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

Heiko Appel, Martin Lüders, Sebastian Ohlmann, Micael Oliveira, Nicolas Tancogne-Dejean

Octopus Course 2021, MPSD Hamburg

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  - Please, only submit small jobs!

Schedule

- Day 1 (6 Sep):
  - Short presentation of the theory
  - Key features of Octopus and numerical methods used
  - Octopus basics tutorial series
- Day 2 (7 Sep):
  - Running Octopus in HPC systems: parallelization and GPUs
- Day 3-4 (8-9 Sep):
  - Solids tutorial series
  - Optical absorption tutorial series
- Day 5 (10 Sep):
  - Model systems
- Days 6-7 (13-14 Sep):
  - Maxwell tutorials
  - Free project (students choose one or more tutorials that haven't been covered yet)

Theory

A bit of underlying theory: Density Functional Theory

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

Density Functional Theory

Hohenberg-Kohn theorem

- One-to-one mapping: $v(\vec{r}) \overset{W}{\longleftrightarrow} n(\vec{r})$

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- Universal functional:

$$E_{v_0}[n] = \underbrace{\langle\, \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \,\rangle}_{=F[n]} + \int \mathrm{d}^3 r\, n(\vec{r})\, v_0(\vec{r})$$

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- Variational principle:

$$\begin{aligned} E_{v_0}[n_0] &= E_0 && \text{for ground state } n_0 \\ E_{v_0}[n] &> E_0 && \text{for } \quad n \neq n_0 \end{aligned}$$

Density Functional Theory

Kohn-Sham scheme

- Use one-to-one mapping: define effective non-interacting system

$$v(\vec{r}) \underbrace{\longleftrightarrow}_{W} n(\vec{r}) \underbrace{\longleftrightarrow}_{W\equiv 0} v_{\mathrm{s}}(\vec{r})$$

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$$F[n] = T_s[n] + \frac{1}{2}\int \mathrm{d}^3 r \int \mathrm{d}^3 r'\, n(\vec{r}) w(\vec{r},\vec{r}') n(\vec{r}') + E_{xc}[n] \qquad (1)$$

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- Apply variational principle (Euler-Lagrange equations): Kohn-Sham equations

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Kohn-Sham equations

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

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

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- Solve for eigenstates at fixed $v_{\rm Hxc}$, then update n and $v_{\rm Hxc}$
- It is a boundary value problem

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Runge-Gross theorem

- One-to-one mapping (for given initial state):
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- A time-dependent Kohn-Sham system can be defined in analogy to ground-state DFT

Time-dependent Density Functional Theory

Time-dependent Kohn-Sham equation

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

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- Various numerical schemes for doing the time-propagation

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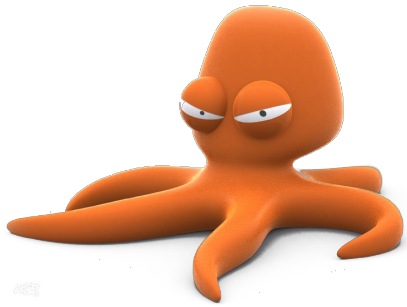
- The exact exchange-correlation functionals are unknown
- The xc functionals have to be approximated

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
- Fortran 2008, C, C++, OpenCL/CUDA 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 11.1.
- Framework to implement and test new ideas

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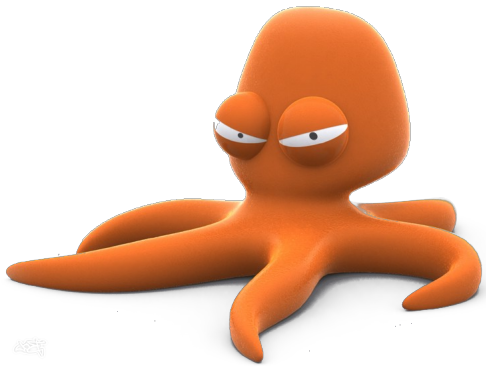

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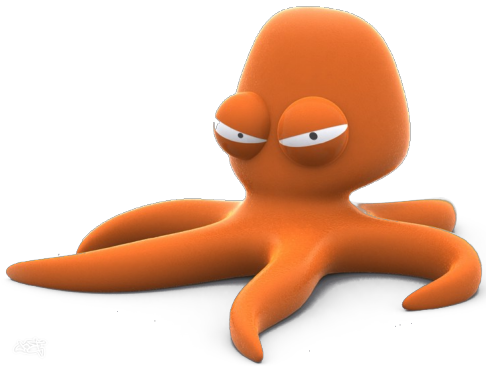

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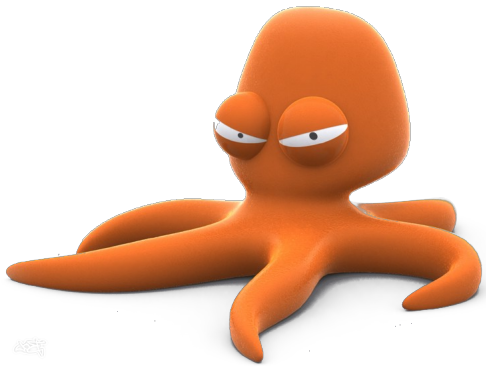

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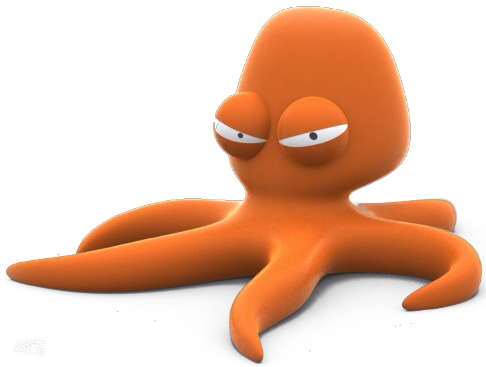

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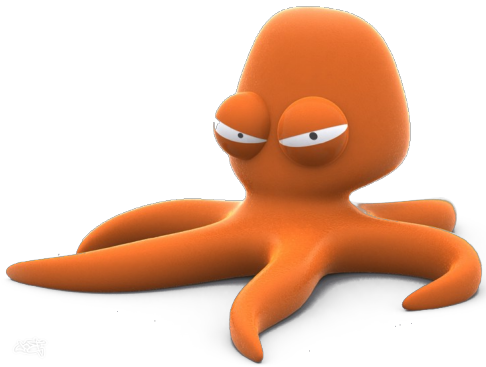
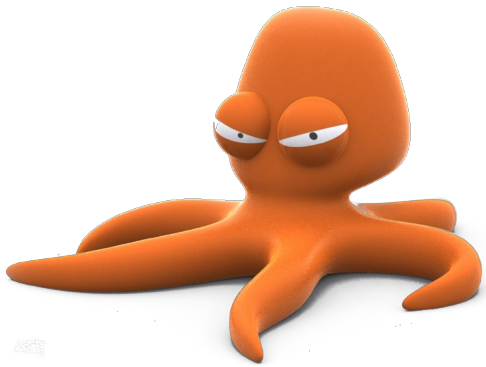


The Octopus code: new features

Big changes going on:

- Multi-system mode



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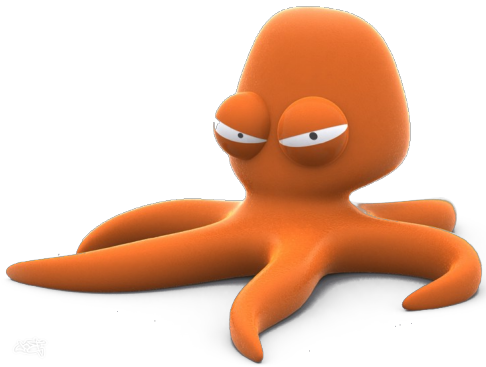
  - Maxwell fields



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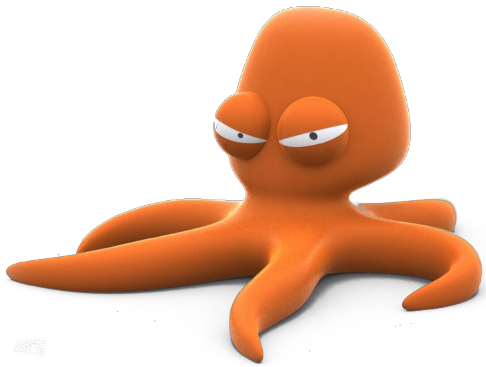

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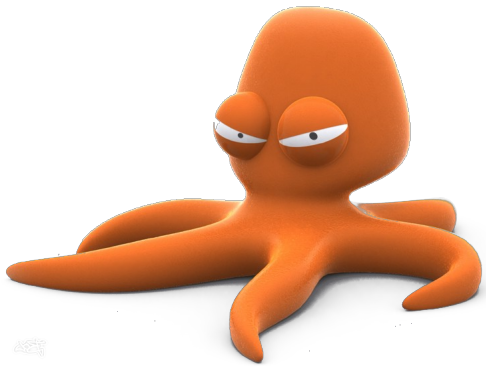

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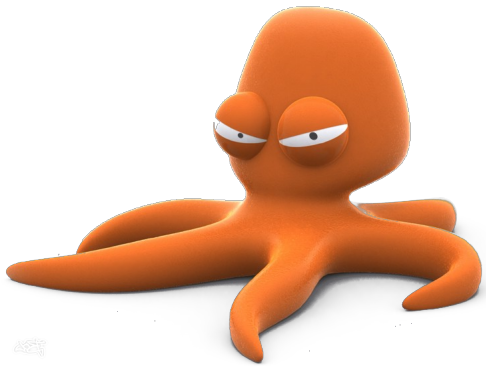

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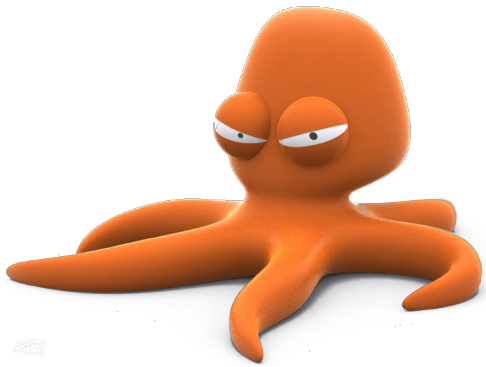

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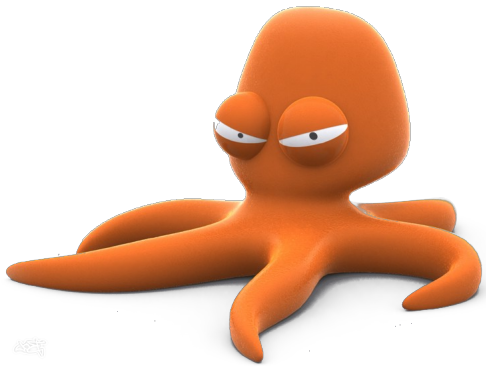

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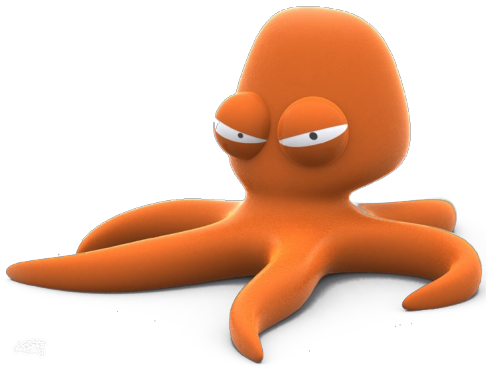

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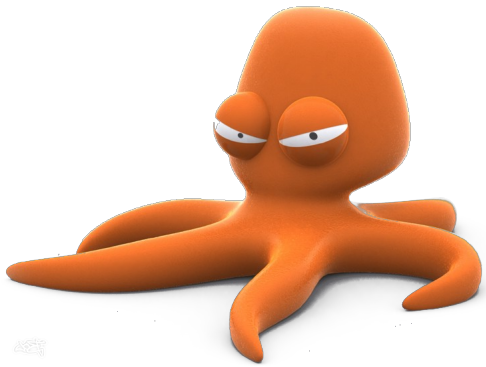

More on that in advanced course.

The Octopus code

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

M.A.L. Marques, A. Castro, G. F. Bertsch, and A. Rubio, "octopus: a first-principles tool for excited electron-ion dynamics", *Comput. Phys. Commun.* **151**, 60-78 (2003).

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Dissecting the animal

- Real-space grid representation

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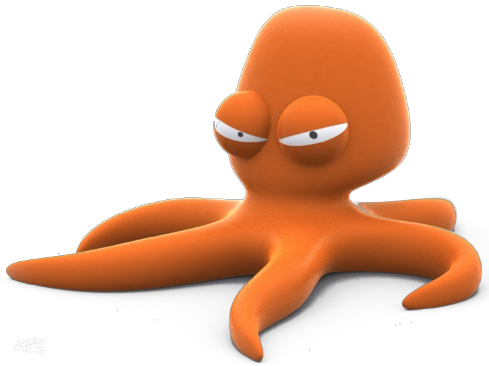
- Finite differences for the calculation of derivatives



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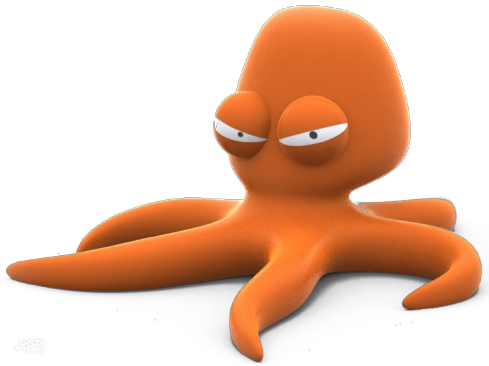

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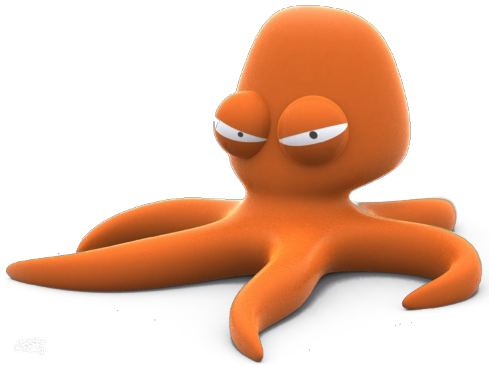

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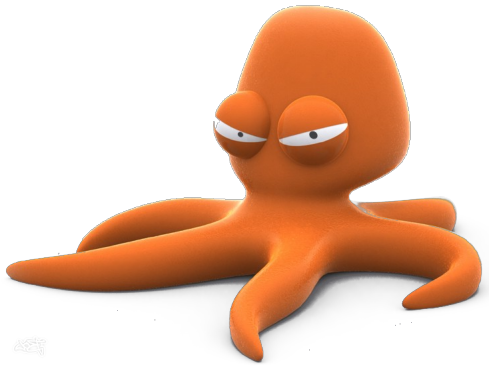

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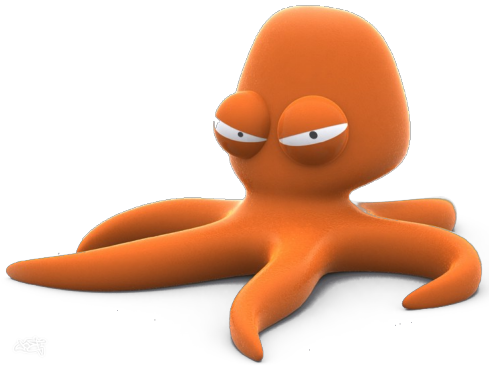

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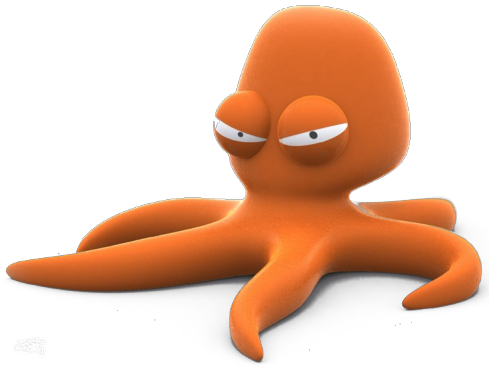

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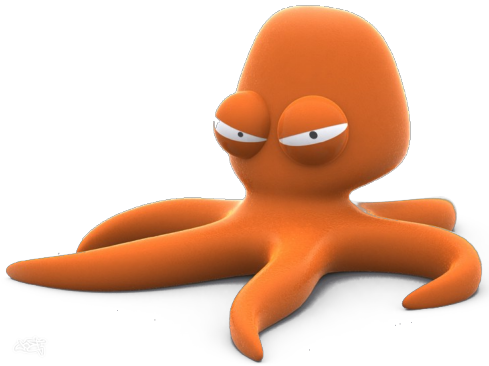

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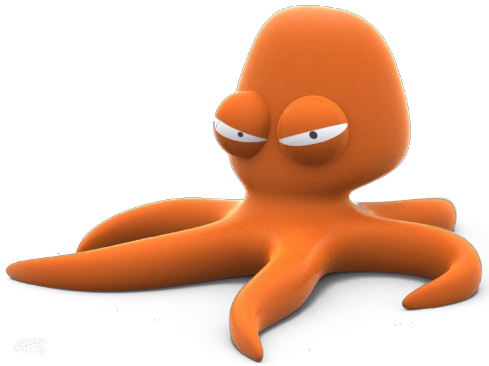

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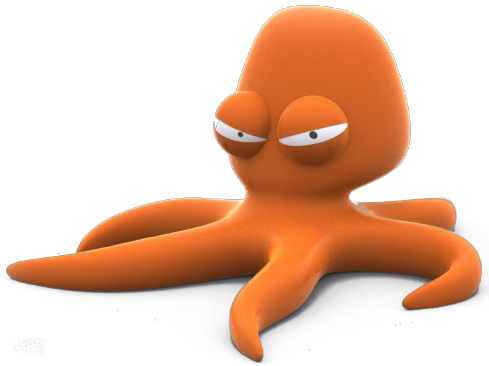

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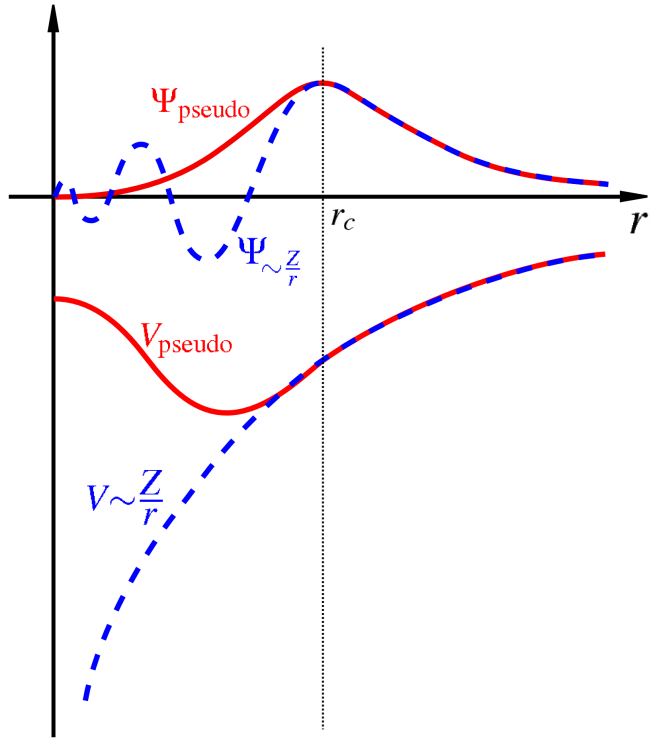
Pseudo-potentials

- The atomic potential is very strong and "hard" (small spacing or high plane-wave cutoff required).



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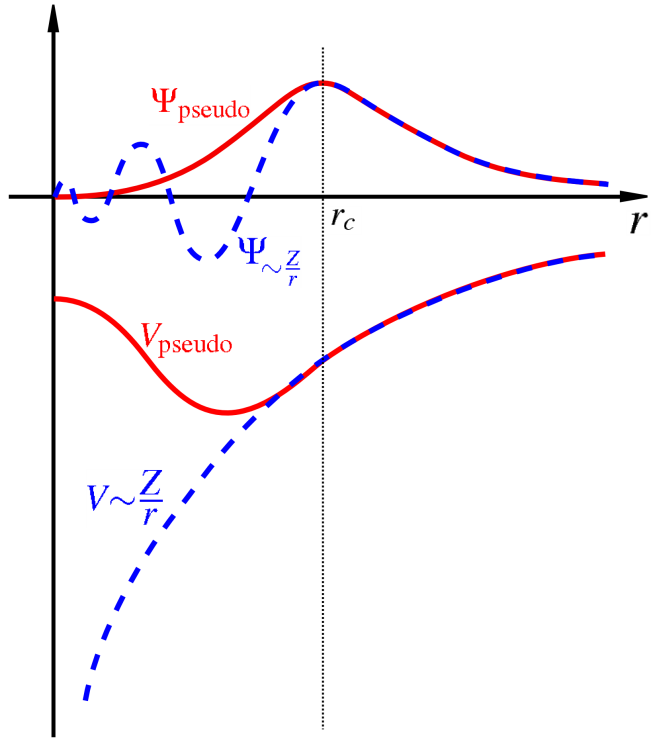

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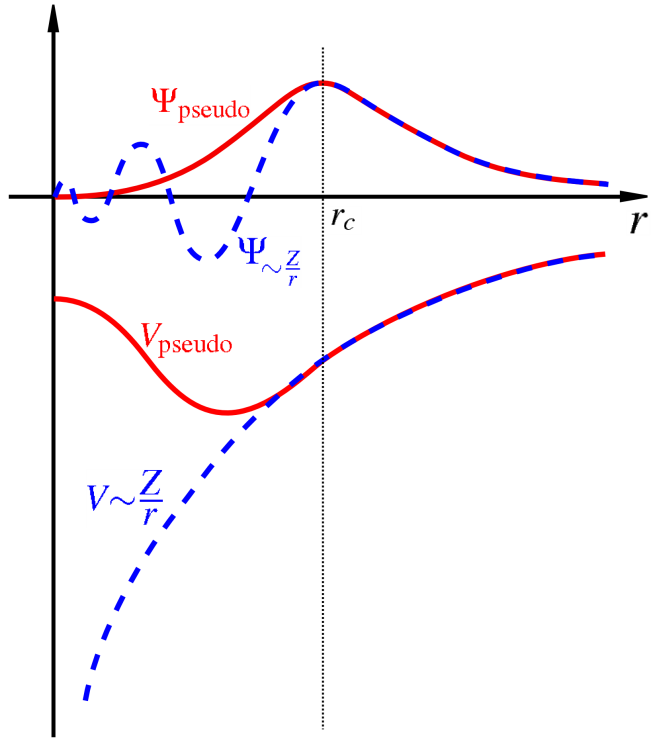

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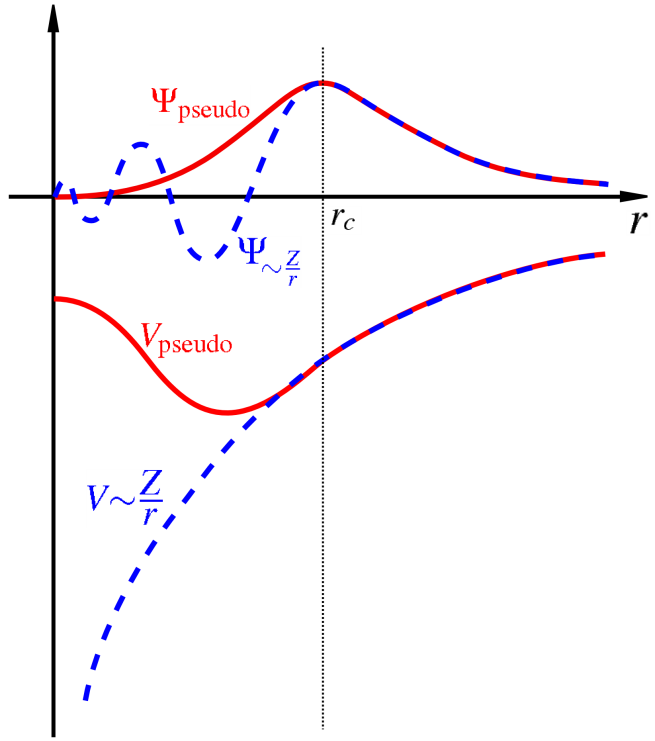

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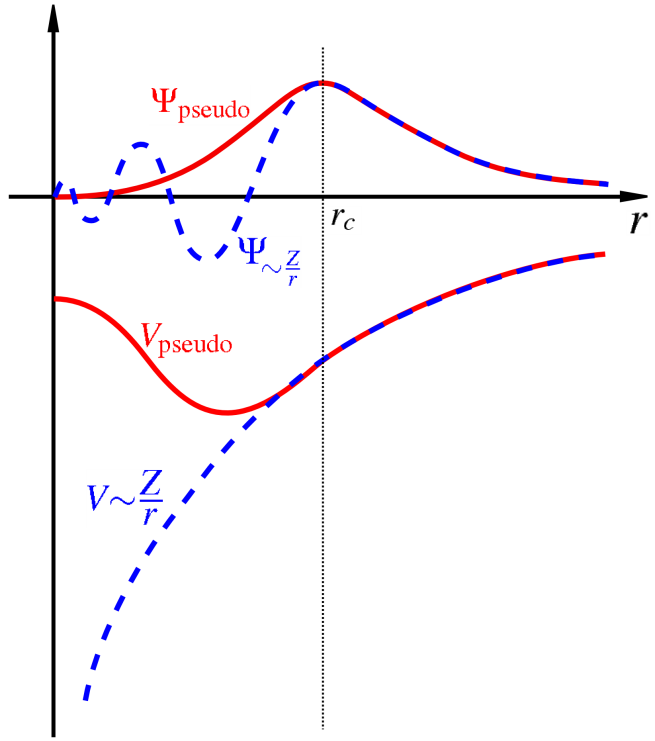

Norm-conserving pseudo-potentials in Kleinman-Bylander form

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

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Can be specified in the `Species` block

- all electron potentials (delta or Gaussian nucleus)

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- Finite region of the space: *Box*

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The Hamiltonian becomes a finite-size matrix

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- Use iterative solvers where only the application of the matrix is required (various options available in the code)

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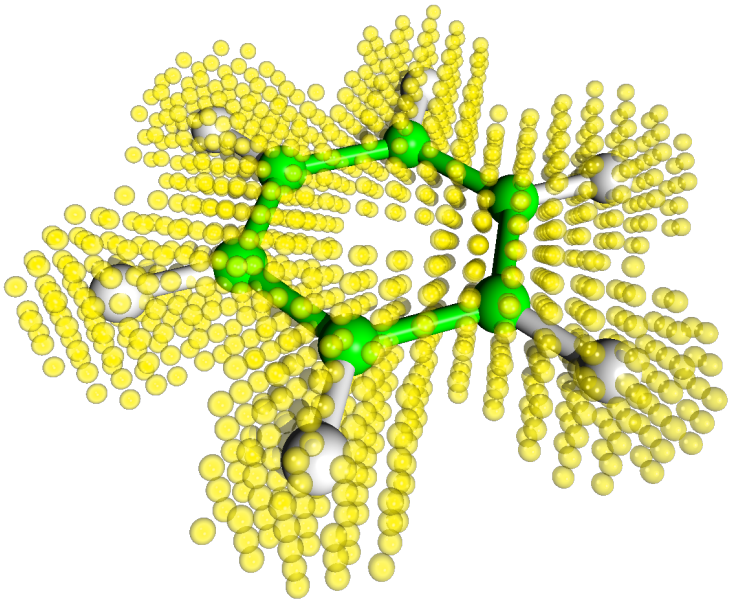
  - absorbing
  - etc

Boundary conditions

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

- Available box shapes:

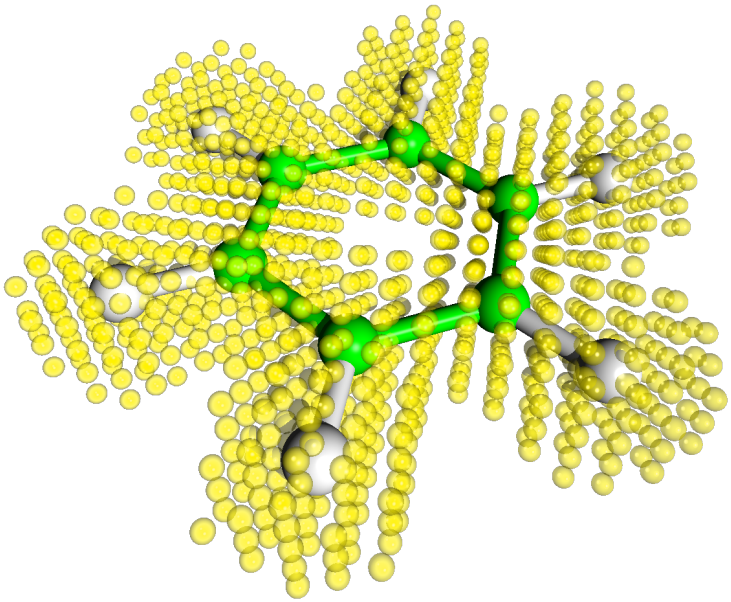


Benzene molecule in minimal box

Boundary conditions

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

- Available box shapes:
  - Sphere



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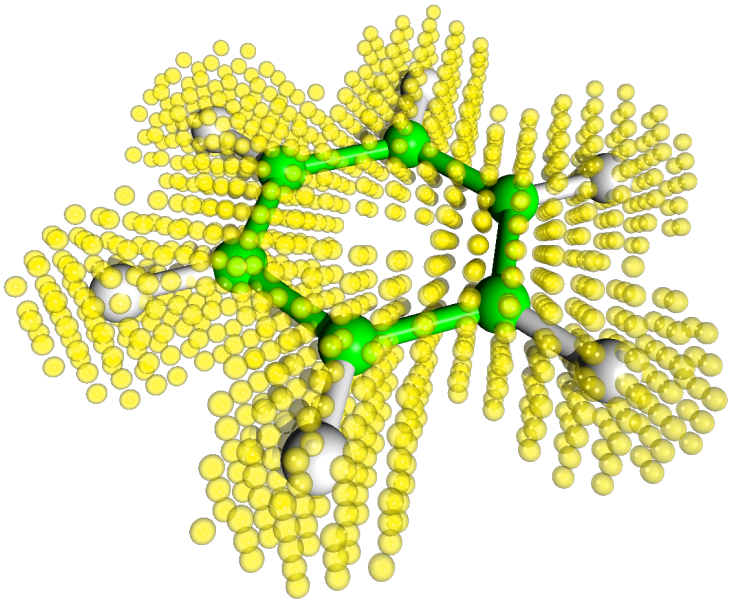

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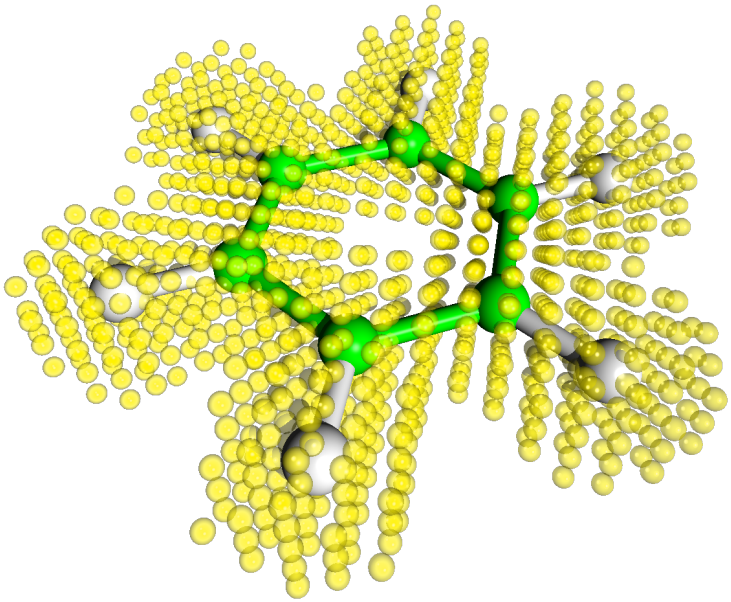

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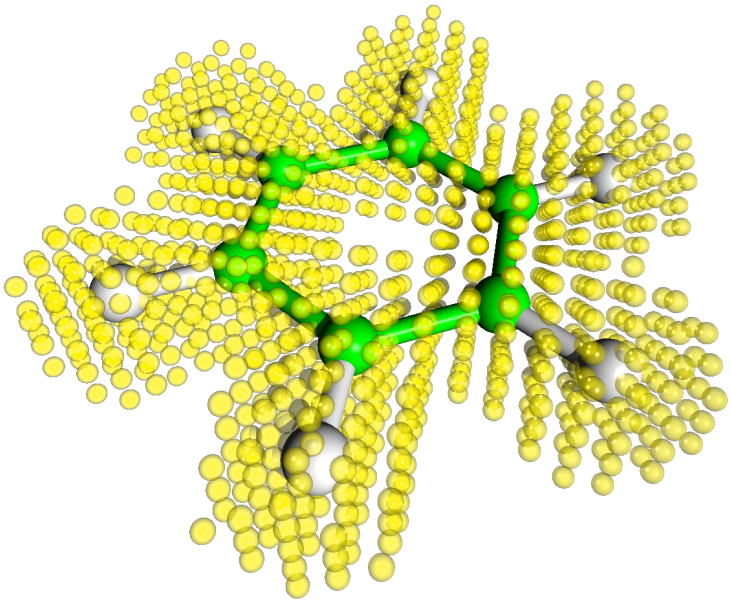

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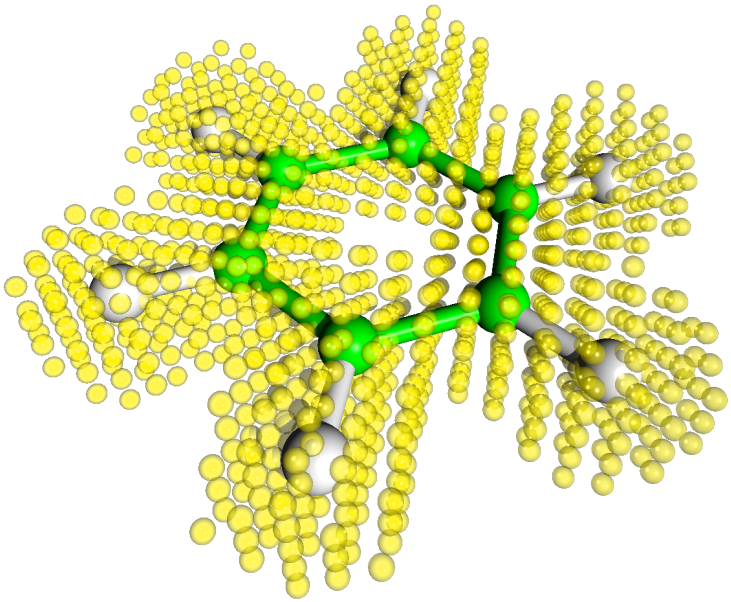

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Time propagation

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

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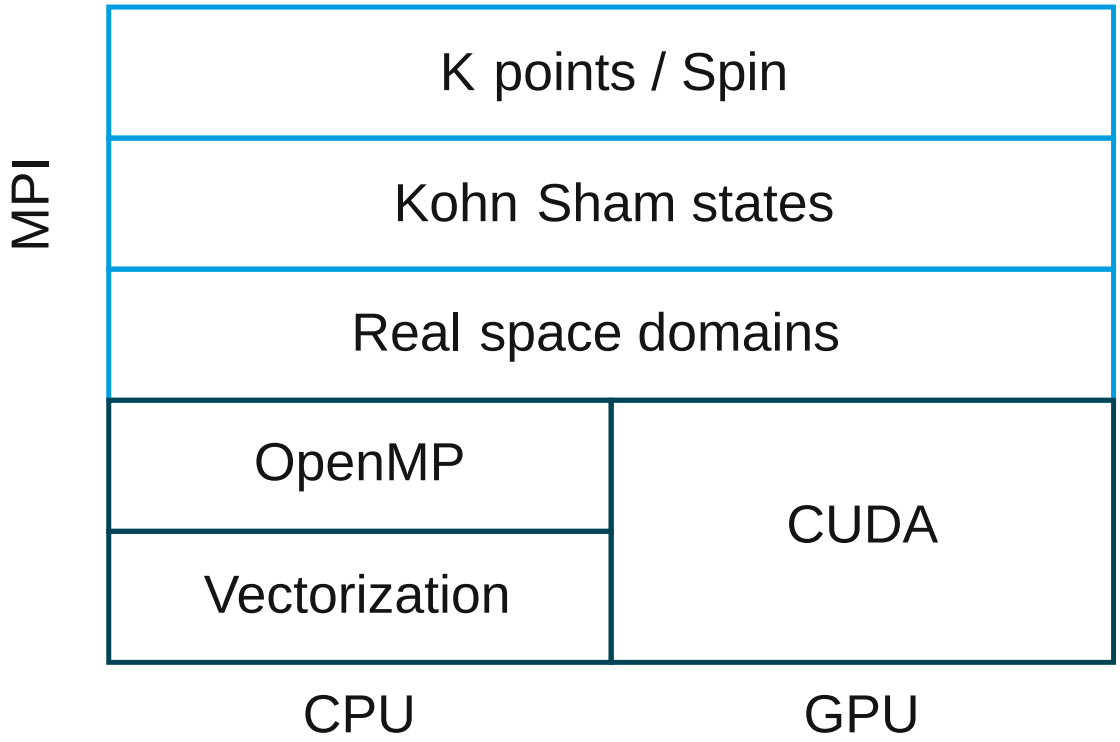
- See e.g. tutorials on optical absorption

Parallelisation strategy



More information in Sebastian's talk.

The tutorials

You can find the tutorials under this link:
`https://octopus-code.org/wiki/Tutorials`

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Have fun!