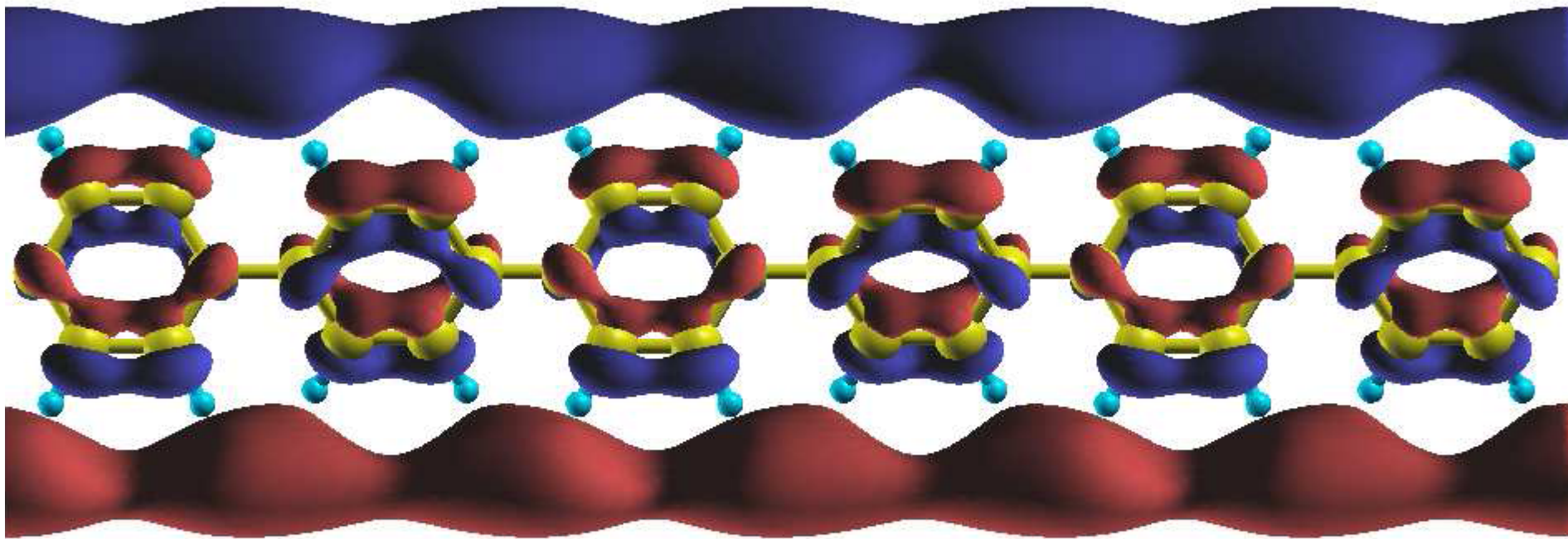
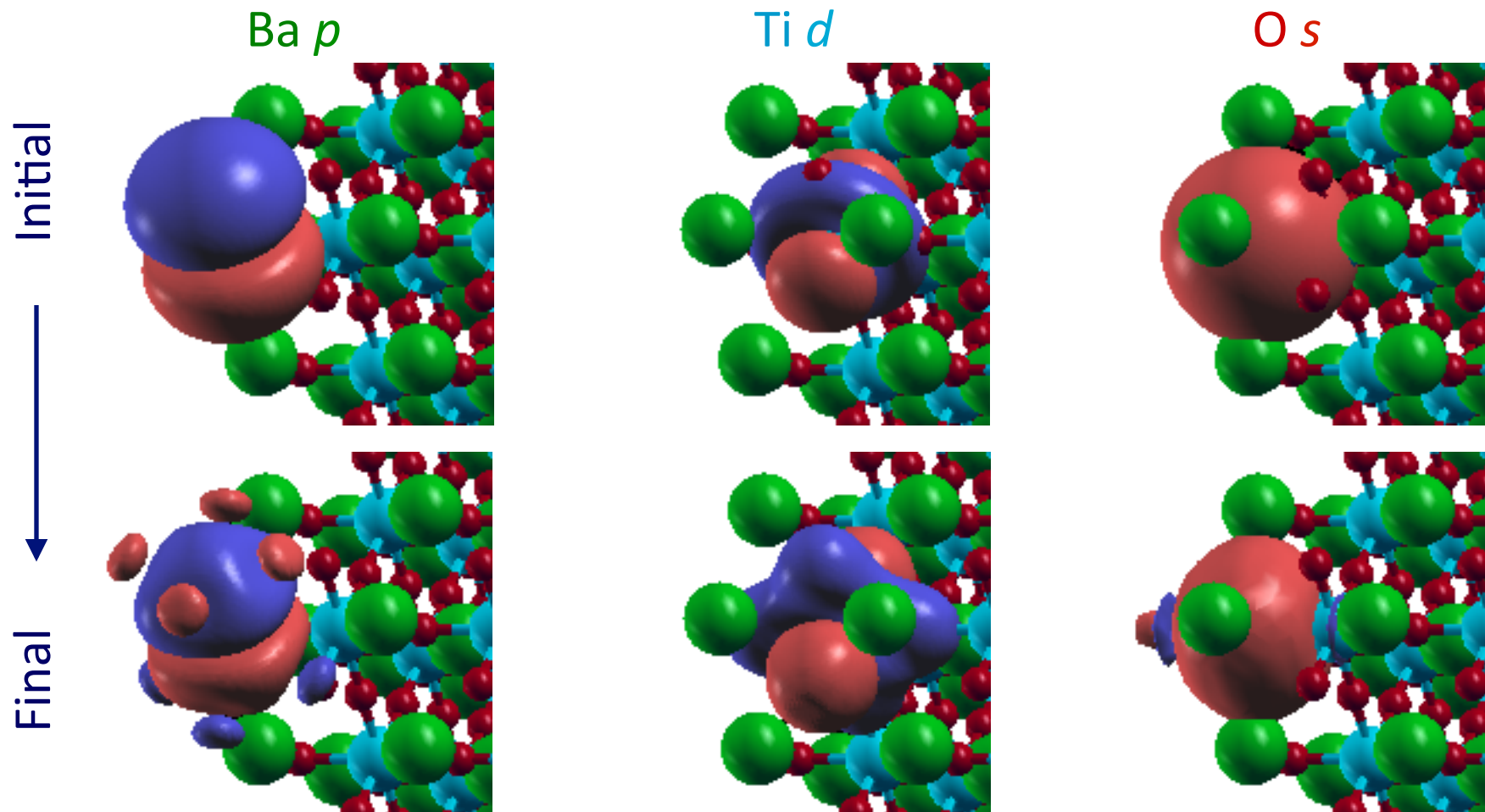


Calculating local orbitals for excited states

Laura Ratcliff, Nick Hine & Peter Haynes

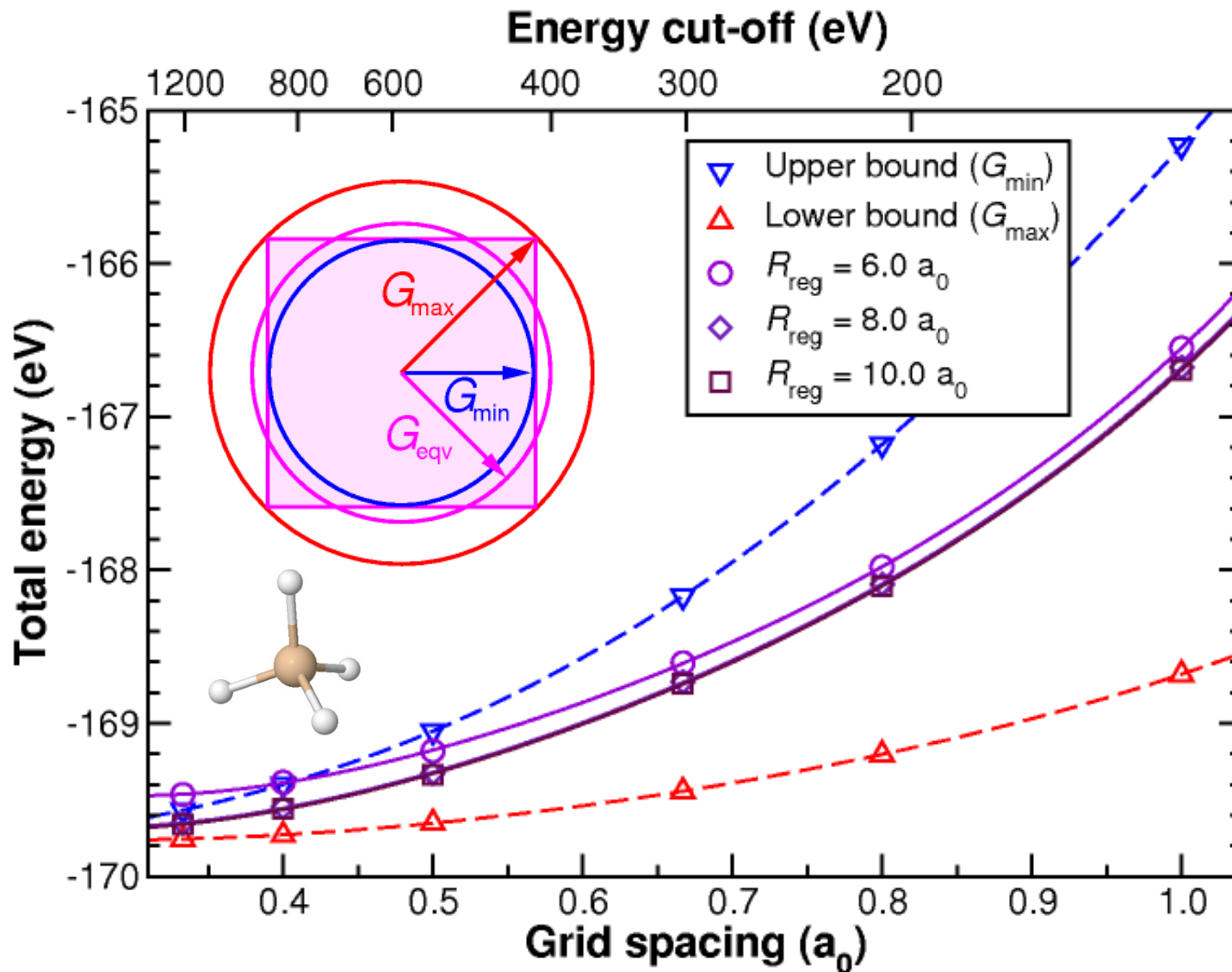


Local orbital optimization

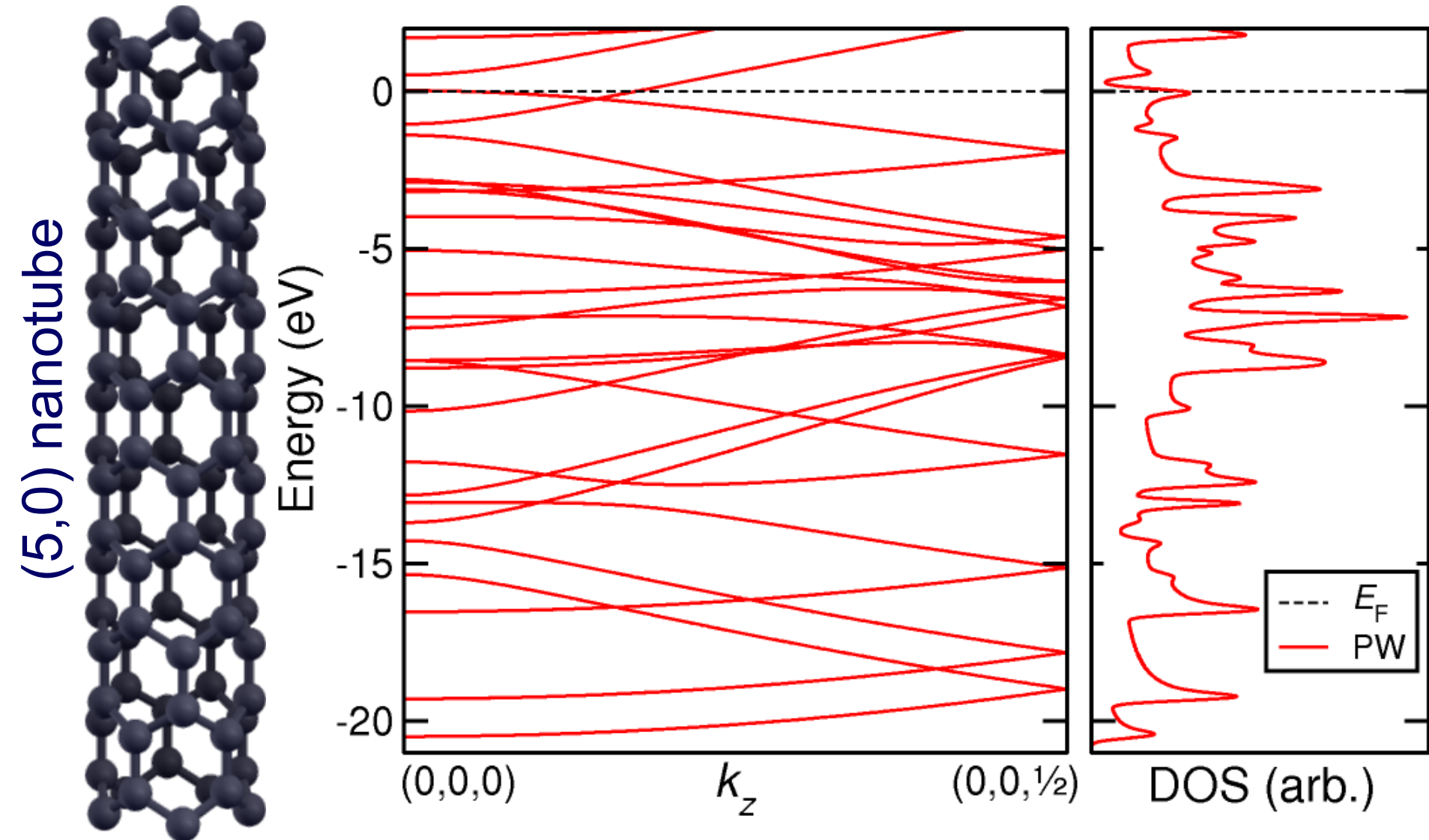


Skylaris, Mostofi, Haynes, Diéguez & Payne, *Phys. Rev. B* **66**, 035119 (2002)
On-site rotation from Foster & Weinhold, *J. Am. Chem. Soc.* **102**, 7211 (1980)

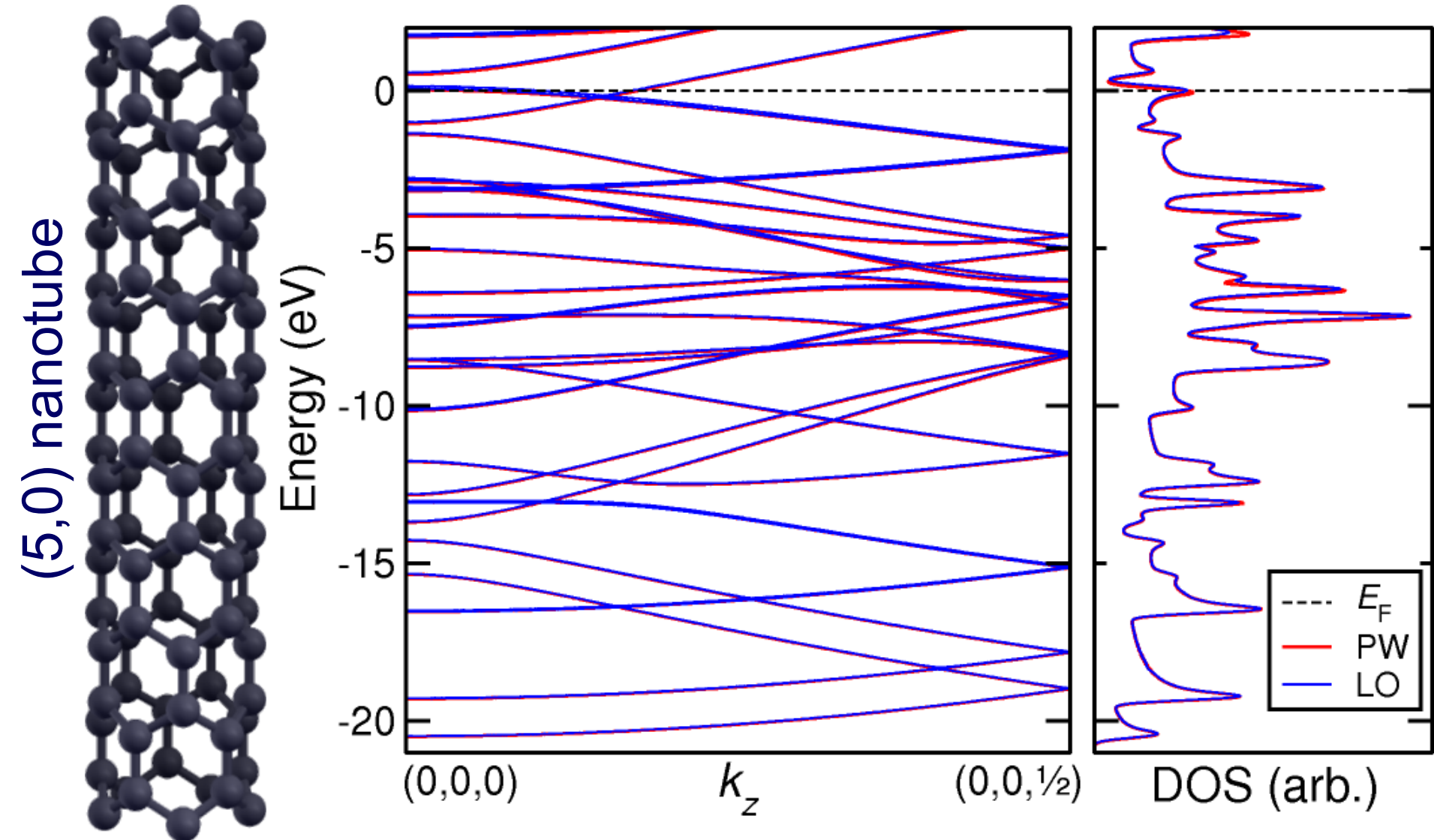
Total energies with plane-wave accuracy



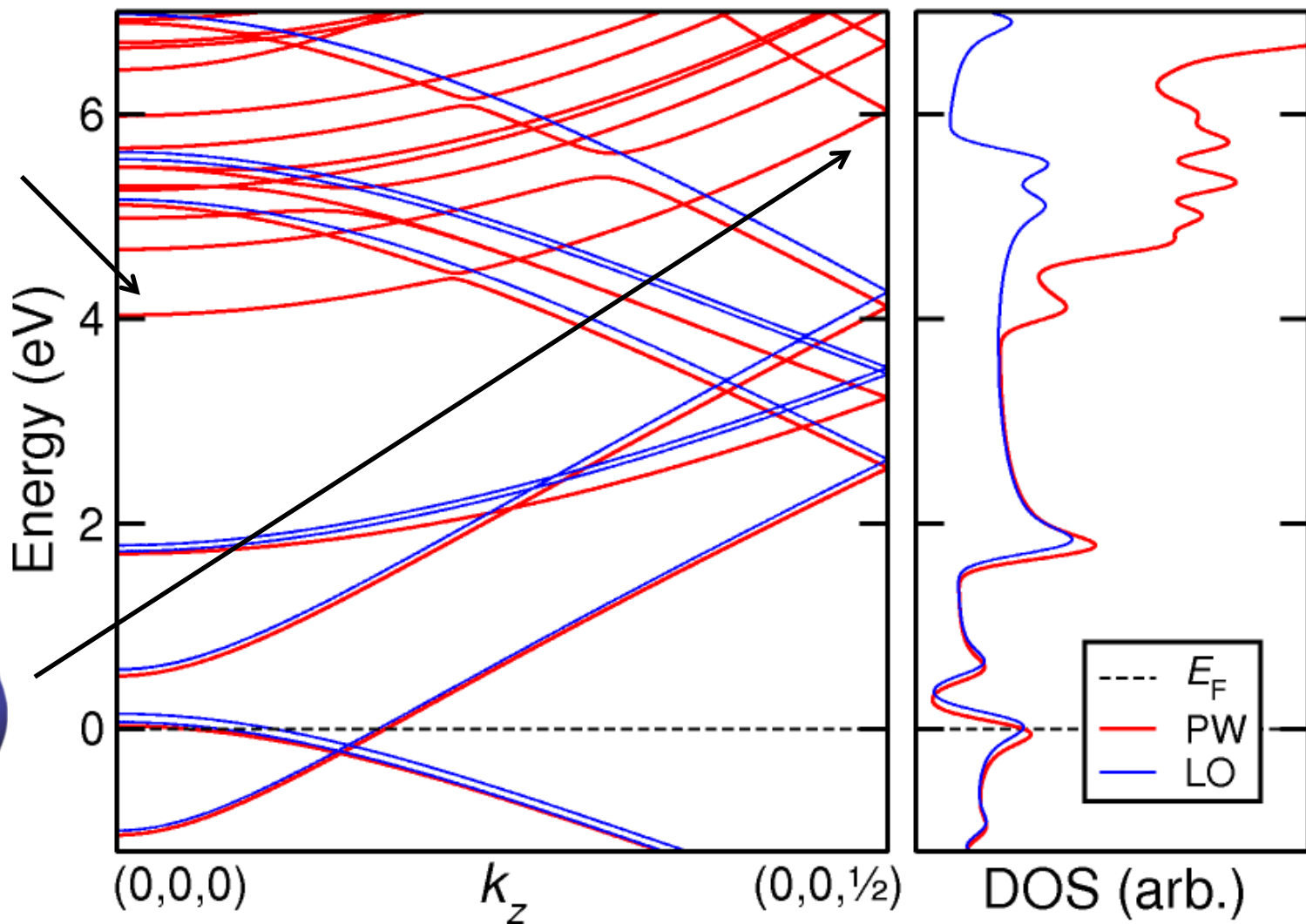
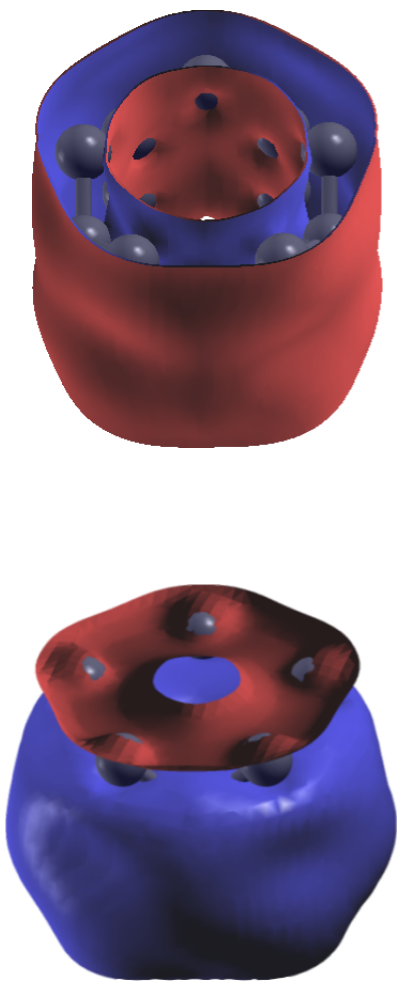
Plane-wave valence band structure



4x 3.7 Å NGWFs / C



Conduction band structure



Calculating unoccupied states

- Ground state DM defines a projection operator:

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

- Use this to define a projected Hamiltonian:

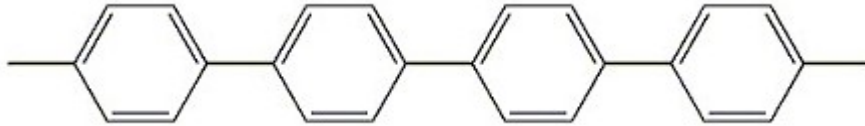
$$\hat{\mathcal{H}} = \left(\hat{H} - \epsilon \hat{1} \right) - \hat{P} \left(\hat{H} - \epsilon \hat{1} \right) \hat{P}$$

- Solve (non-self-consistently) for the new DM:

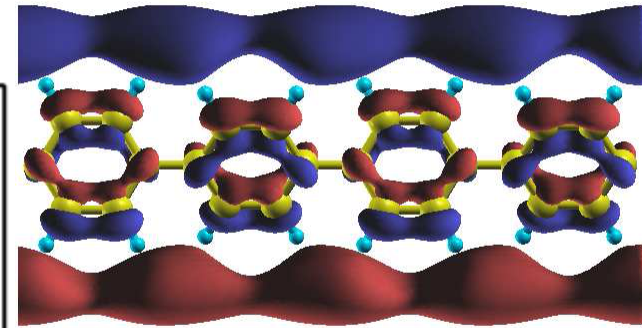
$$\hat{Q} = \sum_{\alpha\beta} |\chi_\alpha\rangle M^{\alpha\beta} \langle\chi_\beta|$$

that minimises $\mathcal{E} = \text{tr} (Q\mathcal{H})$

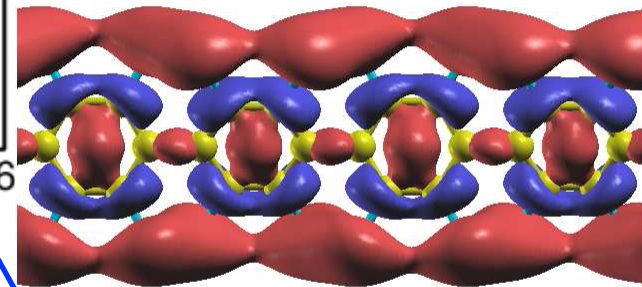
poly(*para*-phenylene) chain



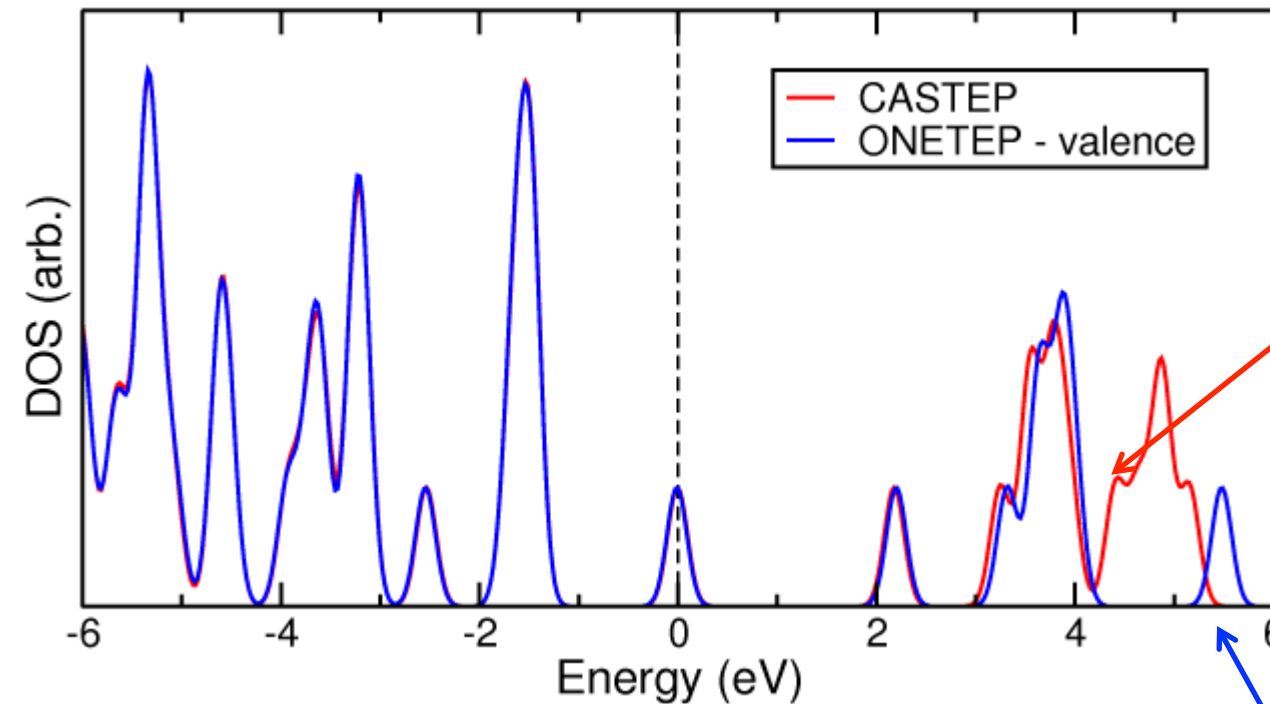
LUMO+8:



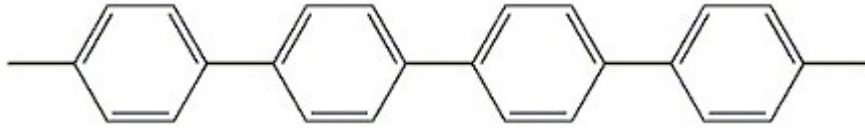
CASTEP



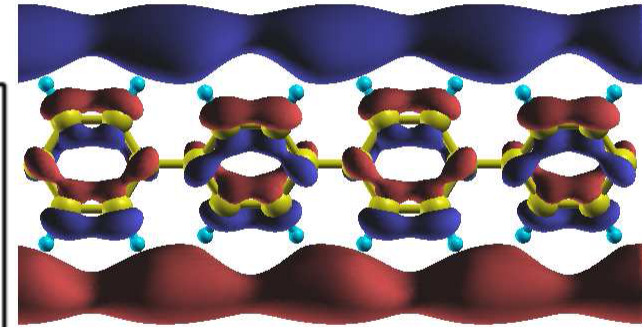
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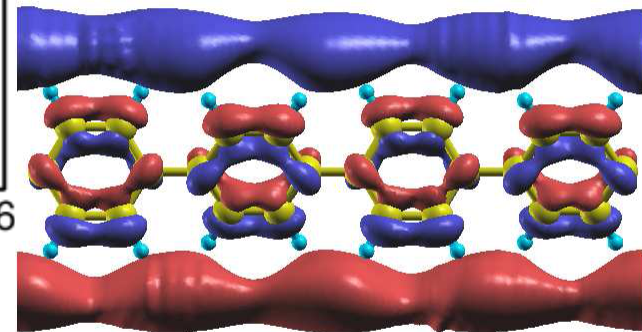
poly(*para*-phenylene) chain



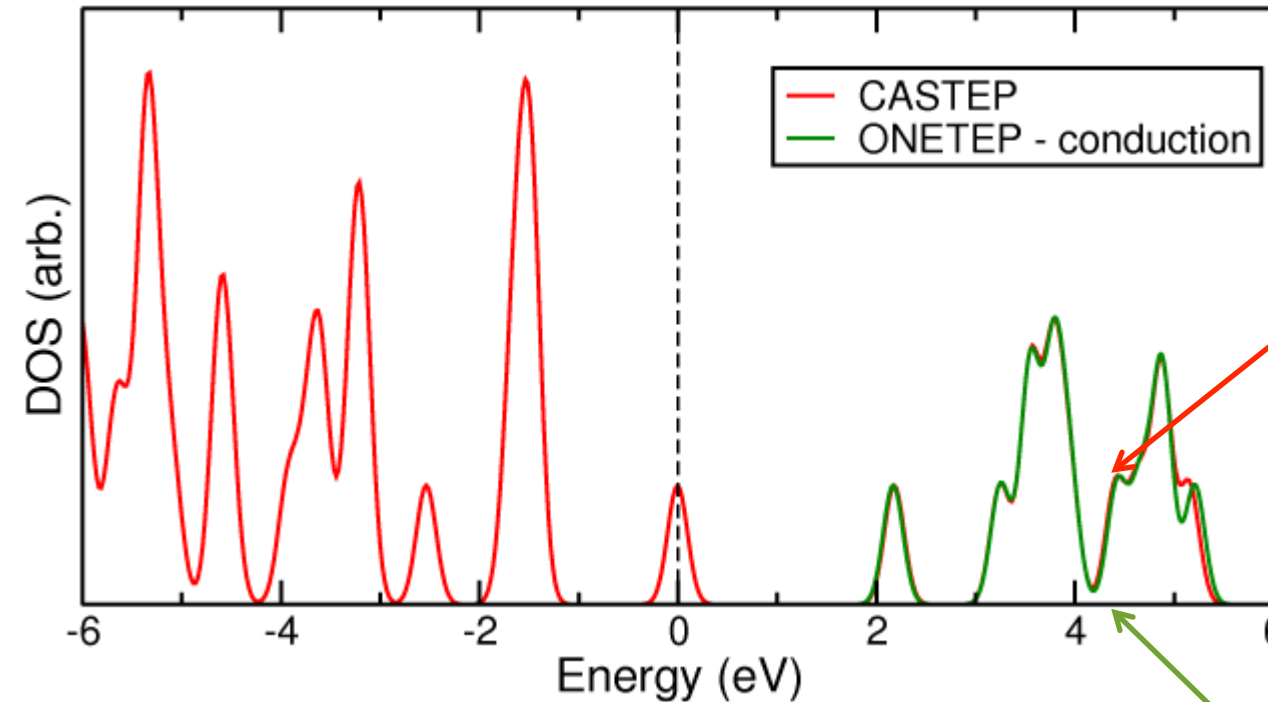
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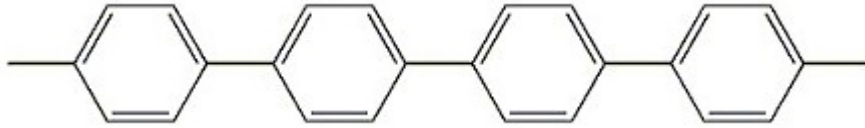
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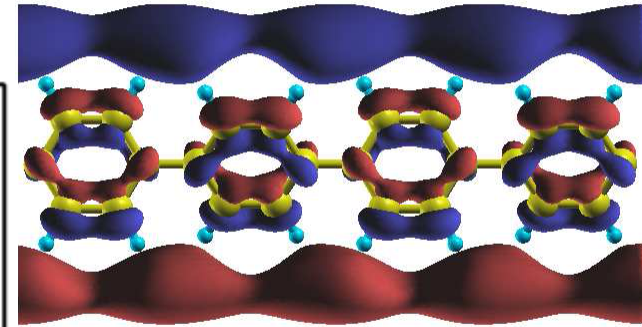
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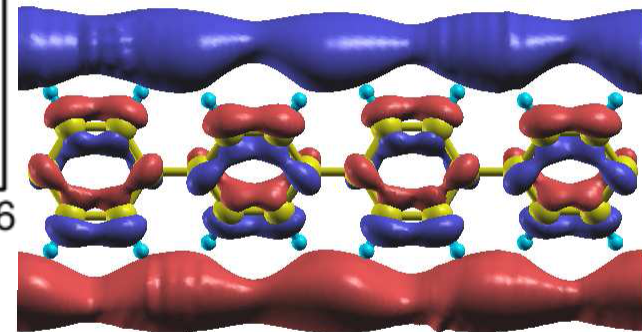
poly(*para*-phenylene) chain



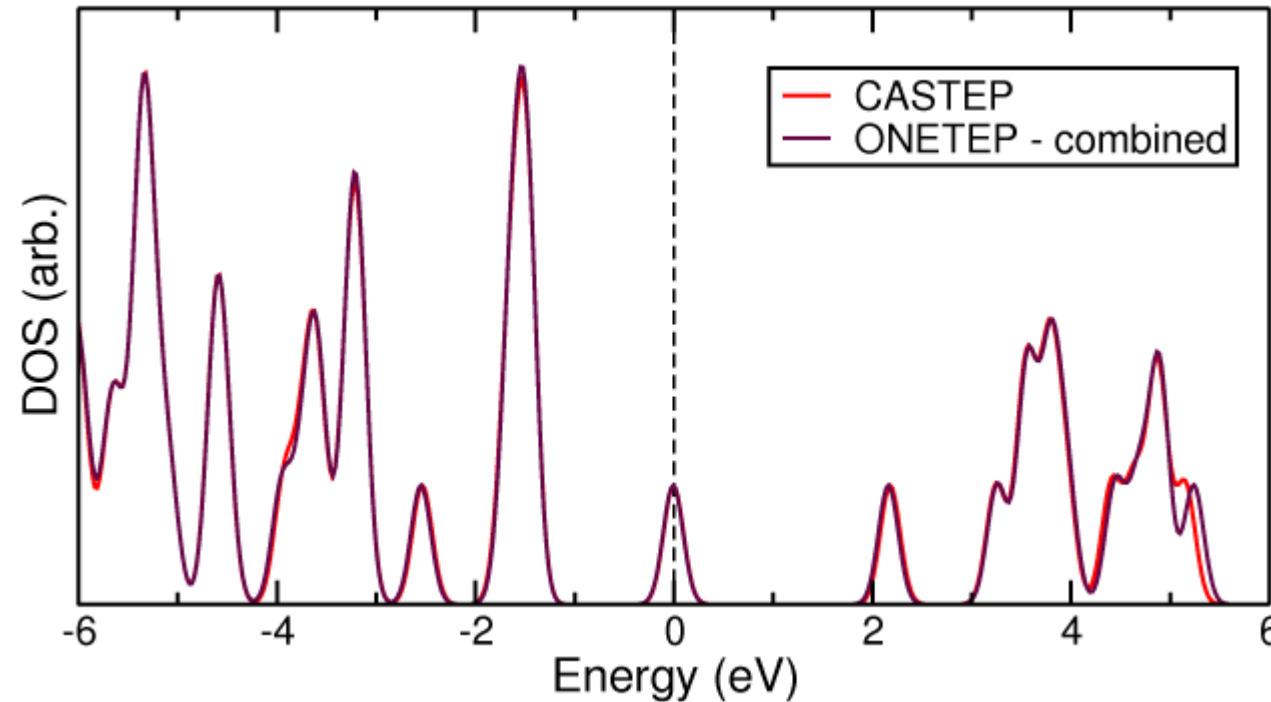
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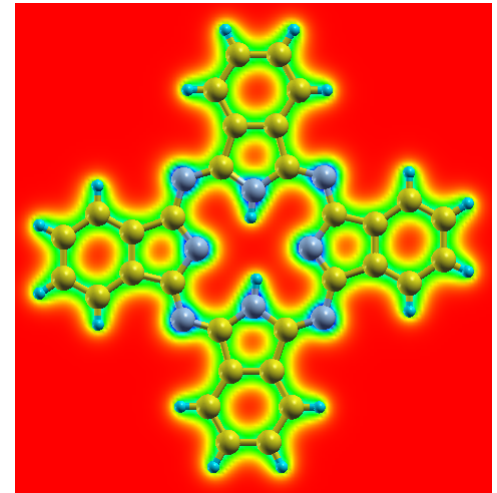
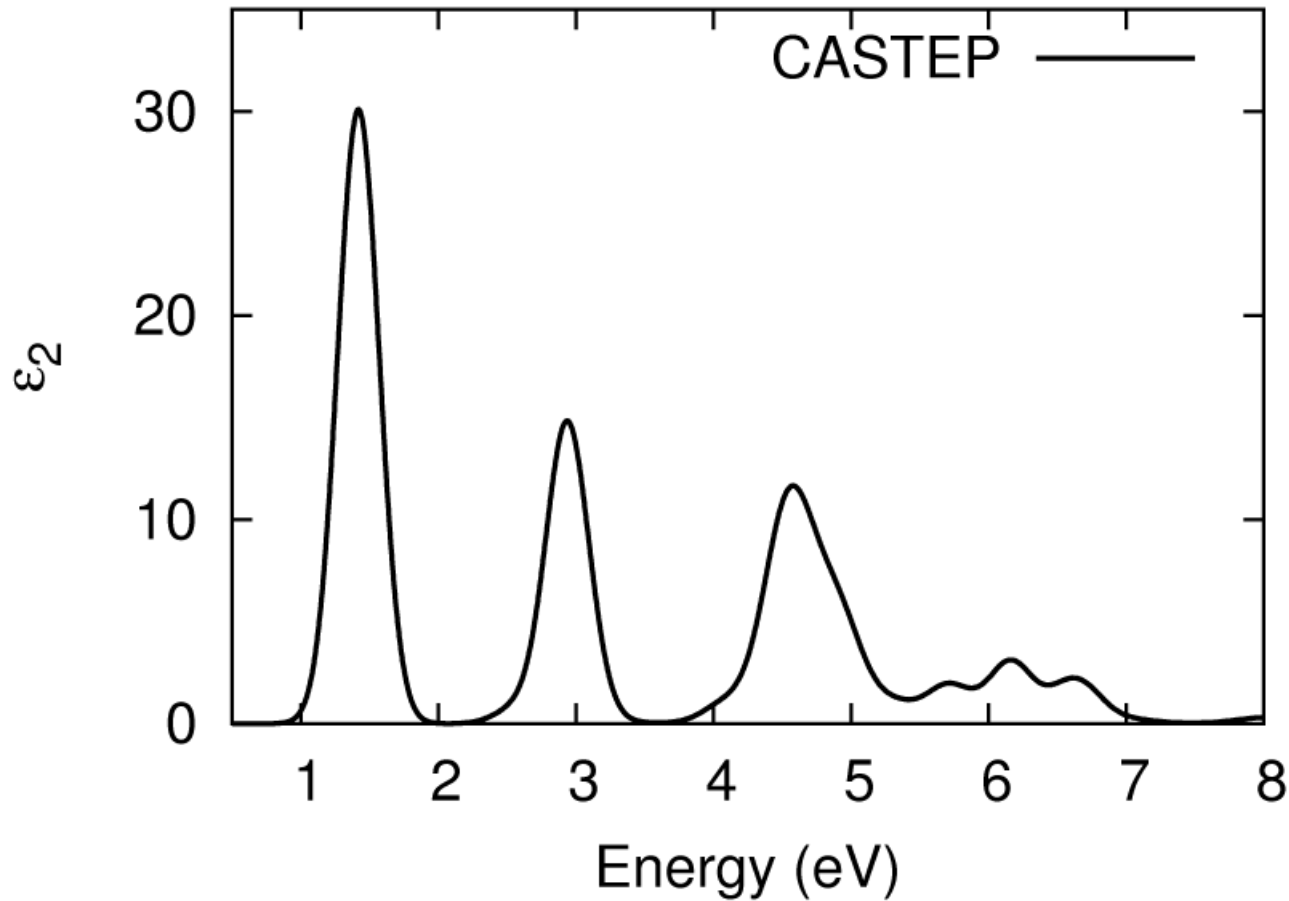
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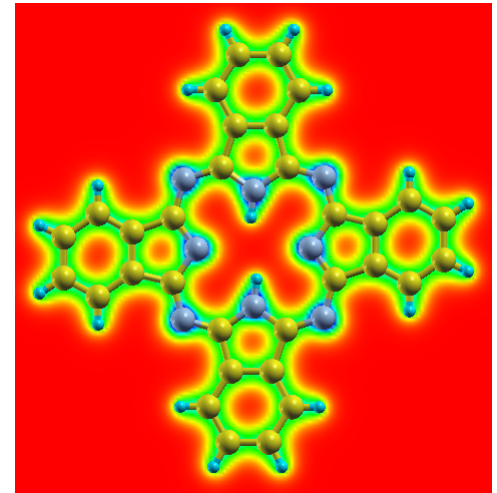
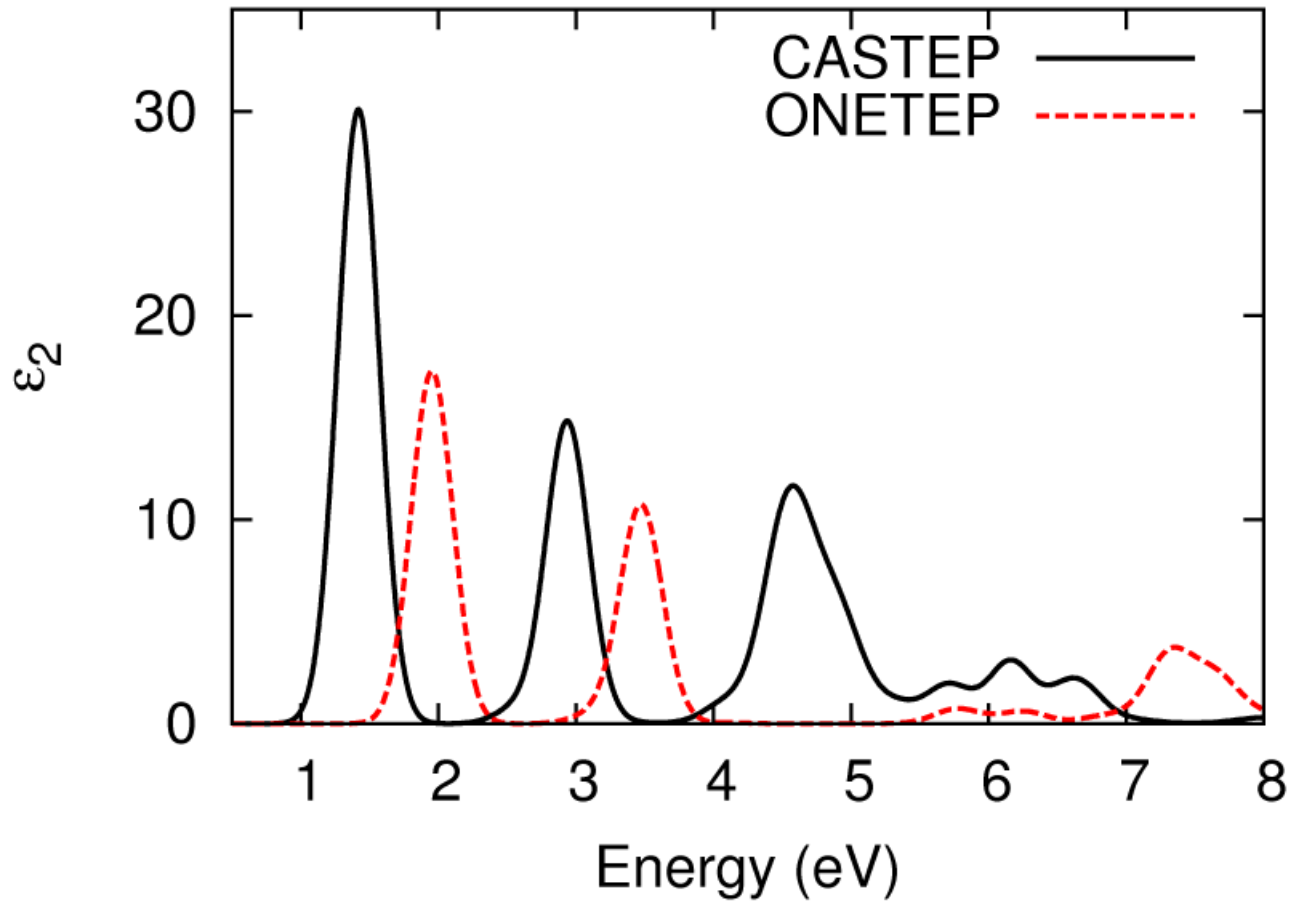
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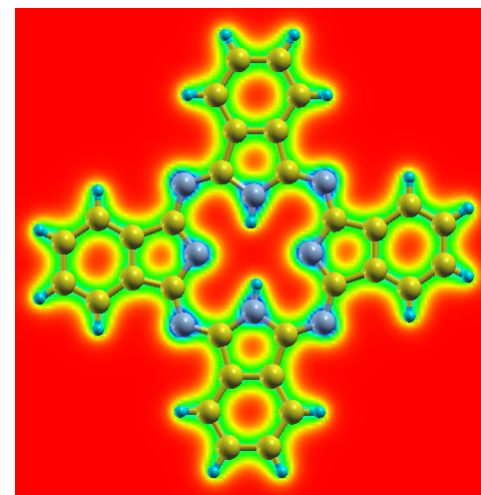
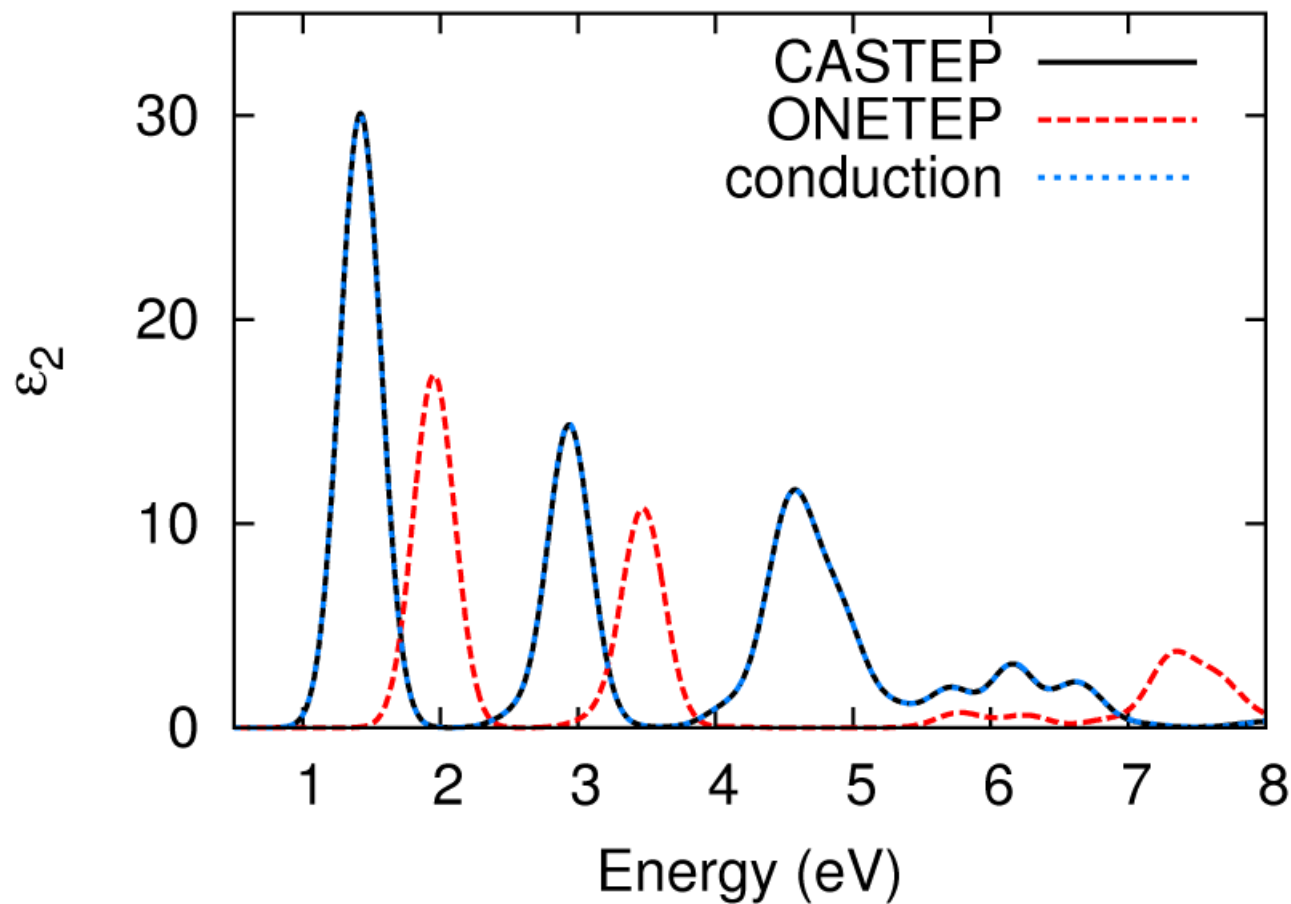
Optical absorption: phthalocyanine



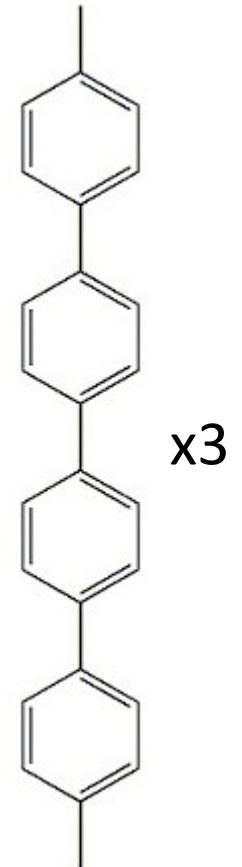
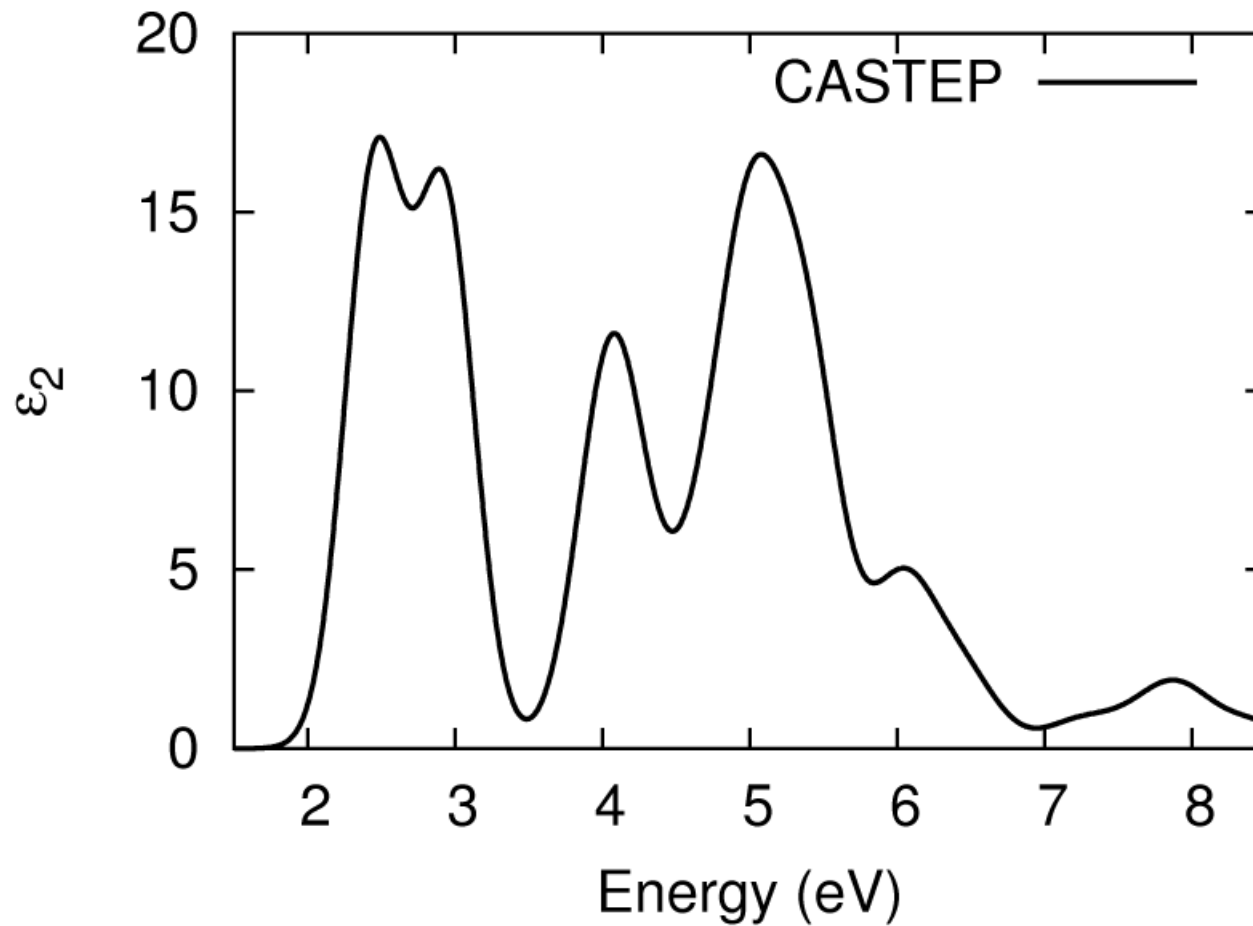
Optical absorption: phthalocyanine



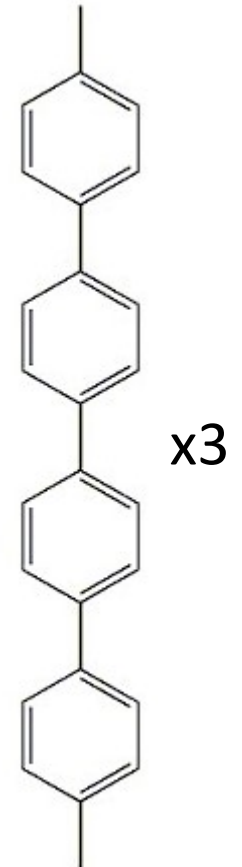
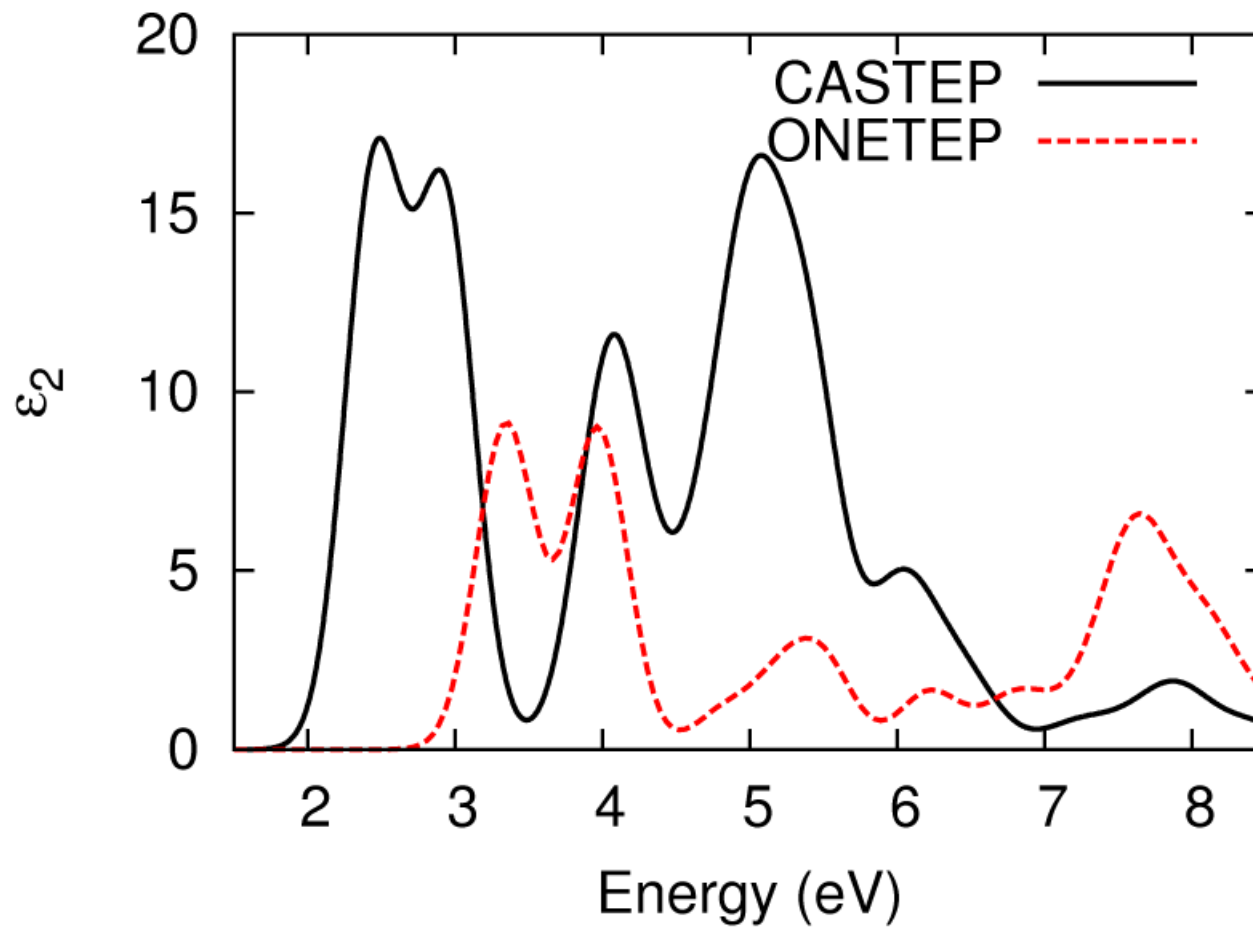
Optical absorption: phthalocyanine



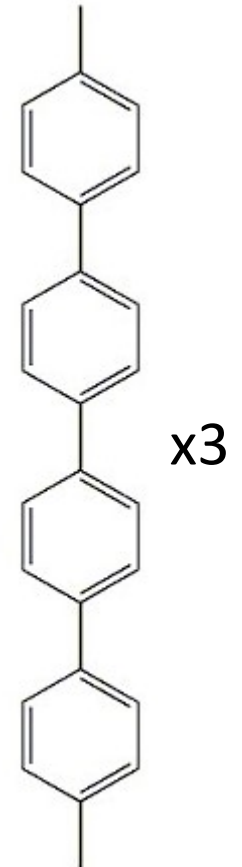
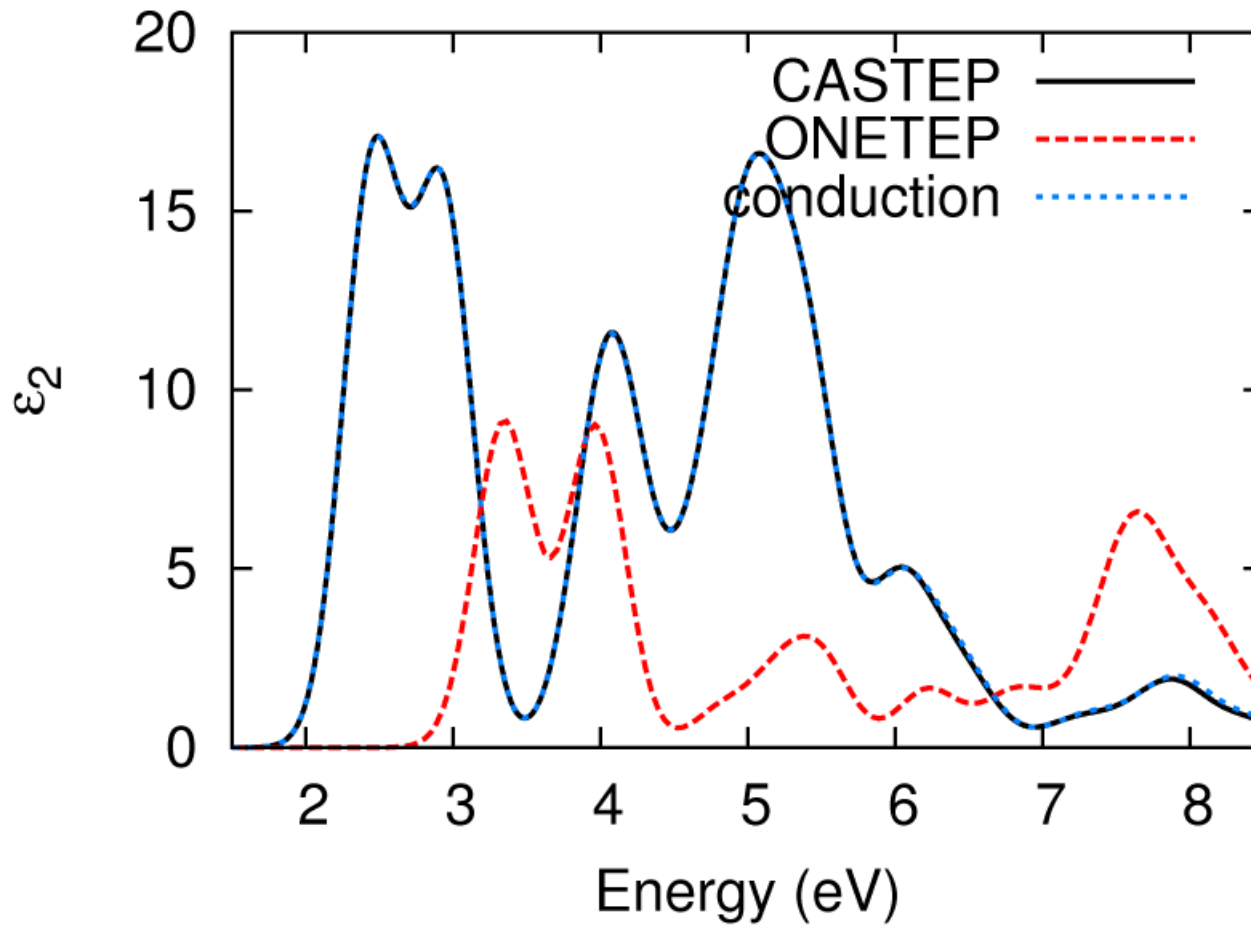
poly(*para*-phenylene-vinylene) chains



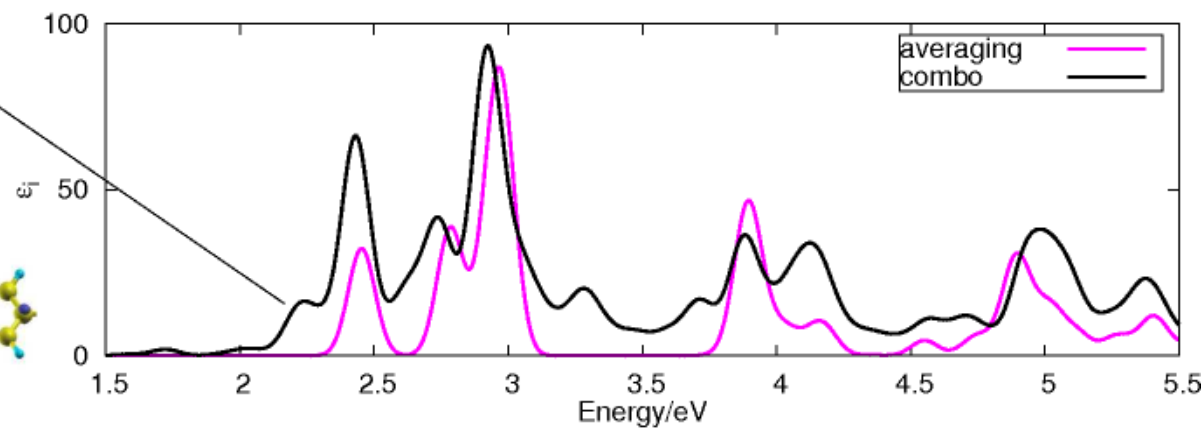
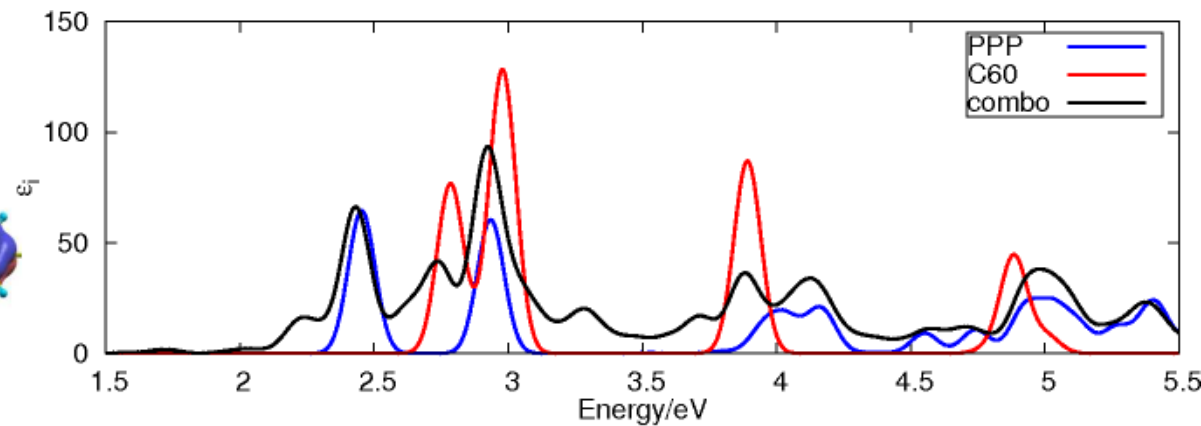
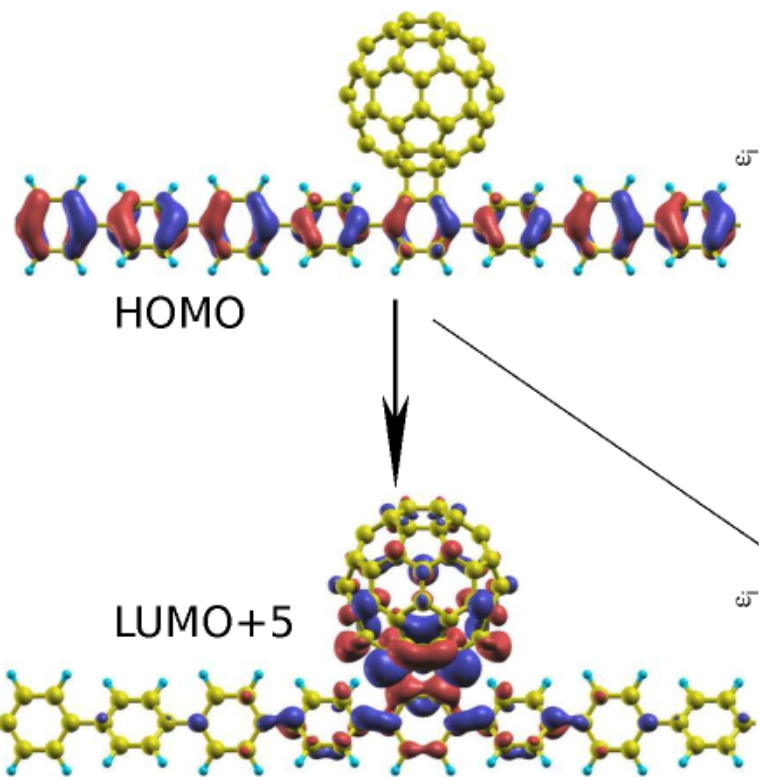
poly(*para*-phenylene-vinylene) chains



poly(*para*-phenylene-vinylene) chains



C₆₀-PPP hybrid



Input file

- Perform a standard single-point energy calculation first to generate “valence” NGWFs
- Then set **TASK=COND**
- Specify radii and numbers of NGWFs in **SPECIES_COND** block
- Set number of unoccupied states to describe using **NUM_COND_STATES**
- Set “conduction” kernel cutoff using **COND_KERNEL_CUTOFF**

Output

- Eigenvalues of valence, conduction and joint Hamiltonians written to **.bands** files
- Plot canonical orbitals using **COND_PLOT_VC_ORBITALS** and **COND_PLOT_JOINT_ORBITALS**

Practical tips

- Higher energy → less localised and slower convergence
- **ODD_PSINC_GRID : T**
- Fixed shift:
 - **COND_INIT_SHIFT**
 - **COND FIXED SHIFT : T**
- Automatically updated shift (recommended):
 - **COND_CALC_MAX_EIGEN : T**
 - **COND_SHIFT_BUFFER**

Local minima

- May occur when ordering of unoccupied states in energy changes during NGWF optimisation
- Identifying the problem:
 - Decrease **NGWF_THRESHOLD_ORIG** and watch for stagnating gradient while energy decreases
 - Rapid changes in energy with conduction NGWF radii
- Solving the problem:
 - Optimise **COND_NUM_EXTRA_STATES** for **COND_NUM_EXTRA_ITS**

References

- See documentation on ONETEP Wiki
- Calculating optical absorption spectra for large systems using linear-scaling density-functional theory, Laura E. Ratcliff, Nicholas D. M. Hine and Peter D. Haynes, *Phys. Rev. B* **84**, 165131 (2011)