

Linear-Scaling Linear-Response Time-Dependent Density Functional Theory in ONETEP

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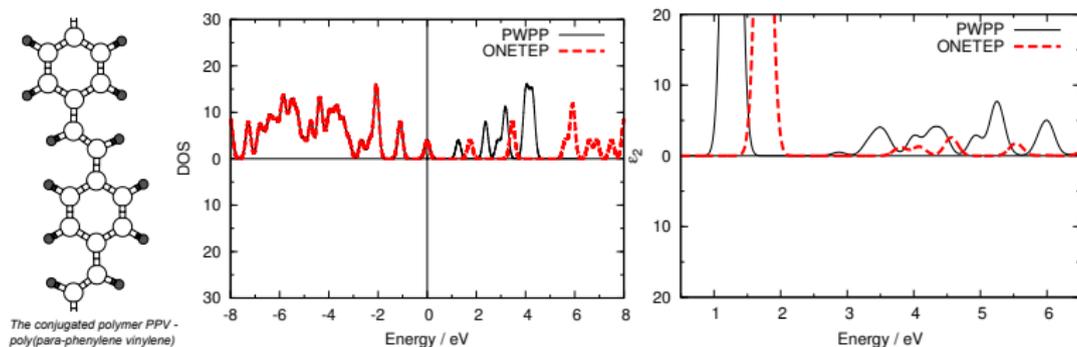
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ONETEP Masterclass 2019



Unoccupied states and Optical Spectra

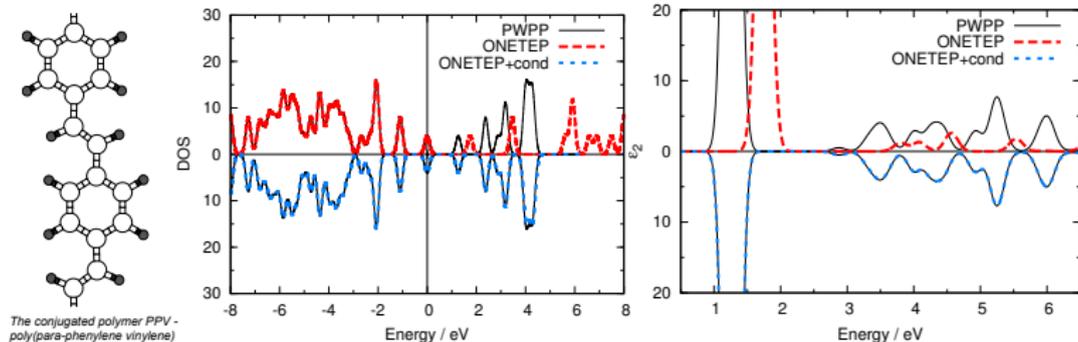
- Unoccupied states (and hence optical spectra) are not well-represented in the valence NGWF representation:



- Construct new set of NGWFs and new 'conduction state' kernel to describe ψ_C ; Project out and shift valence states so that conduction states are lowermost

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 ψ_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)

LR-TDDFT with LS-DFT

Drop ω -dependence of f_{xc} for local functionals (eg ALDA)

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

Make Tamm-Dancoff approximation (ignore de-excitations): $\mathbf{Y} = 0$; $\mathbf{B} = 0$;
Can then use iterative eigensolvers.

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

Write $\mathbf{q} = \mathbf{A}\mathbf{X}$ via effective transition density $\rho^{\{1\}}(\mathbf{r})$ and KS eigenvalues

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

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

T. J. Zuehlsdorff, N. D. M. Hine, [...], P. D. Haynes, J. Chem. Phys. 139 064104 (2013).

Express transition density via NGWFs & response density matrix $\mathbf{P}^{\{1\}}$

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

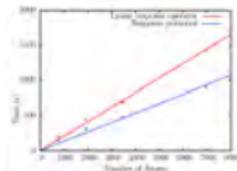
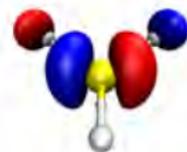
Hole / Electron each well-described by $\{\phi_\alpha(\mathbf{r})\}$ / $\{\chi_\alpha(\mathbf{r})\}$ respectively

TDDFT gradient $\mathbf{q} = \mathbf{A}\mathbf{x}$ in $\{\phi\}$ / $\{\chi\}$ 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 $O(N)$ for each ω if \mathbf{P} 's truncated.

Optimise multiple $\{\mathbf{P}_i\}$ simultaneously
→ Scales as $O(N) \times O(N_\omega)$ with small $O(N) \times O(N_\omega^2)$ orthogonalisation step



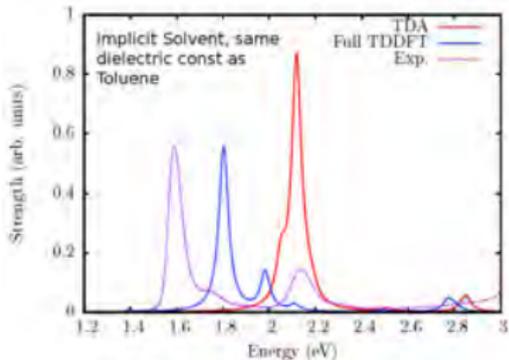
Full TDDFT & Response Kernel Truncation

TDA often inadequate - use full TDDFT with Tziper approach. Define $\mathbf{p} = \mathbf{X} - \mathbf{Y}$ and $\mathbf{q} = \mathbf{X} + \mathbf{Y}$, then minimise Tziper functional:

$$\omega_{\min} = \min_{(\mathbf{p}, \mathbf{q})} \Omega_{\text{Tzip}}(\mathbf{p}, \mathbf{q})$$

$$= \min_{(\mathbf{p}, \mathbf{q})} \frac{(\mathbf{p}^\dagger \quad \mathbf{q}^\dagger) \begin{pmatrix} \mathbf{A} - \mathbf{B} & \mathbf{0} \\ \mathbf{0} & \mathbf{A} + \mathbf{B} \end{pmatrix} \begin{pmatrix} \mathbf{p} \\ \mathbf{q} \end{pmatrix}}{|\mathbf{p}^\dagger \mathbf{q} + \mathbf{q}^\dagger \mathbf{p}|}$$

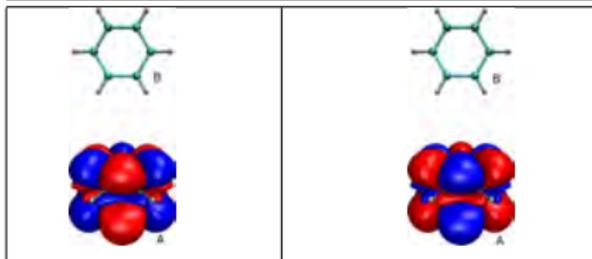
Significant improvement in accuracy (still requires rigid shift for semi-local functionals)



Still have $O(N_\omega)$ scaling, and $N_\omega \propto N^2$ when long-ranged charge transfer excitations are present

Truncation of response kernel can be used to eliminate spurious charge-transfer states

Fully dense $P^{\{1\}}$	$P^{\{1\}}$ on Benzene A
10th excitation:	1st excitation:
$\omega = 5.1950$ eV	$\omega = 5.1953$ eV
$f = 0.177 \times 10^{-6}$	$f = 0.111 \times 10^{-6}$



Atom-centred NGWFs provide natural means to constrain excitations to subspaces

⇒ significant increase in efficiency

Can reintroduce subsystem coupling perturbatively with final subspace

diagonalisation: $\mathbf{P}_{\text{tot}}^{\{1\}} = \sum_I \alpha_I \mathbf{P}_{A_I}^{\{1\}} + \sum_J \beta_J \mathbf{P}_{B_J}^{\{1\}}$

Environmental effects

Except in gas phase, optically-interesting systems are rarely isolated

- Implicit solvent? Change ϵ 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
- Requires extensive sampling - how much?

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

LR-TDDFT Keywords

LR-TDDFT is enabled by setting `TASK=LR_TDDFT`. The LR-TDDFT calculation mode reads in the density kernels and NGWFs of a converged ground state and conduction state calculation, so the `.dkn`, `.dkn_cond`, `.tightbox_ngwfs` and `.tightbox_ngwfs_cond` files all need to be present. The most important keywords in a TDDFT calculation are:

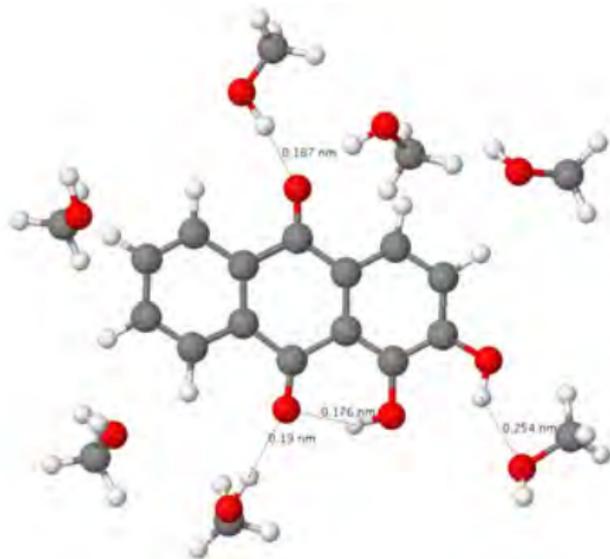
- `lr_tddft_rpa`: T/F.
Boolean, default `lr_tddft_rpa=F`. If set to T, the code performs a full TDDFT calculation without relying on the simplified Tamm-Dancoff approximation.
- `lr_tddft_num_states`: n
Integer, default `lr_tddft_num_states = 1`.
The keyword specifies how many excitations we want to converge. If set to a positive integer n, the TDDFT algorithm will converge the n lowest excitations of the system.
- `lr_tddft_cg_threshold`: x
Real, default `lr_tddft_cg_threshold = 10-6`.
The keyword specifies the convergence tolerance on the sum of the n TDDFT excitation energies. If the sum of excitation energies changes by less than x in two consecutive iterations, the calculation is taken to be converged.
- `lr_tddft_maxit_cg`: n
Integer, default `lr_tddft_maxit_cg = 60`.
The maximum number of conjugate gradient iterations the algorithm will perform.

LR-TDDFT Keywords

- `lr_tddft_triplet`: T/F ; Boolean, default `lr_tddft_triplet = F`.
Flag that decides whether the `lr_tddft_num_states = n` states to be converged are singlet or triplet states.
- `lr_tddft_write_kernels`: T/F ; Boolean, default `lr_tddft_write_kernels = T`.
If the flag is set to T, the TDDFT response density kernels are printed out at every conjugate gradient iteration. These files are necessary to restart a LR_TDDFT calculation.
- `lr_tddft_restart`: T/F ; Boolean, default `lr_tddft_restart = F`.
If the flag is set to T, the algorithm reads in `lr_tddft_num_states = n` response density kernels in .dkn format and uses them as initial trial vectors for a restarted LR_TDDFT calculation.
- `lr_tddft_restart_from_TDA`: T/F ; Boolean, default F.
If the flag is set to T and `lr_tddft_RPA = T`, the code will read in already converged density kernels and use them as a starting guess for a full TDDFT calculation such that $\mathbf{P}_i^{\{p\}} = \mathbf{P}_i^{\{q\}} = \mathbf{P}_i^{\{1\}}$.
- `lr_tddft_init_random` T/F; Boolean, default T.
By default, initial TDDFT eigenvector guesses are random matrices. If `lr_tddft_init_random=F`, the code instead uses the n minimum energy pure Kohn-Sham transitions as initial guesses.
- `lr_tddft_kernel_cutoff`: x ; Real, default `lr_tddft_kernel_cutoff = 1000a_0`.
Keyword sets a truncation radius on all response density kernels in order to achieve linear scaling computational effort with system size.

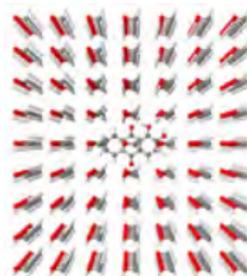
Solvent-Solute interactions

Alizarin — prototypical red dye exhibiting strong solvatochromic shift.
Widely-used implicit solvent methods do not correctly describe solvatochromic shift, particularly when there are specific solvent-solute interactions:

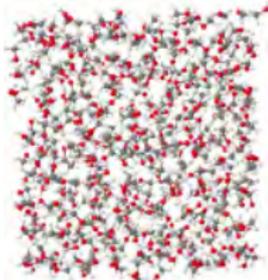


Workflow:

1) Generate large box with solvent and solute:

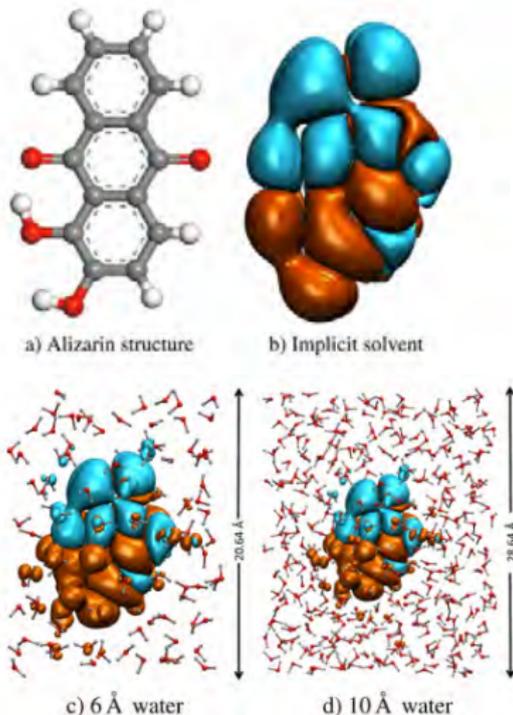


- 2) Determine force-field parameters
- 3) Heat to required temperature over 20ps
- 4) Equilibrate density over 200ps
- 5) Fix box size and re-equilibrate over 40ps
- 6) Generate trajectory of snapshots eg 200, spaced by 10ps each to avoid correlations



Molecular Dynamics calculations can be used to generate an ensemble of configurations

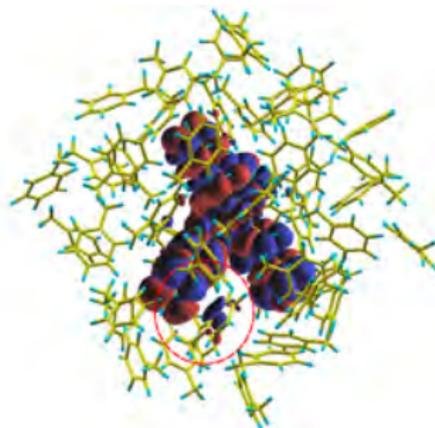
Alizarin: Solvatochromic shifts



S_1 excitation stays mostly localised but fractions of electron and hole delocalise to water

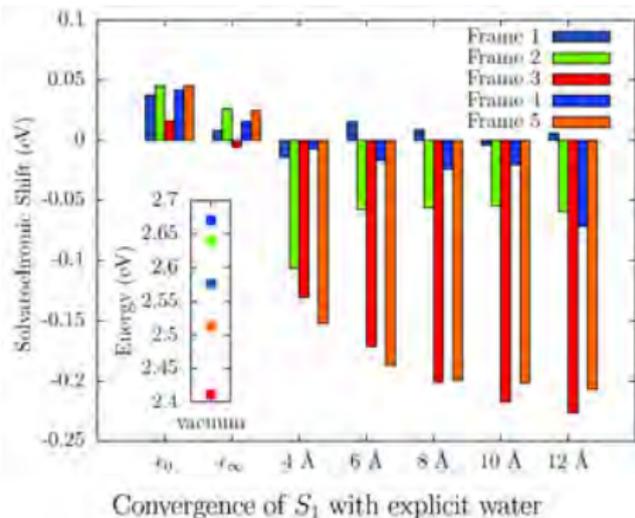
Multiple contributions to solvatochromism:

- Solute configuration influenced by solvent
- Electrostatic potential from dipoles of solvent configuration
- Delocalisation of transition to environment
- Shift due to specific interactions
 - Hydrogen bonding
 - π - π stacking in aromatic solvents

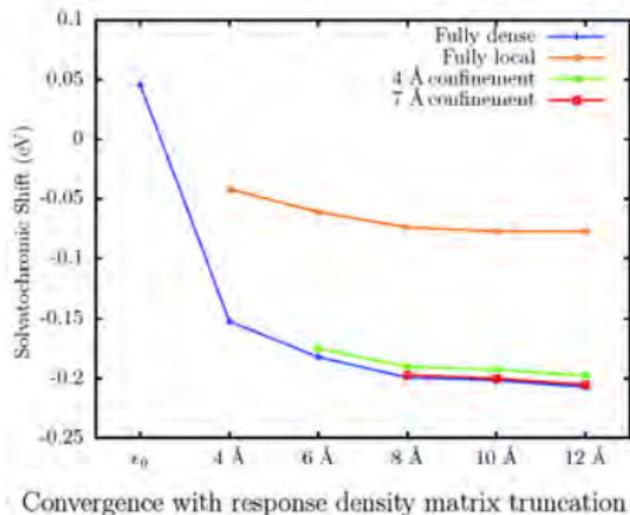


Alizarin: Solvatochromic shifts

Convergence of excitation energy with respect to amount of explicit environment can be slow:



Fortunately, our kernel truncation approach converges more rapidly with amount of water included in the response density kernel:



⇒ Feasible to converge solvatochromic shift with explicit solvent cluster

T. J. Zuehlsdorff, P. D. Haynes, F. Hanke, M. C. Payne, N. D. M. Hine, J. Chem. Theory Comput. 12, 1853 (2016).

DPMes - DPTIPS: Convergence with sampling

Candidate molecules derived from pentacene, exhibiting Singlet Fission

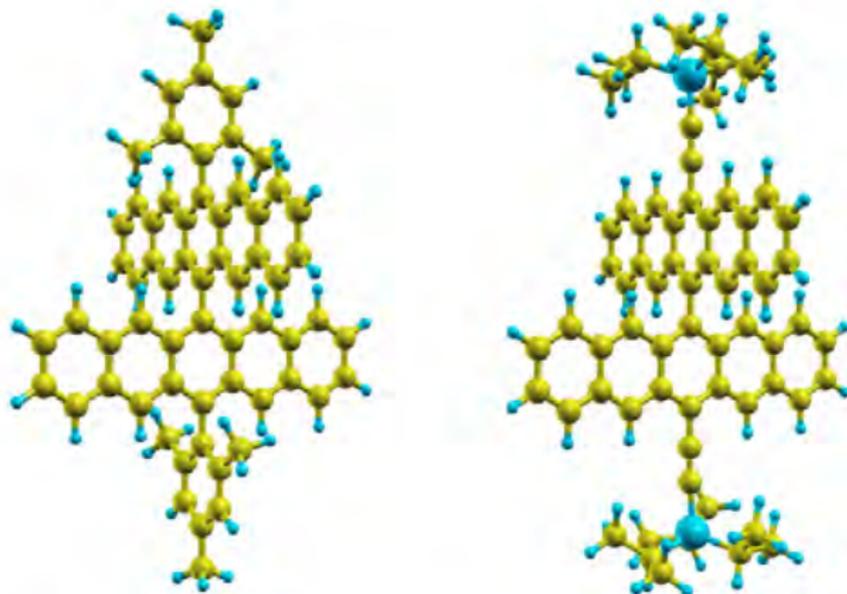
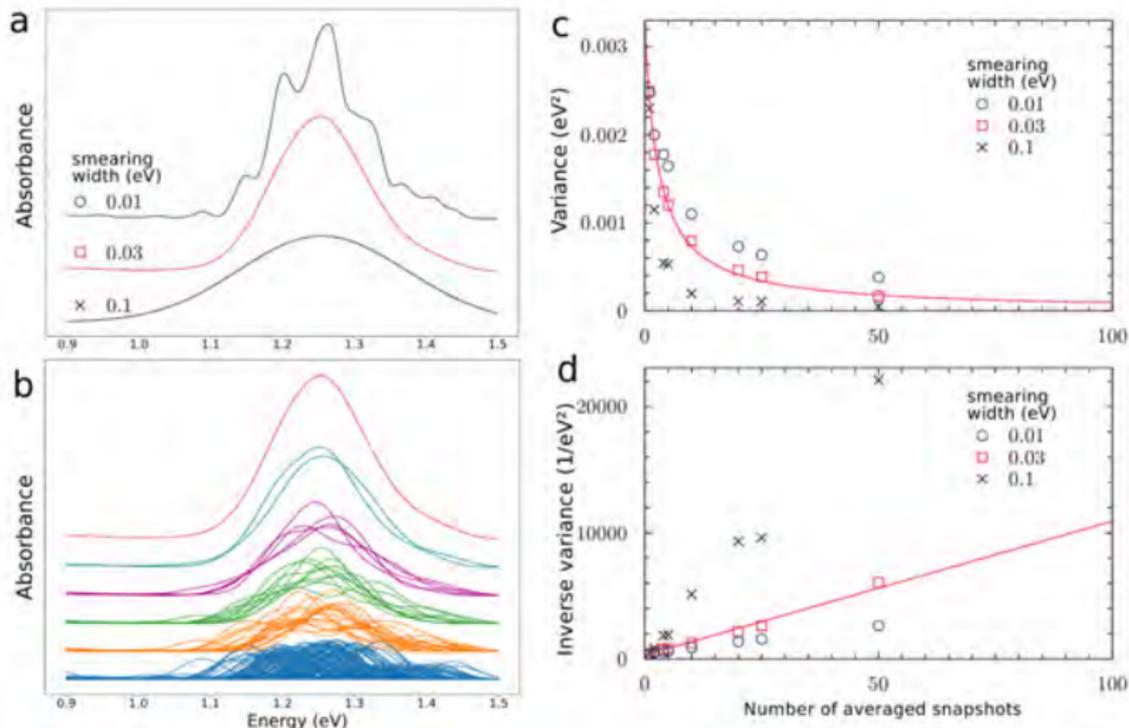


Figure 6.1: DP-Mes (left) and the second dimer DP-TIPS (right), where the mesityl side groups are replaced by triisopropylsilylethynyl. The TIPS side groups contain silicon atoms and link to the pentacene molecules via $C\equiv C$ triple bonds.

Can we converge with respect to number of snapshots, even in a large, flexible system?

DPMes - DPTIPS: Convergence with sampling

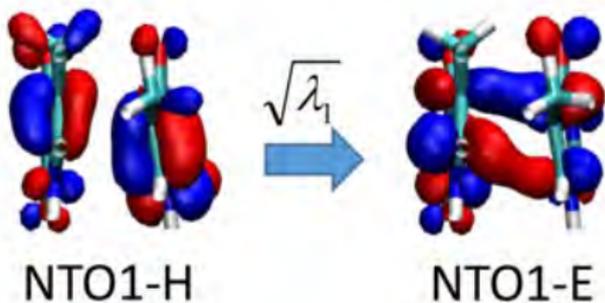
Reasonably quick convergence (40-80 snapshots) to well-defined λ_{\max} for a single excitation



a) DPMES Spectra in ACN; b) Convergence with respect to number of snapshots (1,5,10,20,50,100); c,d) variance extrapolated to 100 snapshots to estimate error on final result

Quantified Natural Transition Orbital Analysis

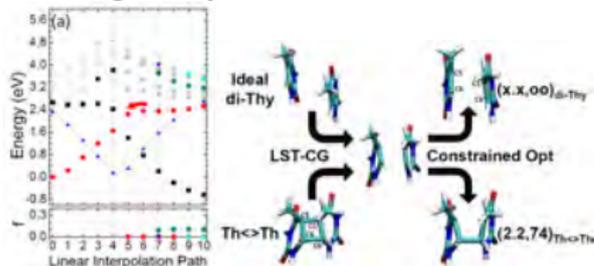
Large systems \rightarrow many low-lying excitations
 How to follow excitation as geometry varies?
 QNTO analysis allows adiabatic PES to be
 “reconnected” by matching transition origins.



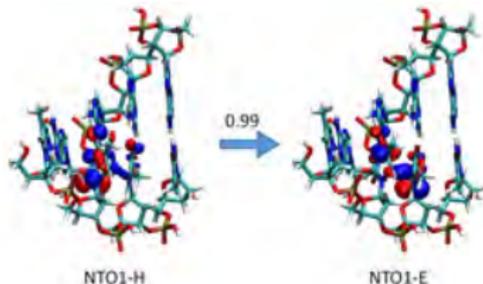
Find \mathbf{U} , \mathbf{V} matrices that diagonalise transition density matrix.

$$P_i^{\{1\}} = \bar{\mathbf{U}}_i \mathbf{D}_i \bar{\mathbf{V}}_i$$

Identify states involved in funnel resulting in thymine dimerisation



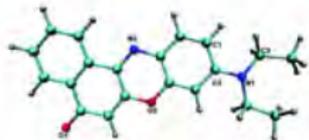
Mechanism then verified in much larger model (4 base pairs of DNA)



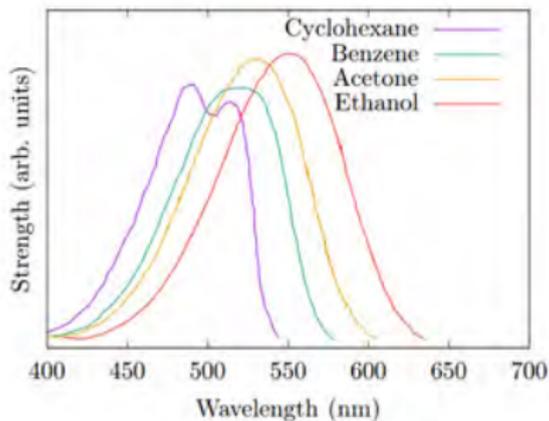
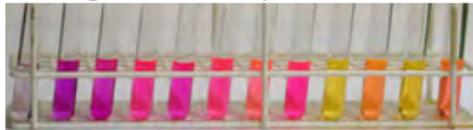
J.-H. Li, T. J. Zuehlsdorff, M. C. Payne and N. D. M. Hine, *Phys. Chem. Chem. Phys.*, 17, 12065 (2015)
 J.-H. Li, T. J. Zuehlsdorff, M. C. Payne and N. D. M. Hine, upcoming (2015)

Colour Prediction

Nile Red (9-diethylamino-5-benzo[*a*]phenoxazinone)

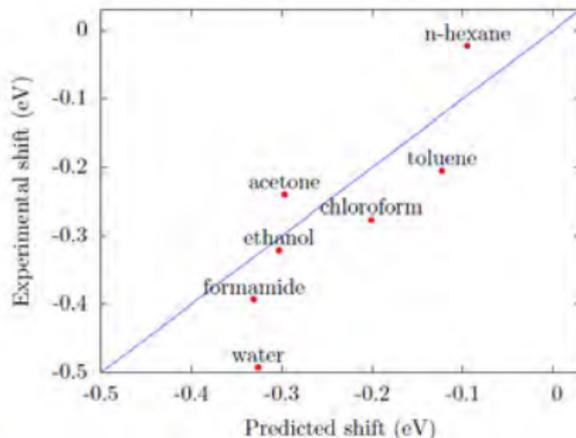


Strong solvent-dependent shift:



Solvatochromic shifts are not well-predicted by electrostatic models

$$\Delta E_{\text{solv}} \left(\frac{\epsilon_{\text{opt}} - 1}{2\epsilon_{\text{opt}} + 1} \right)^{-1} = B \left(\frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_{\text{opt}} - 1}{\epsilon_{\text{opt}} + 2} \right) \left(\frac{\epsilon_{\text{opt}} - 1}{2\epsilon_{\text{opt}} + 1} \right)^{-1} + A$$



Inadequate for colour prediction

Colour Prediction

Nile Red (9-diethylamino-5-benzo[α]phenoxazinone)



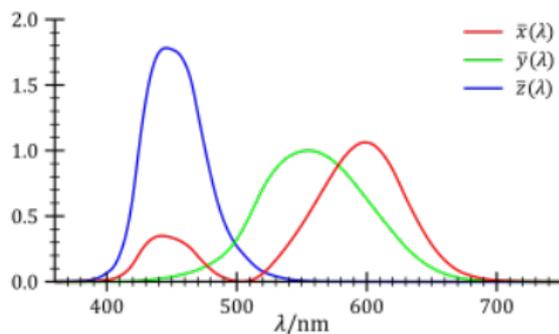
Can we use the absorption spectrum to directly predict the colour?

$$I_{\text{trans}} = I_0(\lambda)e^{-\kappa(\lambda)x}$$

$\kappa(\lambda)$: absorption coefficient;
 $I_0(\lambda)$: spectrum of illuminant;

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = N \int I_{\text{trans}}(\lambda) \begin{pmatrix} \bar{x}(\lambda) \\ \bar{y}(\lambda) \\ \bar{z}(\lambda) \end{pmatrix} d\lambda$$

$\bar{x}(\lambda)$, $\bar{y}(\lambda)$, $\bar{z}(\lambda)$: Tristimulus color matching functions



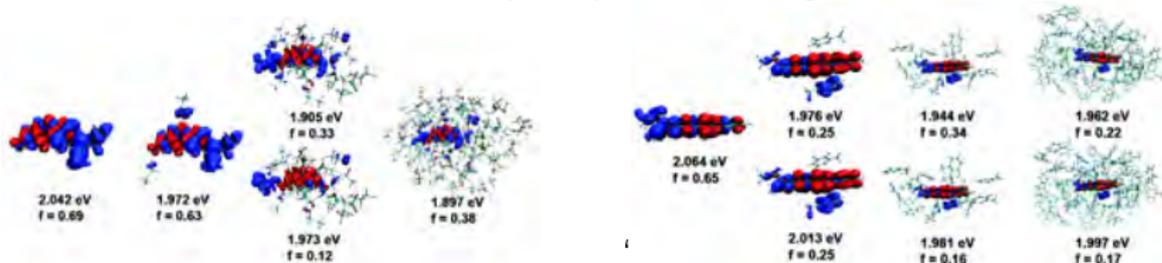
X, Y, Z can be transformed into RGB.

CAM-B3LYP calculations (NWChem code) with well-converged 6-311++G** Gaussian basis set:

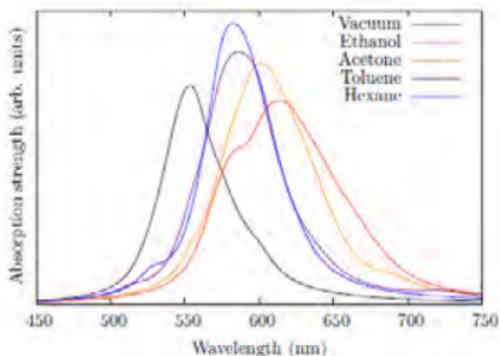
Highly-accurate PES but far too expensive for sampling of solvent configurations

Nile Red Colour Prediction

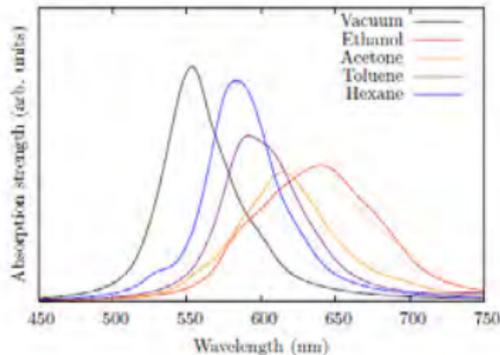
Run long explicit solvent MD. Reparameterise dihedral angle ϕ from AMBER default to match PES of twists. Extract many samples and average.



Ethanol: hydrogen bonded configurations; Toluene: $\pi - \pi$ stacked configuration.



b) Implicit solvent



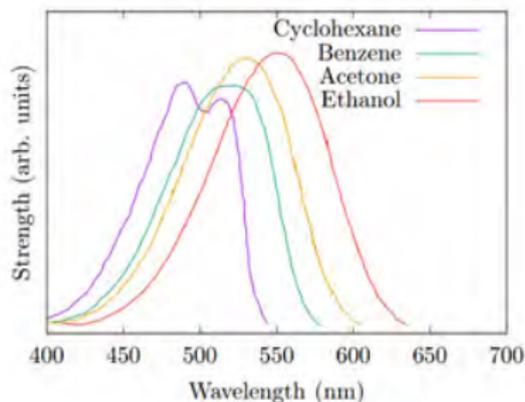
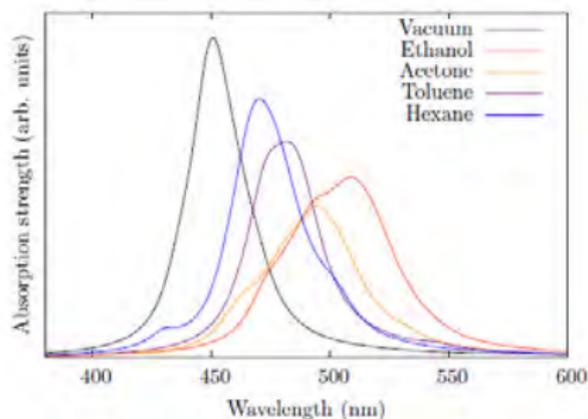
a) Explicit Solvent

T. J. Zuehlsdorff, P. D. Haynes, M. C. Payne, and N. D. M. Hine, *J. Chem. Phys.* 146, 124504 (2017)

Nile Red Colour Prediction

Spectral warping: calculate CAM-B3LYP spectrum (NWChem), apply transformation to PBE spectrum to reproduce PES of CAM-B3LYP:

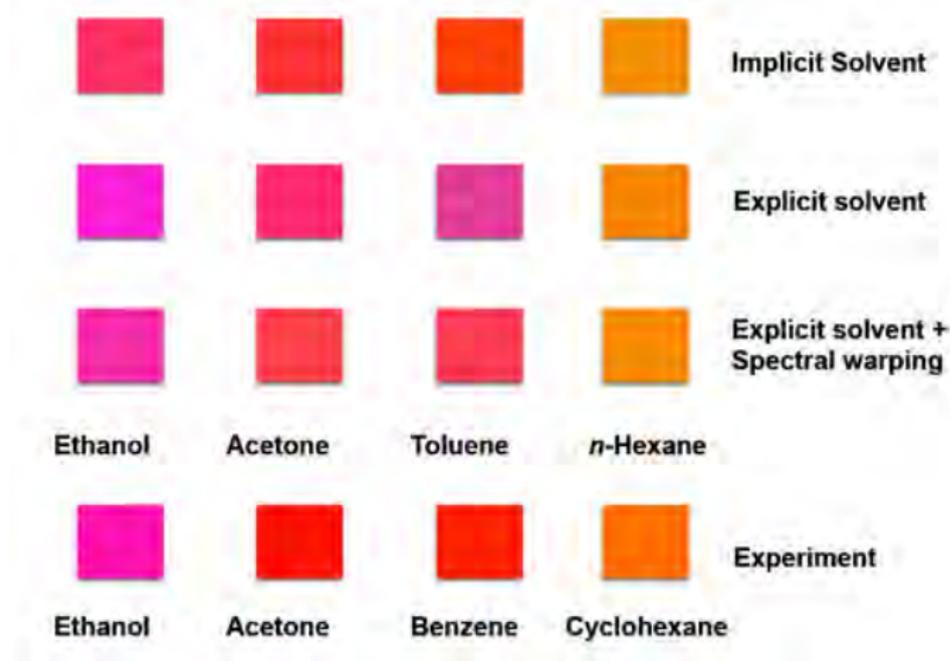
$$\omega_i^{\text{trans}} = \omega_i + \beta + \alpha\phi_i^2$$



T. J. Zuehlsdorff, P. D. Haynes, M. C. Payne, and N. D. M. Hine, *J. Chem. Phys.* 146, 124504 (2017)

Nile Red Colour Prediction

Sufficient accuracy for useful predictive power:



Very good match!

T. J. Zuehlsdorff, P. D. Haynes, M. C. Payne, and N. D. M. Hine, *J. Chem. Phys.* 146, 124504 (2017)

Conclusions

- Linear Scaling DFT with ONETEP (www.onetep.org) allows DFT with plane-wave-equivalent accuracy for simulations of systems comprising hundreds to tens of thousands of atoms
- In theoretical UV/vis spectroscopy, inclusion of both an explicit representation of the environment and a high-accuracy functional are crucial to obtaining quantitative accuracy on predicted spectra.
- **Long-term vision:** simulation toolset enabling computational discovery with true predictive power for nanomaterials spectroscopy.

Acknowledgements



- Funding: EPSRC
- Computing: Warwick CSC (Tinis), Cambridge HPC Facility (Darwin), EPCC (ARCHER)

