GPAW

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Outline

- Introduction to GPAW
  - Projector-augmented wave method
  - Basis sets in GPAW
- Using Atomic Simulation Environment and GPAW
- Hands-on exercises

- Lunch

- Time-dependent DFT with GPAW
- Parallel calculations (+ other features by request)
- Hands-on exercises

GPAW

- Implementation of projector augmented wave method on
  - uniform real-space grids, atomic orbital basis, plane waves
- Density-functional theory, time-dependent DFT, many-body perturbation theory, ...
- Massively parallelized

wiki.fysik.dtu.dk/gpaw

gpaw-users@listserv.fysik.dtu.dk

J. J. Mortensen et al., Phys. Rev. B 71, 035109 (2005)

J. Enkovaara et al., J. Phys. Condens. Matter 22, 253202 (2010)

GPAW

- Open source software licensed under GPL
  - 20-30 developers in Europe and USA

- The main GPAW references cited ~350 times
- ~300 subscribers in users mailing list

GPAW features

- Total energies, forces, structural optimization
  - analysis of electronic structure
- Excited states, optical spectra
  - Non-adiabatic electron-ion dynamics
- Wide range of XC-potentials (thanks to libxc!)
  - LDAs, GGAs, meta-GGAs, hybrids, DFT+U, vdW, RPA
- Electron transport
- GW-approximation, Bethe-Salpeter equation
- ...

Projector-augmented wave method

- Exact all-electron formalism
- “Pseudopotentials done right”
- Good description over the whole periodic table
- Access to full wave functions and density
- Norm-conserving and ultrasoft pseudopotentials can be derived as approximations to PAW

PAW transformation

- Linear transformation from pseudo wave functions to all-electron wave functions

$$|\psi_k\rangle = \widehat{T}|\tilde{\psi}_k\rangle$$

- Transformation operator

$$\widehat{T} = 1 + \sum_{a,i} \left(|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle \right) \langle \tilde{p}_i^a|$$

$|\phi_i^a\rangle$ **all-electron atomic orbital**

$|\tilde{\phi}_i^a\rangle$ **pseudo atomic orbital**

$|\tilde{p}_i^a\rangle$ **projector function**

- Core electrons are frozen

Properties of PAW transformation

- Projector functions are localized inside the augmentation spheres

$$p_i^a(r) = 0, r > R_a$$

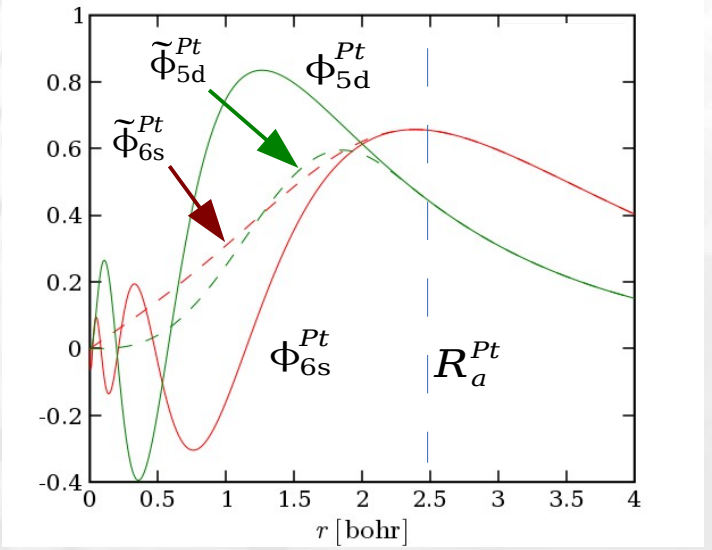
- All-electron orbitals and pseudo orbitals are equal outside the augmentation spheres

$$\phi_i^a(r) = \tilde{\phi}_i^a(r), r > R_a$$

- Projector functions are orthogonal to pseudo orbitals

$$\langle \tilde{p}_i^a | \tilde{\phi}_j^a \rangle = \delta_{ij}$$

Example: Platinum



PAW transformation

- The projector functions and partial waves are constructed from all-electron calculation for spherical symmetric atom
- To be exact, infinite number of projectors and partial waves is needed
  - In practice, 1-2 functions per angular momentum is enough

One center expansion

- Inside augmentation spheres one can define one-center expansions of AE and PS state

$$\psi_n^a(\mathbf{r}) = \sum_i P_{in}^a \phi_i^a(\mathbf{r})$$

$$\tilde{\psi}_n^a(\mathbf{r}) = \sum_i P_{in}^a \tilde{\phi}_i^a(\mathbf{r})$$

  with expansion coefficients

$$P_{in}^a = \langle \tilde{p}_i^a | \tilde{\psi}_n \rangle$$

- All electron wave function can now be written as

$$\psi_n = \tilde{\psi}_n + \sum_a (\psi_n^a - \tilde{\psi}_n^a)$$

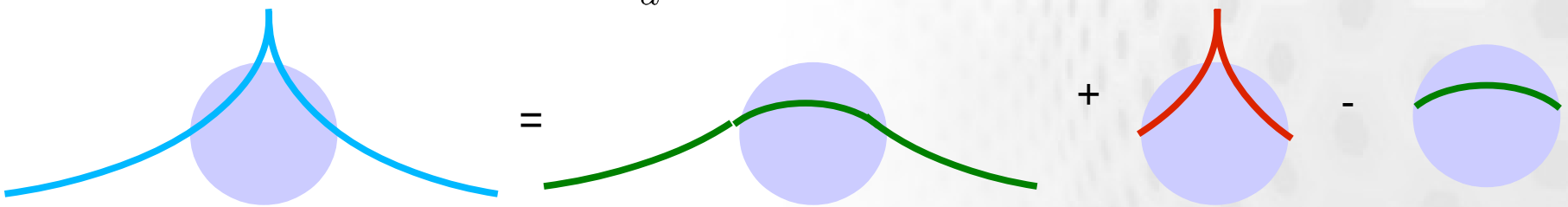
PAW expectation values

- Within frozen core approximation expectation value of operator Ô is

$$\langle \hat{O} \rangle = \sum_{n}^{val} f_n \langle \psi_n | \hat{O} | \psi_n \rangle + \sum_a \sum_\alpha \langle \phi_\alpha^{a,core} | \hat{O} | \phi_\alpha^{a,core} \rangle$$

- By inserting the PAW expression, one obtains for (semi)local operators

$$\begin{aligned} \langle \psi_n | \hat{O} | \psi_n \rangle &= \langle \tilde{\psi}_n | \hat{O} | \tilde{\psi}_n \rangle + \sum_a \left(\langle \psi_n^a | \hat{O} | \psi_n^a \rangle - \langle \tilde{\psi}_n^a | \hat{O} | \tilde{\psi}_n^a \rangle \right) \\ &= \tilde{O} + \sum_a \left(O^a - \tilde{O}^a \right) \end{aligned}$$



PAW Hamiltonian

- PAW Hamiltonian can be written as

$$\hat{H} = -\frac{1}{2}\nabla^2 + \tilde{v}(\mathbf{r}) + \sum_a \sum_{i_1 i_2} |\tilde{p}^a_{i_1}\rangle \Delta H^a_{i_1 i_2} \langle \tilde{p}^a_{i_2}|$$

- Pseudo wave functions are orthonormal only with respect to overlap operator

$$\langle \psi_i | \psi_j \rangle = \langle \tilde{\psi}_i | \hat{T}^\dagger \hat{T} | \tilde{\psi}_j \rangle = \langle \tilde{\psi}_i | \hat{S} | \tilde{\psi}_j \rangle = \delta_{ij}$$

- Generalized eigenvalue equation

$$\hat{H}\tilde{\psi}_n = \epsilon_n \hat{S}\tilde{\psi}_n$$

Approximations in PAW

- Finite number of projectors
  - typically two projectors per angular momentum are used
- Truncated angular momentum expansions
- Overlapping augmentation spheres
- Frozen core

PAW setup

- A set of

  $$\phi^a,\ \tilde{\phi}^a,\ \tilde{p}^a,\ n_c^a,\ \tilde{n}_c^a,\ \bar{v}^a$$

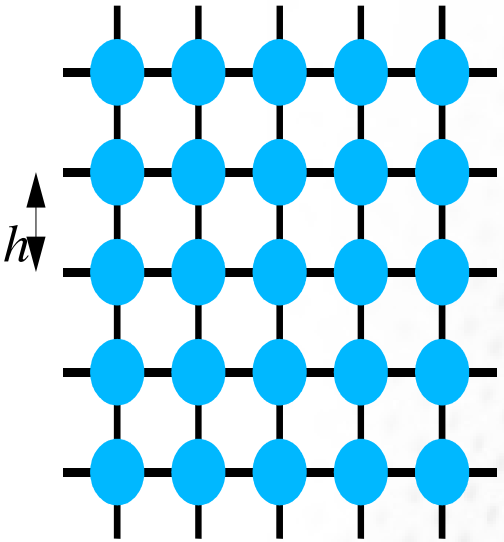
  for a single atom constitutes a PAW setup
- Setups are generated for individual atoms
- The actual PAW calculations use pregenerated setups
- Setup testing is non-trivial and time-consuming
  - correct properties for the particular atom
  - transferability in different molecules and solids

Basis sets in GPAW

- Real-space grids
- Localized atomic orbital basis
- Plane waves

Real-space grids

- Wave functions, electron densities, and potentials are represented on grids.
- Single parameter, grid spacing h



- Accuracy of calculation can be improved systematically
- Derivatives by finite differences

Boundary conditions

- Real-space description allows flexible boundary conditions
- Zero boundary conditions (finite systems)
  - Useful especially in charged systems
- Periodic boundary conditions (bulk systems)
- Boundary conditions can be mixed
  - periodic in one dimension (wires)
  - periodic in two dimensions (surfaces)

Atomic orbital basis

- Linear combination of atomic orbitals (LCAO) provide compact basis set

$$\tilde{\psi}_n = \sum_\nu C_{n\nu} \Phi_\nu(\mathbf{r})$$

$$\Phi^a_{nlm}(\mathbf{r}) = R^a_{nl}(|\mathbf{r} - \mathbf{R}^a|) Y_{lm}(\mathbf{r} - \mathbf{R}^a)$$

- The atomic orbitals are obtained from a free atom in a confining potential well
- Systematic improvement of accuracy is non-trivial
- Possible to switch between localized basis and real-space grids

Plane wave basis

- Functions which are periodic with respect to unit cell can be written as sum of plane waves

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}} \sum_{\mathbf{G}} C_{\mathbf{G},n\mathbf{k}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}$$

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \qquad V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$$

- The expansion is truncated according to

$$\frac{1}{2}|\mathbf{G}+\mathbf{k}|^2 < E_{cutoff}$$

- Only periodic cells (supercells)

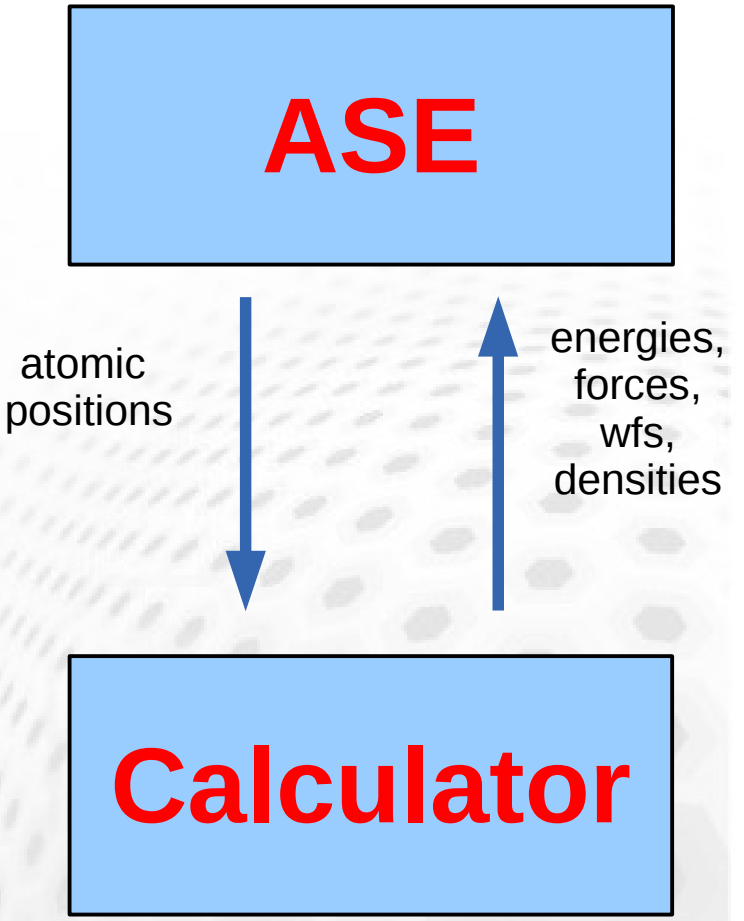
Comparison of basis sets

- Real-space grids
  - systematic convergence with single parameter
  - good parallelization prospects
  - some integrals complicated in real-space
- Localized basis set
  - compact basis
  - systematic convergence can be difficult
- Plane waves
  - systematic convergence with single parameter
  - some integrals simplified in reciprocal space
  - very efficient in small to medium size systems
  - parallelization more limited due FFTs

Using the Atomic Simulation Environment

Atomic Simulation Environment

- ASE is a Python package for
  - building atomic structures
  - structure optimization and molecular dynamics
  - analysis and visualization
- ASE relies on external software which provides total energies, forces, etc.
  - GPAW, Abinit, Siesta, Vasp, Castep, ...
- Input files are Python scripts
  - calculations are run as "python input.py"
  - simple format, no knowledge of Python required
  - knowledge of Python enables great flexibility
- Simple graphical user interface



wiki.fysik.dtu.dk/ase

Setting up the atoms

- Specifying atomic positions directly

```
from ase.all import *  # Setup the atomic simulation environment

d0 = 1.10
x = d0 / sqrt(3)
atoms = Atoms('CH4',
              positions=[(0.0, 0.0, 0.0),  # C
                         (x, x, x),        # H1
                         (-x, -x, x),      # H2
                         (-x, x, -x),      # H3
                         (x, -x, -x)]      # H4
              )
view(atoms)
```

- Reading atomic positions from a file

```
...
atoms = read('CH4.xyz')
view(atoms)
```

  - Several file formats supported

Setting up the unit cell

- By default, the simulation cell of an Atoms object has zero boundary conditions and edge length of 1 Å
- Unit cell can be set when constructing Atoms

```
atoms = Atoms(..., # positions must be now in absolute coordinates
              cell=(1., 2., 3.), pbc=True)# or pbc=(True, True, True)
```

or later on

```
atoms = Atoms(...)   # positions in relative coordinates
atoms.set_cell((2.5, 2.5, 2.5), scale_atoms=True)
atoms.set_pbc(True)  # or atoms.set_pbc((True, True, True))
```

```
atoms = ...
atoms.center(vacuum=3.5) # finite system 3.5 Å empty space around atoms
```

```
atoms = ...
atoms.set_pbc((False, True, True)) # surface slab
atoms.center(axis=0, vacuum=3.5) # 3.5 Å empty space in x-direction
```

Units in ASE

- Length: Å
- Energy: eV

- Easy conversion between units:

```
from ase.units import Bohr, Hartree

a = a0 * Bohr        # a0 in a.u., a in Å
E = E0 * Hartree     # E0 in Hartree, E in eV
```

  - also Rydberg, kcal, nm, ...

Pre-defined molecules and structures

- Database of small molecules (G2-1 and G2-2 sets)

```
from ase.structure import molecule

mol = molecule('C6H6') # coordinates from MP2 calculation
mol.center(3.5)        # molecule() returns unit cell of 1 Å
```

- Bulk structures of elemental materials

```
from ase.lattice import bulk

atoms = bulk('Si') # primitive (2-atom) unit cell with exp. lattice constant
atoms_conv = bulk('Si', cubic=True)  # cubic 8-atom unit cell
atoms_my_a = bulk('Si', a=5.4) # User specified lattice constant
```

Supercells and surfaces

- Existing Atoms objects can be “repeated” and individual atoms removed

```
from ase.lattice import bulk

atoms = bulk('Si', cubic=True)  # cubic 8-atom unit cell
supercell = atoms.repeat((4, 4, 4)) # 512 atom supercell
del supercell[0]  # remove first atom, e.g. create a vacancy
```

- Utilities for working with surfaces

```
from ase.lattice.surface import fcc111, add_adsorbate

slab = fcc111('Cu', size=(3,3,5)) # 5-layers of 3x3 Cu (111) surface
# add O atom 2.5 Å above the surface in the 'bridge' site
add_adsorbate(slab, 'O', 2.5, position='bridge')
```

Performing a calculation

- In order to do calculation, one has to define a calculator object and attach that to Atoms

```
from ase.structure import molecule    # Setup the atomic simulation environment
from gpaw import GPAW  # Setup GPAW

atoms = molecule('CH4')
atoms.center(3.5)
calc = GPAW() # Use default parameters
atoms.set_calculator(calc)
atoms.get_potential_energy() # Calculate the total energy
```

- Specifying calculator parameters

```
...
calc = GPAW(h=0.18, nbands=6,          # 6 bands and grid spacing of 0.20 Å
            kpts=(4,4,4),              # 4x4x4 Monkhorst-Pack k-mesh
            xc='PBE', txt='out.txt') # PBE and print text output to file
...
```

- See wiki.fysik.dtu.dk/gpaw/documentation/manual.html for all parameters

Performing a calculation

- Serial calculations and analysis can be carried out with normal Python interpreter

```
[jenkovaa@flamingo ~]$ python input.py
```

- Parallel calculations with **gpaw-python** executable

```
#PBS -N gpaw_test
#PBS -l select=4
#PBS -l walltime=00:20:00
...
aprun -n 96 gpaw-python input.py
```

Structural optimization


```
from ase.all import *          # Setup the atomic simulation environment
from gpaw import GPAW          # Setup GPAW

atoms = ...
calc = GPAW(...)
atoms.set_calculator(calc)

opt = BFGS(atoms, trajectory='file.traj') # define an optimizer
opt.run(fmax=0.05) # optimize the structure until forces smaller than 0.05 eV / Å
```

- See wiki.fysik.dtu.dk/ase/ase/optimize.html for supported optimizers
- “Best” optimizer is case-dependent

Simple Python scripting


```
atoms = ...
calc = GPAW(...)
atoms.set_calculator(calc)

# Check convergence with grid spacing
for h in [0.35, 0.30, 0.25, 0.20, 0.18]:
    txtfile = 'test_h' + str(h) + '.txt'
    calc.set(h=h, txt=txtfile)
    e = atoms.get_potential_energy()
    print h, e
```

```
import numpy as np
atoms = ...
calc = GPAW(...)
atoms.set_calculator(calc)

# lattice constant for different XC-functionals
for xc in ['LDA', 'PBE']:
    for a in np.linspace(3.8, 4.3, 5):
        txtfile = 'test_xc_' + xc + '_a' + str(s) + '.txt'
        atoms.set_cell((a, a, a), scale_atoms=True)
        calc.set(xc=xc, txt=txtfile)
        e = atoms.get_potential_energy()
```

Saving and restarting

- Saving full state of calculation: .gpw-files (or .hdf5-files)

```
...
calc = GPAW(...)
atoms.set_calculator(calc)
atoms.get_potential_energy() # Calculate the total energy
calc.write('myfile.gpw')     # Atomic positions, densities, calculator parameters
```

```
...
calc.write('myfile.gpw', mode='all') # Save also wave functions (larger files)
```

```
...
calc.write('myfile.hdf5', mode='all') # If GPAW is build with HDF5 support
```

- Restarting

```
from ase.all import *   # Setup the atomic simulation environment
from gpaw import restart  # Setup GPAW

atoms, calc = restart('file.gpw')
e0 = atoms.get_potential_energy() # no calculation needed
calc.set(h=0.20)
e1 = atoms.get_potential_energy() # calculation total energy with new grid
```

Saving and restarting

- Trajectories: atomic positions, energies, forces

```
...
calc = GPAW(...)
atoms.set_calculator(calc)
traj = PickleTrajectory('file.traj', 'w', atoms) # define a trajectory file
for a in np.linspace(3.8, 4.3, 5):
    txtfile = 'test_xc_' + xc + '_a' + str(s) + '.txt'
    atoms.set_cell((a, a, a), scale_atoms=True)
    atoms.get_potential_energy()
    traj.write()  # write cell and energy to trajectory file
```

- Reading atomic positions

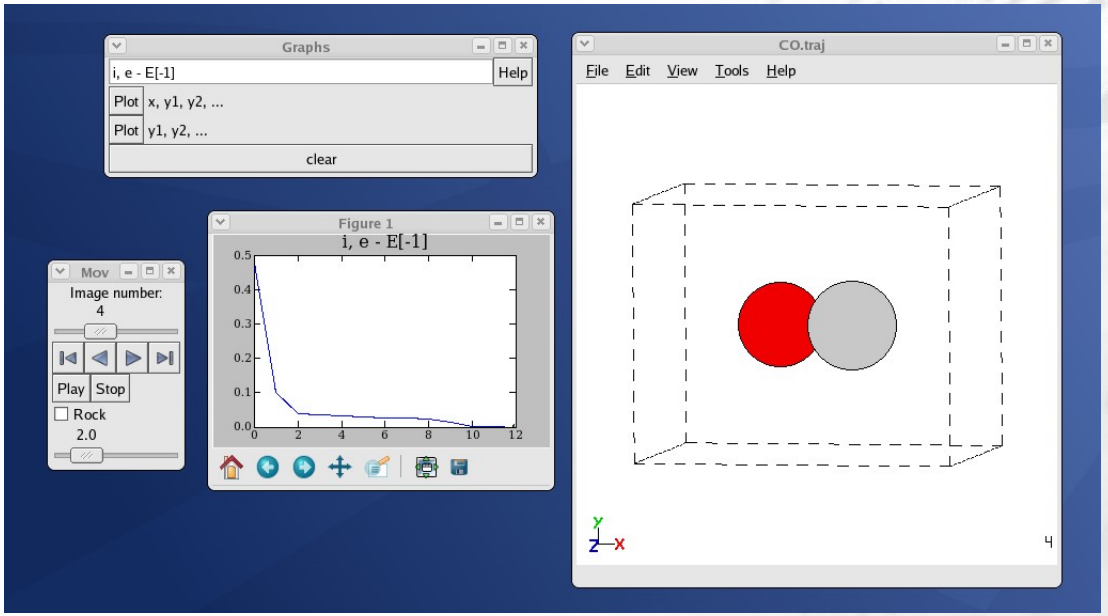
```
from ase.all import *   # Setup the atomic simulation environment
from gpaw import GPAW  # Setup GPAW

atoms = read('file.traj')     # read the last image
first = read('file.traj', 0) # first image
calc = GPAW(...)
atoms.set_calculator(calc)    # calculator has to be attached
```

Simple graphical interface (ase-gui)

- Trajectory can be investigated with **ase-gui** tool

```
[jenkovaa@flamingo ~]$ ase-gui file.traj
```

- Investigate how total energy, forces, bond lengths etc. vary during simulation



Exercises

- Go to wiki.fysik.dtu.dk/gpaw/exercises/exercises.html and get your hands dirty!

Time-dependent DFT with GPAW

Time-dependent DFT

- Generalization of density-functional theory also to time-dependent cases
- Runge-Gross theorem PRL 52 (1984)
  - one-to-one mapping between the time-dependent potential and the density
- Excited state properties
  - excitation energies, optical spectra, ...
- Time-dependent Kohn-Sham equations

$$i\frac{\partial\psi_i(r,t)}{\partial t} = H\psi_i(r,t)$$

$$H = -\frac{\nabla^2}{2} + V_{eff}(r,t)$$

$$n(r,t) = \sum_i |\psi_i(r,t)|^2$$

Real-time propagation

- Direct integration of time-dependent Kohn-Sham equations in time-domain

$$i\frac{\partial\psi_i(r,t)}{\partial t} = H(t)\psi_i(r,t)$$

$$n(r,t) = \sum_i |\psi_i(r,t)|^2$$

- Integration is done with Crank-Nicholson type scheme:

$$\left[1 + iH(t)\Delta t\right]\psi_i(t+\Delta t) = \left[1 - iH(t)\Delta t\right]\psi_i(t)$$

- Initial value problem, the starting value $\psi_i(t=0)$ is obtained from ground state calculation

Optical absorption spectra from real-time TDDFT

- Excite the system with delta pulse $E(t) = \epsilon \mathbf{k}^{\mathrm{o}} \delta(t)$
- Wave functions change instantaneously to

$$\psi(t = 0^+) = \exp\left(i\epsilon \mathbf{k}^{\mathrm{o}} \cdot \mathbf{r}\right) \psi(t = 0)$$

- Time-propagate wave functions and record the time-dependent dipole moment
- Spectra can be obtained via Fourier transform of the time-dependent dipole-moment

Practice

- Perform ground state calculation and save the wave functions

```
from ase.all import *
from gpaw import GPAW

atoms = ...
atoms.center(5.0) # may need to be larger in real calculations
calc = GPAW(h=0.30)
atoms.set_calculator(calc)
atoms.get_potential_energy()
calc.write('gs.hdf5', mode='all')
```

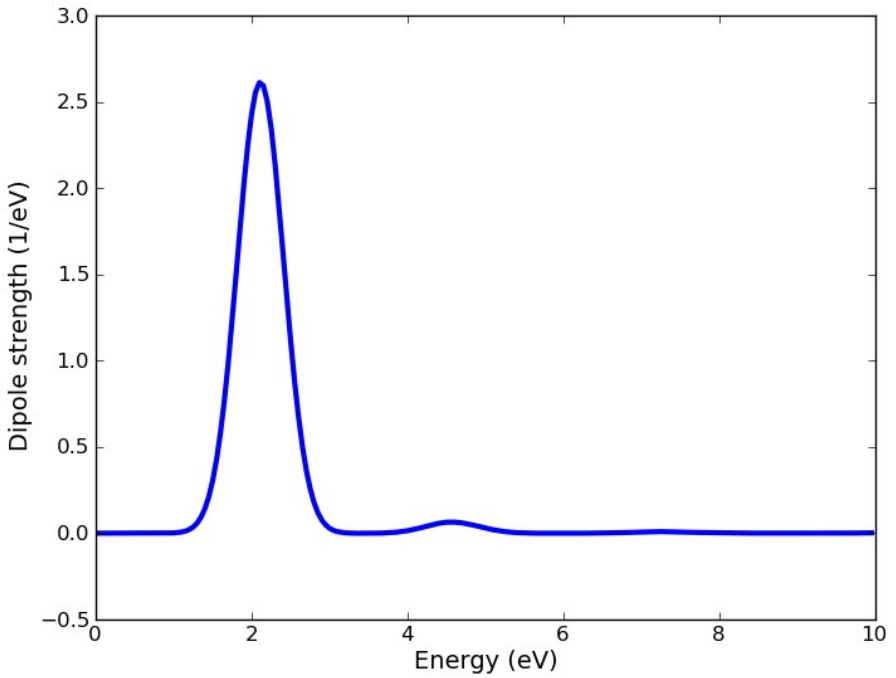
- Time-propagate

```
from gpaw.tddft import TDDFT

time_step = 16.0  # as
iters =  650      # 650 x 16 as 10.4 fs
kick = [0,0,1e-3] # Weak delta kick to z-direction

td_calc = TDDFT('gs.hdf5')
td_calc.absorption_kick(kick)
td_calc.propagate(time_step, iters, 'dmz.dat')
```

Practice

- Calculate the optical spectra

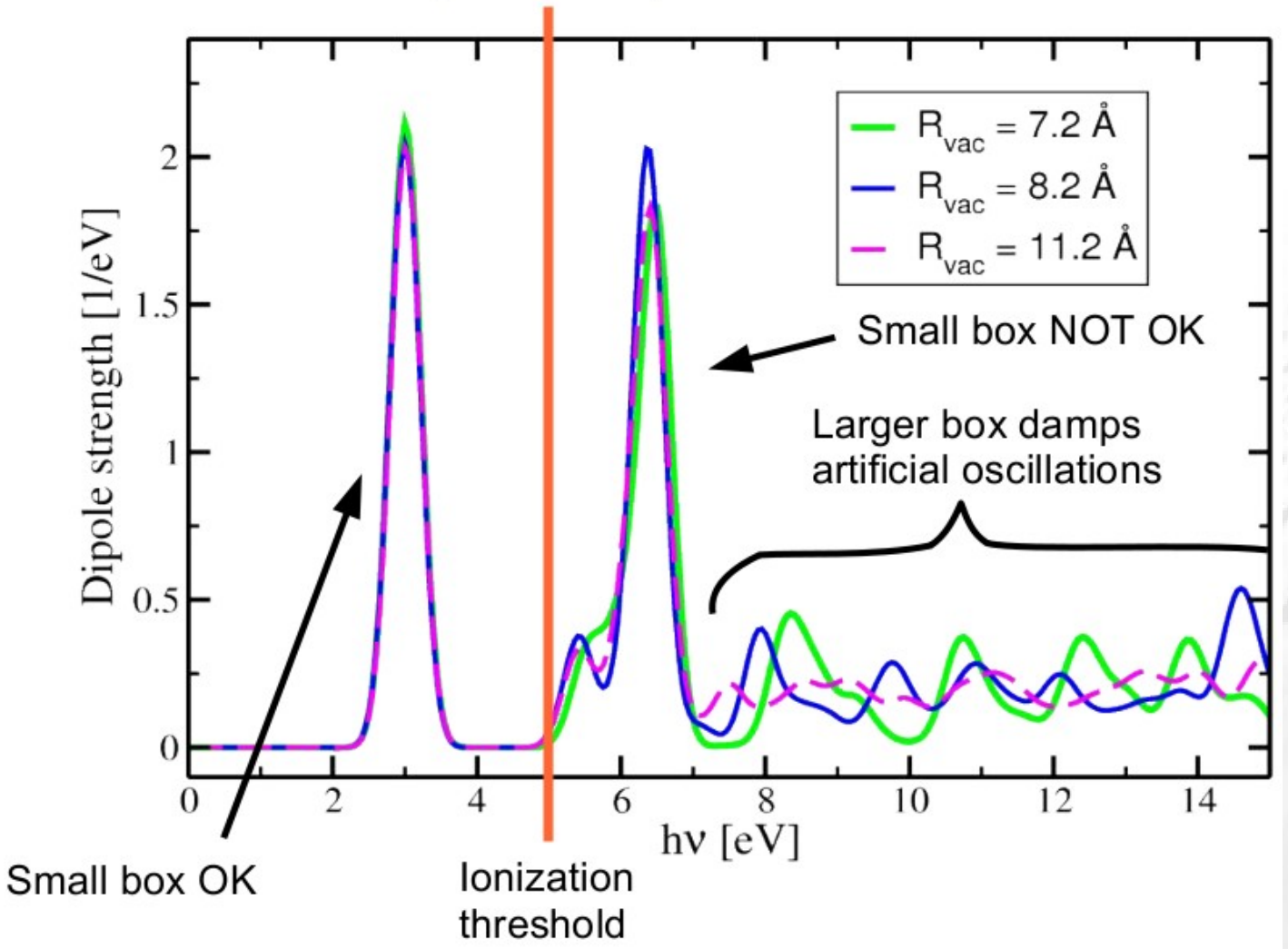
```
from gpaw.tddft import photoabsorption_spectrum

photoabsorption_spectrum('dmz.dat', 'spectrum_z.dat', width=0.2)
```



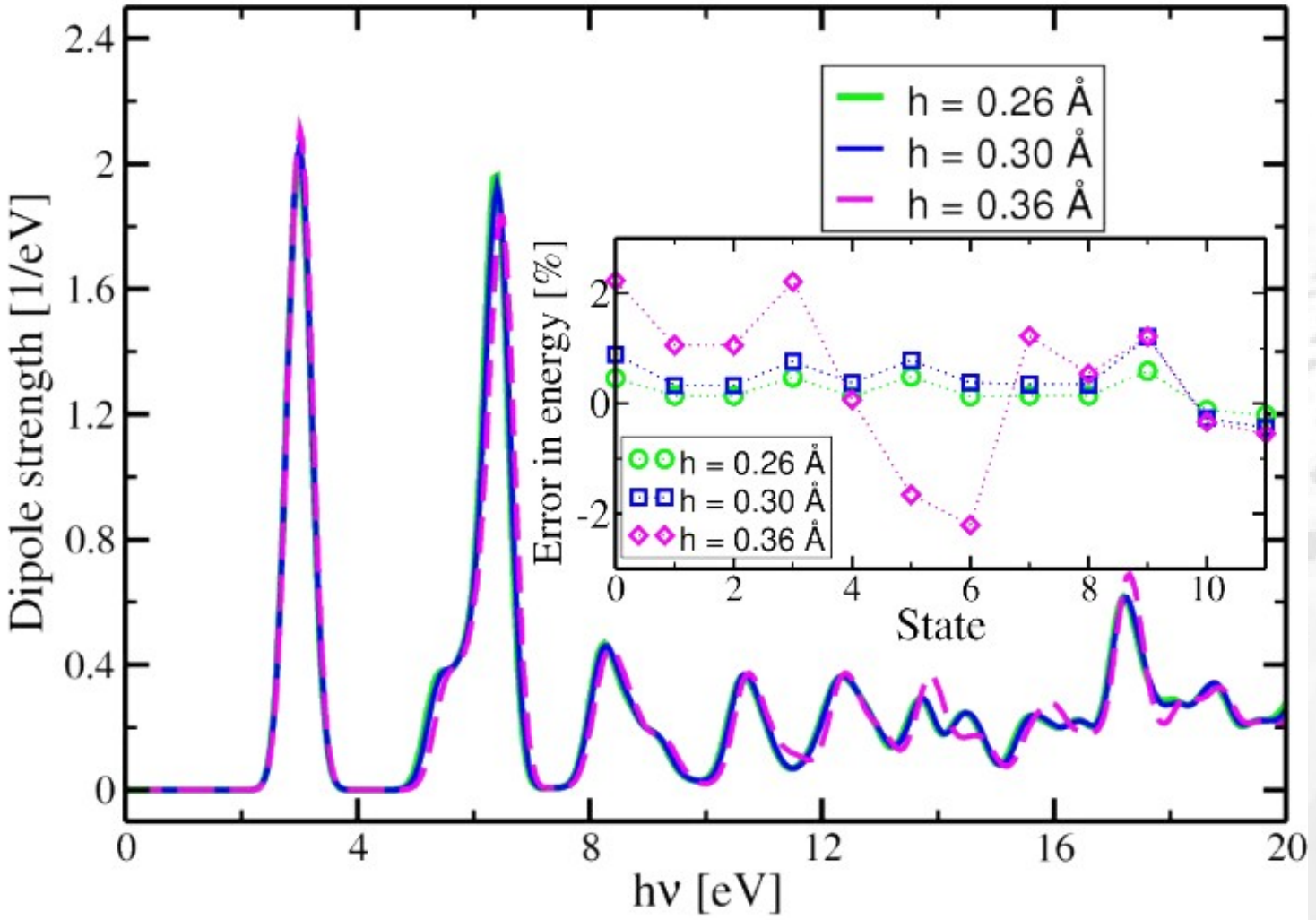
Practical details

- Depending on the symmetry of system, separate kick in all x,y,z directions may be needed.
- Normally, the size of simulation box has to be larger than in ground state calculations
- Grid spacing can often be larger than in ground state calculations
- Time-step affects the accuracy of spectra (too large time-step may lead into unstable propagation)
- Total simulation time affects the resolution of spectra.

Box size

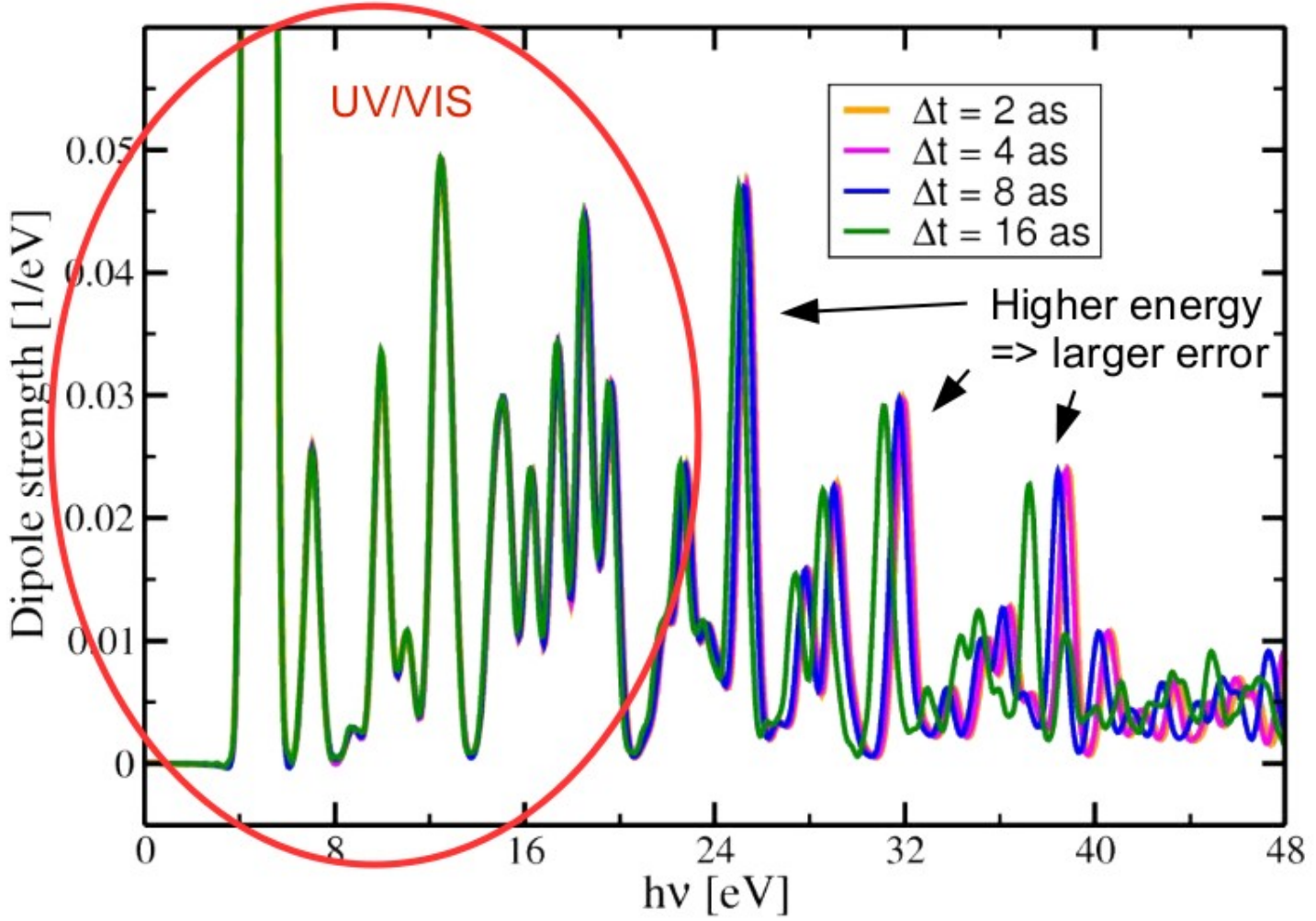

R_{vac} = 7.2 Å
R_{vac} = 8.2 Å
R_{vac} = 11.2 Å
Small box NOT OK
Larger box damps
artificial oscillations
Dipole strength [1/eV]
hν [eV]
0
0.5
1
1.5
2
0
2
4
6
8
10
12
14
Small box OK
Ionization
threshold

Grid spacing

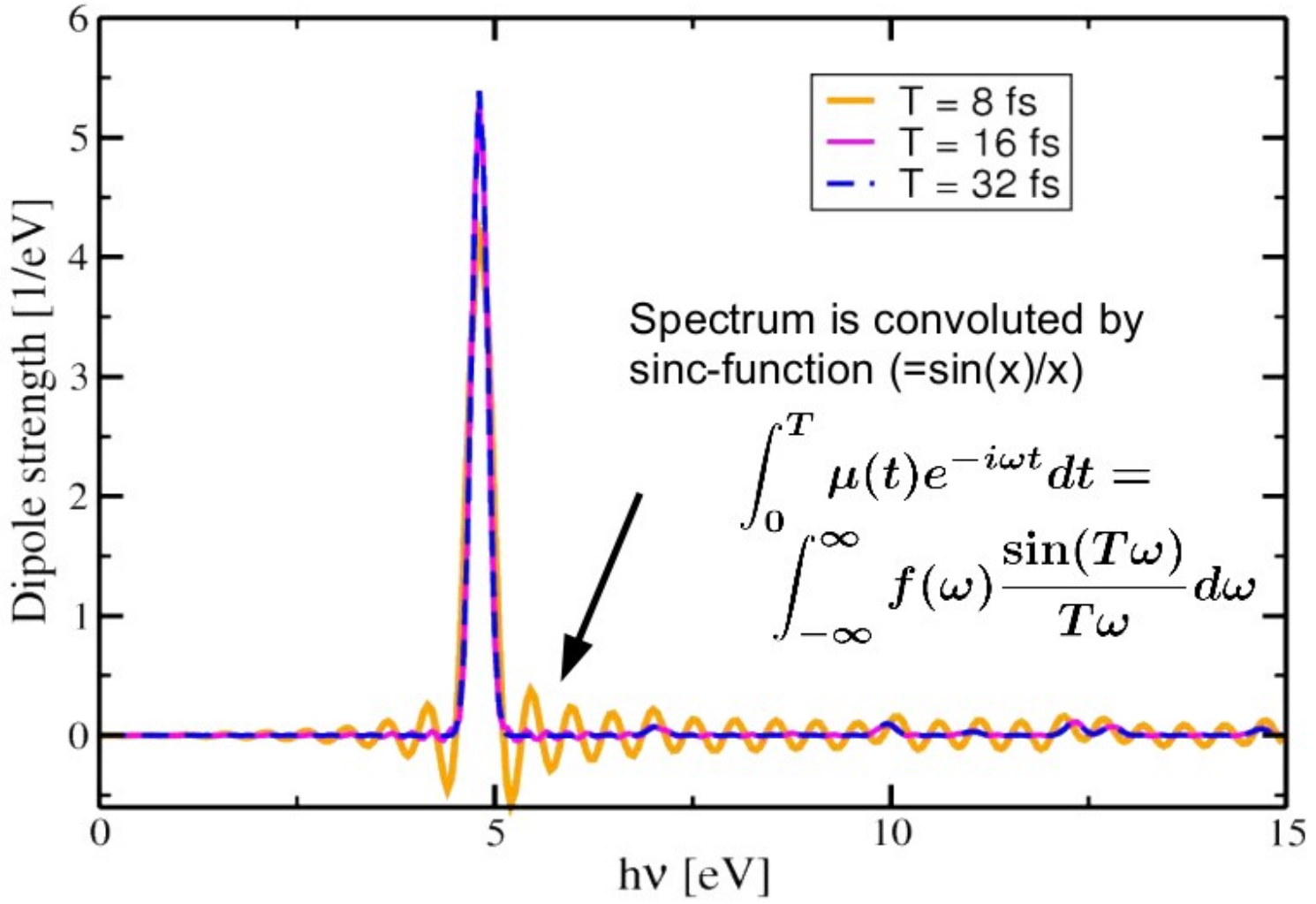


Eigenvalues are important, not forces or total energy!

Time step


UV/VIS
Δt = 2 as
Δt = 4 as
Δt = 8 as
Δt = 16 as
Higher energy
=> larger error
Dipole strength [1/eV]
0.05
0.04
0.03
0.02
0.01
0
0
8
16
24
32
40
48
hν [eV]

Total simulation time



Double simulation time => double resolution

Linear response TD-DFT

- Small perturbation to ground state potential

$$V_{ext} = V_{ext,0} + \delta V_{ext}(t)$$

  results a change in density

$$n(r,t) = n_0(r) + n_1(r,t)$$

- Within linear response:

$$n_1(r,\omega) = \int d^3r \chi(r,r',\omega)\delta V_{ext}(r',\omega)$$

- TD-DFT:

$$n_1(r,\omega) = \int d^3r \chi_0(r,r',\omega)\delta V_{eff}(r',\omega)$$

- The interacting response function can be obtained from the non-interacting one

Response function

- Dyson-like equation for density-density response:

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \chi_0(\mathbf{r},\mathbf{r}',\omega) + \iint_\Omega d\mathbf{r}_1 d\mathbf{r}_2 \; \chi_0(\mathbf{r},\mathbf{r}_1,\omega) K(\mathbf{r}_1,\mathbf{r}_2) \chi(\mathbf{r}_2,\mathbf{r}',\omega)$$

- Non-interacting response function is constructed from ground state Kohn-Sham orbitals

- Coupling kernel is: $K(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{xc}[n](\mathbf{r}_1,\mathbf{r}_2)$

  with XC kernel $f_{xc}(r_1,r_2) = \frac{\partial v_{xc}[n](r_1)}{\partial n(r_2)}$

Response function

- Non-interacting response function is given by

$$\chi^0(\mathbf{r},\mathbf{r}',\omega) = \sum_{\mathbf{k},\mathbf{q}}^{\mathrm{BZ}} \sum_{n,n'} \frac{f_{n\mathbf{k}} - f_{n'\mathbf{k}+\mathbf{q}}}{\omega + \epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}+\mathbf{q}} + i\eta} \psi^*_{n\mathbf{k}}(\mathbf{r})\psi_{n'\mathbf{k}+\mathbf{q}}(\mathbf{r})\psi_{n\mathbf{k}}(\mathbf{r}')\psi^*_{n'\mathbf{k}+\mathbf{q}}(\mathbf{r}')$$

- Occupation numbers, eigenvalues and ground state orbitals of occupied and unoccupied states
- In extended systems one solves the Dyson equation in plane wave basis
  - ground state calculation can be done in any basis

Dielectric matrix

- Dielectric matrix is related to the interacting response function

$$\epsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \delta_{\mathbf{G}\mathbf{G}'} + \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$$

- Macroscopic dielectric function

$$\epsilon_M(\mathbf{q},\omega) = \frac{1}{\epsilon^{-1}_{00}(\mathbf{q},\omega)}$$

- Optical spectra

$$\mathrm{ABS} = \mathrm{Im}\epsilon_M(\mathbf{q}\to 0,\omega)$$

- Electron-energy loss spectra

$$\mathrm{EELS} = -\mathrm{Im}\frac{1}{\epsilon_M(\mathbf{q},\omega)}$$

Excitation energies in finite systems

- Excitation energies can be calculated from eigenvalue equation:

$$\mathbf{\Omega} F_I = \omega_I^2 F_I,$$

where

$$\Omega_{ij\sigma,kl\tau} = \delta_{ik}\delta_{jl}\delta_{\sigma\tau}\varepsilon_{ij\sigma}^2 + 2\sqrt{\varepsilon_{ij\sigma}\varepsilon_{kl\tau}}K_{ij\sigma,kl\tau},$$

$$\varepsilon_{ij} = \varepsilon_i - \varepsilon_j$$

with the coupling kernel

$$K_{ij\sigma,kl\tau} = \int dr_1 dr_2 n^*_{ij\sigma}(r_1) \left[\frac{1}{|r_1 - r_2|} + f_{xc}(r_1, r_2)\right] n_{kl\tau}(r_2)$$

$$n_{ij\sigma}(r) = \psi_{i\sigma}(r)^* \psi_{j\sigma}(r)$$

- i and j indexes go through occupied and unoccupied states, respectively

Optical spectra in finite systems

- Dipole oscillator strengths of excitations can be calculated from the eigenvectors

$$f_{I\alpha} = \left| \sum_{ij\sigma} \langle \psi_{i\sigma} | r_\alpha | \psi_{j\sigma} \rangle \sqrt{\varepsilon_{ij\sigma}} F_I \right|^2$$

- Spectra with finite peak widths are obtained by folding the oscillators strengths e.g. with Gaussian

$$S_\alpha(\omega) = \sum_I f_{I\alpha} g(\omega - \omega_I)$$

Practice

- Perform ground state calculation and include also unoccupied states

```
from ase.all import *                  # Setup the atomic simulation environment
from gpaw import GPAW                  # Setup GPAW
from gpaw.eigensolvers import CG       # Conjugate gradient eigensolver

atoms = ...
atoms.center(vacuum=5.0) # More vacuum might be needed in reality...
calc = GPAW(nbands=1, h=0.30, txt='Na2_gs.txt')
atoms.set_calculator(calc)
e = atoms.get_potential_energy()

# Calculate also unoccupied states with the fixed density
eig = CG() # unoccupied states converge often better with cg
calc.set(nbands=20, convergence={'bands': 'all'}, # converge unoccupied states
         eigensolver=eig,
         fixdensity=True)
e = atoms.get_potential_energy()
# write the wave functions to a file
calc.write('na2_gs.gpw', 'all')
```

Practice

- Calculate Ω matrix

```
from gpaw import *  # Setup GPAW
from gpaw.lrtddft import *

atoms, calc = restart('na2_gs.gpw') # read in a ground state calculation

# Calculate the omega matrix
lr = LrTDDFT(calc, xc='LDA')
# Save the omega matrix
lr.write('Omega_Na2.gz')
```

- Diagonalization can be performed in separate step

```
from gpaw.lrtddft import *

# Read the omega matrix from a file
lr = LrTDDFT(filename='Omega_Na2.gz')
# Diagonalize the matrix
lr.diagonalize()
# Print out five lowest excitations
lr.analyse(range(5))
# Calculate the absorption spectrum and save it to a file
photoabsorption_spctrum(lr, 'Na2_spectrum.dat', e_min=0.0, e_max=10, width=0.1)
```

Practical details

- In addition to the box size and grid spacing, accuracy is controlled by the number of electron-hole pairs
- The computational intensity of the calculation is $O(N_{eh}^{3})$
- The size of electron-hole basis can be reduced:

```
lr = LrTDDFT(calc, xc='LDA',
             istart=5,          # first occupied state to consider
             jend=20)           # last unoccupied state to consider
```

- The proper number of eh-pairs is very system dependent

Real-time vs. linear response

- Real-time
  - only excitations corresponding to given perturbation
  - non-linear effects
  - scales $O(N^2)$ with the system size, large prefactor
  - time step controls the accuracy relatively straightforwardly
- Linear response
  - all excitations (within linear response)
  - scales $O(N^6)$ with the system size, small prefactor
  - control of accuracy by the electron-hole basis size can be complex

Parallel calculations with GPAW

Parallelization levels

$$H_{k,s}\psi_{i,k,s}(r) = e_i S\psi_{i,k,s}(r)$$

$$i\partial_t \psi_{i,s}(r,t) = H_s \psi_{i,s}(r,t)$$

$$n(r) = \sum_{i,k,s} |\psi_{i,k,s}(r)|^2$$

- Parallelization over all degrees of freedom
  - real-space grid
  - k-points and spin
  - electronic states
- Additional trivial parallelizations possible
  - Electron-hole pairs
  - different atomic configurations or unit cells

Parallelization over k-points and spin

$$H_{k,s}\psi_{i,k,s}(r) = e_i\psi_{i,k,s}(r)$$

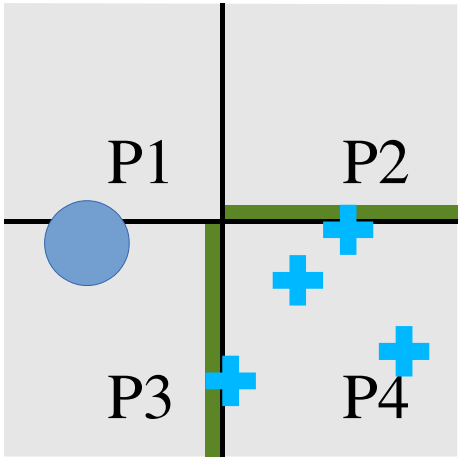
$$n(r) = \sum_{i,k,s} |\psi_{i,k,s}(r)|^2$$

- Spin and k-points are treated equivalently
- Trivial parallelization
- Limited scalability
  - k-points only in (small) periodic systems
  - spin only in magnetic systems
- All basis sets

Parallelization over real-space grid

$$H_{k,s}\psi_{i,k,s}(r) = e_i\psi_{i,k,s}(r)$$
$$n(r) = \sum_{i,k,s} |\psi_{i,k,s}(r)|^2$$

- Domain decomposition



Finite difference Laplacian

PAW augmentation sphere

- Only local communication
- Good parallel scalability down to domain sizes ~16 x 16 x 16
- Not available in plane wave mode

Parallelization over electronic states

$$H_{k,s}\psi_{i,k,s}(r) = e_i\psi_{i,k,s}(r)$$

$$n(r) = \sum_{i,k,s} |\psi_{i,k,s}(r)|^2$$

- Nearly trivial parallelization in real-time TDDFT
  - (similar to k-points)
  - good scalability down to 20 states per process
- Orthonormalizations are complicated in ground state DFT
  - communication of all wave functions to all processes
  - parallel scalability down to 150-250 states per process
  - all basis sets

Parallelization over electron-hole pairs

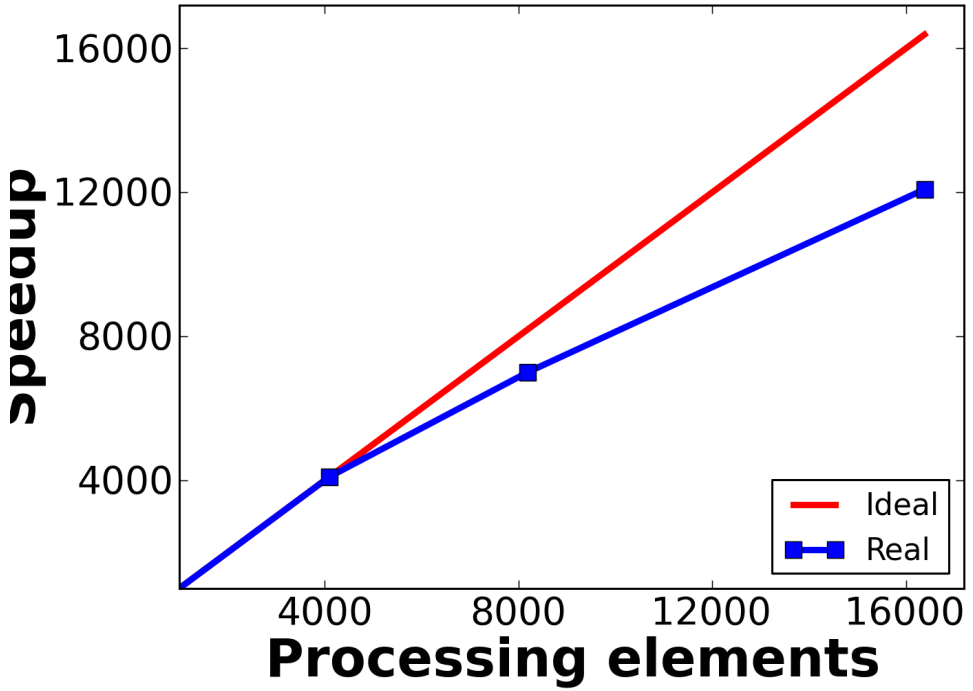
- Casida equation in linear response TD-DFT:

$$\mathbf{\Omega} F_I = \omega_I^2 F_I,$$

$$\Omega_{ij\sigma,kl\tau} = \delta_{ik}\delta_{jl}\delta_{\sigma\tau}\varepsilon_{ij\sigma}^2 + 2\sqrt{\varepsilon_{ij\sigma}\varepsilon_{kl\tau}}K_{ij\sigma,kl\tau}$$

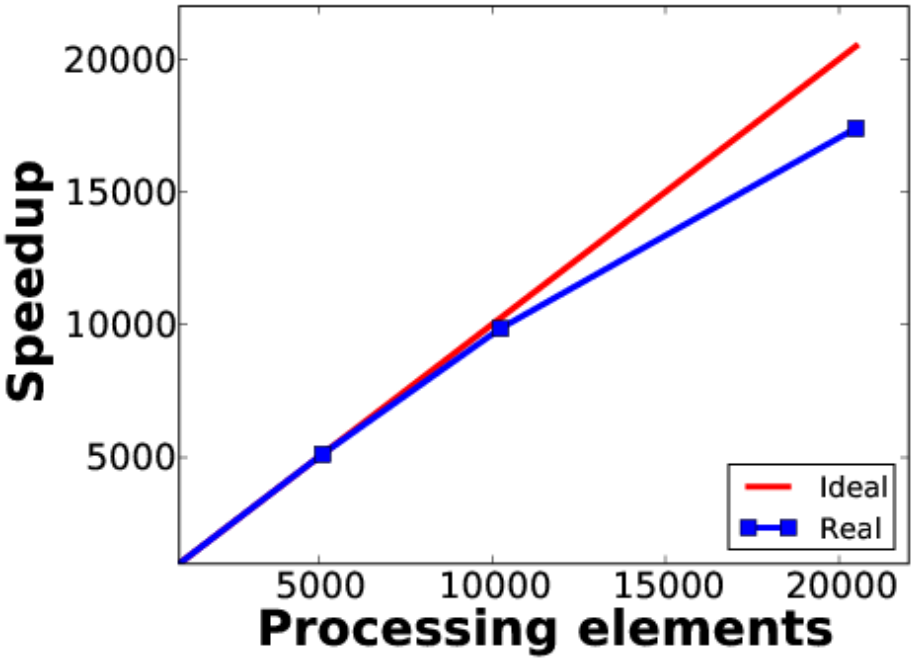
- Matrix elements can be calculated independently
- Nearly trivial parallelization over electron-hole pairs ij
- Domain decomposition for individual matrix elements

Parallel scalability



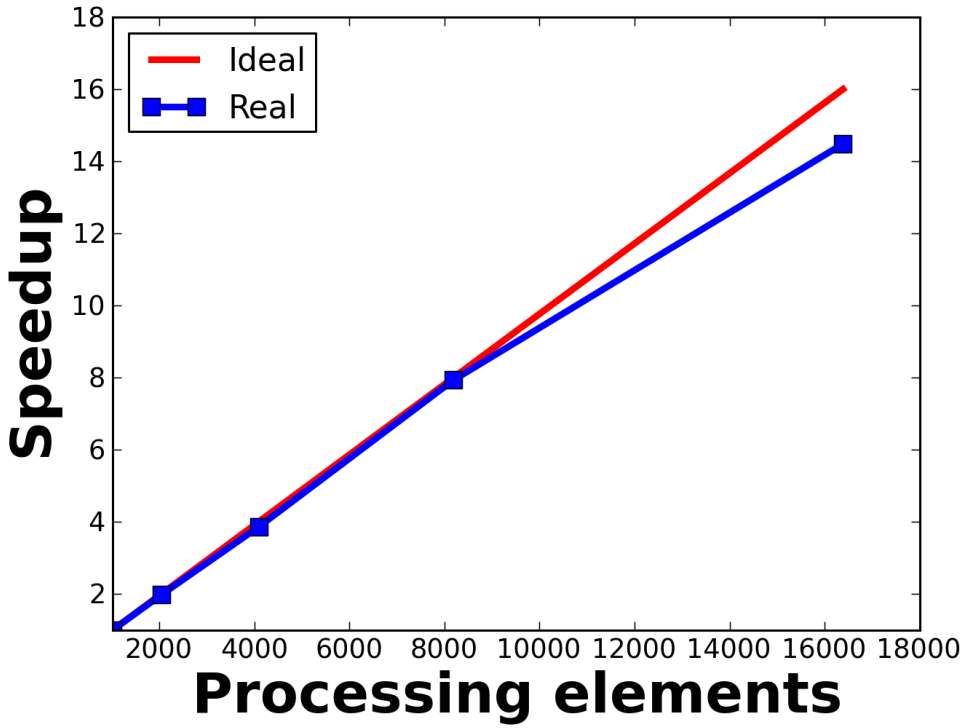
- Ground state DFT
  - 561 Au atom cluster
  - ~6200 electronic states
  - Blue Gene P, Argonne

Parallel scalability



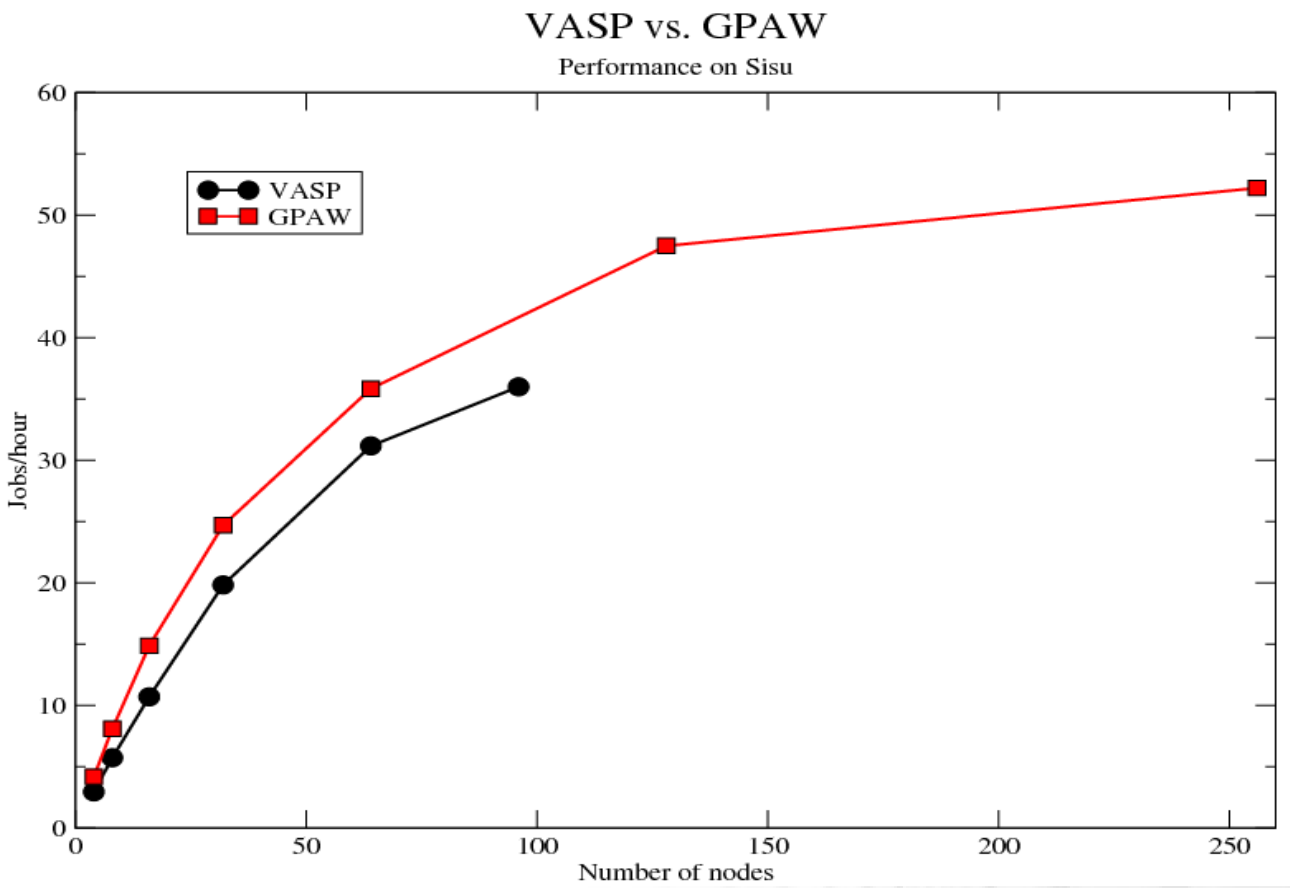
- Real-time TD-DFT
  - 702 Si atom cluster
  - ~2800 electronic states
  - Cray XT5 Jaguar, Oak Ridge

Parallel scalability



- Linear-response TD-DFT
  - Au38(SCH3)24 cluster ~160 atoms
  - ~680 electronic-hole pairs
  - Cray XE6 Hermit, HLRS, Germany

Parallel performance



- Ground state DFT
  - Large MgH2 cell, 1296 atoms
  - Cray XC30, CSC (node=16 cores)

Practical details

- k-points have to be distributed evenly
  - same number of k-points in each process
- Electronic states have to be distributed evenly
  - same number of states in each process
- In principle, arbitrary number of processes can be used for domain decomposition
  - recommended to use cubic domains e.g. 4 x 4 x 4
  - recommended to use domain dimensions which factor the number of grid points

Practical details

- By default, k-point and spin are distributed first, and the remaining processors are used for domain decomposition
- Example: magnetic system, 5 k-points
  - with 20 processors: 10 (=2x5) processors for spin/k-point and 2 processors for domain decompostion (2x1x1 layout)
  - with 24 processors: 2 processors for spin, 12 processors for domain decomposition (3x2x2 layout)

Practical details

- Electronic state parallelization has to specified explicitly

```
aprun -n 512 gpaw-python input.py --state-parallelization=2
```

  - 2 processors for states, 256 to k-points/spin/domains
- For large calculations (> 1000 states) one more command line argument:

```
aprun -n 512 gpaw-python input.py --sl_default=4,4,64
```

  - some large matrix diagonalizations are done in parallel with 16 (=4x4) processes
  - 4x4 or 8x8 are typically good values (block size 64 has only small effect)

Practical details

- Parallelization options can be given also as GPAW calculator parameters

```
...
calc = GPAW(...
            parallel={kpt : 4,          # k-point parallelization with 4 MPI tasks
                      domain : 8,       # domain decomposition with 8 MPI tasks
                      band : 2          # band parallelization with 2 MPI tasks
                      sl_default : (4,4,64)} # parallel matrix diagonalization
            ...
            )
```

- Command line arguments precede calculator parameters

“dry-run” mode

- Often, it is desirable to check system parameters without an actual calculation
- GPAW offers a dry-run mode

```
[cscuser@cobol ~]$ python input.py --state-parallelization=2 --dry-run=512
```

  - only unexpensive initializations, can be run serially
  - simulates parallel calculations and shows the parallelization scheme
  - estimates the memory usage