(TD)DFT: From the theory to practical numerical implementations

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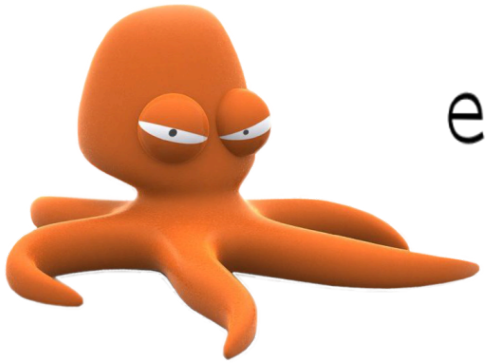
Why do we have so many real-time TDDFT codes?



and many more....

Part 1: Density Functional Theory

How to do Kohn-Sham Density Functional Theory?

Kohn-Sham equations

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

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

- We need to choose an approximation for $v_{\text{xc}}[n]$
- We need to solve a Poisson equation to get $v_{\text{H}}[n]$

How to do Kohn-Sham Density Functional Theory?

Kohn-Sham equations for noncollinear magnetism

$$\left[\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\boldsymbol{r}) + v_{\text{H}}[n](\boldsymbol{r}) + v_{\text{xc}}[n,\mathbf{m}](\boldsymbol{r})\right)\sigma_0 + \frac{1}{2c}\mathbf{B}_{\text{xc}}[n,\mathbf{m}](\boldsymbol{r})\cdot\boldsymbol{\sigma} + \frac{1}{4c^2}\boldsymbol{\sigma}\cdot(\nabla v_s(\boldsymbol{r})\times -i\nabla)\right]\varphi_i(\boldsymbol{r}) = \epsilon_i\varphi_i(\boldsymbol{r})$$

$$n_{\sigma,\sigma'}(\boldsymbol{r}) = \sum_{i=1}^{N}\sum_{\sigma=\uparrow,\downarrow}\varphi_{i,\sigma}(\boldsymbol{r})\varphi^*_{i,\sigma'}(\boldsymbol{r})$$

- We need to choose an approximation for $v_{\text{xc}}[n,\mathbf{m}]$ and $\mathbf{B}_{\text{xc}}[n,\mathbf{m}]$
- We need to solve a Poisson equation to get $v_{\text{H}}[n]$

How to do Kohn-Sham Density Functional Theory?

Kohn-Sham equations

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

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

- It is a boundary value problem $\rightarrow$ We need to specify the boundary conditions

Boundary conditions

- For finite systems, functions go to zero away from the center of mass of the system:
  - Force the functions to vanish at the boundaries of the simulation box
  - The simulation box must be sufficiently large to encompass the wavefunctions
- Other BCs are possible:
  - periodic (Born-von Kármán)
  - zero derivative
  - absorbing
  - semi-periodic
  - etc

What about the wavefunctions?

We need to know the total electronic density

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

And hence we need to know the Kohn-Sham wavefunctions $\rightarrow$ Freedom in the choice of representations, as long as a (complete) basis is used !

- Real-space sampling, splines, ...
- Boundary-condition adapted basis (planewaves, localized orbitals)

Most TDDFT codes use different bases for representing the wavefunctions. The basis also affects the calculation of the Laplacian, but also the forces and stress tensor.

How to do Kohn-Sham Density Functional Theory?

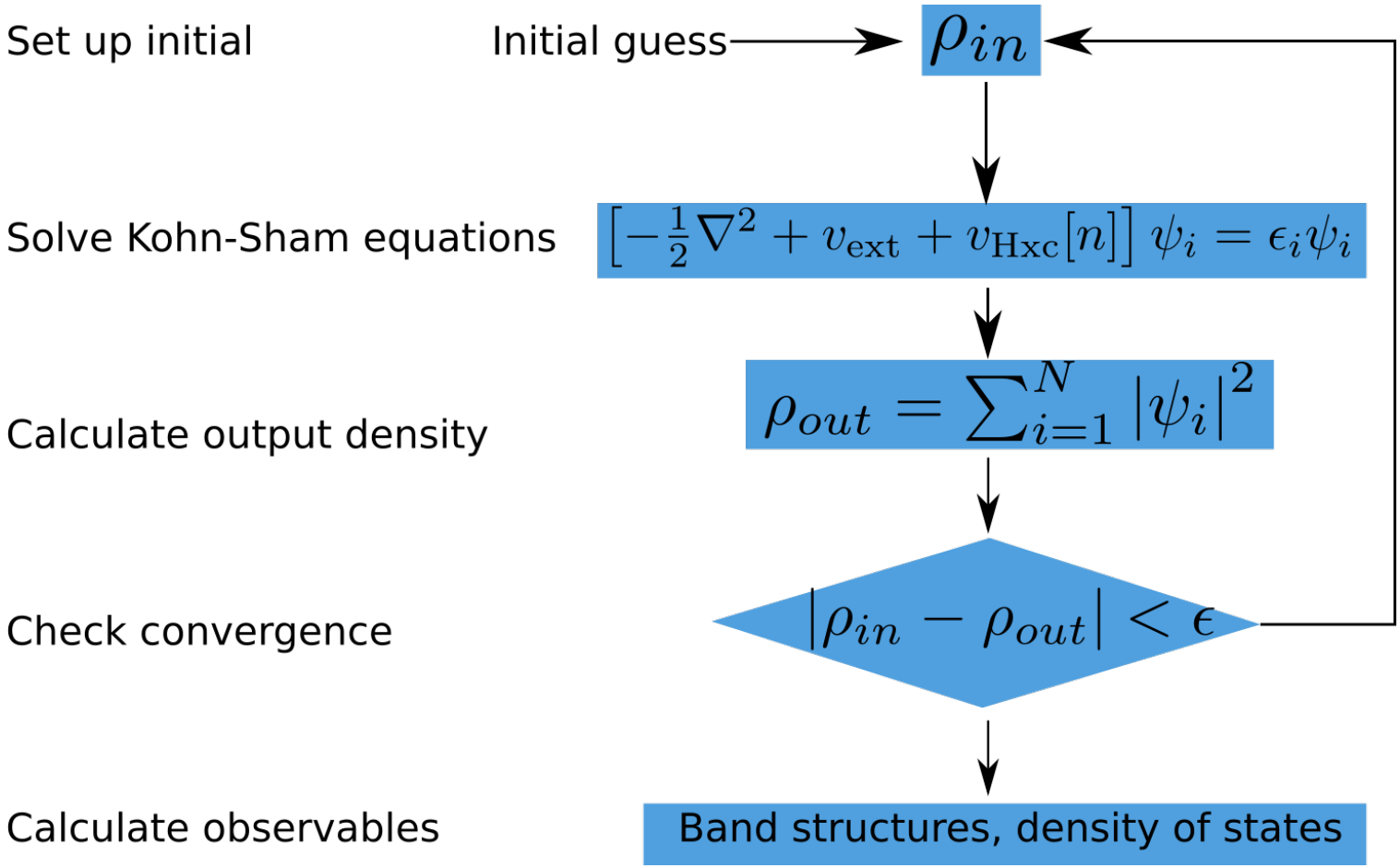
Kohn-Sham equations

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

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

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

Self-consistent field calculation



and many possible variations of this....

Other decisions to make

- Do we need all the electrons? $\rightarrow$ all electrons vs pseudopotentials
- Do you care about spin-degrees of freedom? $\rightarrow$ collinear or non-collinear spin-DFT

Summary for the DFT part

- Boundary-value problem $\rightarrow$ the boundaries need to be specified
- The representation of the wavefunctions needs to be chosen
- An algorithm to achieve self-consistency needs to be specified (mixing, preconditioning, subspace diagonalization, convergence criteria, . . .).

Part 2: Time-dependent Density Functional Theory

Time-dependent Density Functional Theory

Time-dependent Kohn-Sham equation

$$\mathrm{i}\frac{\partial}{\partial t}\varphi_i(\boldsymbol{r},t) = \left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ext}}(\boldsymbol{r},t) + v_{\mathrm{Hxc}}[n,\Psi_0,\Phi_0](\boldsymbol{r},t)\right)\varphi_i(\boldsymbol{r})$$

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

- We need to choose an approximation for $v_{\mathrm{xc}}[n] \rightarrow$ adiabatic approximation used almost all the time
- We need to solve a Poisson equation to get $v_{\mathrm{H}}[n]$

Time-dependent Density Functional Theory

Time-dependent Kohn-Sham equation

$$\mathrm{i}\frac{\partial}{\partial t}\varphi_i(\boldsymbol{r},t) = \left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ext}}(\boldsymbol{r},t) + v_{\mathrm{Hxc}}[n,\Psi_0,\Phi_0](\boldsymbol{r},t)\right)\varphi_i(\boldsymbol{r})$$

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

- It is an initial value problem
- Usually the ground-state is used as initial state
  $v_{\mathrm{Hxc}}[n,\Psi_0,\Phi_0] \to v_{\mathrm{Hxc}}[n]$
- Various numerical schemes for doing the time-propagation

Time propagation

Propagation of the wavefunctions in time:

$$\varphi_i(\boldsymbol{r}, t') = \hat{T}\exp\left\{-\mathrm{i}\int_t^{t'} \mathrm{d}\tau\, \hat{H}(\tau)\right\}\varphi_i(\boldsymbol{r}, t) = U(t', t)\varphi_i(\boldsymbol{r}, t)$$

which means

$$\varphi_i(\boldsymbol{r}, t') = \left\{\sum_{n=0}^{\infty} \frac{(-i)^n}{n!}\int_t^{t'} \mathrm{d}\tau_1 \ldots \int_t^{t'} \mathrm{d}\tau_n\, \hat{T}\hat{H}(\tau_1)\ldots\hat{H}(\tau_n)\right\}\varphi_i(\boldsymbol{r}, t)$$

Time propagation

If the Hamiltonian commutes with itself at different times, we can drop the time-ordering product and we have

$$\varphi_i(\boldsymbol{r}, t') = \exp\left\{-\mathrm{i}(t'-t)\hat{H}\right\}\varphi_i(\boldsymbol{r}, t)$$

This is not the case in TDDFT, as we have external time-dependent perturbations fluctuations of the electronic density.
Solution: split the propagation into short-time propagation using the composition property:

$$U(t', t) = U(t', \tau)U(\tau, t)\,, \quad t' \geq \tau \geq t \quad \rightarrow \quad U(t', 0) = \prod_{i=0}^{N-1} U(t_i + \Delta t, t_i)$$

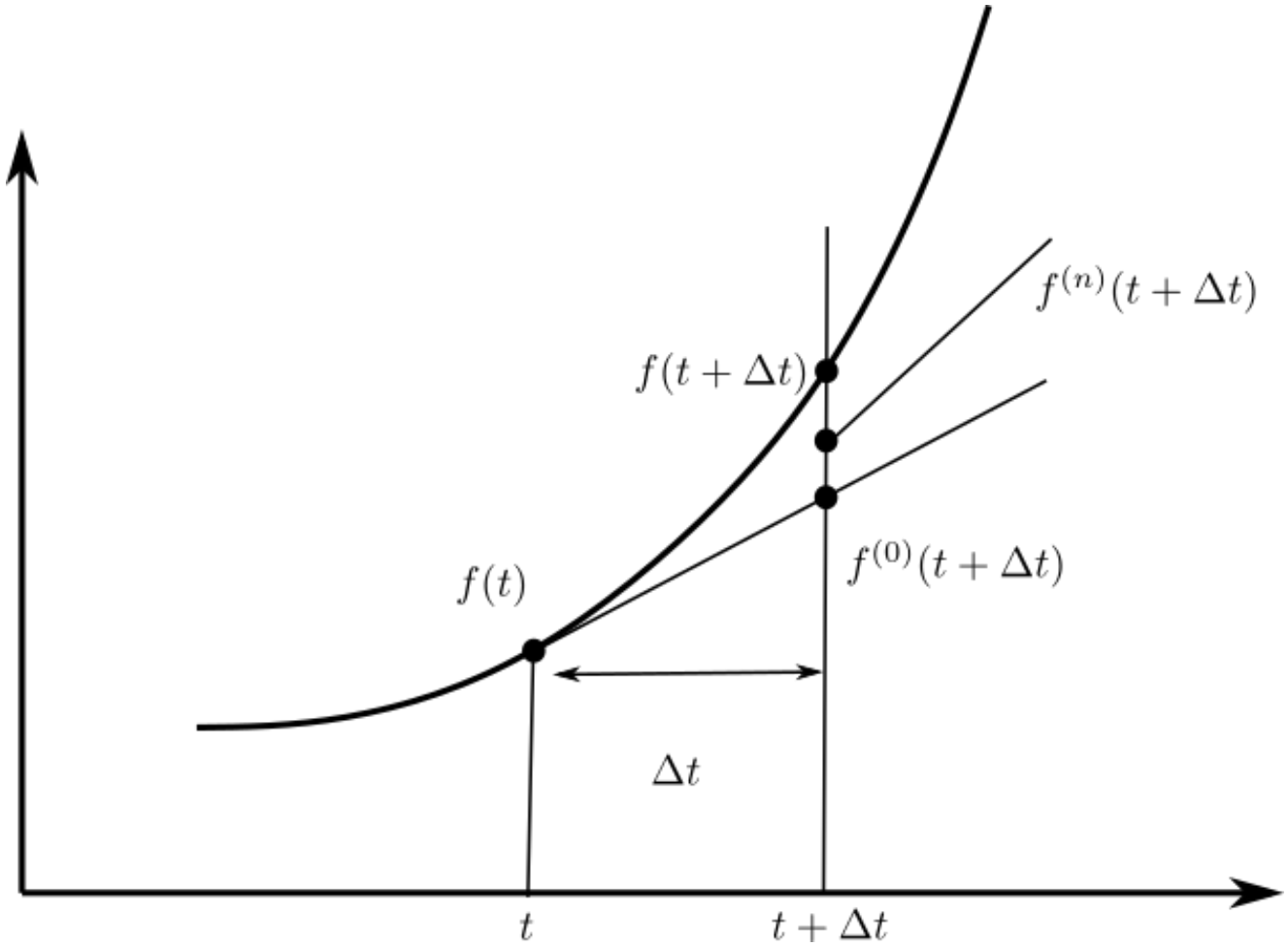
A practical scheme for the time propagation

The orbitals $\varphi_j(t + \Delta t)$ are computed from the knowledge of $\varphi_j(\tau)$ and $H(\tau)$ for $0 \leq \tau \leq t$.

- Approximate $H(\tau)$, for example when τ in between t and $t + \Delta t$
- Propagate $\varphi_j(t)$ to get $\varphi_j(t + \Delta t)$
- Calculate $H(t + \Delta t)$ from the orbitals $\varphi_j(t + \Delta t)$
- Interpolate the required $H(\tau)$ from $H(t)$ and $H(t + \Delta t)$
- Repeat steps 2-4 until self consistency is reached

In practice, simpler schemes are often used, and self-consistency is typically neglected. Instead, we rely on a sufficiently small Δt.

A practical scheme for the time propagation



$$\varphi_i(\boldsymbol{r}, t') = \hat{T}\exp\left\{-\mathrm{i}\int_t^{t'} \mathrm{d}\tau\, \hat{H}(\tau)\right\}\varphi_i(\boldsymbol{r}, t)$$

Example of a time propagation: exponential mid-point

The exponential mid-point propagator is given by

$$U(t+\Delta t,t) \approx U_{EM}(t+\Delta t,t) = \exp\left\{-\mathrm{i}\Delta t \hat{H}(t+\Delta t/2)\right\}$$

Well grounded theoretically:

- Unitary (if the exponential is properly computed)
- Preserves time-reversal symmetry (if the self-consistency is achieved)

A last remaining point: the exponential of the Hamiltonian

If the Hamiltonian matrix can be stored in memory, one can compute exactly $\exp\{H\}$.
If not, the exponential must be approximated, *e.g.* via a Taylor expansion

$$\exp\{A\} = \sum_{k=0}^{\infty} \frac{1}{k!} A^k$$

A fourth-order Taylor expansion appears to yield good results for some TDDFT codes.
Other choices are possible: Chebyshev basis expansion, Krylov-subspace projection (Lanczos method), ...

Summary for the TDDFT part

- Initial value problem $\rightarrow$ the starting point needs to be specified
- An approximation to the time-evolution operator needs to be specified (exponential mid-point, Runge-Kutta, Magnus expansions, Crank-Nicolson method, ...).
- A method for computing the exponential is needed (Taylor, Chebyshev, Krylov,...)
- You might want to include self consistency
- Should ionic motion be included? $\rightarrow$ Ehrenfest dynamics or methods beyond Ehrenfest?

Acknowledgements

Thank you for your attention