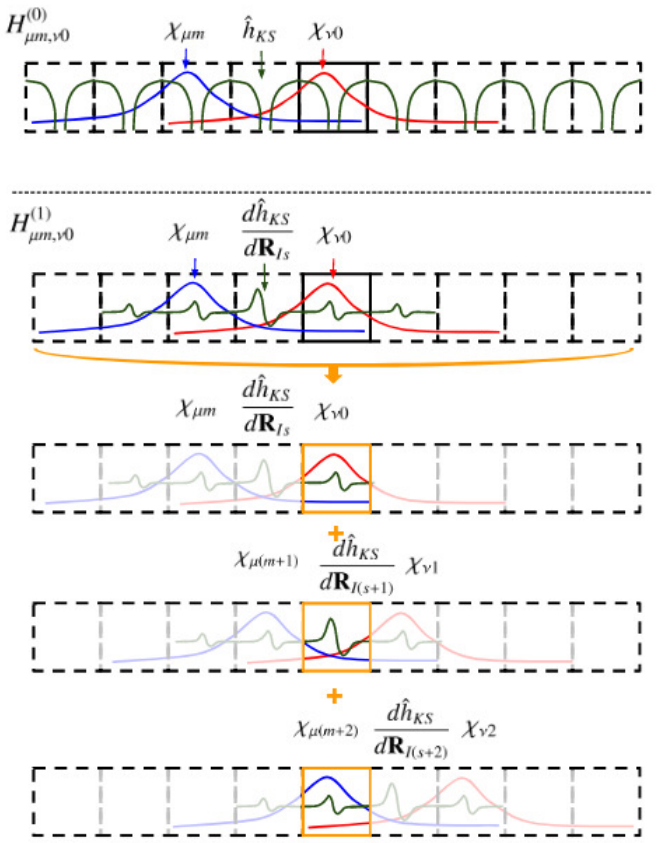
- In a full real space calculation, we get all k-points in a single run!
- Reduced localized basis set

CONS:

- Integration is non-trivial for periodic systems(reciprocal space trick)



DFPT-phonon integration scheme



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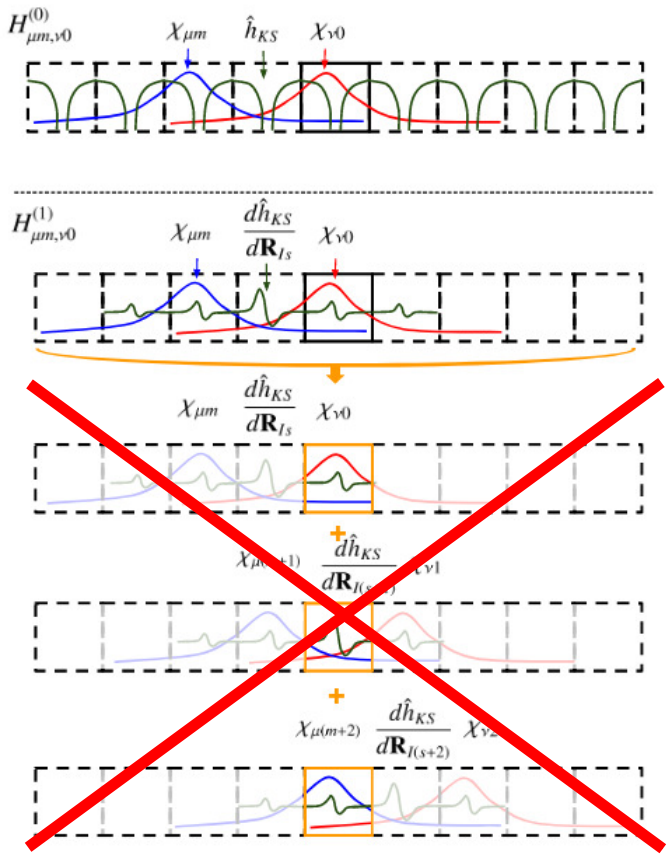


Scaling

Phonons

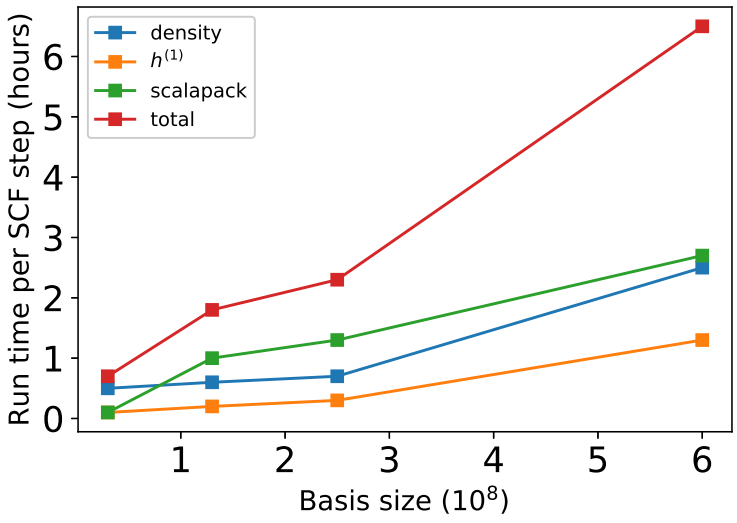


Figure 1: DFPT distributed (Si, AlP, GaAs, Zirconia all tight+tier1 basis set)

Dielectric

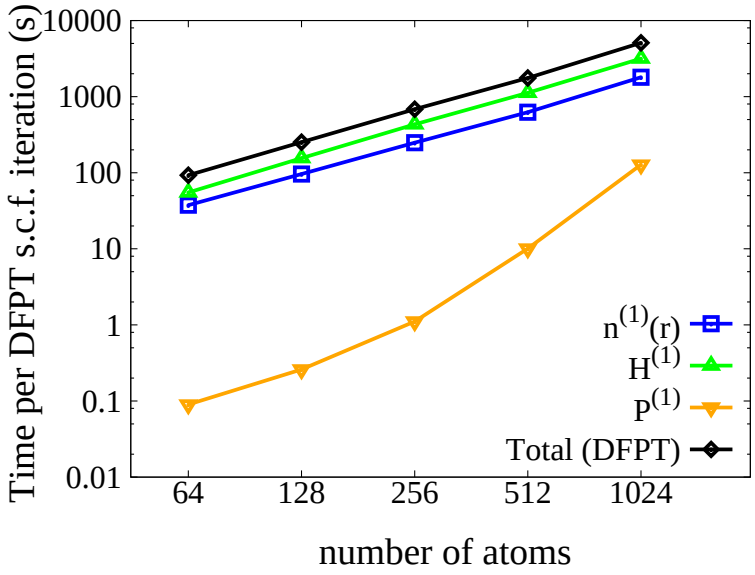


Figure 2: Periodic diamond

Scaling

Phonons

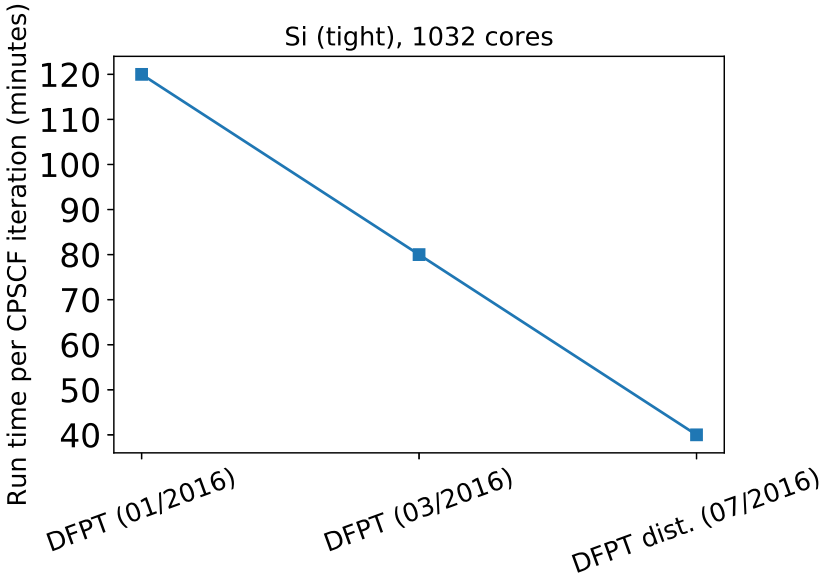


Figure 3: 1024 Cores (Draco), tight basis set, tier 1

Dielectric

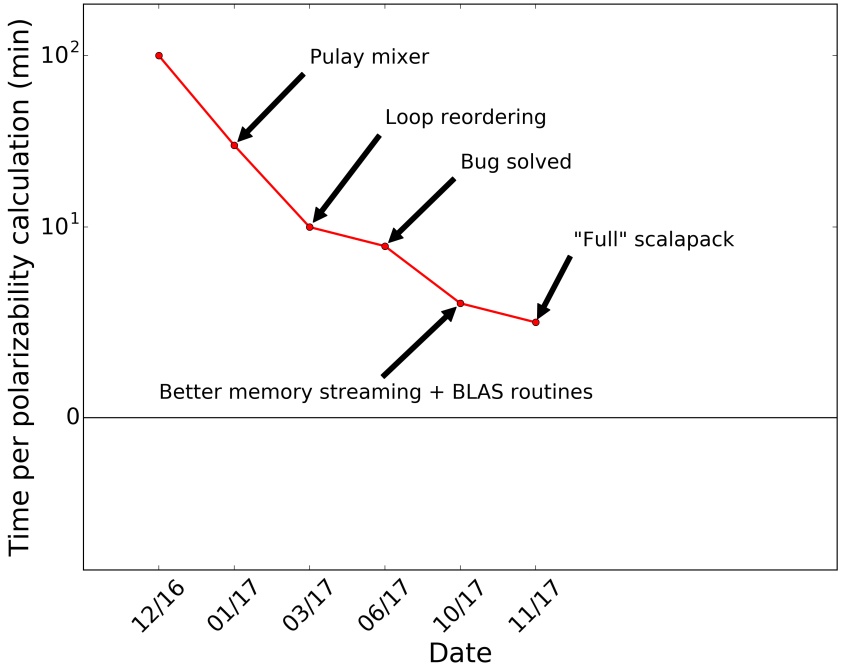


Figure 4: Paracetamol I, 72 cores (PBE, light settings)

Scaling dielectric

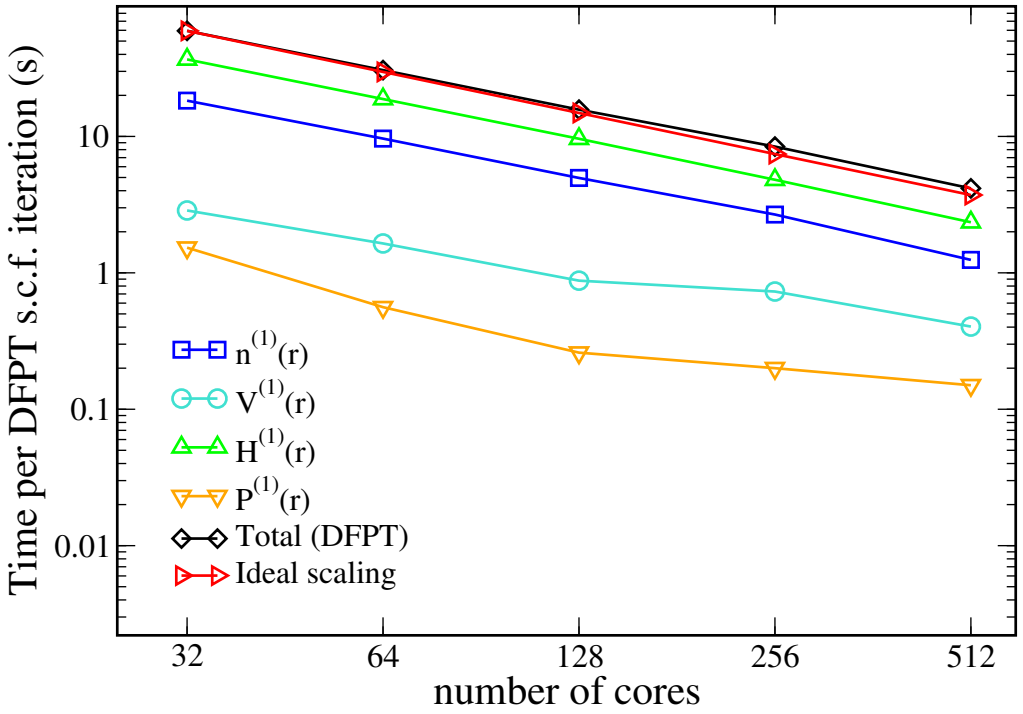
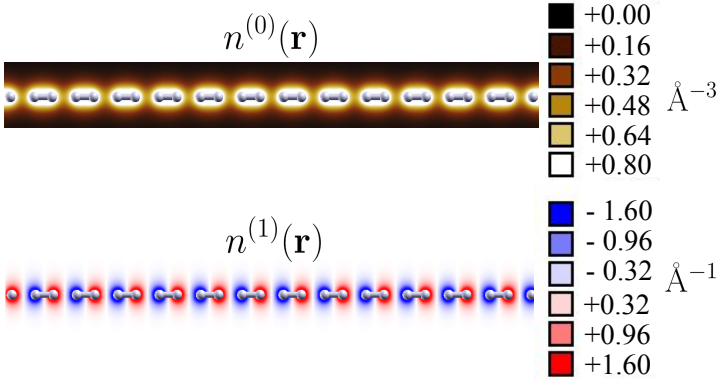


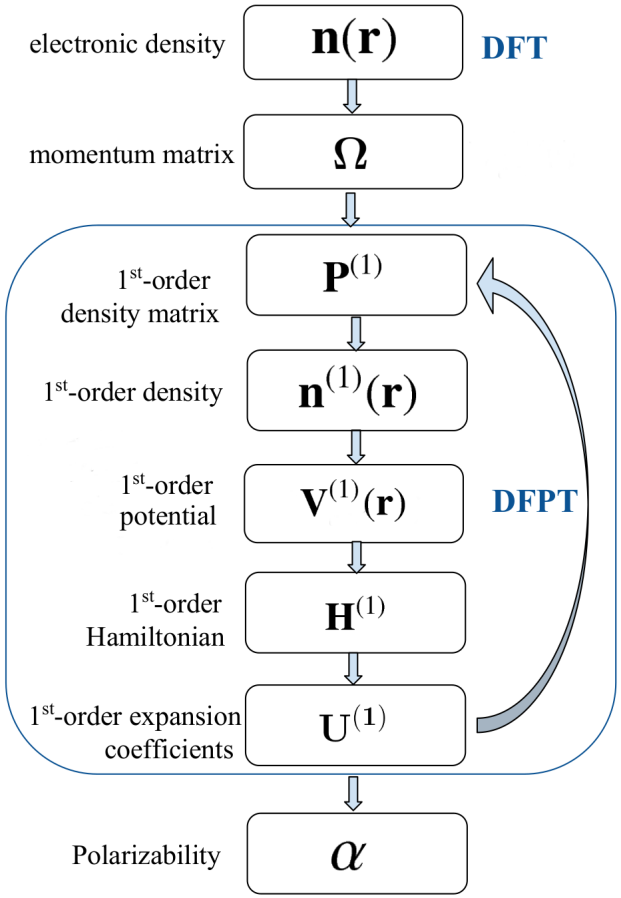
Figure 5: Paracetamol II

Typical timings (paracetamol II) for 1 polarizability calculation (256 cores, LDA, 1600 basis functions):

- DFT cycle $\approx$ 1 minute
- DFPT cycle $\approx$ 4 minutes

DFPT dielectric in FHI-aims





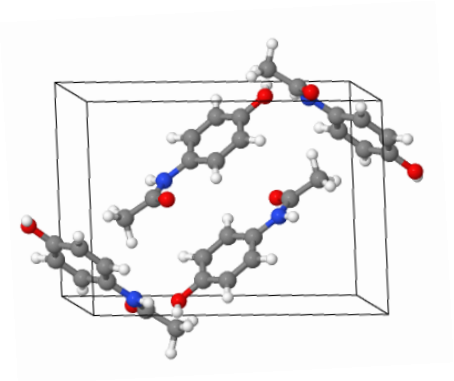
Since the density response $n^{(1)}$ is perfectly periodic, we can use the same machinery as that of ground-state DFT.

See arXiv:1803.00924

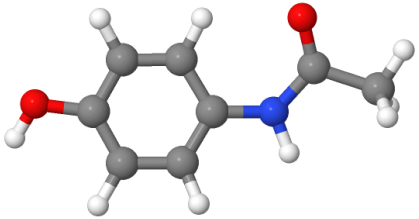
Molecular crystals

- Class of crystals built from molecular units, held together mainly by hydrogen bonds and weak dispersion forces.
- Widely used in pharmaceutics, organic electronics, ...
- Polymorphs have very similar binding energies, but very different physicochemical properties.
- Experimentally, polymorphs can be distinguished by Raman spectroscopy.

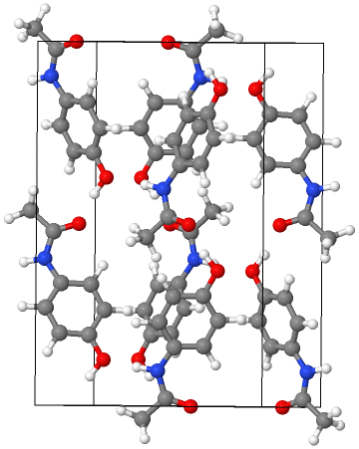
Form I (monoclinic)
(4 mol. in unit cell)



Paracetamol molecule
(20 atoms)



Form II (orthorhombic)
(8 mol. in unit cell)



Raman intensity: 2 roads

α can be divided into an isotropic ($\bar{\alpha}$) and an anisotropic part (β):

$$\alpha = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} = \bar{\alpha} I + \beta$$

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Harmonic Raman intensity

$$I(\omega) \propto \left| \frac{\partial \alpha}{\partial R_a} \right|^2$$

R_a: small displacements over atomic positions

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Anharmonic Raman intensity

$$I(\omega) \propto \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} (\underbrace{\langle \alpha(0)\alpha(t) \rangle}_{\text{autocorr. func.}})$$

Autocorrelation function:
$\langle A(0)A(\tau) \rangle =$
$\lim_{T\to\infty} \frac{1}{T} \int_0^T dt A(t)A(t+\tau)$ tell us how much a property at time $t+\tau$ is related to that at time t

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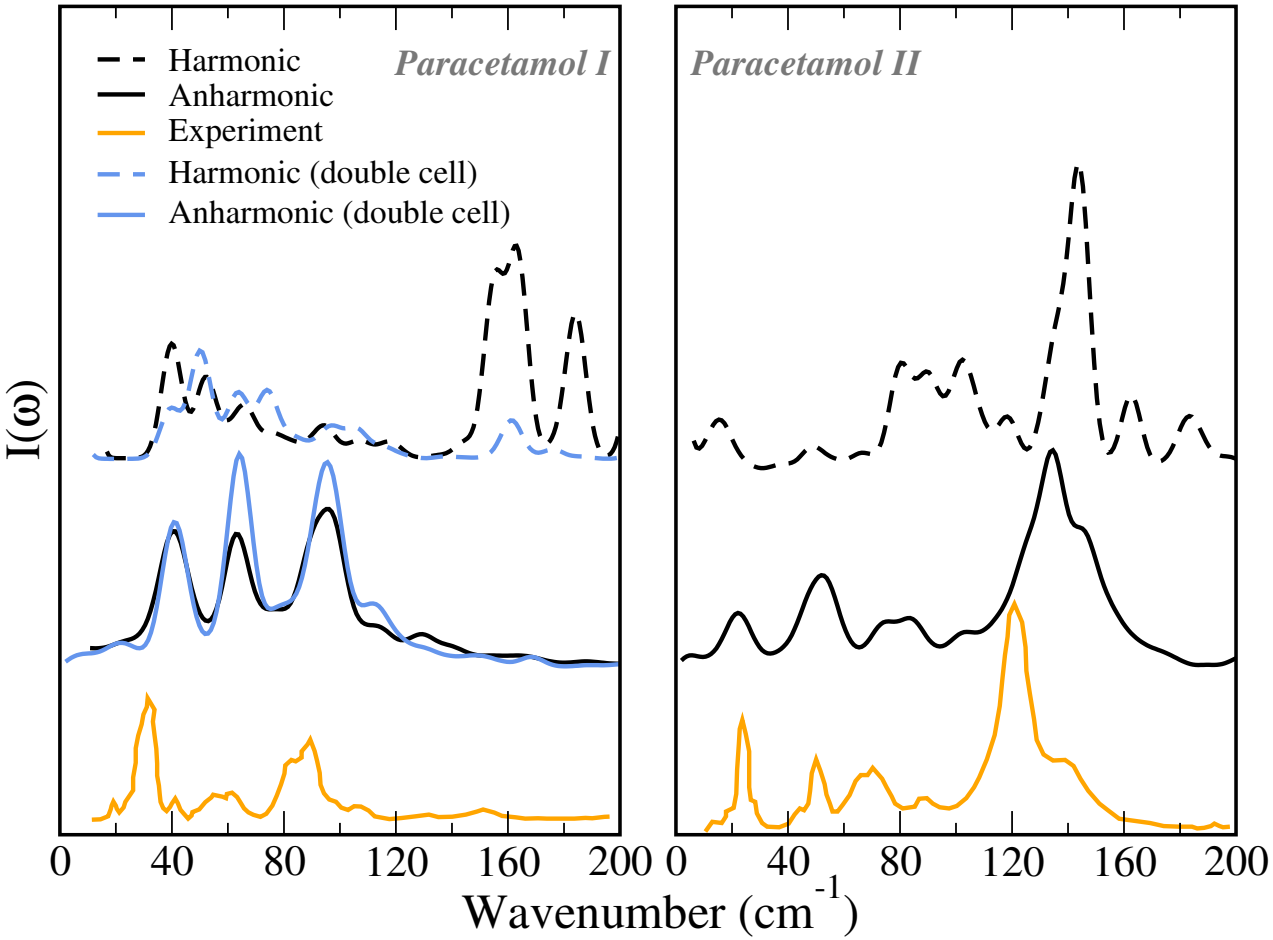
Ab initio Molecular Dynamics (MD) trajectories $\Rightarrow$ Polarizabilities time series $\Rightarrow$ Polarizability autocorrelation function.
Full anharmonicity (at the classical nuclei level) taken into account

Raman spectra: theory vs experiment

To get the harmonic spectrum:

```
make vibrations[.scalapack.mpi]
perl aims.vibrations.xxxxxx.[...].pl name displ polar
```



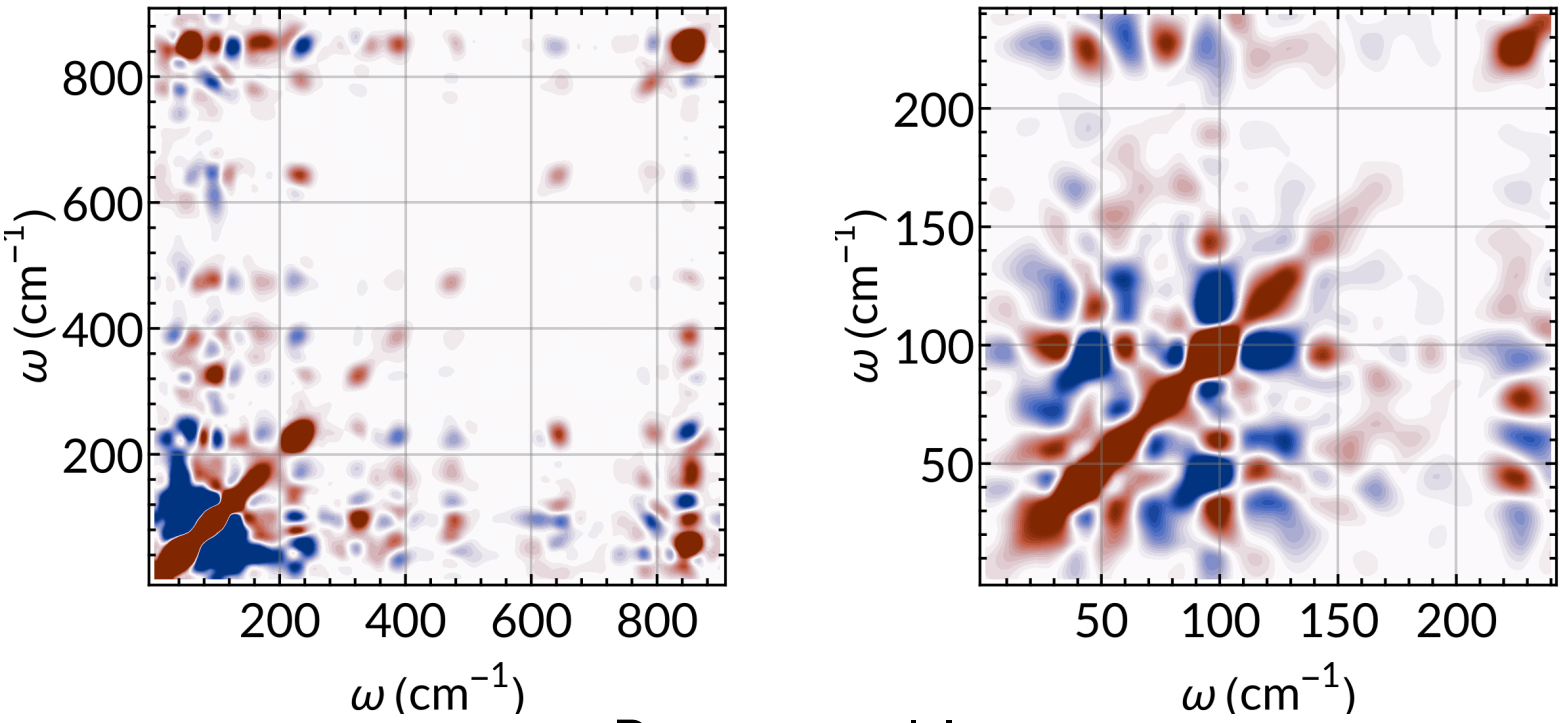
PBE+MBD/LDA

MD: 2x15ps, @300 K

Low-frequency modes: high sensitivity to anharmonicity and to polymorphic forms

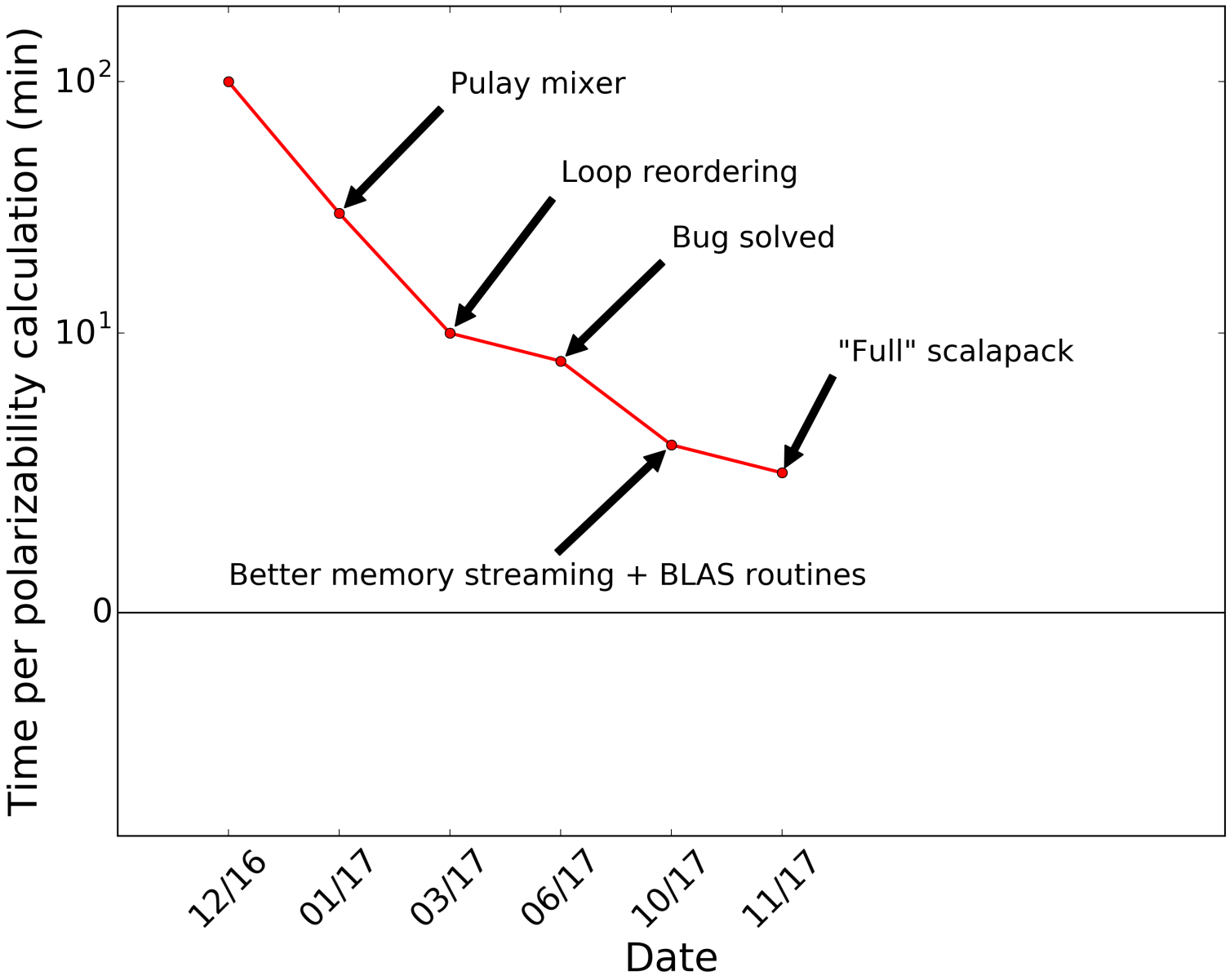
2D-spectroscopy

How do vibrational modes couple to each other ?

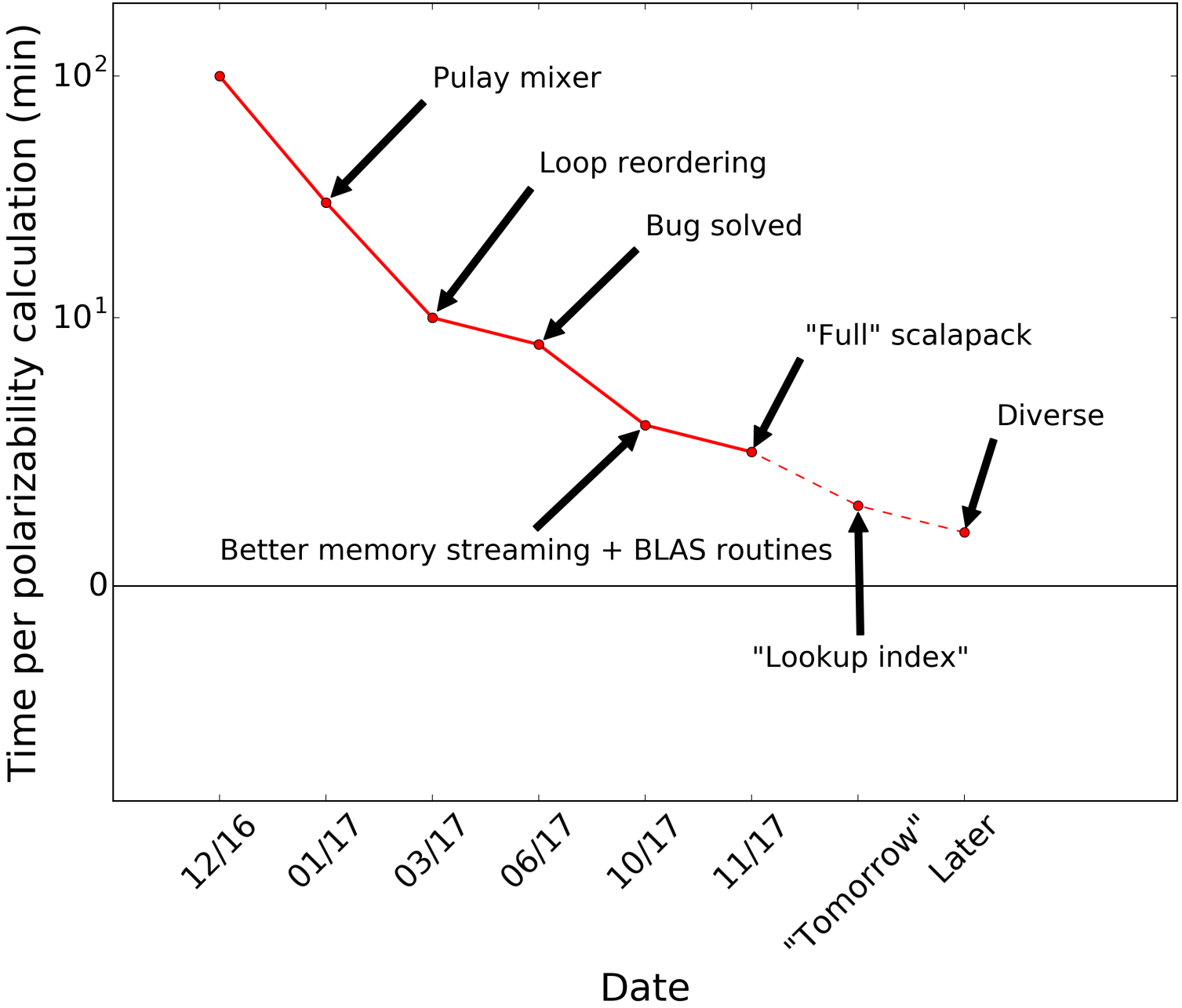


Paracetamol I

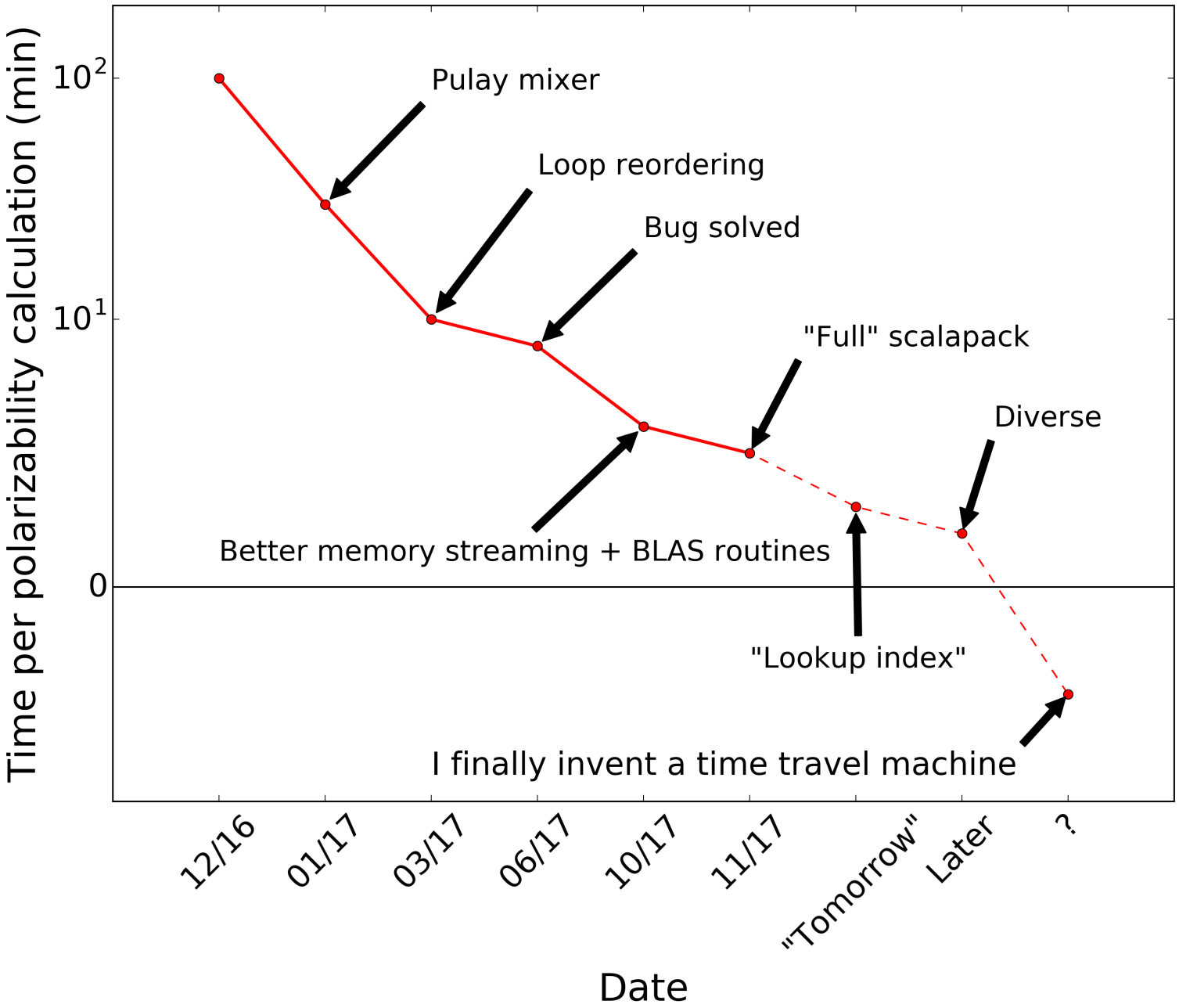
Speed (dielectric)



Speed (dielectric)



Speed (dielectric)



Things missing/wishes

Phonons

- Improve performance
- PBE0 for both periodic and cluster
- Treat metals (See `DFPT_width` keyword for dielectric)
- ...

Dielectric

- Born-effective charges → Partially there
- PBE0 for periodic case → Will be there later this year
- (Dipole moment for periodic case) → Very soon in principle
- ...

Thank you