

Towards the calculation of experimental spectra using $O(N)$ DFT

Laura Ratcliff and Peter Haynes



Imperial College
London

Aim

The goal

The calculation of experimental spectra in ONETEP, such as EELS, x-ray and optical spectra.

Why the calculation of spectra is useful

- The **prediction** of experimental results
- Spatial decomposition of spectra to determine the **origin of features**
- The effect on spectra of making **changes to the electronic structure**

Methods for calculating spectra

Time-dependent density-functional theory (TDDFT)

- Good for finite systems
- Complications when applying to periodic systems

Many body perturbation theory and the *GW* method

- Good level of accuracy
- Applicable only to smaller systems

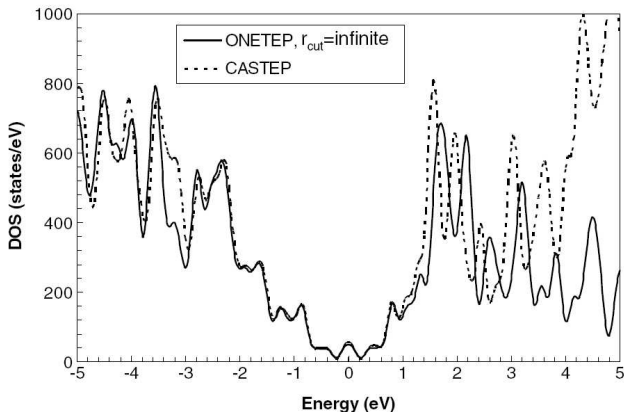
Density-functional perturbation theory (DFPT)

- Less accurate than the *GW* method
- **But** can be applied to **larger systems**

Conduction state methods

Why do we need conduction states?

- For complete **band structures** and **densities of states**
- For correct **spectra**

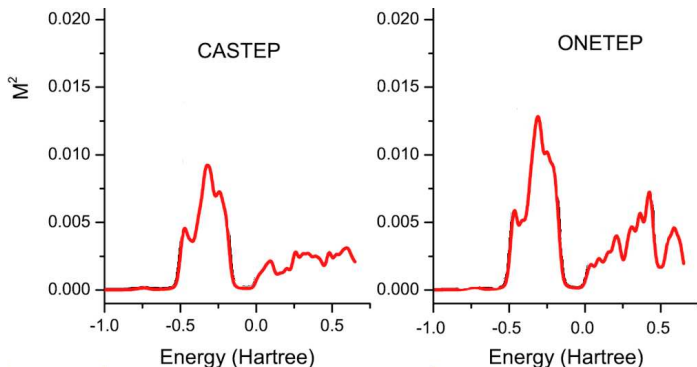


Conduction state methods

Why do we need conduction states?

- For complete **band structures** and **densities of states**
- For correct **spectra**

Example x-ray absorption spectra in CASTEP and ONETEP:



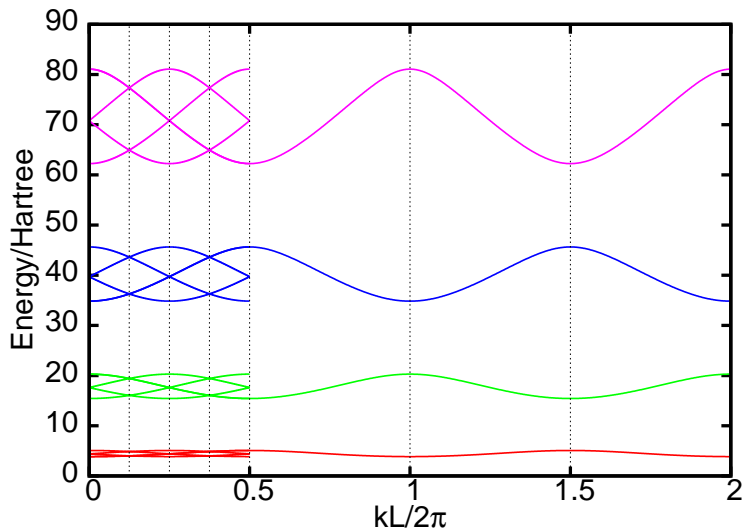
The test program

What does it need to achieve?

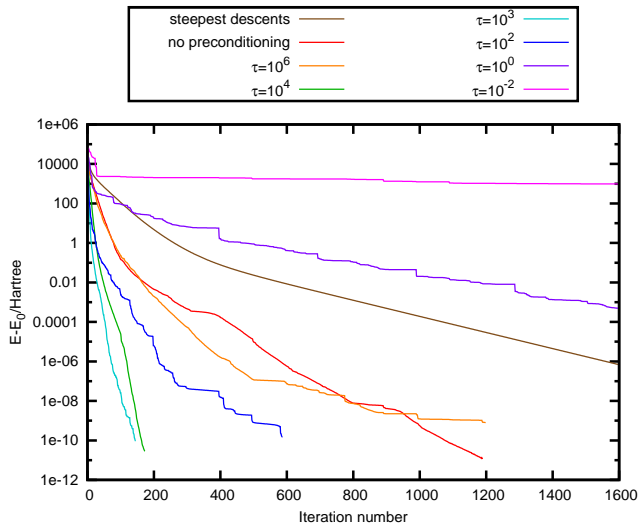
Imitate the **main elements** of ONETEP and be as **simple** as possible:

ONETEP	Test program
3 dimensions conjugate gradients preconditioning psinc basis localized NGWFs DFT	1 dimension conjugate gradients preconditioning B-spline basis extended eigenstates Kronig-Penney potential

The test program



The test program



Conduction state methods

How can we add conduction states?

We want a second non self-consistent calculation following a ground state calculation.

The possible methods

- Folded spectrum method
- Shift invert
- Projectors

The requirements

- Accuracy
- Efficiency
- Scaling

The folded spectrum method

The new eigenvalue equation

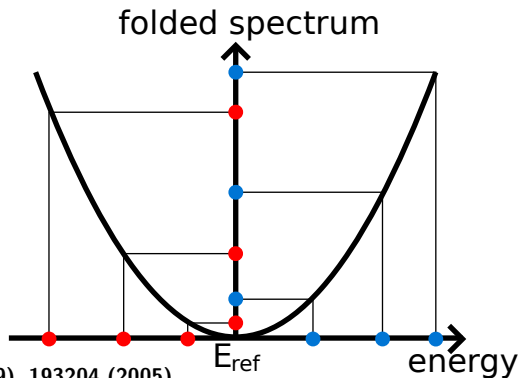
$$(\mathbf{H} - E_{ref}\mathbf{S})\mathbf{S}^{-1}(\mathbf{H} - E_{ref}\mathbf{S})\mathbf{x} = (\epsilon - E_{ref})^2\mathbf{S}\mathbf{x}$$

Advantages

- Known to work e.g. using tight-binding to find Si conduction band minimum [1]

Disadvantages

- Poor condition number
- Need to find good E_{ref}



[1] A.S. Martins et al. *Phys. Rev. B* 72(19), 193204 (2005)

Shift invert

The new eigenvalue equation

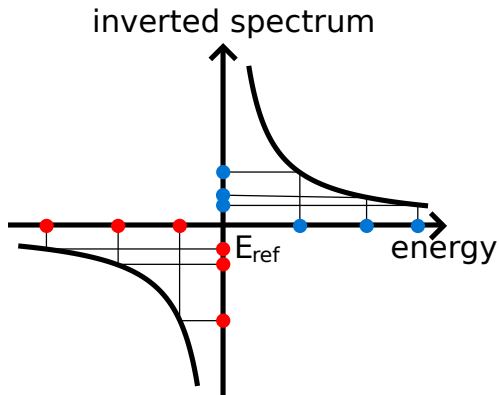
$$\mathbf{S} (\mathbf{H} - E_{ref}\mathbf{S})^{-1} \mathbf{S}\mathbf{x} = \left(\frac{1}{\epsilon - E_{ref}} \right) \mathbf{S}\mathbf{x}$$

Advantages

- Better condition number

Disadvantages

- Need to find good E_{ref}
- Small eigenvalues so rescaled
- 3 different variants



Projectors

The density operator as a projection operator

$$\text{where } \hat{\rho} = \sum_n f_n |\psi_n\rangle \langle \psi_n|$$

The new eigenvalue equation

$$\begin{aligned} (1 - \hat{\rho}) \hat{H} |\psi_n\rangle &= 0 && \text{if } n \text{ is a valence state} \\ &= \epsilon_n |\psi_n\rangle && \text{if } n \text{ is a conduction state} \end{aligned}$$

Advantages

- No use of E_{ref}
- Efficient?

Disadvantages

- Accuracy will be affected by valence calculation

Results

Comparison of the methods

Method	Time taken (s)	Average Number of iterations
Folded spectrum	2.39	181.85
Shift invert 1	2.34	158.13
Shift invert 2	5.48	462.80
Shift invert 3	2.23	169.69
Projection	1.21	35.72

Where each method has an absolute error of less than 10^{-10}

Shift invert equations:

$$\mathbf{S} (\mathbf{H} - E_{ref} \mathbf{S})^{-1} \mathbf{S} \mathbf{x} = \left(\frac{1}{\epsilon - E_{ref}} \right) \mathbf{S} \mathbf{x} \quad (1)$$

$$-\mathbf{S} \left[\mathbf{H} \mathbf{S}^{-1} \mathbf{H} - 2E_{ref} \mathbf{H} + (E_{ref}^2 + \mu^2) \mathbf{S} \right]^{-1} \mathbf{S} \mathbf{x} = - \left(\frac{1}{\epsilon - E_{ref}} \right)^2 \mathbf{S} \mathbf{x} \quad (2)$$

$$-\mathbf{S} (\mathbf{H} - E_{ref} \mathbf{S})^{-1} \mathbf{S} \mathbf{x} = - \left(\frac{1}{\epsilon - E_{ref}} \right) \mathbf{S} \mathbf{x} \quad (3)$$

What next?

ONETEP

In ONETEP everything is represented in terms of the density matrix (DM), with a basis of NGWFs.

The test program

ONETEP	Test program
3 dimensions	1 dimension
conjugate gradients	conjugate gradients
preconditioning	preconditioning
psinc basis	B-spline basis
localized NGWFs	extended eigenstates
DFT	Kronig-Penney potential

NGWFs

How can we add NGWFs to the test program?

- We now want 2 sets of NGWFs
- We can modify the projection method to include NGWFs
- Represent them in terms of B-splines

New definitions

$$\hat{P} = \sum_{n=1}^N |\psi_n\rangle\langle\psi_n| = \sum_{\alpha\beta} |\phi_\alpha\rangle K^{\alpha\beta} \langle\phi_\beta|$$

$$\hat{Q} = \sum_{n=N+1}^M |\psi_n\rangle\langle\psi_n| = \sum_{\alpha\beta} |\chi_\alpha\rangle L^{\alpha\beta} \langle\chi_\beta|$$

Optimizing the new density kernel

Density matrix

- **Idempotent:**

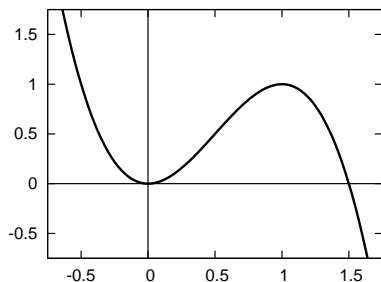
$$\rho^2 = \rho$$

- **Normalised:**

$$N = \text{Tr}[\rho]$$

- **Separable:**

$$\hat{\rho} = \sum_{\alpha\beta} |\phi_\alpha\rangle K^{\alpha\beta} \langle\phi_\beta|$$



Purification transformation

$$\rho_{k+1} = 3\rho_k^2 - 2\rho_k^3$$

The new scheme

1) Optimize the kernel for fixed NGWFs

- **Project the Hamiltonian** using $1 - \hat{P}$, and shift by some reference energy so that all conduction states are lower in energy
- Use **PM** to get the conduction DM

2) Optimize the NGWFs for a fixed kernel:

- Minimize the energy $E = Tr[\hat{Q}\hat{H}]$ wrt the conduction NGWFs
- Use the **projected Hamiltonian** to stay in conduction space
- Use the **LVN purification method** to impose idempotency

3) Repeat

...until converged

Summary and future work

What I've done so far

- Created a 1D test program with a localised basis set and an efficient energy minimization scheme
- Looked at 5 different methods for calculating conduction states
- Implemented a density matrix formalism with optimized NGWFs

What I still have left to do...

- Consider the effects of localization and truncation
- Implement the best conduction state method in ONETEP
- Add the calculation of theoretical spectra

The end!