Introduction to Octopus: a real-space (TD)DFT code

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Theory

Underlying theory: Density Functional Theory

- Hohenberg-Kohn theorem
- Kohn-Sham system
- time-dependent DFT

Density Functional Theory

Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + v_{\rm ext}(\boldsymbol{r}) + v_{\rm H}[n](\boldsymbol{r}) + v_{\rm xc}[n](\boldsymbol{r})\right]\psi_i(\boldsymbol{r}) = \epsilon_i\psi_i(\boldsymbol{r})$$

$$n(\boldsymbol{r}) = \sum_{i=1}^{N} |\psi_i(\boldsymbol{r})|^2$$

- A self-consistency scheme is used to treat the non-linearity
- Solve for eigenstates at fixed $v_{\rm Hxc}$, then update n and $v_{\rm Hxc}$
- It is a boundary value problem

Time-dependent Density Functional Theory

Time-dependent Kohn-Sham equation

$$\mathrm{i}\frac{\partial}{\partial t}\psi_i(\boldsymbol{r},t) = \left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ext}}(\boldsymbol{r},t) + v_{\mathrm{H}}[n](\boldsymbol{r},t) + v_{\mathrm{xc}}[n](\boldsymbol{r},t)\right)\psi_i(\boldsymbol{r})$$

$$n(\boldsymbol{r},t) = \sum_{i=1}^{N} |\psi_i(\boldsymbol{r},t)|^2$$

- It is an initial value problem
- Usually the ground-state is used as initial state
- Various numerical schemes for doing the time-propagation

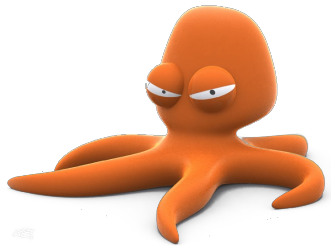
The Octopus code

Purpose: simulate the dynamics of electrons and nuclei under the influence of external time-dependent fields in the framework of Time-Dependent Density Functional Theory (TDDFT)

- DFT with many functionals (from `Libxc`), Hartree-Fock, Hartree, RDMFT
- Fortran 2008, C, C++, OpenCL/CUDA/HIP and some Python and Perl.
- extensive use of mathematical libraries: `BLAS/LAPACK`, `FFTW`, `GSL`, etc.
- Interfaces to external libraries: `libxc`, `libvdwxc`, `wannier90`, `berkeleygw`, etc.
- Free open-source software (GNU Public License).
- Current version is 16.0.

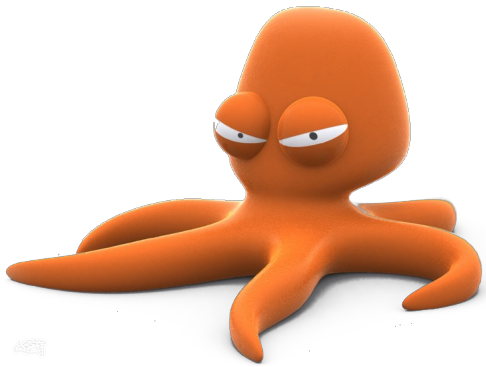
The Octopus code: features and functionalities

- Ground-state DFT calculations
- Excited states calculations (real-time propagation, linear response)
  - optical
  - photoemission
  - magnetic (magnons)
  - vibrations
- electric and thermal conductivities
- Theory levels include:
  - Kohn-Sham with LDA, GGA
  - generalized Kohn-Sham: MGGA, hybrid functionals
  - Optimized effective potentials (OEP)
  - self-interaction corrected functionals
  - reduced density matrix functional theory (RDMFT)
  - van der Waals interactions



The Octopus code: new and upcoming features

- Multi-system mode
  - classical particles (nuclei)
  - electrons and ions
  - Maxwell fields
- Matter coupled to Maxwell fields
  - forward and backward coupling
- Multitrajectory Ehrenfest dynamics



The Octopus code

- `https://octopus-code.org`
- `https://gitlab.com/octopus-code`

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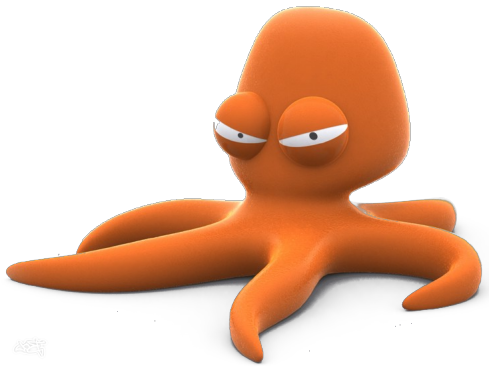
Dissecting the animal

- Real-space grid representation
- Finite differences for the calculation of derivatives
- Pseudopotential approximation
- Finite systems and periodic systems
- Arbitrary number of dimensions
- Three methods to obtain excited states properties within TDDFT:
  - Real-time TDDFT
  - Casida Linear response
  - Sternheimer linear response
- Quantum optimal control theory
- Many other features



Real-space grid

- We have a partial differential equation with infinite degrees of freedom
- We want a finite number of degrees of freedom
- Discretization: functions are represented by values on a set of points
- Point distribution:
  - Uniformly spaced grid
  - Distance between points is constant: *Spacing*
  - (Non-uniform grids also possible)
- Finite region of the space: *Box*

Real-space grid

- Can systematically improve discretization quality:
  - Decrease the spacing
  - Increase the box size (for non-periodic directions)
- Orthogonal "basis set"
- Unbiased, independent of atomic positions (no Pulay forces)
- Problems:
  - Breaking of translational invariance: egg-box effect
  - Breaking of rotational invariance
  - (Decreasing spacing helps both)

Discretization of the Hamiltonian

We use finite differences to evaluate the Laplacian (kinetic energy):

- Derivative at a point: weighted sum over neighboring points
- General form for the Laplacian:

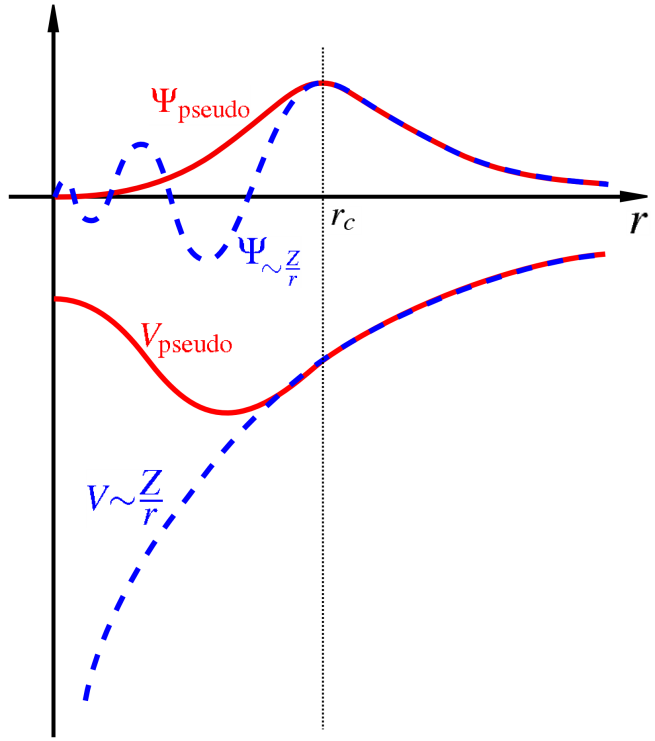
$$\nabla^2 f(n_x h,\, n_y h) = \sum_i^n \sum_j^n \frac{c_{ij}}{h}\, f(n_x h + ih,\, n_y h + jh)$$

- The coefficients c_{ij} depend on the mesh and number of points used: *the stencil*
- More points $\rightarrow$ more precision

The Hamiltonian becomes a finite-size, sparse matrix

Pseudo-potentials

- The atomic potential is very strong and "hard" (small spacing or high plane-wave cutoff required).
- Core electrons are strongly bound and do not play a significant role in the chemical binding of atoms.
- Replace the potential and core electrons by a pseudo-potential.



Norm-conserving pseudo-potentials in Kleinman-Bylander form

$$V = V_{\text{loc}} + \sum_{lm} |lm\rangle (V_l - V_{\text{loc}}) \langle lm|$$

Other potential types

Can be specified in the `Species` block

- all electron potentials (delta or Gaussian nucleus)
- user defined potentials
- jellium spheres
- and others...

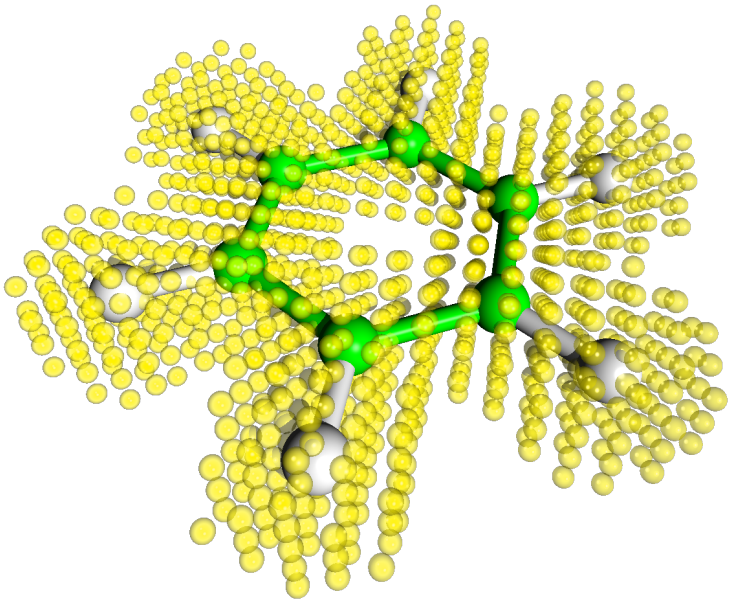
Boundary conditions

- For finite systems, functions go to zero:
  - Force functions to go to zero on the border of the box
  - The box has to be large enough to contain the functions
- Other BCs are possible:
  - periodic
  - zero derivative
  - absorbing
  - etc

Boundary conditions

- Optimize the shape of the box to minimize the number of points needed

- Available box shapes:
  - Sphere
  - Cylinder
  - Parallelepiped
  - Minimum box: union of spheres around each atom
  - Arbitrary



Benzene molecule in minimal box

Ground state calculation: The eigenvalue problem

- Find the eigenvectors and eigenvalues of a matrix
- Very large matrix with lots of zero components (*Sparse*)
- Use iterative solvers where only the application of the matrix is required (various options available in the code)

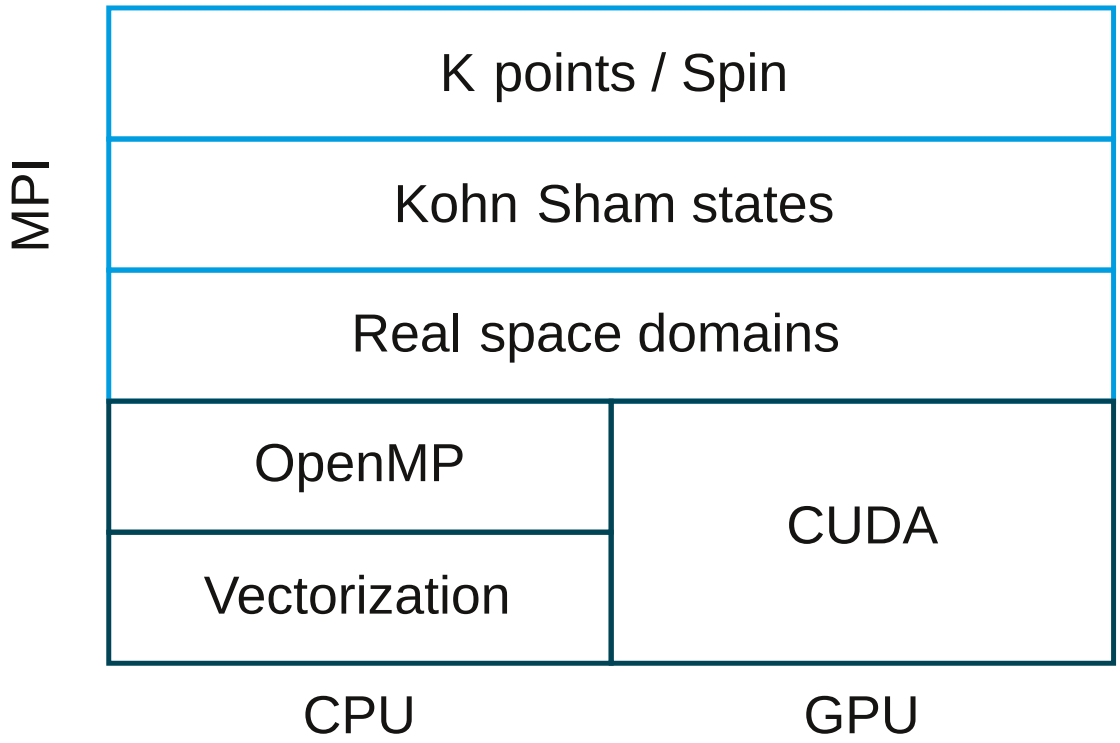
Time propagation

Propagation of the wavefunctions in time:

$$\varphi_i(\boldsymbol{r}, t + \Delta t) = \hat{T} \exp\left\{ -\mathrm{i} \int_t^{t+\Delta t} \mathrm{d}t \, \hat{H} \varphi_i(\boldsymbol{r}, t) \right\}$$

- Several numerical methods available for doing the time-propagation
- Exponential must also be calculated numerically
- Many properties can be obtained
- Response to time-dependent fields: lasers
- See e.g. tutorials on optical absorption

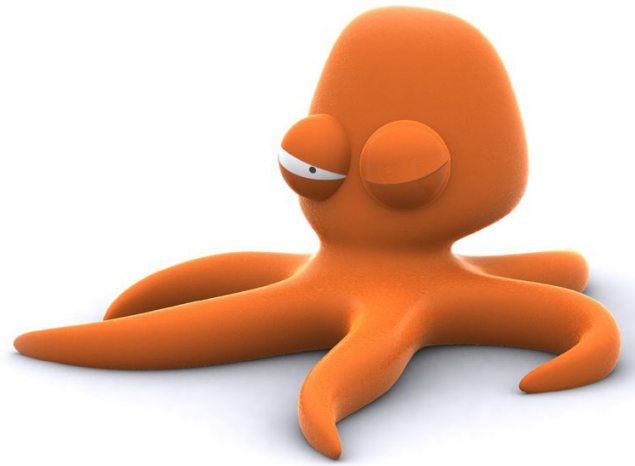
Parallelisation strategy



Examples and tutorials

Some tutorials:

- Getting started
- Convergence
- Periodic systems



Spectroscopy

- Optical absorption spectra
- High Harmonic generation
- Transient (pump probe) spectroscopy
- (time-resolved) ARPES
- Magnon spectroscopy
- Phonon/vibrational spectroscopy

Electronic response of finite systems to external fields

The dynamical polarizability is the ratio of the induced dipole moment to the perturbing electric field:

$$\alpha(\omega) = \frac{\delta \boldsymbol{p}(\omega)}{\boldsymbol{E}(\omega)} = \frac{1}{\boldsymbol{E}(\omega)} \int \mathrm{d}\boldsymbol{r}\, \boldsymbol{r}\, \delta n(\boldsymbol{r}, \omega)$$

$\alpha(\omega)$ is related to the optical absorption cross-section:

$$\sigma(\omega) = \frac{4\pi\omega}{c} \mathfrak{Im} \left\{ \mathrm{Tr} \left[\alpha(\omega) \right] \right\}$$

Real-time TDDFT

The dynamical polarizability can be computed by solving directly the time-dependent Kohn-Sham equations:

- Take the DFT ground state wavefunctions $\varphi_i(\boldsymbol{r})$.
- Excite all the frequencies of the system by applying the appropriate instantaneous perturbation $\delta v(\boldsymbol{r}, t) = -E x_j \delta(t)$.
- Use TDDFT to propagate the wavefunctions in time:

$$\varphi_i(\boldsymbol{r}, t + \Delta t) = \hat{T} \exp\left\{ -\mathrm{i} \int_t^{t+\Delta t} \mathrm{d}t \, \hat{H}_{\mathrm{KS}} \varphi_i(\boldsymbol{r}, t) \right\}$$

  and keep track of the density $n(\boldsymbol{r}, t)$.
- Compute the polarizability $\alpha_{ij}(\omega) = \frac{1}{E(\omega)} \int \mathrm{d}\boldsymbol{r} \, x_i \delta n(\boldsymbol{r}, \omega)$.

Optical absorption in solids

- Wavelength of the light is much larger than the lattice constant.
- Treat electric field as spatially uniform.
- This cannot be described by scalar potential: use velocity gauge.
- In velocity gauge the time-dependent electric field is described by: $\mathbf{E}(t) = -\frac{\partial}{\partial t}\mathbf{A}(t)$.

Treatment of the velocity gauge in Octopus

Time dependent Kohn-sham equation within velocity gauge

$$i\frac{\partial}{\partial t}|\psi_{n,\mathbf{k}}(t)\rangle = \hat{H}_{\mathrm{KS}}(t)|\psi_{n,\mathbf{k}}(t)\rangle,$$

with

$$\langle \mathbf{r}|\hat{H}_{\mathrm{KS}}(t)|\mathbf{r}'\rangle = \left[\frac{1}{2}\left(-i\nabla - \frac{1}{c}\mathbf{A}(\mathbf{r},t)\right)^2 + v_{\mathrm{s}}(\mathbf{r},t)\right]\delta(\mathbf{r}-\mathbf{r}')\,.$$

Treatment of the velocity gauge in Octopus

Within dipole approximation, Octopus uses an accelerated wavefunction

$$\psi^{\mathbf{A}}_{n,\mathbf{k}}(\mathbf{r},t) = e^{i\mathbf{A}(t).\mathbf{r}}\psi_{n,\mathbf{k}}(\mathbf{r},t).$$

It is easy to show that

$$e^{-i\mathbf{A}(t).\hat{\mathbf{r}}}\left[\frac{\hat{\mathbf{p}}^2}{2}+\hat{v}_{\mathrm{s}}\right]|\psi^{\mathbf{A}}_{n,\mathbf{k}}(t)\rangle = \left[\frac{1}{2}(\hat{\mathbf{p}}-\frac{1}{c}\mathbf{A}(t))^2+\hat{v}_{\mathrm{s}}\right]|\psi_{n,\mathbf{k}}(t)\rangle.$$

The time-evolution of $|\psi_{n,\mathbf{k}}(t)\rangle$ is described using the ground-state Hamiltonian $\hat{H}_0 = \left[\frac{\hat{\mathbf{p}}^2}{2}+\hat{v}_{\mathrm{s}}\right]$ applied to the accelerated wavefunction.

Other methods implemented in Octopus

Casida equations:

- Pseudo-eigenvalue equation of the form:

$$\hat{R}F_q = \Omega_q^2 F_q$$

- Eigenvalues Ω_q^2 are the square of the excitation energies
- Eigenvectors are related to the oscilator strenghts
- $\hat{R}$ is a matrix that involves pairs of occupied and unoccupied KS states

Other methods implemented in Octopus

Sternheimer equations:

- Relies on the calculation of the first order variations of the KS wavefunctions $\psi'_m(\boldsymbol{r}, \pm\omega)$
- Equations have the following form

$$\left[\hat{H}_{\mathrm{KS}} - \epsilon_m \pm \omega + \mathrm{i}\eta\right] \psi'_{m,i}(\boldsymbol{r}, \pm\omega) = -\hat{P}_c \hat{H}'(\pm\omega)\psi_m(\boldsymbol{r})\,,$$

- $\hat{H}'$ is the first order variation of the Kohn-Sham Hamiltonian:

$$\hat{H}'(\omega) = x_i + \int \mathrm{d}\boldsymbol{r}' \, \frac{\delta n_i(\boldsymbol{r}', \omega)}{|\boldsymbol{r} - \boldsymbol{r}'|} + \int \mathrm{d}\boldsymbol{r}' \, f_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}', \omega)\delta n_i(\boldsymbol{r}', \omega)\,.$$

Pros and cons

Real time propagation

Pros

- Favourable scaling with system size
- Does not require the calculation of empty states
- Easy to extend to other perturbations/responses
- Allows to go beyond linear-response
- Only requires knowledge of v_{xc}

Cons

- Slow for small systems

Pros and cons

Casida equations

Pros

- Fast for small systems

Cons

- Requires calculation of empty states
- Requires computation of large matrices
- Unfavourable scaling with system size

Pros and cons

Sternheimer equations

Pros

- Favourable scaling with system size
- Does not require the calculation of empty states
- Allows to go beyond linear-response

Cons

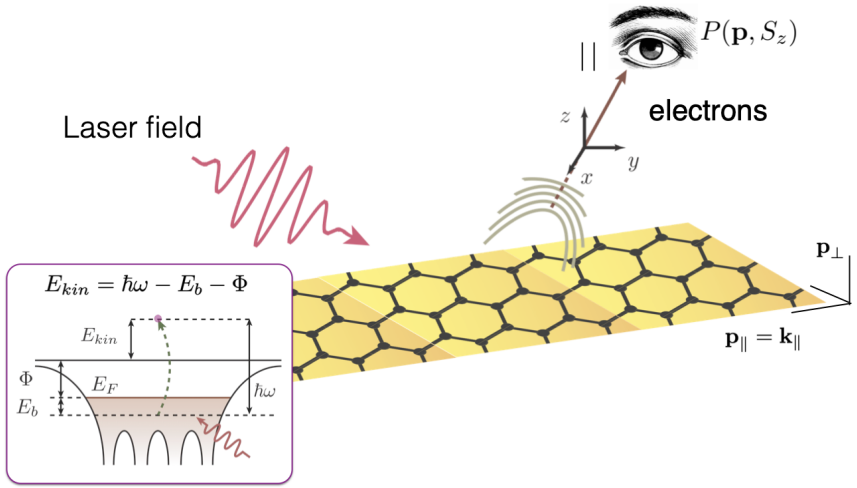
- Equations needs to be solved one frequency at a time

High Harmonic Generation

- HHG is a nonlinear optical process in which an intense laser field interacts with a material, leading to the emission of high-frequency harmonics.
- The emitted harmonics can be used to probe electronic and structural properties of materials.
- We calculate the induced current (by real-time propagation) and analyze by Fourier transforming it to obtain the HHG spectrum.

(Time-resolved) ARPES

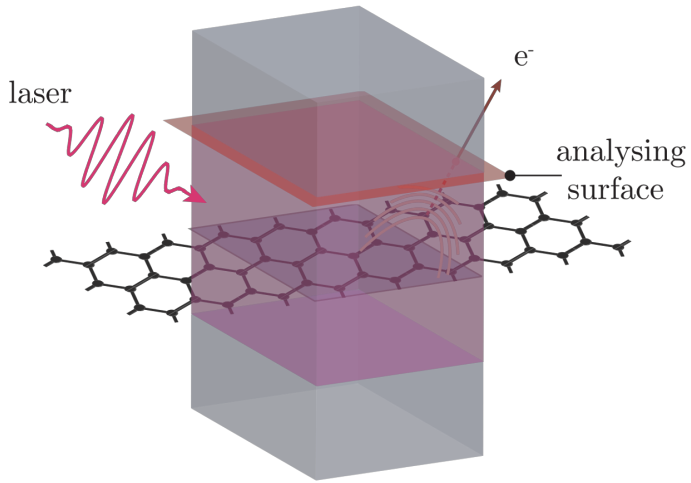
- Angle-resolved photoemission spectroscopy (ARPES) is a powerful technique to study the electronic structure of materials.
- It measures the energy and momentum of electrons emitted from a material after being excited by photons.
- Time-resolved ARPES extends this technique to study ultrafast dynamics in materials.



(Time-resolved) ARPES

Basic idea:

- propagate wave functions excited by laser pulse
- integrate current through 'analysing surface'
- absorb electrons above this surface
- corresponds to 'one-step model': matrix elements are naturally included.

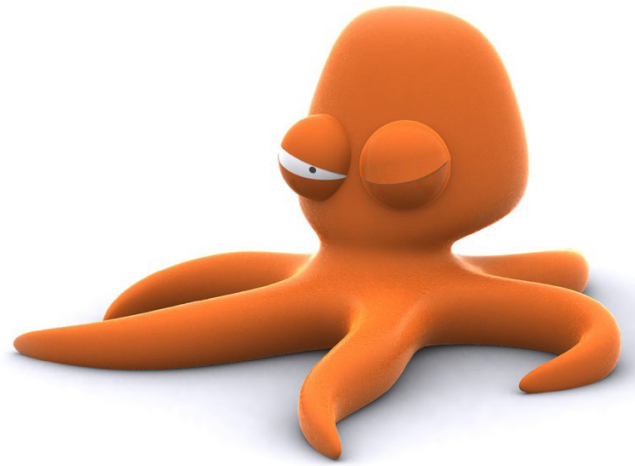


N. Tancogne-Dejean et al. JCP 152, 124119 (2020)
U de Giovannini et al. JCTC 13, 265 (2017)

Examples and tutorials

Some tutorials:

- Optical absorption
- Pump-probe spectroscopy
- HHG in solids
- ARPES



Examples and tutorials

You can try the tutorials yourself using the notebooks, provided by the binder, which is hosted at MPCDF

https://notebooks.mpcdf.mpg.de/binder/v2/gl/mpsd.training%2Ftimes-school-2025/HEAD?labpath=jupyter-notebooks%2F

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