

# Linear-scaling time-dependent density-functional theory in the linear response formalism <sup>1</sup>

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ONETEP Masterclass, August 2013

# Outline

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Linear-scaling TDDFT

Results

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Motivation

Linear-scaling DFT

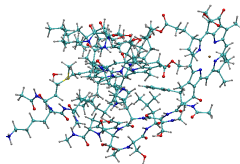
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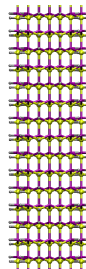
# Optical properties of large systems

## Bacteriochlorophyll in FMO



- ▶ Effects due to protein environment
- ▶ Optical properties different from isolated molecule

## Semiconductor nanorod



- ▶ Surface effects and quantum confinement
- ▶ Optical properties different from bulk crystal

Ideally, we want to treat the entire system to include all effects



# Optical properties of large systems: How?

There are a number of different methods to compute optical spectra. Which one is the most appropriate depends on a number of different factors:

- ▶ Time dependent density functional theory (TDDFT) vs. Many-Body techniques (GW+BSE)
- ▶ System sizes accessible vs. accuracy of the method
- ▶ Computational complexity of the algorithm: For large systems, we ideally require a method scaling **linearly** with system size

For the large scale systems of interest, TDDFT is the most promising since it is computationally cheap in its simplest approximation.

# TDDFT: Time-domain vs. linear response

## Time-domain

$$i\frac{\partial}{\partial t}\psi_v^{\text{KS}}(\mathbf{r}, t) = \mathbf{H}\psi_v^{\text{KS}}(\mathbf{r}, t)$$

- ▶ Explicit propagation of the KS orbitals in time
- ▶ The entire spectrum is obtained, but no information on individual excitations
- ▶ Linear-scaling algorithms are known, but still challenging

## Linear-response

$$\mathbf{A}\vec{\mathbf{X}} = \omega\vec{\mathbf{X}}$$

- ▶ Eigenvalue equation for an effective 2-particle Hamiltonian
- ▶ Yields energies, transition densities and oscillator strength for each excitation
- ▶ Linear-scaling algorithms in principle possible but harder to achieve

# The TDDFT eigenvalue equation

In linear response TDDFT (Tamm-Dancoff approximation), the excitation energies are solutions to the eigenvalue equation

$$\mathbf{A}\vec{\mathbf{X}} = \omega\vec{\mathbf{X}}$$

where

$$A_{cv,c'v'} = \delta_{c,c'}\delta_{v,v'}(\epsilon_c^{\text{KS}} - \epsilon_v^{\text{KS}}) + K_{cv,c'v'}$$

$$K_{cv,c'v'} = \int d^3r d^3r' \left[ \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega) \right] \psi_c^*(\mathbf{r})\psi_v(\mathbf{r})\psi_{v'}^*(\mathbf{r}')\psi_{c'}(\mathbf{r}')$$

- ▶ The ALDA approximation:  $f_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega) = f_{\text{xc}}^{\text{LDA}}(\mathbf{r})$
- ▶ Iterative solutions: Only require the action  $\mathbf{q} = \mathbf{A}\vec{\mathbf{X}}$

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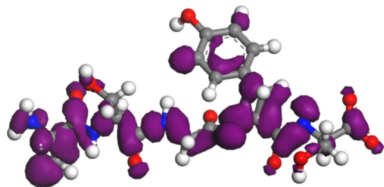
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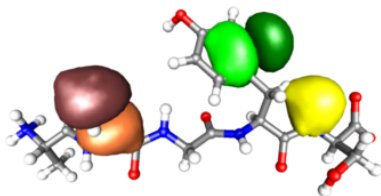
# DFT vs. Linear-scaling DFT

## DFT



- ▶ KS-orbitals are delocalised over the entire system
- ▶ Keeping  $O(N)$  orbitals orthogonal to each other  $\rightarrow O(N^3)$  scaling

## LS-DFT



- ▶ Use atom-centered nonorthogonal orbitals that are very localised
- ▶ Move from a KS state formalism to a density matrix formalism

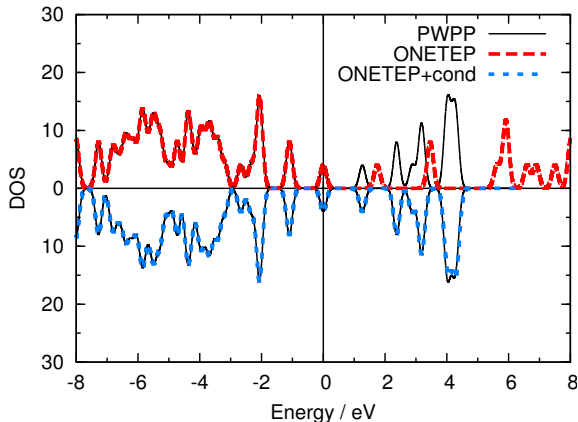
# Linear-scaling DFT

In linear-scaling DFT, the valence density matrix is expanded in terms of atom-centered nonorthogonal localised functions  $\{\phi_\alpha\}$

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_v^{\text{occ}} \psi_v^{\text{KS}}(\mathbf{r}) \psi_v^{\text{KS}*}(\mathbf{r}') = \phi_\alpha(\mathbf{r}) \mathbf{P}^{\{v\}\alpha\beta} \phi_\beta^*(\mathbf{r}')$$

- ▶  $\{\phi_\alpha\}$  are optimised *in situ* during a ground state calculation  
→ minimal number is needed to span valence space
- ▶ Linear scaling is achieved by truncating the density matrix with distance →  $\mathbf{P}^{\{v\}}$  is sparse
- ▶ No reference to individual Kohn-Sham eigenstates and energies

# Conduction optimisation



- Optimisation of a second set of localised functions  $\{\chi_\alpha\}$  and effective density matrix  $\mathbf{P}^{[c]}$  to represent **low energy** part of conduction space<sup>2</sup>

<sup>2</sup>L. E. Ratcliff, N. D. M. Hine, and P. D. Haynes, Phys. Rev. B **84**, 165131(2011)

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# Response density matrix

The transition density  $\rho^{\{1\}}$  associated with canonical eigenvector  $\vec{\mathbf{X}}$  of a **low energy** excitation  $\omega$  can be expressed as

$$\rho^{\{1\}}(\mathbf{r}) = \chi_{\alpha}(\mathbf{r}) \mathbf{P}^{\{1\}\alpha\beta} \phi_{\beta}(\mathbf{r})$$

where  $\mathbf{P}^{\{1\}}$  is the response density matrix

- ▶  $\mathbf{P}^{\{1\}}$  is a representation of  $\vec{\mathbf{X}}$  expressed in terms of  $\{\chi_{\alpha}\}$  and  $\{\phi_{\alpha}\} \rightarrow$  very efficient representation
- ▶ Define the action  $\mathbf{q} = \mathbf{A}\vec{\mathbf{X}}$  in mixed  $\{\chi_{\alpha}\}$  and  $\{\phi_{\alpha}\}$  representation
- ▶ If calculating  $\mathbf{q}$  is linear-scaling, lowest excitation energy can be found in  $O(N)$  operations using iterative techniques

# The TDDFT operator in $\{\phi\}$ and $\{\chi\}$ representation

The action  $\mathbf{q} = \mathbf{A}\vec{\mathbf{X}}$  in mixed  $\{\phi\}$  and  $\{\chi\}$  representation can be written:

$$\mathbf{q}^{\chi\phi} = \mathbf{P}^{\{c\}} \mathbf{H}^{\chi} \mathbf{P}^{\{1\}} - \mathbf{P}^{\{1\}} \mathbf{H}^{\phi} \mathbf{P}^{\{v\}} + \mathbf{P}^{\{c\}} \mathbf{V}_{\text{SCF}}^{\{1\}\chi\phi} \mathbf{P}^{\{v\}}$$

- ▶ Fully  $O(N)$  if all involved density matrices are truncated
- ▶ Can be used to generate a gradient for conjugate gradient algorithm
- ▶ Multiple excitations: Optimise  $\{\mathbf{P}_i^{\{1\}}\}$  simultaneously  $\rightarrow O(N_{\omega}^2)$  due to orthonormalisations

In practice, we minimise the function:

$$\Omega = \sum_i^{N_\omega} \omega_i = \sum_i^{N_\omega} \frac{\mathbf{x}^\dagger \mathbf{A} \mathbf{x}}{\mathbf{x}^\dagger \mathbf{x}} = \sum_i^{N_\omega} \left[ \frac{\text{Tr} \left[ \mathbf{P}_i^{\{1\}\dagger} \mathbf{S}^\chi \mathbf{q}_i^{\chi\phi} \mathbf{S}^\phi \right]}{\text{Tr} \left[ \mathbf{P}_i^{\{1\}\dagger} \mathbf{S}^\chi \mathbf{P}_i^{\{1\}} \mathbf{S}^\phi \right]} \right]$$

by constructing the (tensorially correct) gradients of  $\Omega$  with respect to all response density matrices  $\{\mathbf{P}_i^{\{1\}}; i = 1, \dots, N_\omega\}$ :

$$(g_i^\perp)^{\alpha\beta} = (q_i^{\chi\phi})^{\alpha\beta} - \sum_j \text{Tr} \left[ \mathbf{P}_j^{\{1\}\dagger} \mathbf{S}^\chi \mathbf{q}_j^{\chi\phi} \mathbf{S}^\phi \right] (P_j^{\{1\}})^{\alpha\beta}$$

The gradients can be used to construct search directions for a conjugate gradients algorithm.

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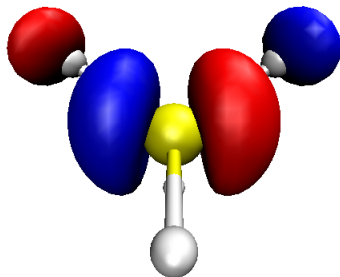
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**Results**

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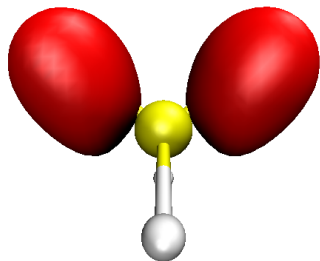
## Silane (SiH<sub>4</sub>): Transition density



$$\rho^{\{1\}}(\mathbf{r}) = \chi_{\alpha}(\mathbf{r}) P^{\{1\}\alpha\beta} \phi_{\beta}(\mathbf{r})$$

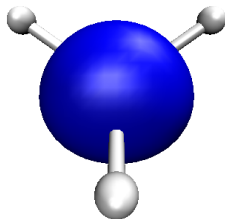
# Silane ( $\text{SiH}_4$ ): Electron and hole densities

Hole density



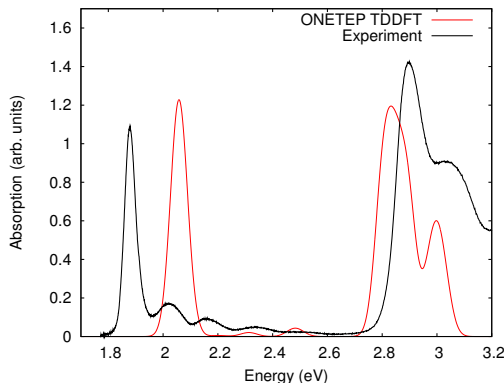
$$\mathbf{P}^{\{\text{hole}\}} = \mathbf{P}^{\{1\}} \mathbf{S}^x \mathbf{P}^{\{1\}^\dagger}$$

Electron density



$$\mathbf{P}^{\{\text{elec}\}} = \mathbf{P}^{\{1\}^\dagger} \mathbf{S}^0 \mathbf{P}^{\{1\}}$$

# Chlorophyll a



- Absorption spectrum of chlorophyll a generated from the 12 lowest excitation energies compared with the experimental spectrum of chlorophyll a in diethyl ether <sup>3</sup>

<sup>3</sup>H. Du, R. C. A. Fuh, J. Li, L. A. Corkan, and J. S. Lindsey, Photochem. Photobiol. **68**, 141 (1998)

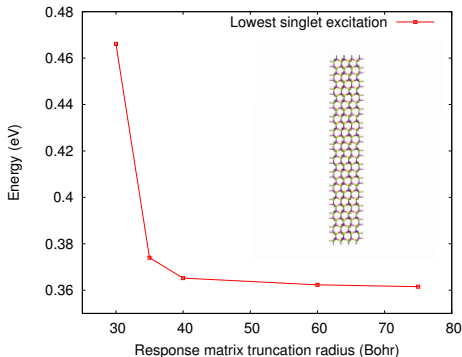
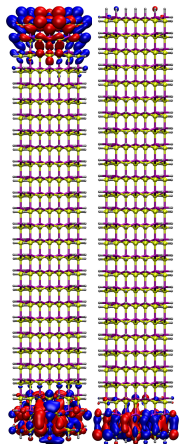
# Pentacene

ONETEP (1 H)	ONETEP (2 H)	NWCHEM(aug-cc-pVTZ)
1.883 (0.050)	1.855 (0.049)	1.844 (0.044)
2.416	2.402	2.408
2.961	2.942	2.961
3.143	3.121	3.115
3.419	3.405	3.412
3.852 (0.034)	3.831 (0.035)	3.839(0.030)
3.918	3.900	3.908
4.003	4.000	4.002
4.029 (0.011)	4.032 (0.013)	4.029(0.012)
4.162	4.106	4.159
⋮	⋮	⋮
4.311(2.58)	4.281(3.87)	4.270(3.88)

Lowest excitation energies of Pentacene. Energies are given in eV, oscillator strengths in brackets



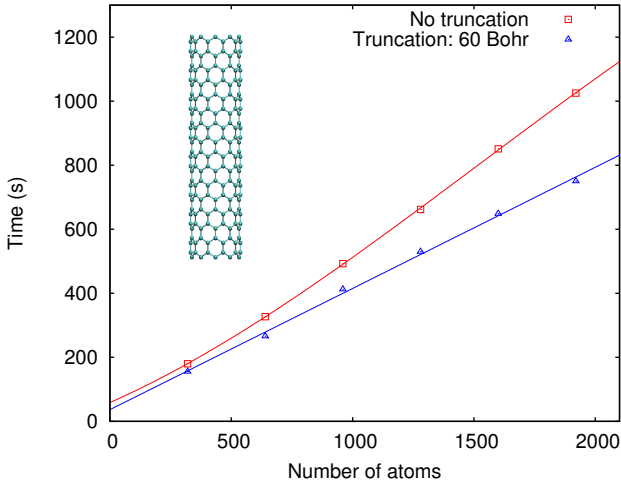
# GaAs nanorod with Hydrogen termination



- Convergence of excitation energy with respect to response matrix truncation

Response matrix truncation accurate for **localised** excitations, but misses **delocalised** excitations

# (10,0) Carbon nanotube: Linear scaling test



- ▶ Time taken for a single conjugate gradient iteration vs. system size
- ▶ Clear linear scaling for truncated response density matrix

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# Hybrid functionals

Hybrid functionals can be included in the formalism in a straightforward fashion by adding an extra term

$$(g_{HF}^{\alpha\beta})_i = P^{\{c\}\alpha\gamma} \left( \frac{\partial E_{HF}}{\partial \mathbf{P}_i^{\{1\}}} \right)_{\gamma\delta} P^{\{v\}\delta\beta}$$

to the gradient, with

$$\left( \frac{\partial E_{HF}}{\partial \mathbf{P}_i^{\{1\}}} \right)_{\alpha\gamma}^i = -2c_{HF} P_i^{\{1\}\beta\delta} \int \int \frac{\chi_\alpha(\mathbf{r}) \phi_\gamma(\mathbf{r}') \chi_\beta(\mathbf{r}) \phi_\delta(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

- ▶ Very similar expression to the one needed for Hybrid functionals in ground state DFT
- ▶ For truncated density matrices, evaluating  $g_{HF}^{\alpha\beta}$  can be made to scale linearly with system size

# TDDFT forces

Forces for each excitation energy can be found by differentiating

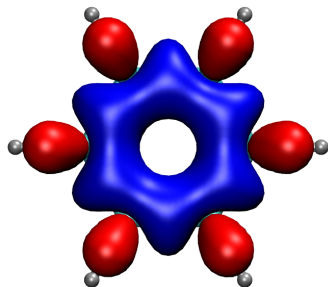
$$\begin{aligned}\mathcal{L}[X, \psi_p^{\text{KS}}, \omega, Z, \Lambda] = & E_{\text{KS}}[\psi_v^{\text{KS}}] + \mathcal{L}_{\text{TDDFT}}[X, \psi_p^{\text{KS}}, \omega] \\ & + Z_{cv} \langle \psi_c^{\text{KS}} | \hat{H} | \psi_v^{\text{KS}} \rangle - \Lambda_{pq} (\langle \psi_p^{\text{KS}} | \psi_q^{\text{KS}} \rangle - \delta_{pq})\end{aligned}$$

with respect to nuclear coordinates.

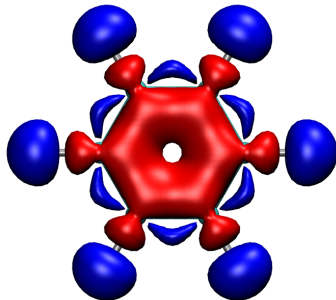
- ▶ Allows for excited state geometry optimisations
- ▶ Can be written in form of the linear-scaling TDDFT formalism  $\rightarrow O(N)$  effort per excitation energy
- ▶ Requires the calculation of effective Lagrange multipliers  $Z_{cv}$  and  $\Lambda_{pq}$

# TDDFT forces: Preliminary results (Benzene)

Electron-Hole Density



Relaxation Density  $\rho^{\{z\}}$



# Non-adiabatic coupling terms

Non-adiabatic coupling vector  $\mathbf{d}_i$  between a ground state  $\Psi_0$  and excited state  $\Psi_i$  is defined as

$$\mathbf{d}_i = \langle \Psi_0 | \frac{\partial \Psi_i}{\partial \mathbf{R}_\gamma} \rangle$$

In linear response TDDFT formalism the expression reduces to

$$\mathbf{d}_i = \frac{1}{\omega_i} \int d\mathbf{r} v_\gamma^{ne}(\mathbf{r}) \rho_i^{\{1\}}(\mathbf{r})$$

- ▶ Allows for calculating hopping probabilities between excited states potential energy surfaces
- ▶ NAC vectors and excited state forces are the main ingredients to non-adiabatic molecular dynamics simulations

# Conclusion

- ▶ We have introduced a linear-scaling TDDFT algorithm capable of solving for low energy excitations of systems of thousands of atoms
- ▶ Main limitation: Excitations with large contributions from **continuum** conduction states are unlikely to be representable in terms of  $\{\chi_\alpha\}$  and  $\{\phi_\alpha\}$
- ▶ A truncation of the response density matrix (and thus  $O(N)$  calculations) is possible for relatively localised excitations but fails for very delocalised excitations
- ▶ The dual representation approach is flexible and efficient even for dense  $\mathbf{P}^{\{1\}}$
- ▶ Future developments will allow calculations involving fully non-adiabatic molecular dynamics



# Acknowledgements

- ▶ Thanks to Keith Refson, Leonardo Bernasconi and Dominic Jochym from Rutherford Appleton Laboratory (RAL) for helpful discussions and Jian-Hao Li for extensive testing of earlier implementations
- ▶ This research was funded by the EPSRC grant EP/G036888/1
- ▶ All calculations were performed using the ONETEP code: J. Chem. Phys. **122**, 084119 (2005)
- ▶ A detailed description of the work shown here can be found in J. Chem. Phys. **139**, 064104(2013)

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