

# Excited state calculations and theoretical spectroscopy of complex nanomaterials using Linear-Scaling Density Functional Theory

**N. D. M. Hine**, T. J. Zuehlsdorff, L. E. Ratcliff, D. J. Cole, A. W. Chin, M. C. Payne, P. D. Haynes

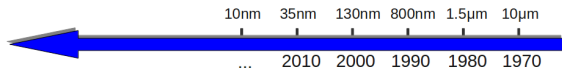
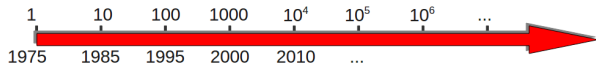
Assistant Professor, Department of Physics, University of Warwick

Warwick Centre for Predictive Modelling, 25/06/15

# Nanomaterials: Convergence of Lengthscales

## Convergence of experimental and computational lengthscales

Number of Atoms feasible with DFT



Semiconductor fabrication technology

Resolution of analytic methods (microscopy, tomography, etc) shows similar trend.

# Traditional DFT

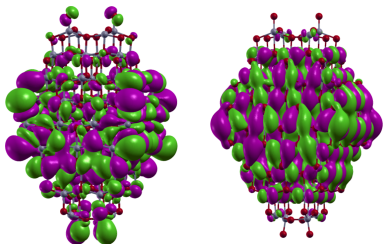
Traditional Kohn-Sham DFT:

$$E_{KS}[\rho(\mathbf{r})] = T_s[\rho] + E_H[\rho] + E_{xc}[\rho] + E_{ext}[\rho]$$

Minimise w.r.t.  $\rho$  with  $\rho = \sum_n |\psi_n(\mathbf{r})|^2$  for orthogonal single-particle states  $\psi_n(\mathbf{r})$ :  
Becomes Eigenvalue problem:

$$\hat{H}_{KS}[\rho(\mathbf{r})]\psi_n(\mathbf{r}) = \varepsilon_n \psi_n(\mathbf{r})$$

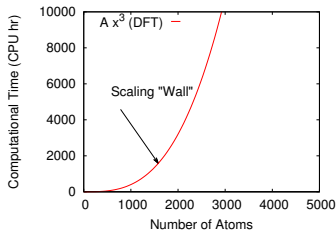
where  $\hat{H}_{KS}[\rho(\mathbf{r})] = -\frac{1}{2}\nabla^2 + V_{\text{eff}}[\rho(\mathbf{r})]$   
seeks eigenstates  $\psi_n(\mathbf{r})$ , eigenvalues  $\varepsilon_n$ .



## Scalability Problem:

For  $N$  atoms, eigenstate-based approaches are inherently  $O(N^3)$ :

- Number of eigenstates  $\propto O(N)$
- Number of basis functions  $\propto O(N)$
- Each must stay mutually orthogonal to number of others  $\propto O(N)$



# Linear-Scaling approaches to DFT

Density matrix expresses same information as eigenstates:

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_n \psi_n(\mathbf{r}) f_n \psi_n(\mathbf{r}')$$

Introduce localised nonorthogonal support functions:

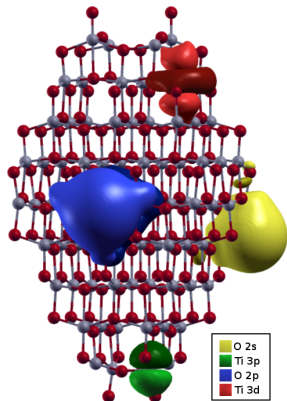
$$\psi_n(\mathbf{r}) = \sum_{\alpha} M_n^{\alpha} \phi_{\alpha}(\mathbf{r})$$

Density kernel  $K^{\alpha\beta}$  replaces occupation number:

$$K^{\alpha\beta} = \sum_n (M_n^{\dagger})^{\alpha} f_n M_n^{\beta}$$

Represent DM using these:

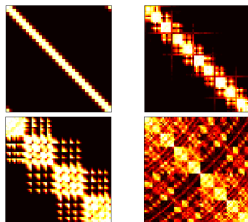
$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{\alpha\beta} \phi_{\alpha}(\mathbf{r}) K^{\alpha\beta} \phi_{\beta}(\mathbf{r}')$$





# Linear-Scaling DFT

- Using local orbitals, Hamiltonian  $H_{\alpha\beta} = \langle \phi_\alpha | \hat{H} | \phi_\beta \rangle$  and overlap  $S_{\alpha\beta} = \langle \phi_\alpha | \phi_\beta \rangle$  are *sparse*
- Density matrix *nearsighted* for insulators:  $\rho(\mathbf{r}, \mathbf{r}') \propto \exp(-\gamma|\mathbf{r} - \mathbf{r}'|)$  so  $K^{\alpha\beta}$  can be *sparse*



Minimise total energy subject to constraints on Density Matrix:

Energy:  $E_T = K^{\alpha\beta} H_{\beta\alpha} - E_{dc}[\rho]$

- normalisation (right number of electrons)

$$N_e = \int \rho(\mathbf{r}) d\mathbf{r} = K^{\alpha\beta} S_{\beta\alpha}$$

- idempotency (orthogonality of states)

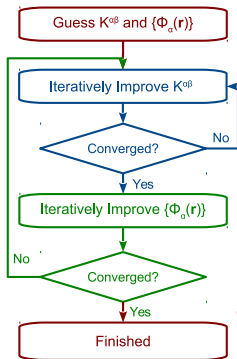
$$\begin{aligned} \rho^2(\mathbf{r}, \mathbf{r}') &= \int \rho(\mathbf{r}, \mathbf{r}'') \rho(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'' \\ &= \sum_{nm} \psi_n(\mathbf{r}) f_n \int \psi_n(\mathbf{r}'') \psi_m(\mathbf{r}'') d\mathbf{r}'' f_m \psi_m(\mathbf{r}') \\ &= \sum_{nm} \psi_n(\mathbf{r}) f_n \delta_{nm} f_m \psi_m(\mathbf{r}') = \rho(\mathbf{r}, \mathbf{r}') \end{aligned}$$

$$\begin{aligned} \rho^2(\mathbf{r}, \mathbf{r}') &= \phi_\alpha(\mathbf{r}) K^{\alpha\gamma} \int \phi_\gamma(\mathbf{r}'') \phi_\delta(\mathbf{r}'') d\mathbf{r}'' K^{\delta\beta} \phi_\beta(\mathbf{r}') \\ \Rightarrow K^{\alpha\beta} &= K^{\alpha\gamma} S_{\gamma\delta} K^{\delta\beta} \end{aligned}$$

# Linear-Scaling DFT

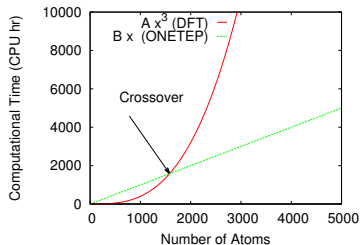
Initial guesses based on pseudoatomic orbitals for  $\{\Phi_\alpha(\mathbf{r})\}$  and non-SC solution of  $H_{\text{orb}}$  for atomic densities

Outer loop: Optimise total energy wrt  $\{\Phi_\alpha(\mathbf{r})\}$ , minimising wrt  $K^{\alpha\beta}$  at each step



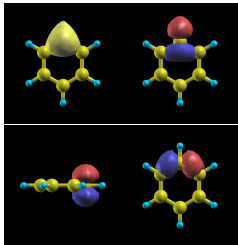
Inner loop: Optimise total energy wrt  $K^{\alpha\beta}$  for fixed  $\{\Phi_\alpha(\mathbf{r})\}$  (constraints of normalisation and idempotency)

Output energy, forces, populations etc. Can post-process for eigenstates if req'd.



Optimise kernel  $K^{\alpha\beta}$  and spatial form of  $\phi_\alpha(\mathbf{r})$  in underlying basis: No need for eigenstates!

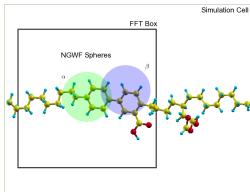
## NGWFs



Minimal basis of local orbitals optimised in-situ, systematic wrt real & recip-space cutoffs

## FFT Box Approximation

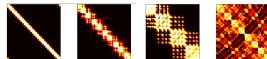
Local  $\phi_\alpha \Rightarrow$  moving FFT box



Strictly  $O(N)$   $H_{\alpha\beta}$  and  $n(\mathbf{r})$  evaluation

## Sparse Matrix Algebra

Excellent parallelisation and load balance



Adaptive Kernel Optimisation  
Purification / Penalty / LNV

$O(N)$  matrix algebra and kernel optimisation

## Main Goals

Controllable accuracy wrt variational parameters: equivalent to plane waves

Computational effort linear-scaling with system size: all parts  $O(N)$

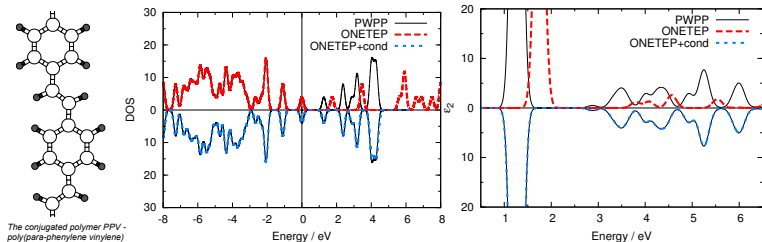
High parallel efficiency: strong-scaling to thousands of cores

Vacuum is 'free'

www.onetep.org; CK Skylaris, PD Haynes, AA Mostofi and MC Payne, J. Chem. Phys. 122, 084119 (2005)  
NDM Hine, PD Haynes, AA Mostofi, C-K Skylaris, MC Payne, Comput. Phys. Commun. 180, 1041 (2009)

# Unoccupied states and Optical Spectra

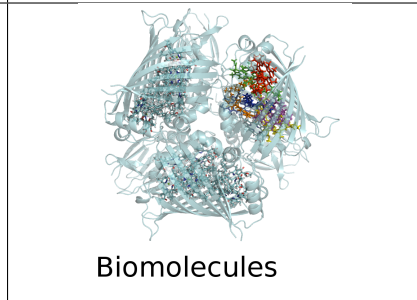
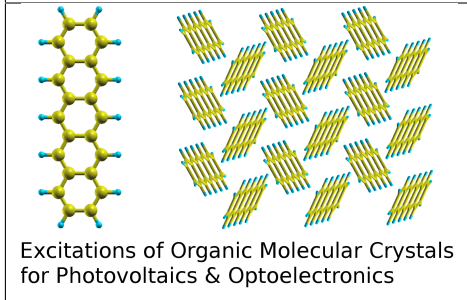
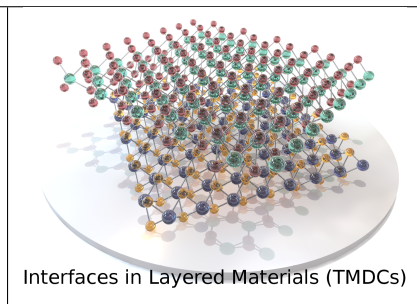
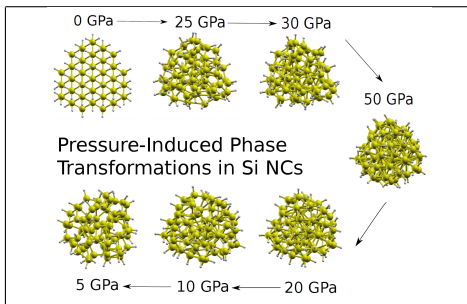
- Unoccupied states (and hence optical spectra) are not well-represented in the valence NGWF representation:



- Construct new set of NGWFs  $\chi_\alpha(\mathbf{r})$  and new 'conduction state' kernel  $K_{\{C\}}^{\alpha\beta}$  to describe  $\psi_C$ ; Project out and shift valence states so that conduction states are lowermost
- Optimised conduction NGWFs can describe all localised states of a molecule (but not vacuum states)
- However, limitations of DFT mean bandgaps underestimated. TDDFT can improve this for small systems and localised excitations

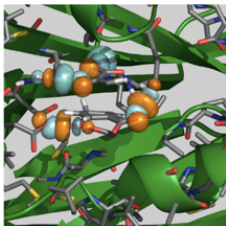
L. E. Ratcliff, N.D.M. Hine, P.D. Haynes, Phys. Rev. B **84**, 165131 (2012)

# Recent Applications

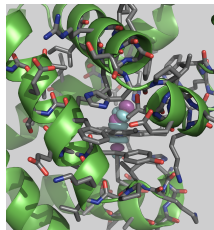


# Fully 'Ab Initio' Biomolecular Simulations

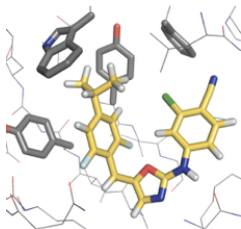
Images: D. J. Cole, Cambridge



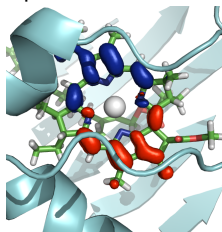
Transition Searching State in Enzymes



Protein-ligand binding in metalloproteins



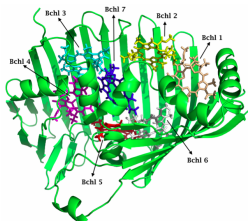
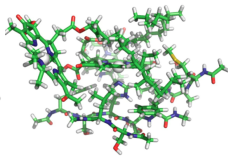
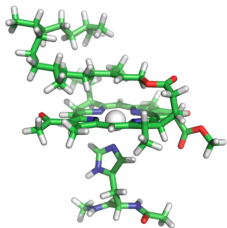
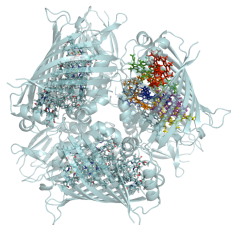
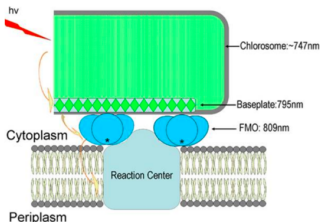
Parameterisation of classical force fields



Theoretical spectroscopy of pigment-protein complexes

# Energy Transport in the FMO Complex

Fenna Matthews Olson Pigment-Protein Complex: widely-studied paradigm for quantum coherent transport



Pigments held in place via non-bonded interactions with the protein.

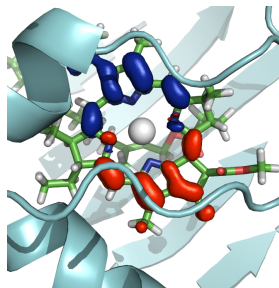
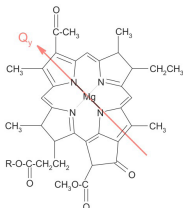
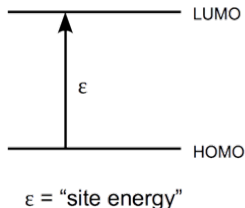
⇒ Local environment 'tunes' site energies.

# Quantum Coherent Transport

Evidence of quantum coherent energy transfer in FMO: may explain near 100% photon-to-electron conversion rate.

Electronic excitation transfer through FMO often modelled by parameterising a Hamiltonian of the form:

$$H = \sum_i \epsilon_i |i\rangle \langle i| + \sum_{i \neq j} J_{ij} |i\rangle \langle j|$$



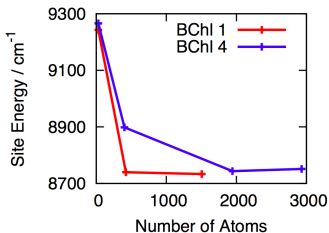
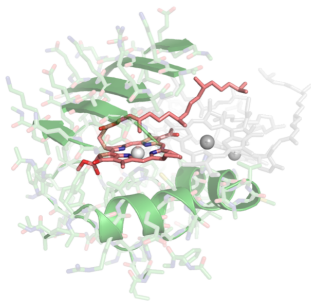
- Optimise NGWFs to describe valence states
- Optimise second set of NGWFs to describe low energy unoccupied states
- Calculate matrix elements corresponding to allowed optical transitions in joint basis, via Fermi's Golden Rule
- Project out the contribution to the absorption spectrum from the Bchl site of interest

Ratcliff, Hine, Haynes, Phys. Rev. B, **84**, 165131 (2011).



# Site Energy Convergence

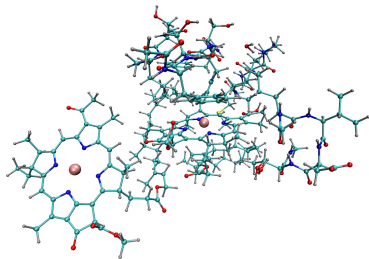
Trimeric structure, each monomer containing 7-8 bacteriochlorophyll pigments.  
How large a system do we need to study to obtain accurate (relative) site energies?



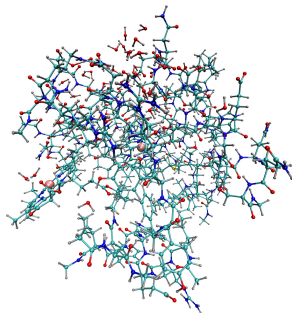
Resulting systems are 1600-2200 atoms (largest includes 6 BChla pigments, 92 protein residues, and 25 water molecules). Calculations can also be performed on whole monomer (>7000 atoms).

# Site Energy Convergence

BChl1 model systems: inclusion of protein environment



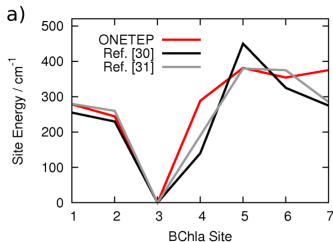
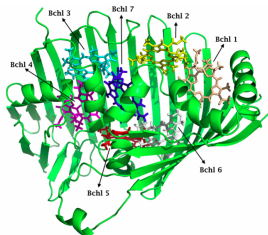
**562 atoms**  
10 Å radius



**1646 atoms**  
15 Å radius

# Calculated Site Energies

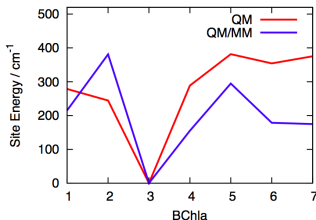
Good agreement between site energies and those obtained by careful empirical fitting to experimental absorption data [30,31];



Identification of Bchl3 as the lowest energy “exit” pigment fits with alignment in membrane.

D. J. Cole, A. W. Chin, N. D. M. Hine, P. D. Haynes and M. C. Payne, *J. Phys. Chem. Lett.* 4, 4206 (2013).

NB: Poor agreement with QM/MM:



# Couplings

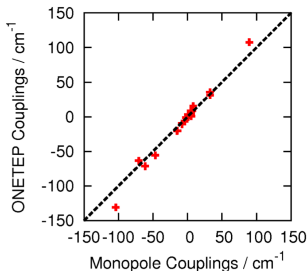
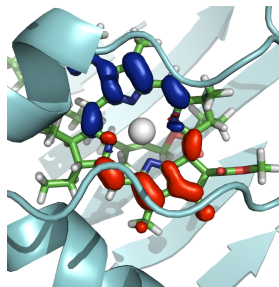
For pigments with no orbital overlap, energy transfer is mediated by Coulombic coupling between transition densities:

$$J_{ij} = \frac{1}{\epsilon} \int d\mathbf{r} \phi_{10}^{(i)}(\mathbf{r}) \rho_{10}^{(j)}(\mathbf{r})$$

$$\rho_{10}^{(j)}(\mathbf{r}) = \psi_0^{(j)*}(\mathbf{r}) \psi_1^{(j)}(\mathbf{r})$$

ONETEP couplings close to those from fitted classical point charge models.

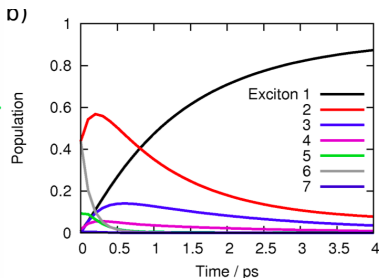
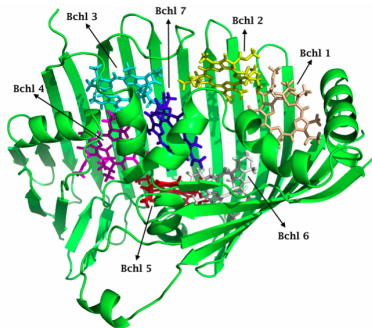
NB: Empirical parameter  $\epsilon = 4$  has to be introduced to account for dielectric screening of protein environment



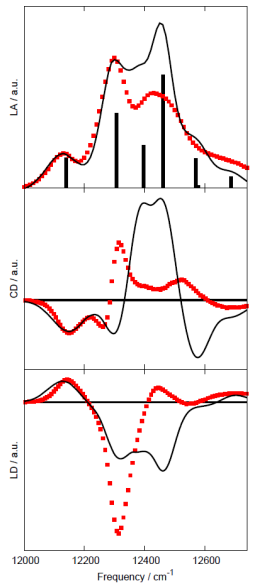
# Energy Transport in FMO

BChla	1	2	3	4	5	6	7
1	12444	-131	5	-7	9	-20	-11
2	-131	12410	36	8	1	15	3
3	5	36	12165	-56	0	-10	7
4	-7	8	-56	12454	-64	-20	-71
5	9	1	0	-64	12547	108	-1
6	-20	15	-10	-20	108	12519	31
7	-11	3	7	-71	-1	31	12540

Full Hamiltonian can be solved for dynamics of excitons:  
 Exciton created on Bchl1 relaxes down to Bchl3 in  $\sim 5$ ps  
 Rigid shift  $\Delta\omega = 3710\text{cm}^{-1}$  applied to all site energies to align with experimental spectrum



# Optical Spectra



- Master equation techniques to produce Optical Absorption, Linear Dichroism and Circular Dichroism Spectra. Inhomogeneous disorder by averaging over realisations with site energies individually broadened by Gaussian distribution.
- Fair agreement reasonable over much of the range: near-degeneracy delocalises exciton states and boosts dipole.
- Hints that couplings of very nearby sites may not be adequate
- Can investigate effect of individual mutations on site energies to elucidate the role of the backbone: specific H-bond donors red shift by up to  $130\text{cm}^{-1}$

LS-DFT: D. J. Cole, A. W. Chin, N. D. M. Hine, P. D. Haynes and M. C. Payne, *J. Phys. Chem. Lett.* 4, 4206 (2013).  
Rigidity Analysis: A. S. Fokas, D. J. Cole, A. W. Chin, *Photosynthesis Research.* 122, 275 (2014)

# Predictive Power of Theoretical Spectroscopy

- Original goal was to predict spectrum for Fenna-Matthews-Olson complex fully *ab initio*
- NB: Bacteriochlorophyll in DFT is not even Green!
- Ended up with just two empirical parameters:  $\Delta\omega$ ,  $\epsilon_r$  to generate reasonable agreement
- How can we improve the predictive power without resorting to further empiricism?
- Linear-Response Time-Dependent DFT (Casida Formalism) allows solution for individual excitations, treats interaction of electron and hole explicitly
- Significantly improved-accuracy for localised (Frenkel-like) excitations
- Traditional methods generally not applied to anything bigger than small molecules
- Experimental results almost always for pigments in solvent: solvatochromic shifts
- LR-TDDFT does not handle charge-transfer states well!

How best to take environment into account, given that it is complex, dynamic, polarisable?

# Linear-Response TDDFT

Casida Formalism: 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

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

and

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

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.

$\omega$ -dependence of  $f_{xc}$  is generally dropped (eg ALDA)



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

Express as an optimisation problem in terms of TDDFT operator  $\mathbf{A}$  (self-consistent)

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

Differentiating the Rayleigh-Ritz value yields an energy gradient:

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

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

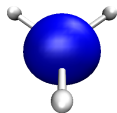
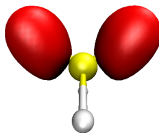
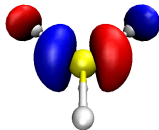
$$q_{cv} = (\epsilon_c^{\text{KS}} - \epsilon_v^{\text{KS}})x_{cv} + \left( V_{\text{SCF}}^{\{1\}} \left[ \rho^{\{1\}} \right] \right)_{cv}$$

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

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

- 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  $\{\chi_\beta\}$



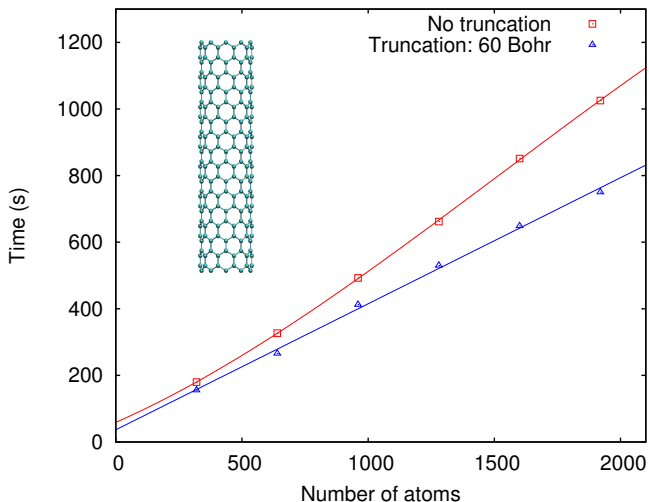
## The TDDFT gradient in $\{\phi\}$ and $\{\chi\}$ representation

The TDDFT gradient  $\mathbf{q} = \mathbf{A}\mathbf{x}$  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

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



- Time taken for a single conjugate gradient iteration vs. system size (64 cores)

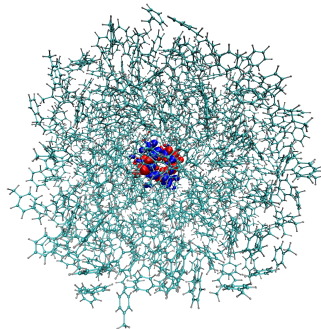
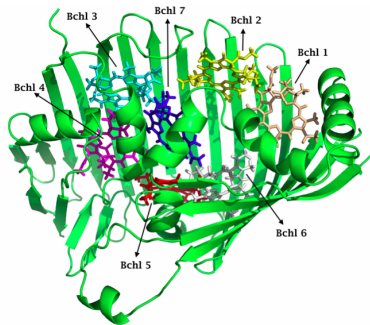
# Environmental effects

- Implicit solvent? Change  $\epsilon$  of environment (screening by polarisable medium)
- Classical explicit solvent? Add classical counter-ions?
- Fully quantum-mechanical explicit solvent?
- Hard to define cavity, prevents delocalisation of electron/hole
- Provides influence of polar environment but does not screen the transition densities
- Charge transfer excitations will swamp the excitations of interest
- Sampling???

How can we add a QM description of the environment while still studying only a subsystem?

# Simulating the whole FMO complex

Do we need to extract individual pigment sites? Full system  $\sim 8000$  atoms.



Largest LR-TDDFT simulation ever performed?

# Conclusions

Efficient framework for calculating low energy excited states in systems containing thousands of atoms

- 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. System sizes of hundreds to thousands of atoms seem to be necessary in pigment-protein complexes

LS-DFT methods with ONETEP applied to biomolecules can be hugely valuable in situations where QM/MM is insufficient, eg:

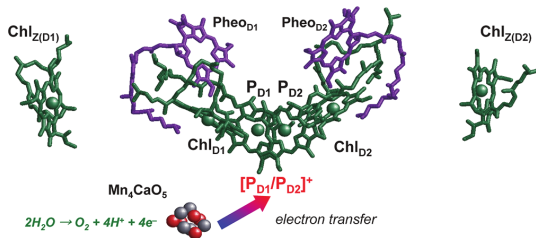
- Showing how PPCs create and protect quantum coherence enabling high-efficiency energy transport
- Explaining how protein structure influences site energies
- Predicting effect of low-energy vibrational modes on site energies
- Explaining how structure makes energy transport robust against long-timescale dynamics

# Future Work

More rigorous error control to understand propagation of errors from snapshots to spectra

- Localisation of excitations
- Truncation of kernels
- Functional error (ALDA vs CAM-B3LYP)
- Sampling of molecule & solvent configurations
- Convergence wrt to range of environment

Can we learn to replicate protection of quantum coherence in devices?  $\Rightarrow$  Influence on design of organic photovoltaic materials?



Future work: Understand energy transport and charge separation in Photosystem II



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