Current* status of DFPT within FHI-aims

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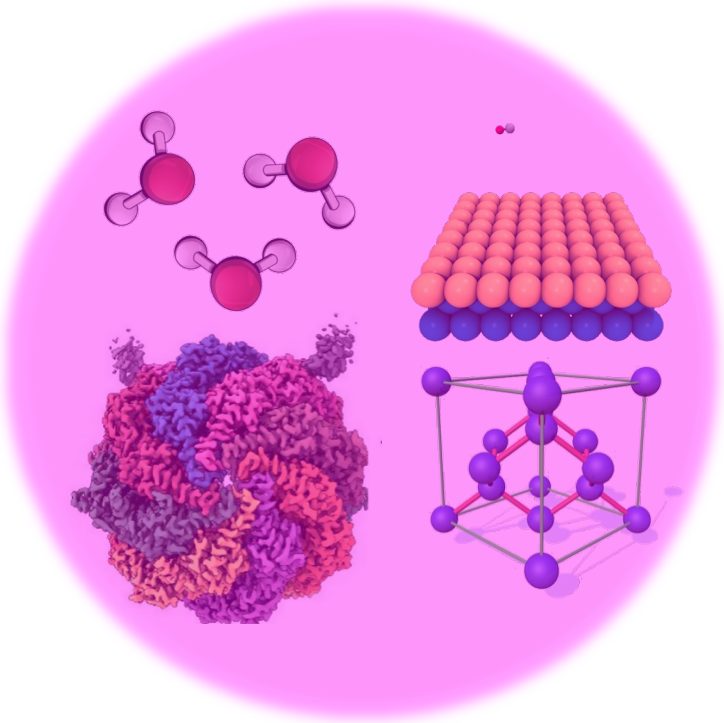
DFPT project (2020-2021) co-supervised by: Dr Andrew Logsdail (*Cardiff University*), Dr Volker Blum (*Duke University*), Dr Mariana Rossi (*MPI for the Structure and Dynamics of Matter*) and Dr Christian Carbogno (*Fritz-Haber-Institut der Max-Planck-Gesellschaft*)

Perturbation theory

$$H(\lambda) = H^{(0)} + V_{\text{ext}}(\lambda)$$

Perturbation (λ)

- Atomic displacement
- Electric field
- Magnetic field
- Strain
- Alchemical change



Response functions

- Thermal expansion
- Vibrational lifetimes
- Raman intensities
- Phonons

Density functional perturbation theory (DFPT)

DFT: solve the Kohn-Sham equations by minimizing the **total energy**.

1st order properties: forces, stress, dipole moment, ...

DFPT: minimizing **the second order perturbation** in the **total energy**

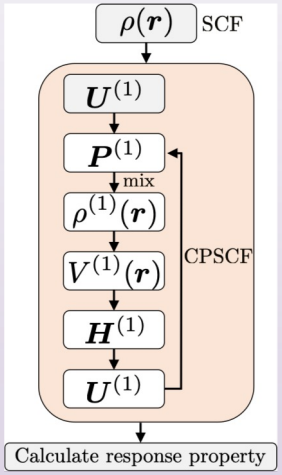
$$(H^{(0)} - \epsilon_i^{(0)})|\psi_i^{(1)}\rangle = -(H^{(1)} - \epsilon_i^{(1)})|\psi_i^{(0)}\rangle$$

2nd order properties: phonon dynamical matrix, elastic constants, dielectric susceptibility, Born effective charges, piezoelectricity, internal strain

3rd order properties: non-linear dielectric susceptibility, phonon-phonon interaction, anharmonic elastic constants, ...

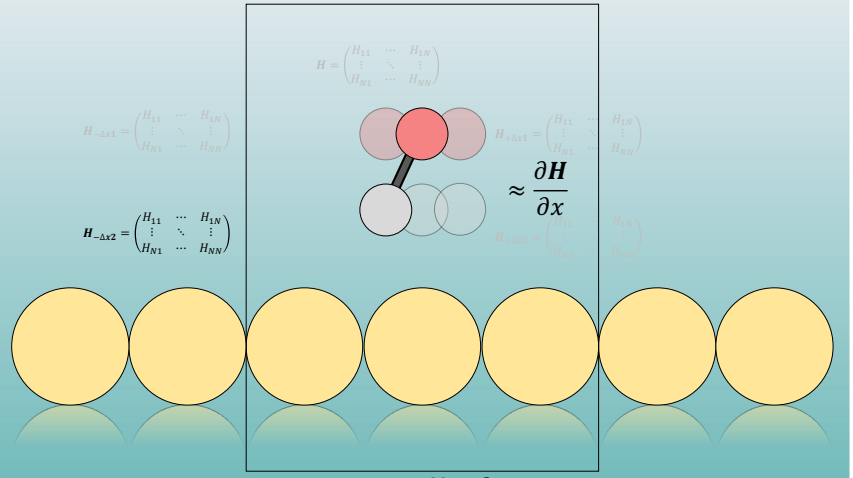
Finite difference or DFPT?

DFPT



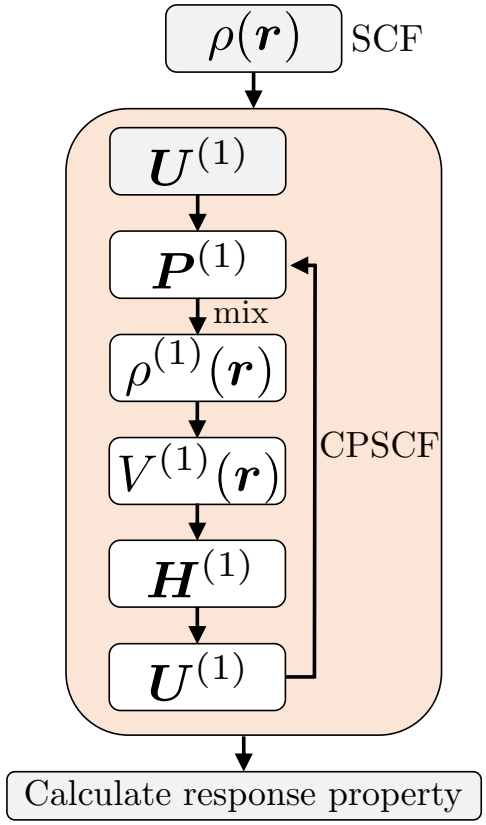
- Non-zero momentum response
- Faster in *theory*
- Involved programming required

Finite difference

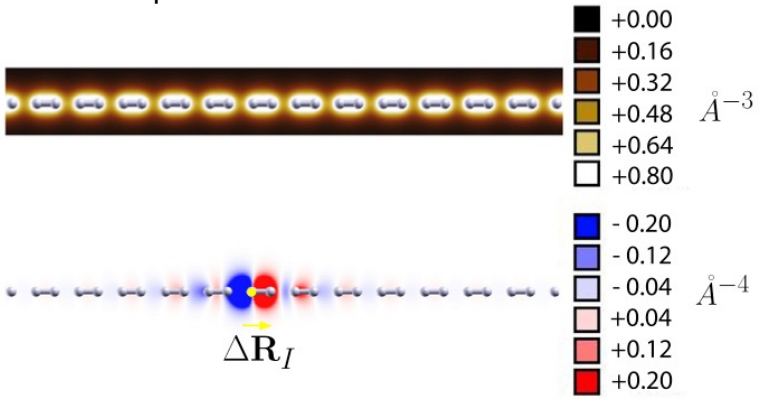


- **q**=0 (requires supercells for **q**>0)
- +2N SCF cycles (with less steps potentially)
- Numerical issues can be present – e.g atomic perturbation crossing symmetry planes
- Easy to program/script for any underlying methods (hybrids etc)

FHI-aims implementation

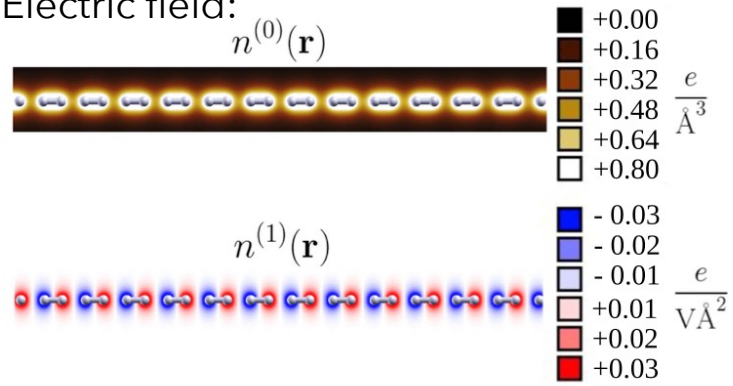


Atomic perturbations:



H. Shang et al, *Comput. Phys. Commun.*, (2017)

Electric field:



H. Shang et al, *New J. Phys.*, (2018)

DFPT ecosystem in FHIaims

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`DFPT polarizability`

`DFPT dielectric`

Electric field response: Polarizability tensors and dielectric constants

`DFPT vibration`

`DFPT vibration_reduce_memory`

`DFPT phonon`

`DFPT phonon_reduce_memory`

Atomic perturbation response: IR spectrum, Hessian, **q**≥0 phonons

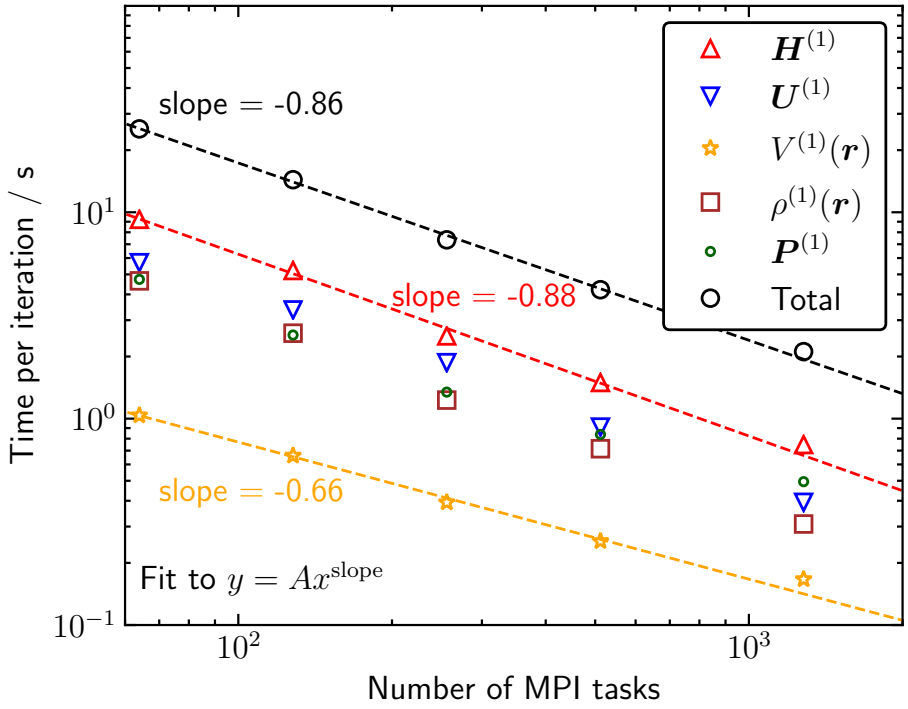
`calculate_friction`

Atomic perturbation response: Electronic friction tensor , electron-phonon coupling matrix elements, phonon linewidths. Also *finite difference* implemented.

`magnetic_response`

Magnetic field response: NMR shielding tensors, magnetizability tensor

Time breakdown



Time per CPSCF iteration for evaluation of key matrices as a function of the number of MPI tasks (cores) used. This is calculated for electric field response of bulk Si with 128 atoms on ARCHER2 with the new interface.

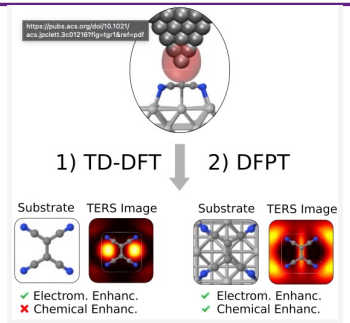
`DFPT dielectric`

Applications we've heard so far …

Simulation of Tip-enhanced Raman Spectroscopy – Yair Litman

`DFPT polarizability`

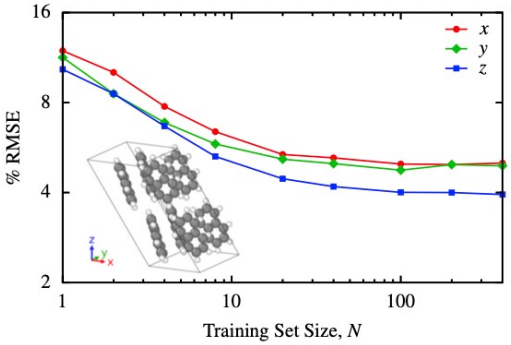
`DFPT dielectric`



Y. Litman et al, *J. Phys. Chem. Lett.*, (2023)

Machine Learning for the Electronic Structure – Alan Lewis

`DFPT dielectric`



A. M. Lewis et al, *arXiv:2304.09057*, (2023)

Basis-set-error free RPA correlations for atoms and diatomic molecules based on the Sternheimer equation – Xinguo Ren

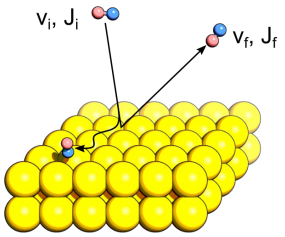
`DFPT vibration`

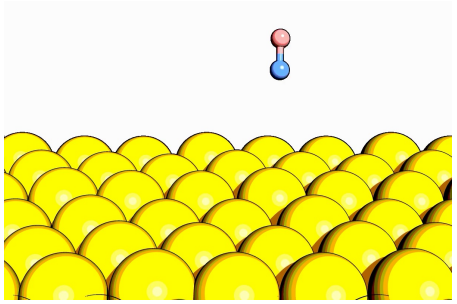
`DFPT vibration_reduce_memory`

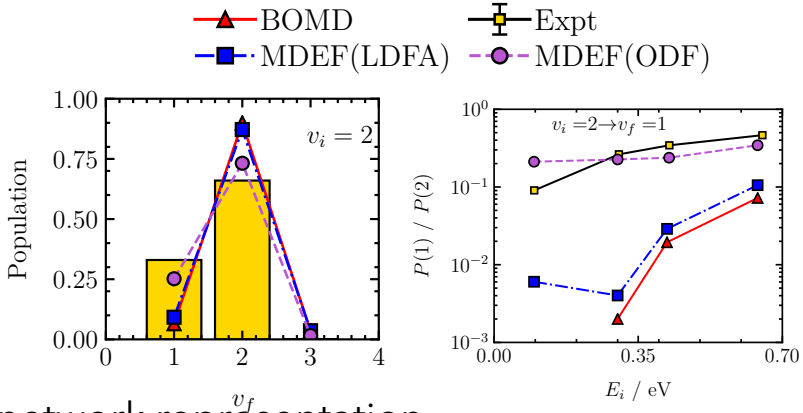
Machine learning of response functions

Electronic friction tensor ---> Vibrational state-to-state scattering

`calculate_friction`







C. L. Box & Y. Zhang et al, *JACS Au*, (2021)

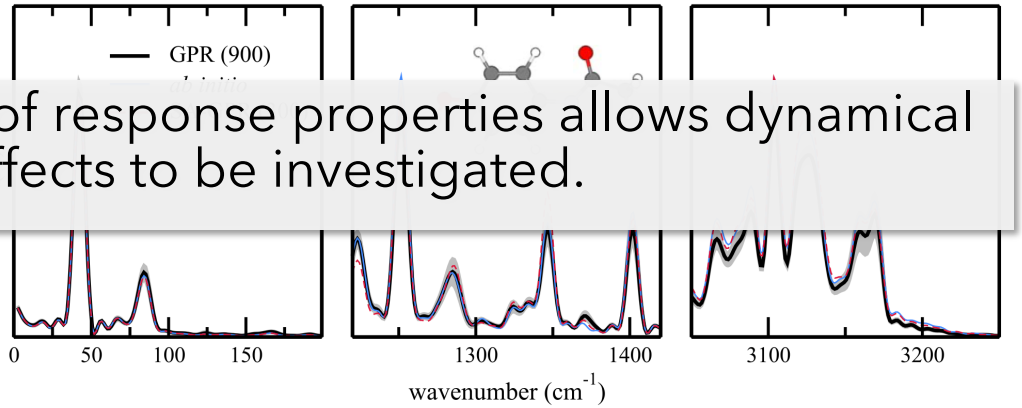
Embedded atom neural network representation

Polari

N. Ra mbault et al, *New J. Phys.*, (2019)

`DFPT polarizability`

`DFPT dielectric`



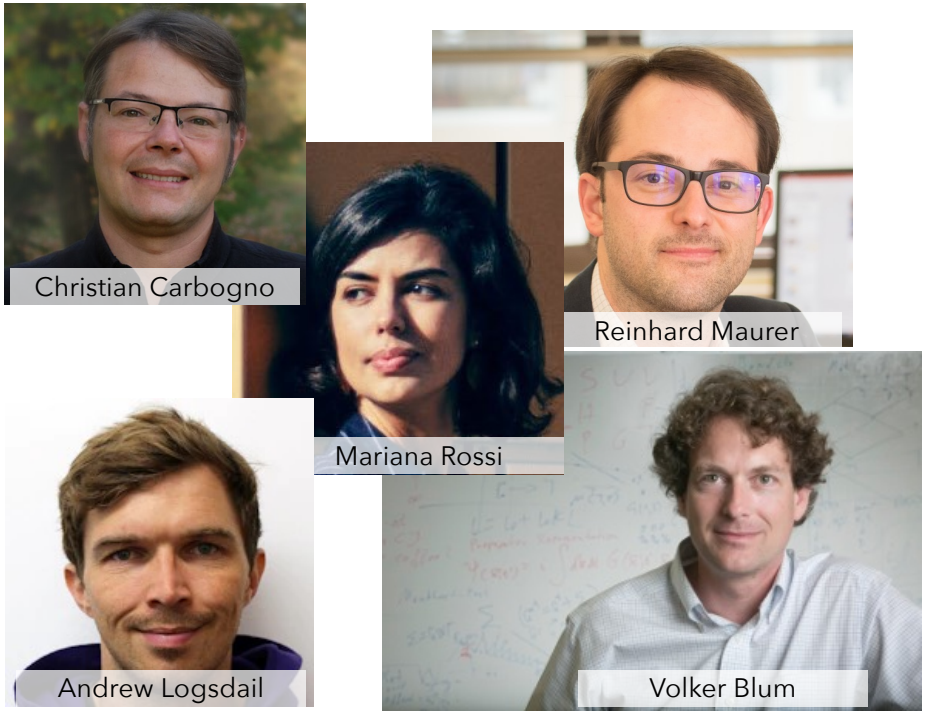
Gaussian process regression representation

Machine learning representations of response properties allows dynamical and anharmonic effects to be investigated.

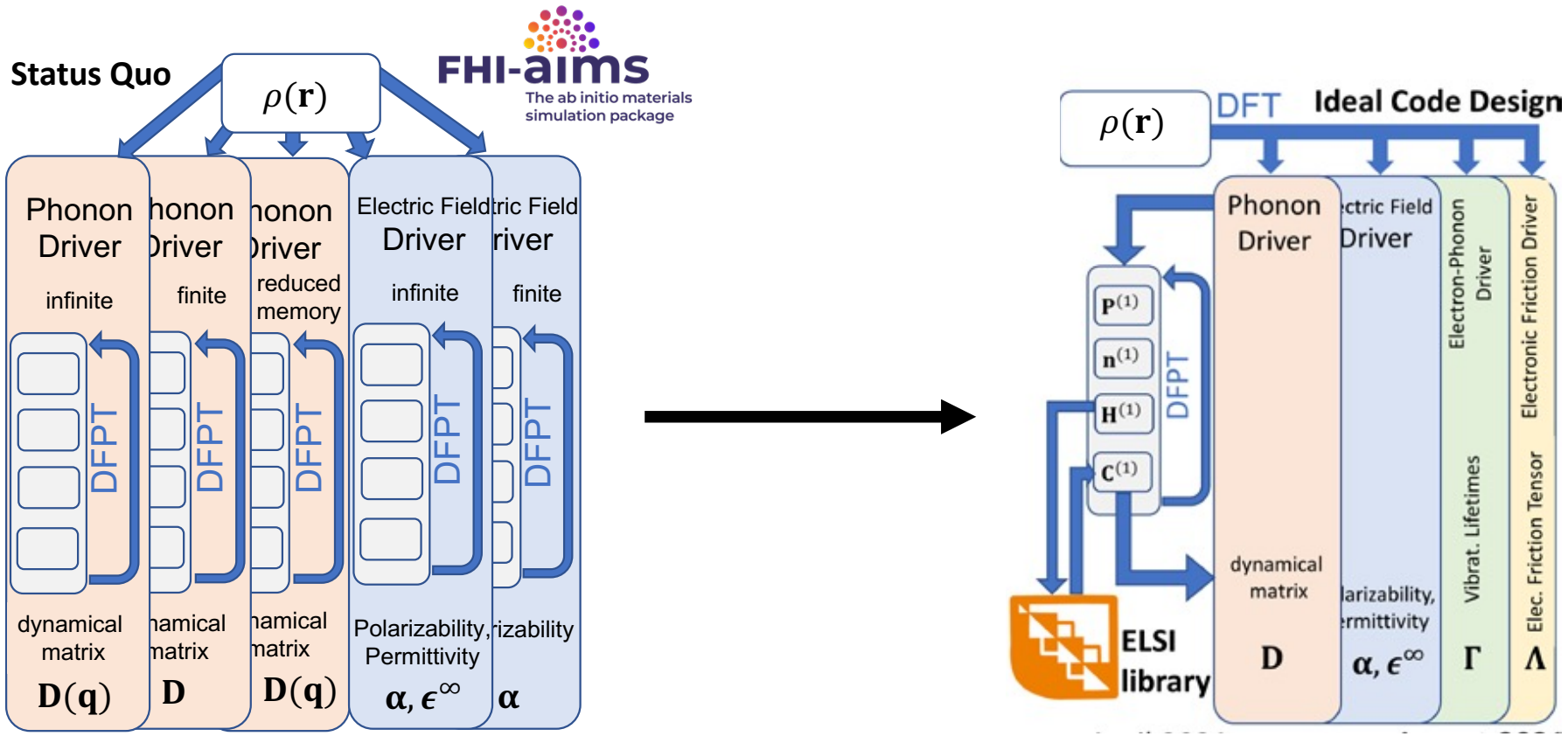
Background to project

ARCHER2 eCSE funded project : Achieving the **sustainability** and scalability of numeric-atomic-orbital-based linear response and electron-phonon functionality in FHI-aims

2020-2021



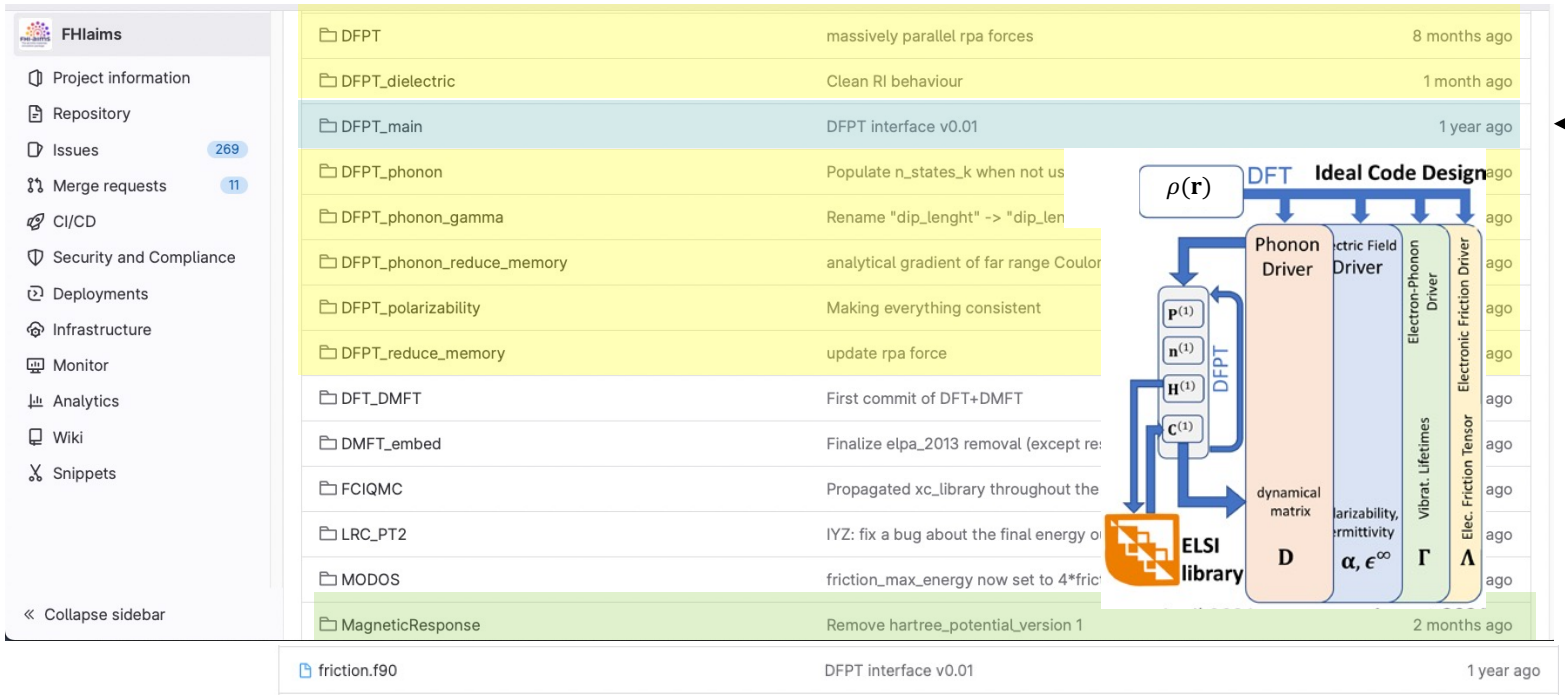
DFPT in FHI-aims



Degeneracy of CPSCF code

- These `cpscf_solver.f90` files are generally similar but also call driver routines (not just the CPSCF)
- In turn, each driver also has different evaluation routines for each first order matrix.

FHI-aims DFPT directory structure



This work (2020)

H. Shang et al, (2017, 2018)

R. Laasner et al, (2018)

DFPT_main: Largely same functionality with reducing code lines by over 60 % compared to various DFPT_XXXs

Calling new DFPT/CPSCF module

```
!DFPT variable, letting the module know we want nuclear (not electric field) response
nuclear_response=.true.

! Run all required perturbations in same CPSCF cycle
! We translate friction atom list to dfpt_perturbation list, which just contains coord info too
perturbation_list = 0
do i_atom = 1, n_atoms
    if (friction_atoms_list(i_atom)) then
        do i_cart =1 ,3
            !We need perturbation for this atomic coordinate
            perturbation_list(i_atom,i_cart) = 1
        enddo !i_cart
    endif !friction_atom
enddo !i_atom

if (n_periodic == 0) then
    i_q_point = 0 !Basically a dummy
else
    i_q_point = 1 !All thats supported right now, unless use a supercell
endif

! Get first order overlap first, we need this for DFPT anyway
call calculate_first_order_S_generic(perturbation_list,i_q_point,one_sided_derivative=.false.,use_supercell=.false.)


converged_cpscf = .false. !initialization

!At the moment it automatically reads first_order_S from first_order_overlap module, so we dont need to pass it in
! reduce_memory = .true.
!TODO: remove need for this
call DFPT_initialization(.false., perturbation_list)
call DFPT_cpscf(converged_cpscf,dfpt_forces_on=.false.,i_q_point=i_q_point)

if ((.not.converged_cpscf).and.(.not.postprocess_anyway==PP_ANYWAY_EVERYTHING)) then
    call aims_stop('CPSCF not converged')
endif
```

- Atomic perturbation
- After `DFPT_cpscf`, `DFPT_first_order_XXX` matrices become populated
- `DFPT centralised .true.` to call the new interface (not yet default)

`friction.f90`

Calling new DFPT/CPSCF module – second example

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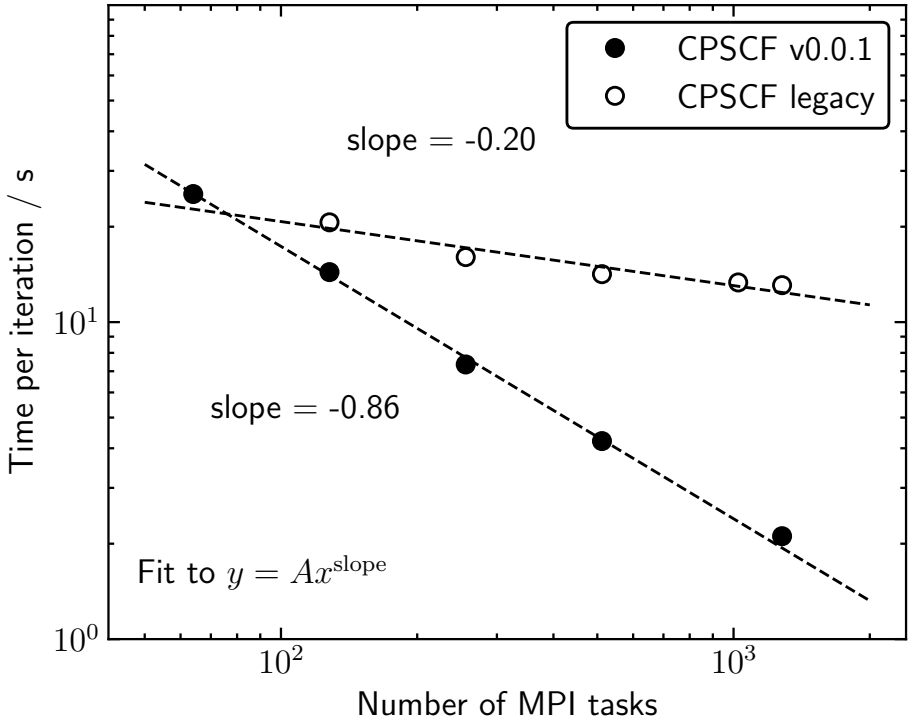
```
do j_coord = 1,3,1 !x, y, z response

    perturbation_list = 0 !(re)initialization
    perturbation_list(1,j_coord) = 1 !we calculate each perturbation in serial

    call DFPT_initialization(.false., perturbation_list)

    if (n_periodic==0) then
        call DFPT_cpscf(converged_cpscf,dfpt_forces_on=.false.) !main CPSCF cycle
    else ! Requiries momentum matrix for periodic

        !only do this once. currently Omega_MO evaluates for all coords (no reduce_mem)
        if (j_coord==1) call elecres_calculate_omega_MO() !momentum matrix required

        ! 2/3 of the Omega_MO* arguments will be dummies, which ones depend on usecase
        call DFPT_cpscf(converged_cpscf, &
            dfpt_forces_on=.false., &
            Omega_MO=Omega_MO, &
            Omega_MO_scalapack=Omega_MO_scalapack, &
            Omega_MO_complex_scalapack=Omega_MO_complex_scalapack)

            !if (myid==0) write(*,*) 'dm1', DFPT_first_order_density_matrix_sparse(1,1,:,1)
    endif !n_periodic

    if (.not.converged_cpscf.and..not.(postprocess_anyway==PP_ANYWAY_EVERYTHING)) then
        call aims_stop('CPSCF not converged')
    endif
```

electric_response.f90

Speedup

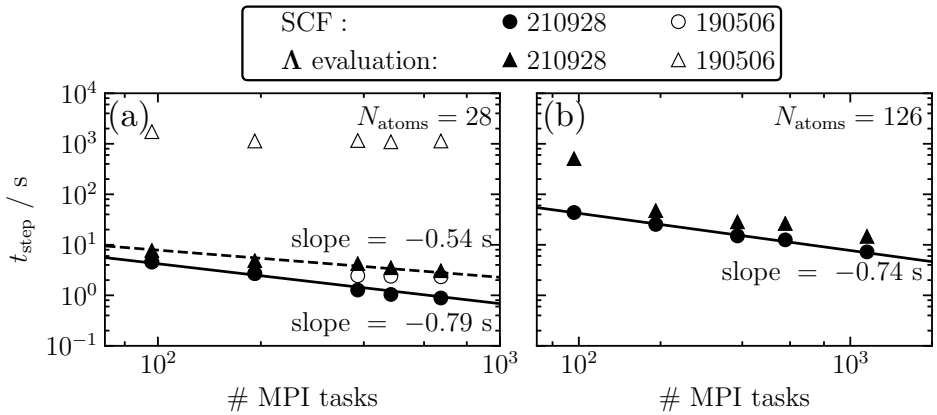
- Fixing ScaLAPACK implementation for periodic electric field
- Electric field response of bulk Si with 128 atoms on ARCHER2



Electronic friction / electron-phonon coupling driver

`calculate_friction` `numerical_friction`

`calculate_friction` `DFPT`

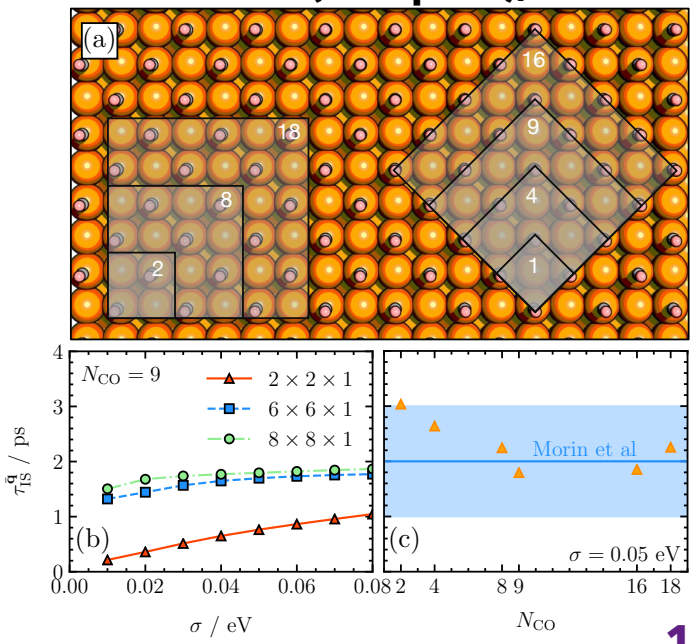


Electron-phonon coupling matrix elements:

`friction_elsi_epc_write .true.`

can then calculate phonon linewidths, superconductivity, carrier transport etc.

- Original finite difference implementation by **R. J. Maurer et al, *PRB*, (2016)**
- Now DFPT enabled for *non-metals*
- Refactored driver to make more scalable
- These recent developments described in **C. L. Box et al, Electron. Struc. (accepted), 2023**



Exp: M. Morin et al, *JCP*, (1992)

Conclusions

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- A more consolidated interface for DFPT in FHI-aims was created for atomic and electric field response.
- Electronic friction /electron-phonon coupling driver was refactored and DFPT enabled, though lacking fix for metallic systems currently.
- “New” interface needs to be made default for atomic and electric field or it will soon become defunct
- I think some small remaining issues remaining stopping electric field response users from switching to the new interface
- RPA DFPT implementation has now significantly diverged from the point where it could be easily switched to the new interface – now somewhat more involved to do this.

Moving forward

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2023

1. Fix bugs in ScaLAPACK-distributed electric field response for new interface (Connor, September)

2. Port recent functionality in electric field response to new interface/driver

3. Set new interface as default for electric field driver, and vibration/phonon drivers (Connor, September)

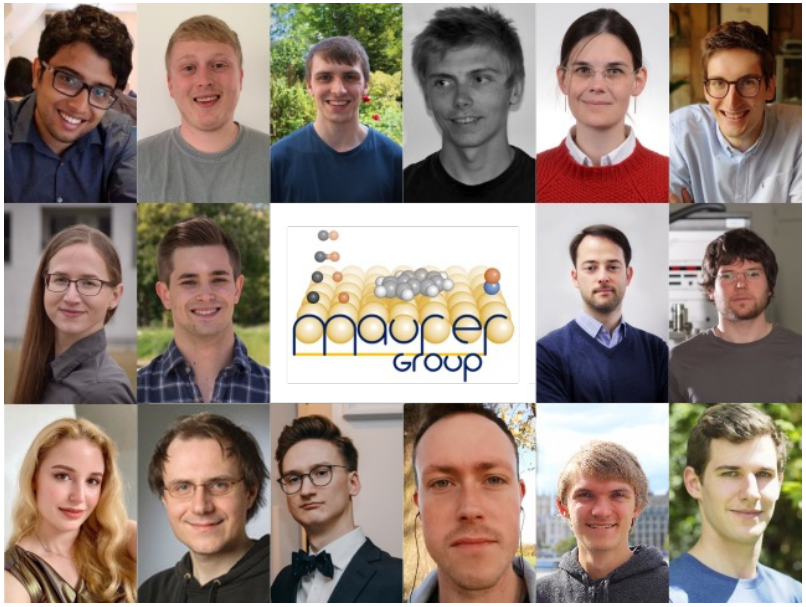
4. Possibly implement metals for atomic response (desirable for electronic friction in Maurer group)

Beyond

5. New drivers should use new interface

6. Evaluation/discussion of porting RPA driver over to new interface

Acknowledgements



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Thank you for your attention

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