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


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

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

Traditional Kohn-Sham DFT:

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

Minimise w.r.t. \( \rho \) with \( \rho = \sum_n |\psi_n(r)|^2 \) for orthogonal single-particle states \( \psi_n(r) \):

Becomes Eigenvalue problem:

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

where \( \hat{H}_{KS}[\rho(r)] = -\frac{1}{2} \nabla^2 + V_{\text{eff}}[\rho(r)] \)

seeks eigenstates \( \psi_n(r) \), eigenvalues \( \varepsilon_n \).

\[ \text{Computational Time (CPU hr)} \]

\[ \text{Number of Atoms} \]

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:

\[ \rho(r, r') = \sum_n \psi_n(r) f_n \psi_n(r') \]

Introduce localised nonorthogonal support functions:

\[ \psi_n(r) = \sum_\alpha M_n^\alpha \phi_\alpha(r) \]

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:

\[ \rho(r, r') = \sum_{\alpha\beta} \phi_\alpha(r) K^{\alpha\beta} \phi_\beta(r') \]
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: $\rho(r, r') \propto \exp -\gamma |r - r'|$ 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)

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

- Idempotency (orthogonality of states)

$$\rho^2(r, r') = \int \rho(r, r'') \rho(r'', r') dr''$$

$$= \sum_{nm} \psi_n(r) f_n \int \psi_n(r'') \psi_m(r'') dr'' f_m \psi_m(r')$$

$$= \sum_{nm} \psi_n(r) f_n \delta_{nm} f_m \psi_m(r') = \rho(r, r')$$

$$\rho^2(r, r') = \phi_\alpha(r) K^{\alpha\gamma} \int \phi_\gamma(r'') \phi_\delta(r'') dr'' K^{\delta\beta} \phi_\beta(r')$$

$$\Rightarrow K^{\alpha\beta} = K^{\alpha\gamma} S_{\gamma\delta} K^{\delta\beta}$$
Initial guesses based on pseudoatomic orbitals for \( \{ \Phi_\alpha(r) \} \) and non-SC solution of \( H_{\alpha\beta} \) for atomic densities

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

Guess \( K_{\alpha\beta} \) and \( \{ \Phi_\alpha(r) \} \)

Iteratively Improve \( K_{\alpha\beta} \)

Converged?

No

Yes

Iteratively Improve \( \{ \Phi_\alpha(r) \} \)

Converged?

No

Yes

Finished

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

Optimise kernel \( K^{\alpha\beta} \) and spatial form of \( \phi_\alpha(r) \) 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 $n(r)$ 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’
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 $K_{\alpha\beta}^{\{c\}}$ 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

Recent Applications

Pressure-Induced Phase Transformations in Si NCs

Interfaces in Layered Materials (TMDCs)

Excitations of Organic Molecular Crystals for Photovoltaics & Optoelectronics

Biomolecules
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:

\[ H = \sum_i \varepsilon_i |i\rangle\langle i| + \sum_{i \neq j} J_{ij} |i\rangle\langle j| \]

- 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

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.


NB: Poor agreement with QM/MM:

D. J. Cole, A. W. Chin, N. D. M. Hine (Warwick)
**Couplings**

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

\[
J_{ij} = \frac{1}{\varepsilon} \int dr \phi_{10}^{(i)}(r) \rho_{10}^{(j)}(r)
\]

\[
\rho_{10}^{(j)}(r) = \psi_{0}^{(j)*}(r) \psi_{1}^{(j)}(r)
\]

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

NB: Empirical parameter $\varepsilon = 4$ has to be introduced to account for dielectric screening of protein environment.
Energy Transport in FMO

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 doners red shift by up to 130 cm\(^{-1}\).


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: $\Delta \omega, \varepsilon_r$ 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

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

where

\[
A_{cv,c'v'}(\omega) = \delta_{cc'}\delta_{vv'}(\varepsilon_{c'}^{KS} - \varepsilon_{v'}^{KS}) + K_{cv,c'v'}(\omega)
\]

\[
B_{cv,c'v'}(\omega) = K_{cv,v'c'}(\omega)
\]

and

\[
K_{cv,c'v'}(\omega) = \left< \psi_c^{KS} \psi_v^{KS} \left| \frac{1}{|r - r'|} + f_{xc}(r, r', \omega) \right| \psi_{c'}^{KS} \psi_{v'}^{KS} \right>
\]

Tamm-Dancoff approximation: \( Y = 0; \ B = 0; \ AX = \omega X \)

Use iterative eigensolvers: Only the action \( q = Ax \) 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 \( A \) (self-consistent)

\[
\omega = \min_x \frac{x^\dagger Ax}{x^\dagger x}
\]

Differentiating the Rayleigh-Ritz value yields an energy gradient:

\[
\frac{\partial \omega}{\partial x} = 2Ax - [x^\dagger Ax]x
\]

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

\[
q_{cv} = (\varepsilon_c^{KS} - \varepsilon_v^{KS})x_{cv} + \left( V_{SCF}^{\{1\}} \rho^{\{1\}} \right)_{cv}
\]

where \( \rho^{\{1\}}(r) = \sum_{cv} \psi_c^{KS}(r)x_{cv} \psi_v^{KS}(r) \)
Transition density matrix in ONETEP

\[ \rho^{\{1\}}(r) = \sum_{cv} \psi_{c}^{\text{KS}}(r) \chi_{cv} \psi_{v}^{\text{KS}}(r) \]

\[ = \sum_{\alpha\beta} \chi_{\alpha}(r) P^{\{1\}}_{\alpha\beta} \phi_{\beta}(r) \]

- Express the transition density in terms of density matrix \( P^{\{1\}} \)
- Hole well described by \( \{\phi_{\alpha}\} \)
- Electron well described by \( \{\chi_{\alpha}\} \)
- \( \rho^{\{1\}}(r) \) well described by \( \{\phi_{\alpha}\} \) and \( \{\chi_{\beta}\} \)
The TDDFT gradient in $\{\phi\}$ and $\{\chi\}$ representation

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

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

- Fully $O(N)$ if all involved density matrices are truncated
- Can be used to generate a gradient for conjugate gradient algorithm
- Multiple excitations: Optimise $P_i^{1}$ 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 $\varepsilon$ 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 $P^{(1)}$ 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? ⇒ Influence on design of organic photovoltaic materials?

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

- ONETEP Developers Group: J. Dziedzic, P. Haynes, N. Hine, A. Mostofi, M. Payne, C. Skylaris
- Funding: EPSRC, Leverhulme, Winton Programme for the Physics of Sustainability
- Computing: ARCHER, Cambridge HPC (DARWIN), STFC Hartree Centre (BlueJoule)

THE UNIVERSITY OF WARWICK