

Linear-scaling time-dependent density-functional theory (LS-TDDFT): Implementation and applications

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Outline

Motivation

Linear-scaling DFT in ONETEP

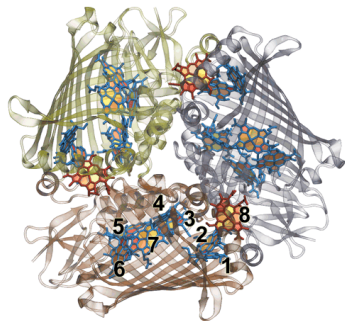
Linear-scaling TDDFT

Converging targeted localised excitations

Applications

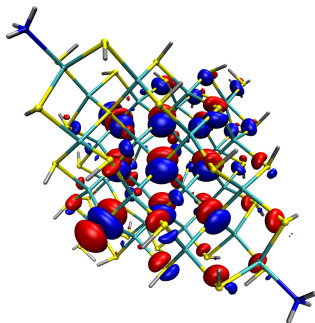
Optical properties of large systems

Bacteriochlorophyll in FMO



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

Semiconductor nanoparticle



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

Linear Response TDDFT

Solve

$$\begin{pmatrix} \mathbf{A}(\omega) & \mathbf{B}(\omega) \\ -\mathbf{B}(\omega) & -\mathbf{A}(\omega) \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

where

$$A_{c\nu, c' \nu'}(\omega) = \delta_{cc'} \delta_{\nu\nu'} (\epsilon_{c'}^{\text{KS}} - \epsilon_{\nu'}^{\text{KS}}) + K_{c\nu, c' \nu'}(\omega)$$

$$B_{c\nu, c' \nu'}(\omega) = K_{c\nu, \nu' c'}(\omega)$$

and

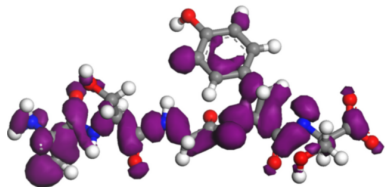
$$K_{c\nu, c' \nu'}(\omega) = \left\langle \psi_c^{\text{KS}} \psi_{\nu}^{\text{KS}} \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega) \right| \psi_{c'}^{\text{KS}} \psi_{\nu'}^{\text{KS}} \right\rangle$$

Tamm-Dancoff approximation: $\mathbf{Y} = 0$; $\mathbf{B} = 0$; $\mathbf{A}\mathbf{X} = \omega\mathbf{X}$

Use iterative eigensolvers: Only the action $\mathbf{q} = \mathbf{A}\mathbf{x}$ is required.

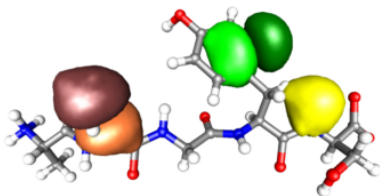
DFT vs. Linear-scaling DFT

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 ONETEP

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

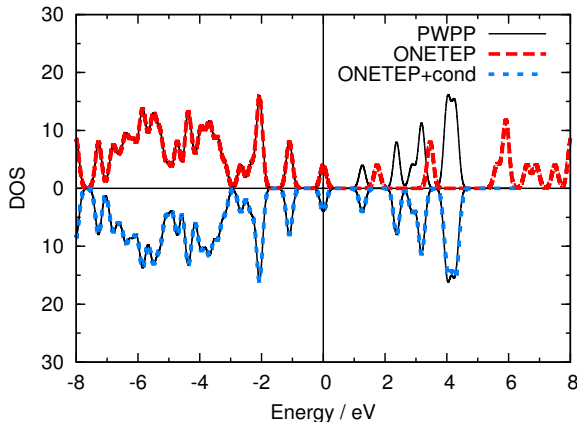
$$\rho(\mathbf{r}, \mathbf{r}') = \sum_v^{\text{occ}} \psi_v^{\text{KS}}(\mathbf{r}) \psi_v^{\text{KS}*}(\mathbf{r}') = \sum_{\alpha\beta} \phi_\alpha(\mathbf{r}) \mathbf{P}^{\{v\}\alpha\beta} \phi_\beta^*(\mathbf{r}')$$

- ▶ $\{\phi_\alpha\}$ are optimised *in situ* during a ground state calculation
→ minimal number is needed to span valence space

$$E_{\text{DFT}} = E_{\text{DFT}} \left[\mathbf{P}^{\{v\}}, \{\phi_\alpha\} \right]$$

- ▶ 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 of phthalocyanine



- ▶ 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 ¹

¹L. E. Ratcliff, N. D. M. Hine, and P. D. Haynes, Phys. Rev. B **84**, 165131(2011)

Optimisation of the Rayleigh-Ritz value in Kohn-Sham space

$$\omega = \min_{\mathbf{x}} \frac{\mathbf{x}^\dagger \mathbf{A} \mathbf{x}}{\mathbf{x}^\dagger \mathbf{x}}$$

Differentiating the Rayleigh-Ritz value yields an energy gradient:

$$\frac{\partial \omega}{\partial \mathbf{x}} = 2\mathbf{A}\mathbf{x} - \left[\mathbf{x}^\dagger \mathbf{A} \mathbf{x} \right] \mathbf{x}$$

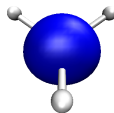
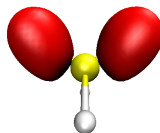
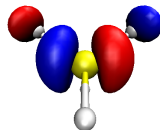
Write $\mathbf{q} = \mathbf{A}\mathbf{x}$ in terms of an effective transition density $\rho^{\{1\}}(\mathbf{r})$ and the Kohn-Sham eigenvalue differences

$$q_{cv} = (\epsilon_c^{\text{KS}} - \epsilon_v^{\text{KS}}) x_{cv} + \left(V_{\text{SCF}}^{\{1\}} \left[\rho^{\{1\}} \right] \right)_{cv}$$

where $\rho^{\{1\}}(\mathbf{r}) = \sum_{cv} \psi_c^{\text{KS}}(\mathbf{r}) x_{cv} \psi_v^{\text{KS}}(\mathbf{r})$

Transition density matrix in ONETEP

$$\begin{aligned}\rho^{\{1\}}(\mathbf{r}) &= \sum_{c\nu} \psi_c^{\text{KS}}(\mathbf{r}) \chi_{c\nu} \psi_\nu^{\text{KS}}(\mathbf{r}) \\ &= \sum_{\alpha\beta} \chi_\alpha(\mathbf{r}) \mathbf{P}^{\{1\}\alpha\beta} \phi_\beta(\mathbf{r})\end{aligned}$$



- ▶ Express the transition density in terms of density matrix $\mathbf{P}^{\{1\}}$
- ▶ Hole well described by $\{\phi_\alpha\}$
- ▶ Electron well described by $\{\chi_\alpha\}$
- ▶ $\rho^{\{1\}}(\mathbf{r})$ well described by $\{\phi_\alpha\}$ and $\{\chi_\beta\}$

The Tamm-Dancoff TDDFT gradient in $\{\phi\}$ and $\{\chi\}$ representation

The TDDFT gradient $\mathbf{q} = \mathbf{Ax}$ in mixed $\{\phi\}$ and $\{\chi\}$ representation:

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

- ▶ 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

Full TDDFT: An effective variational principle

In full TDDFT, define an effective variational principle for the *positive* eigenvalues:

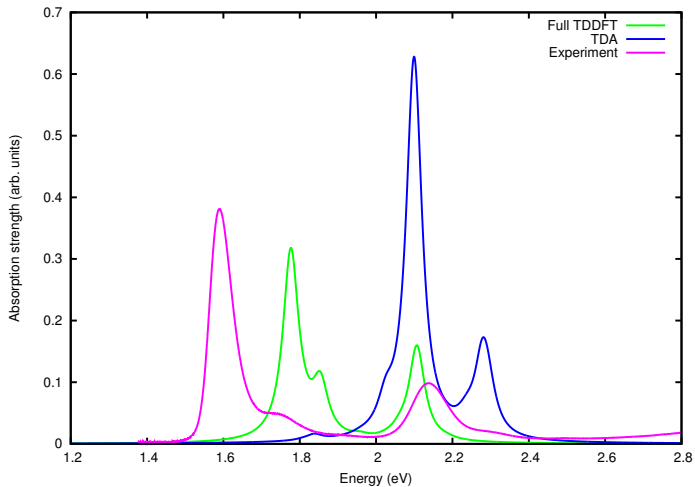
$$\omega_{\min} = \min_{\{\mathbf{P}\{\rho\}, \mathbf{P}\{q\}\}} \left\{ \frac{\text{Tr} [\mathbf{P}\{\rho\}^\dagger \mathbf{S}^\chi \mathbf{q}_{\{\rho\}}^{\chi\phi} \mathbf{S}^\phi]}{2 \left| \text{Tr} [\mathbf{P}\{\rho\}^\dagger \mathbf{S}^\chi \mathbf{P}\{q\} \mathbf{S}^\phi] \right|} + \frac{\text{Tr} [\mathbf{P}\{q\}^\dagger \mathbf{S}^\chi \mathbf{q}_{\{q\}}^{\chi\phi} \mathbf{S}^\phi]}{2 \left| \text{Tr} [\mathbf{P}\{\rho\}^\dagger \mathbf{S}^\chi \mathbf{P}\{q\} \mathbf{S}^\phi] \right|} \right\}$$

where

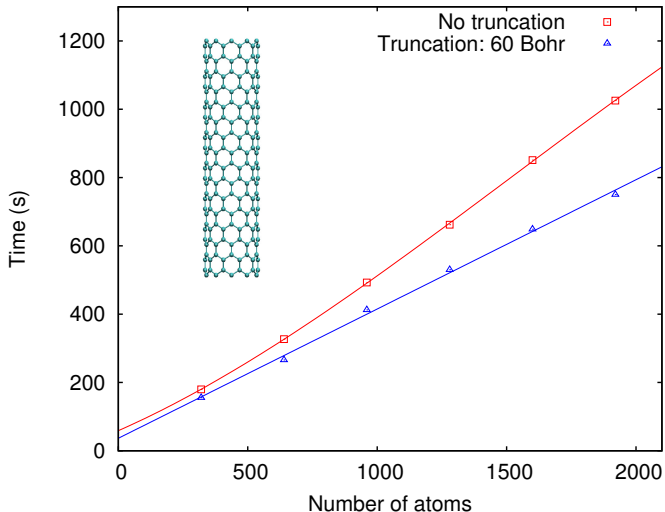
$$\mathbf{q}_{\{\rho\}}^{\chi\phi} = \mathbf{P}\{c\} \mathbf{H}_{\text{KS}}^\chi \mathbf{P}\{1\} - \mathbf{P}\{1\} \mathbf{H}_{\text{KS}}^\phi \mathbf{P}\{v\}$$

$$\mathbf{q}_{\{q\}}^{\chi\phi} = \mathbf{P}\{c\} \mathbf{H}_{\text{KS}}^\chi \mathbf{P}\{1\} - \mathbf{P}\{1\} \mathbf{H}_{\text{KS}}^\phi \mathbf{P}\{v\} + 2\mathbf{P}\{c\} \mathbf{V}_{\text{SCF}}^{\{1\}\chi\phi} \mathbf{P}\{v\}$$

Full TDDFT vs. Tamm-Dancoff: Bacteriochlorophyll



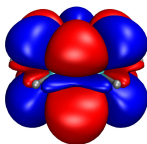
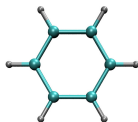
(10,0) Carbon nanotube: Linear scaling test



- ▶ Time taken for a single conjugate gradient iteration vs. system size

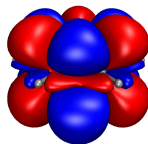
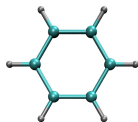
Constraining the TDDFT transition density matrix

Fully dense $P^{\{1\}}$



- ▶ $P^{\{1\}}$ filling: 100.0 %
- ▶ $\omega = 5.1950$ eV
- ▶ $f = 0.177 \times 10^{-6}$
- ▶ 10th excitation converged

$P^{\{1\}}$ only on one Benzene

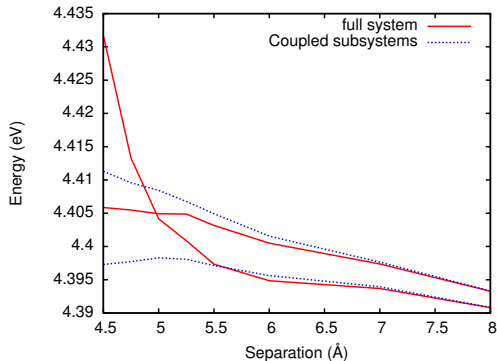


- ▶ $P^{\{1\}}$ filling: 25.0 %
- ▶ $\omega = 5.1953$ eV
- ▶ $f = 0.111 \times 10^{-6}$
- ▶ Lowest excitation converged

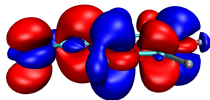
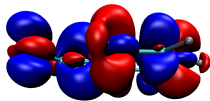
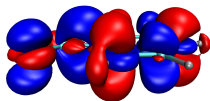
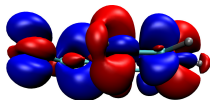
Interactions between subsystems: Exciton coupling

Reintroduce subsystem coupling perturbatively:

$$\mathbf{P}_{\text{tot}}^{\{1\}} = \sum_i \alpha_i \mathbf{P}_{\mathbf{A}_i}^{\{1\}} + \sum_j \beta_j \mathbf{P}_{\mathbf{B}_j}^{\{1\}}$$

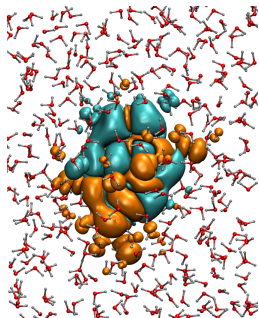
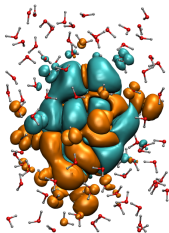
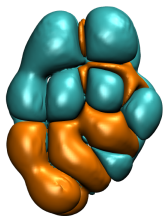


α_j, β_j obtained in a single subspace diagonalisation as a post-processing step



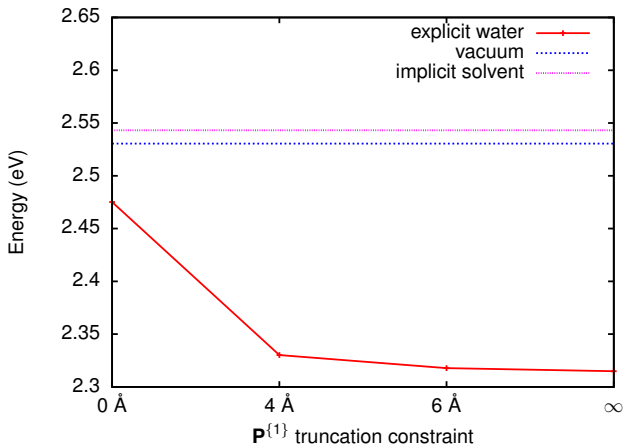
Solvatochromic shift of alizarin ($C_{14}H_8O_4$) in water

How much of the environment has to be treated explicitly in order to converge localised excitations of alizarin?



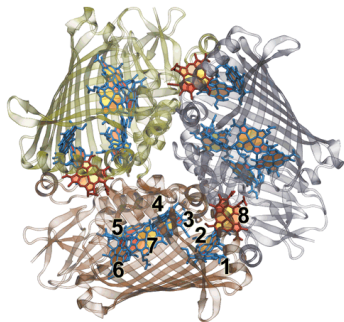
- ▶ Create a model system from a single classical MD snapshot
- ▶ All water within 12 \AA of alizarin is included in the calculation ≈ 1800 atoms

Solvatochromic shift of alizarin ($C_{14}H_8O_4$) in water



- ▶ Strong solvatochromic shift of 0.12 eV due to charge-transfer delocalisation in P^{1} onto the water
- ▶ Delocalisation confined to within 6 Å from alizarin (≈ 300 atoms)

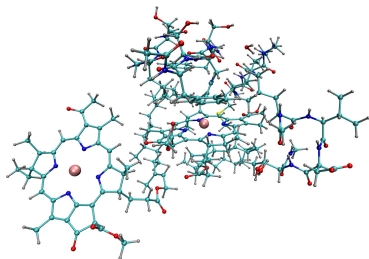
The Fenna-Matthews-Olson (FMO) complex



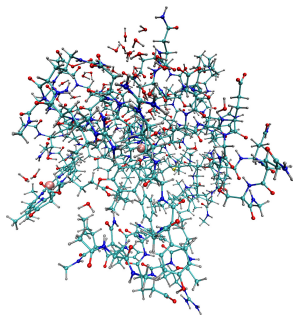
- ▶ 7 Bacteriochlorophyll pigments per monomer
- ▶ Including protein environment ≈ 10.000 atoms per monomer
- ▶ Exciton dynamics studied with model Hamiltonians \rightarrow accurate pigment site energies needed

Site energies from linear-scaling TDDFT: Case study of BChl site 1

Two model systems of the protein environment:

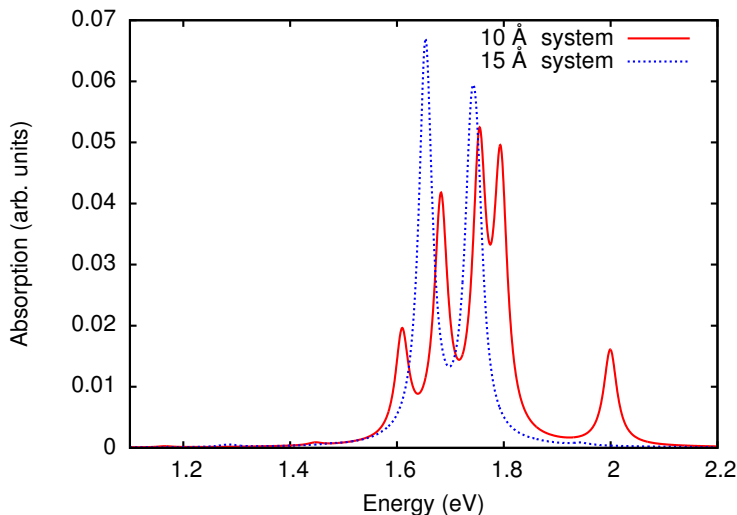


562 atoms
10 Å radius



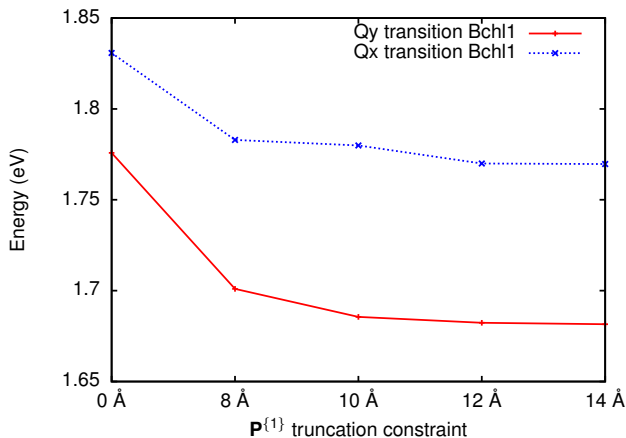
1646 atoms
15 Å radius

Absorption spectrum, full TDDFT



Fully dense $\mathbf{P}^{\{1\}}$: large number of spurious charge-transfer states with local f_{XC} (34 states needed for 15 Å spectrum)

Quantifying exciton delocalisation into the protein



- ▶ 12 Å radius of explicit protein environment necessary to converge localised site energies \approx 1000 atom systems
- ▶ Constraining $P^{(1)}$: Localised site energies become the **lowest** excited states of the system

Conclusion

- ▶ ONETEP provides an efficient framework for calculating low energy excited states in systems containing thousands of atoms (**available features**: (semi)-local functionals, PAW; **Future work**: Hybrid functionals, TDDFT forces → excited states dynamics)
- ▶ Fully linear-scaling for sufficiently large systems
- ▶ Truncation of $\mathbf{P}^{\{1\}}$ can be used to converge targeted, localised excitations of larger systems
- ▶ **Warning**: QM/MM methods can require very large QM regions to converge environmental effects on localised excitations.

Acknowledgements

- ▶ This research was funded by the EPSRC grants EP/G036888/1, EPSRC Grant EP/J017639/1 and the ARCHER eCSE programme
- ▶ All calculations were performed using the ONETEP code: J. Chem. Phys. **122**, 084119 (2005), www.onetep.org
- ▶ Further information and benchmark tests regarding linear-scaling TDDFT in ONETEP: J. Chem. Phys. **139**, 064104(2013)

