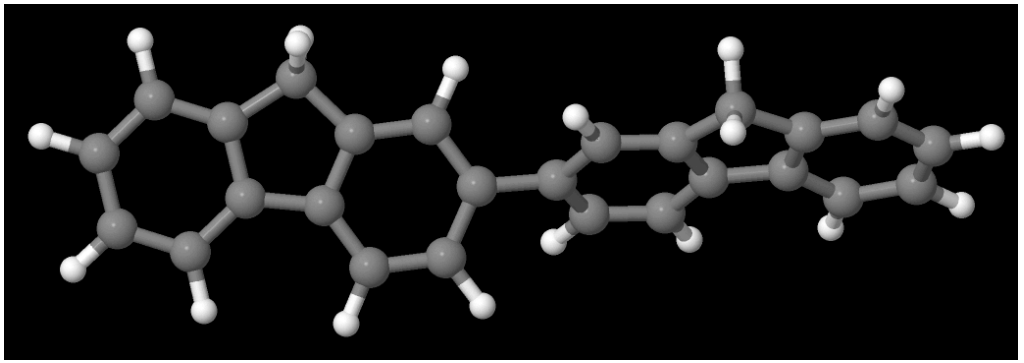
Science & Technology Facilities Council

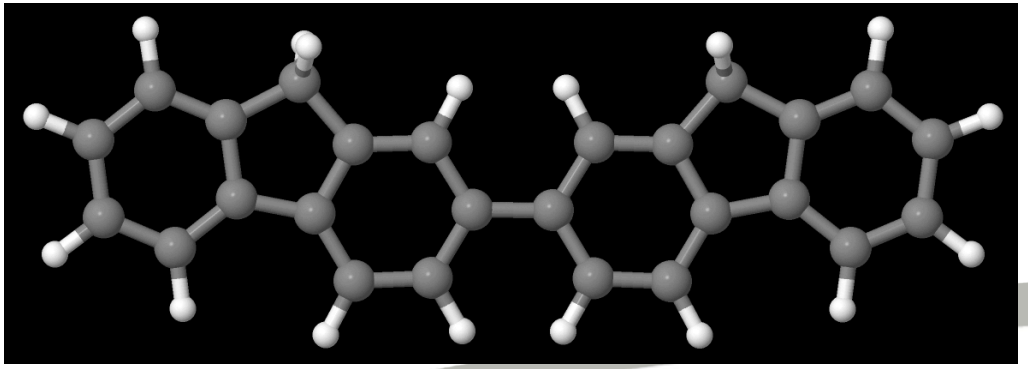
Forces for Electronic Excited States: An Implementation of TD-DFT in CASTEP

ESDG Cambridge 2nd October 2013

Dominik Jochym
STFC Rutherford Appleton Laboratory
dominik.jochym@stfc.ac.uk

Polyfluorene





Science & Technology Facilities Council

Time-Dependent DFT

- One-to-one correspondence between time-dependent one-body densities and time-dependent one-body potentials.

$$n(\mathbf{r},t) \leftrightarrow v_{\mathrm{ext}}(\mathbf{r},t)$$

- Time dependent Kohn-Sham equations

$$i\frac{\partial \phi_j(\mathbf{r},t)}{\partial t} = \left[-\frac{\nabla^2}{2} + v_{\mathrm{KS}}[n](\mathbf{r},t)\right]\phi_j(\mathbf{r},t)$$

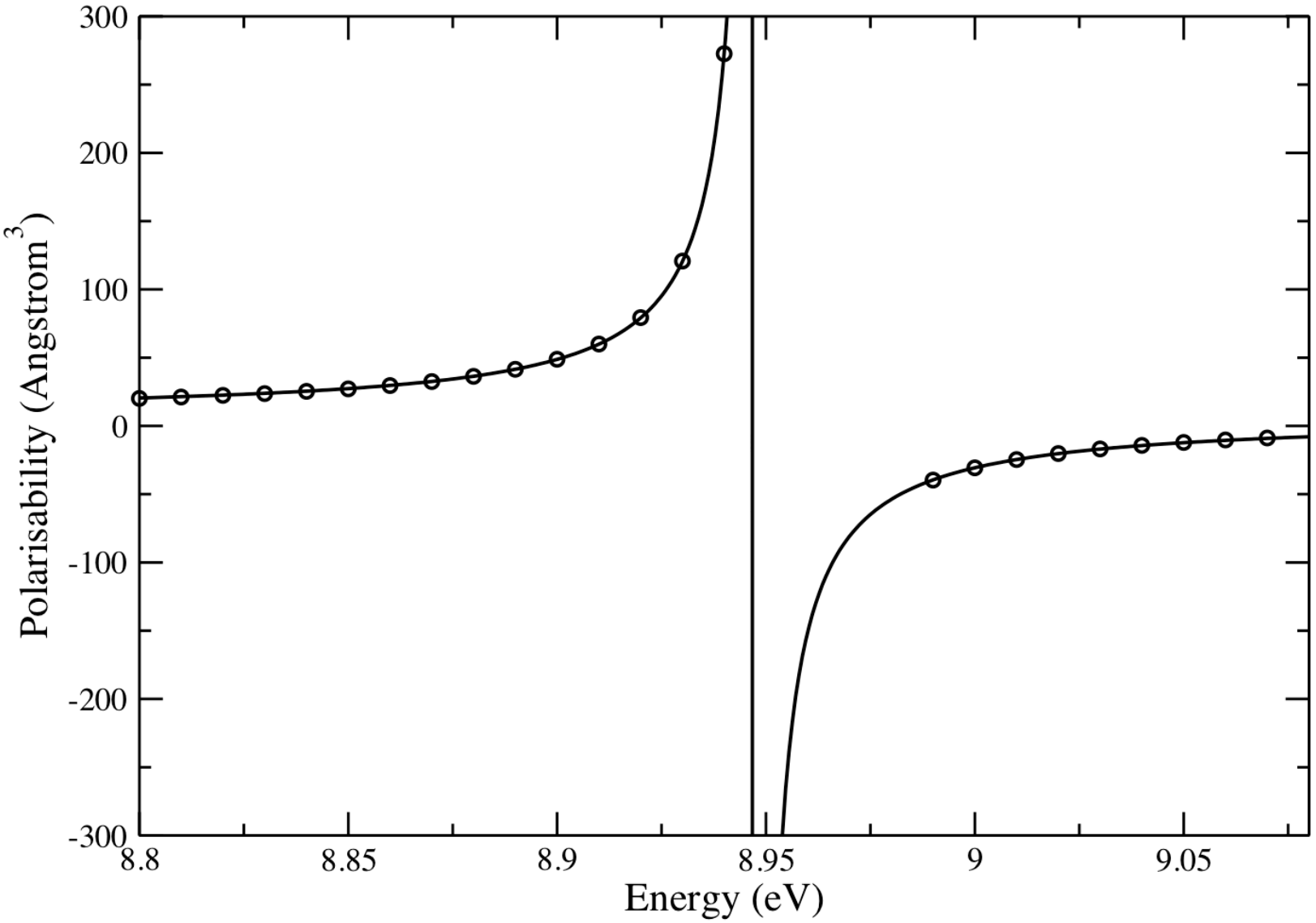
TD Linear Response

- Response to a harmonic perturbation

$$\delta V_{\mathrm{ext}}(\mathbf{r},t) = \delta V^{(+)}(\mathbf{r})e^{i\omega t} + \delta V^{(-)}(\mathbf{r})e^{-i\omega t}$$

- Coupled Sternheimer equations

$$\left(H^{(0)} - \varepsilon_i\right)\left|\Phi_i^{(\pm)}\right\rangle + P_c[\delta V^{(\pm)} + \delta V_{\mathrm{SCF}}(\pm\omega)]\left|\Phi_i^{(0)}\right\rangle = \mp\omega\left|\Phi_i^{(\pm)}\right\rangle$$



Science & Technology Facilities Council

Direct Calculation of Excitations

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

- Tamm-Dancoff approximation

$$\mathbf{AX} = \omega \mathbf{X}$$

where

$$\mathbf{X} = \{X_1 \dots X_i\} \quad X_i = \sum_{a}^{\text{unocc}} x_{ai} \phi_a$$

Science & Technology Facilities Council

TDDFT in CASTEP

- Based on Hutter's formulation

  J. Chem. Phys. **118**, 3928 (2003)

$$\left(H^{(0)} - \varepsilon_i\right)\left|\Phi_i^{(1)}\right\rangle + P_c \delta V_{\mathrm{SCF}}[n^{(1)}]\left|\Phi_i^{(0)}\right\rangle = \omega\left|\Phi_i^{(1)}\right\rangle$$

- Self-consistent response

$$\delta V_{\mathrm{SCF}}[n^{(1)}](\mathbf{r}) = \int d\mathbf{r}' \left\{ \frac{1}{|\mathbf{r}-\mathbf{r}'|} + \left.\frac{\delta E_{\mathrm{XC}}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right|_{n=n^{(0)}} \right\} n^{(1)}(\mathbf{r}')$$

- Response density

$$n^{(1)}(\mathbf{r}) = \sum_i^{\mathrm{occ}} \Phi_i^{*(0)}(\mathbf{r})\Phi_i^{(1)}(\mathbf{r})$$

Science & Technology Facilities Council

Hartree-Fock Contribution

- Contribution to excitation energy

$$\omega_{\mathrm{HF}} = -c_{\mathrm{HF}} \sum_{i}^{\mathrm{occ}} \sum_{j}^{\mathrm{occ}} \iint d\mathbf{r} d\mathbf{r}' \frac{\Phi_i^{*(1)}(\mathbf{r}) \Phi_j^{(1)}(\mathbf{r}) \Phi_j^{(0)}(\mathbf{r}') \Phi_i^{(0)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- Require the gradient w.r.t. response wavefunction

$$\frac{\delta \omega_{\mathrm{HF}}}{\delta \Phi_i^{*(1)}(\mathbf{r})} = -c_{\mathrm{HF}} \sum_{j}^{\mathrm{occ}} \Phi_j^{(1)}(\mathbf{r}) \int d\mathbf{r}' \frac{\Phi_i^{(0)}(\mathbf{r}') \Phi_j^{*(0)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

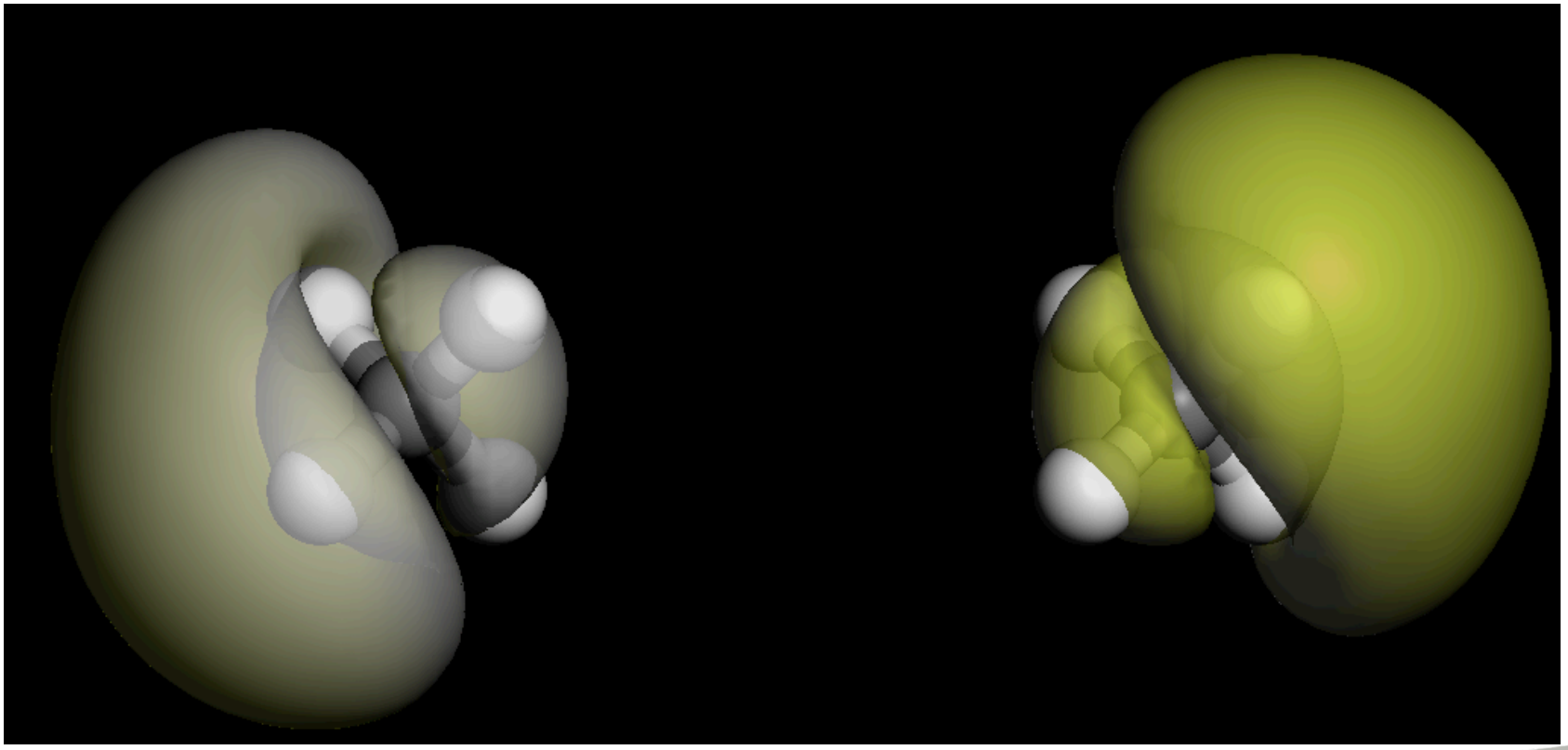
- http://www.hector.ac.uk/cse/distributedcse/reports/castep02/

Validation Tests

- Comparisons with CPMD

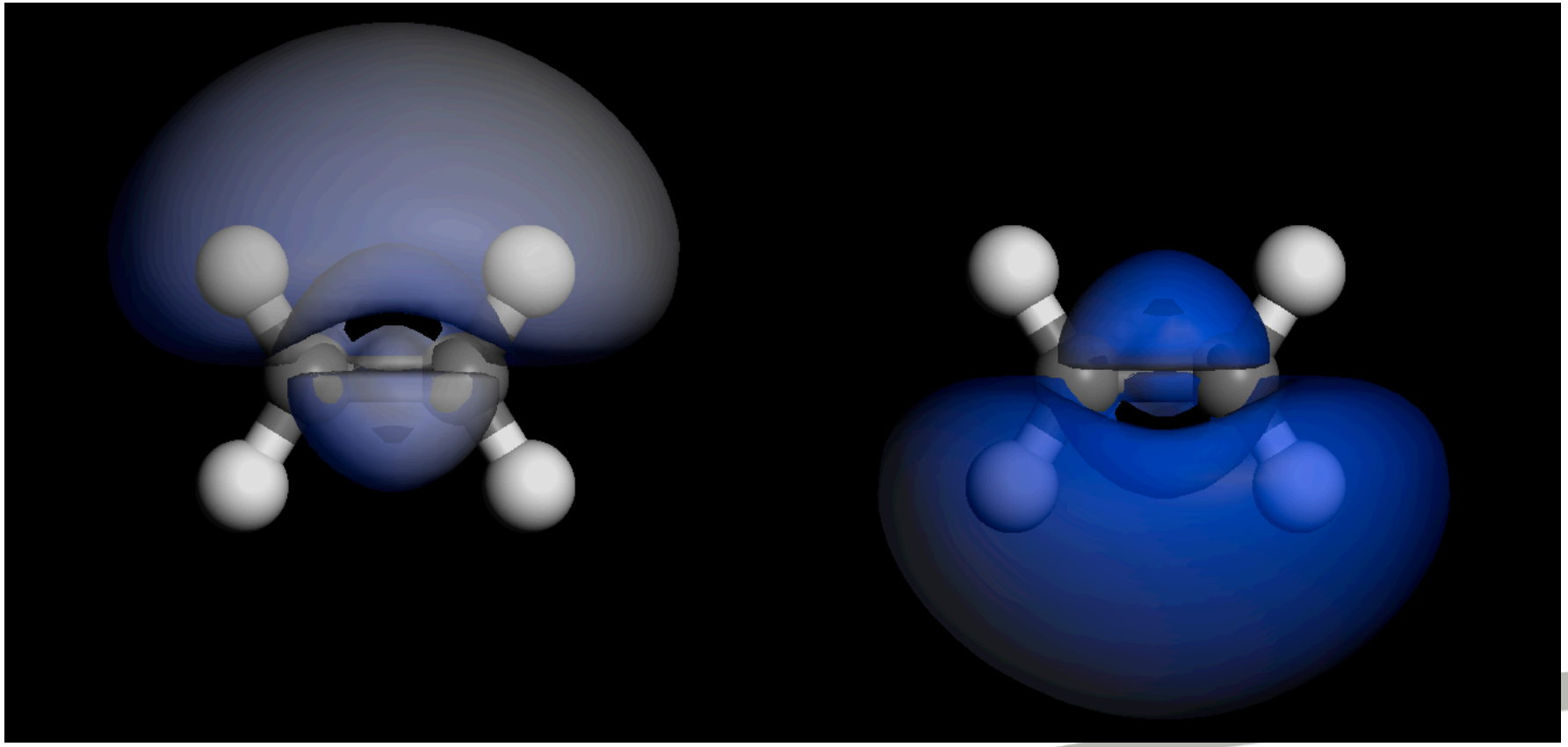
Molecule	State	CASTEP	CPMD
N_2	1	9.282	9.283
	2	9.282	9.283
	3	9.692	9.692
	4	10.259	10.251
	5	10.270	10.269
	6	10.270	10.269
	7	11.495	11.488
	8	11.495	11.488
H_2	1	9.988	9.997
	2	10.840	10.831
	3	11.024	11.014
	4	11.024	11.014
	5	11.403	11.392

Response Densities



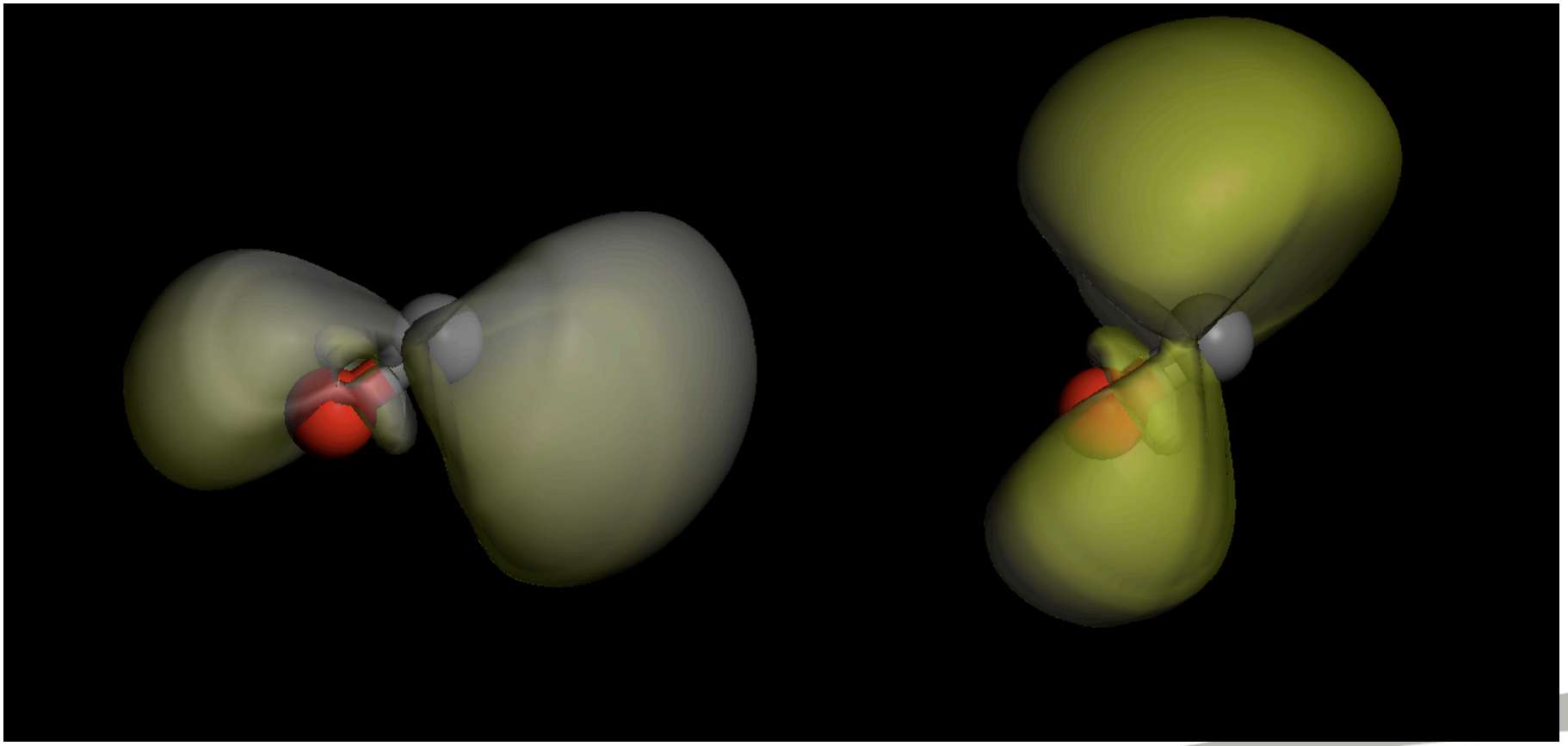
Science & Technology Facilities Council

Response Densities



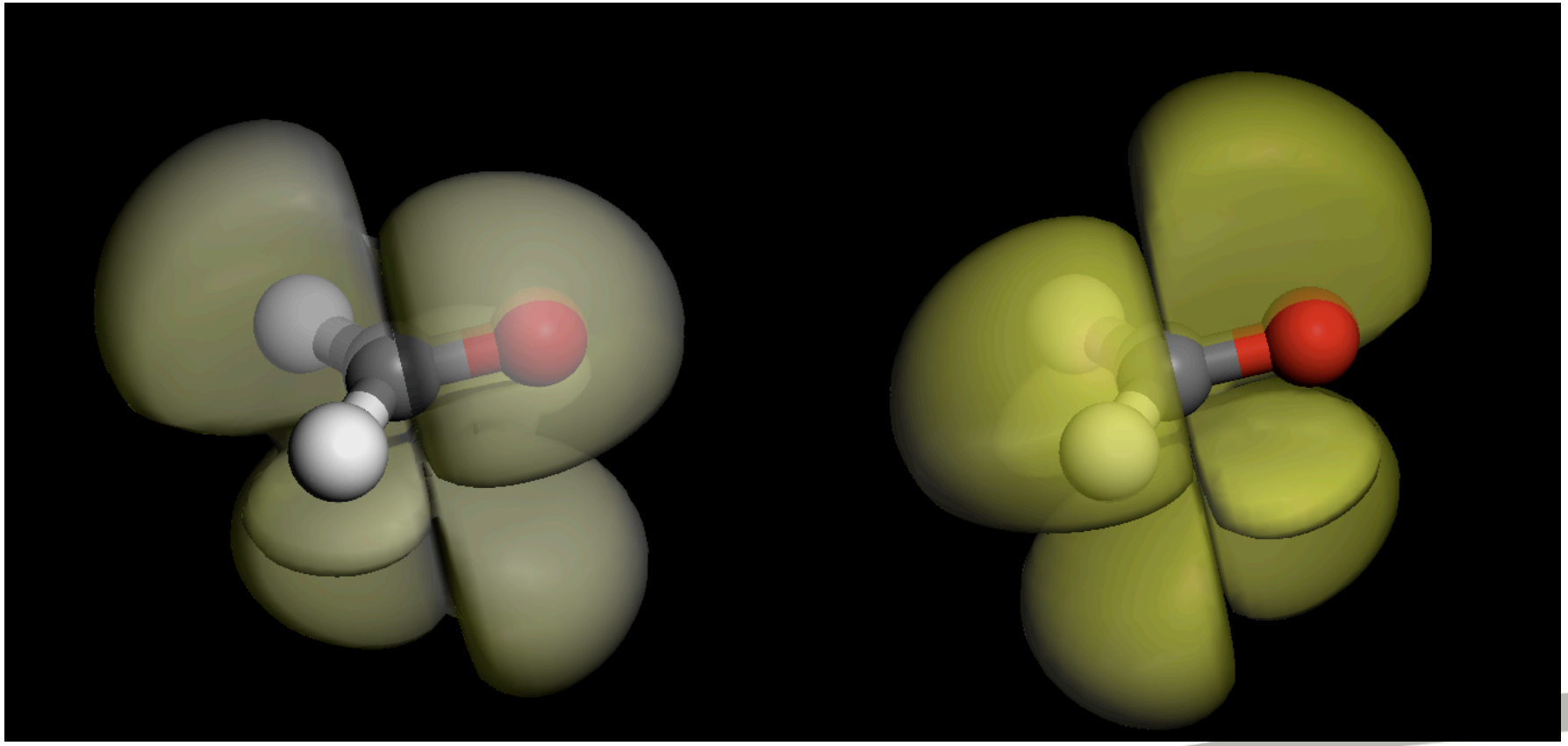
Science & Technology Facilities Council

Response Densities



Science & Technology Facilities Council

Response Densities



Science & Technology Facilities Council

Characterisation of States

- Singlet or Triplet
- Projection onto unoccupied Kohn-Sham bands

$$\left\langle \Phi_i^{(1)} \middle| \Phi_a^{(0)} \right\rangle$$

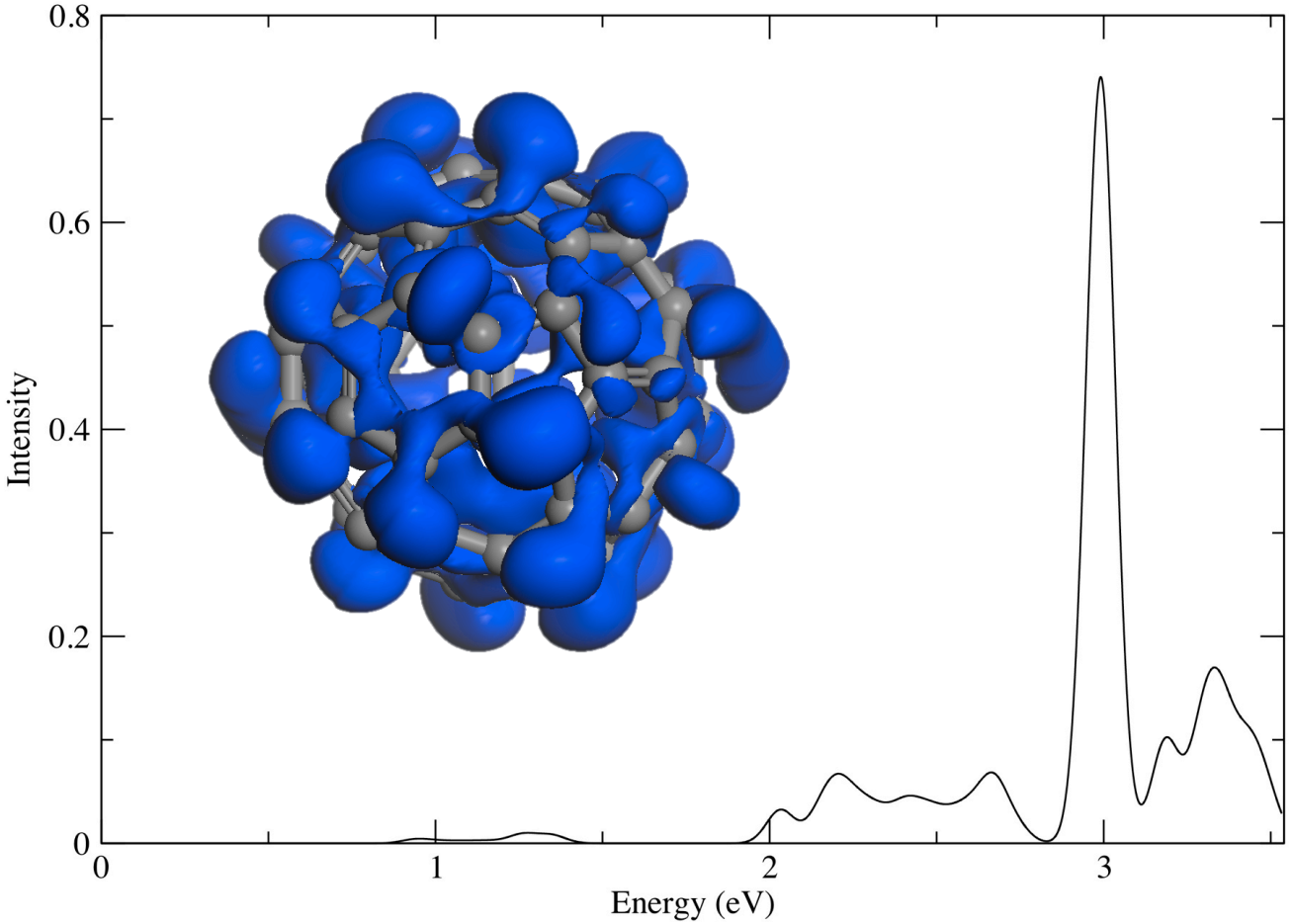
- “Spurious” states

$$\left(H^{(0)} - \varepsilon_i\right) \left|\Phi_i^{(1)}\right\rangle + P_c \delta V_{\mathrm{SCF}}[n^{(1)}] \left|\Phi_i^{(0)}\right\rangle = \omega \left|\Phi_i^{(1)}\right\rangle$$

  - Heßelmann and Görling PRL **102**, 233003 (2009)

Science & Technology Facilities Council

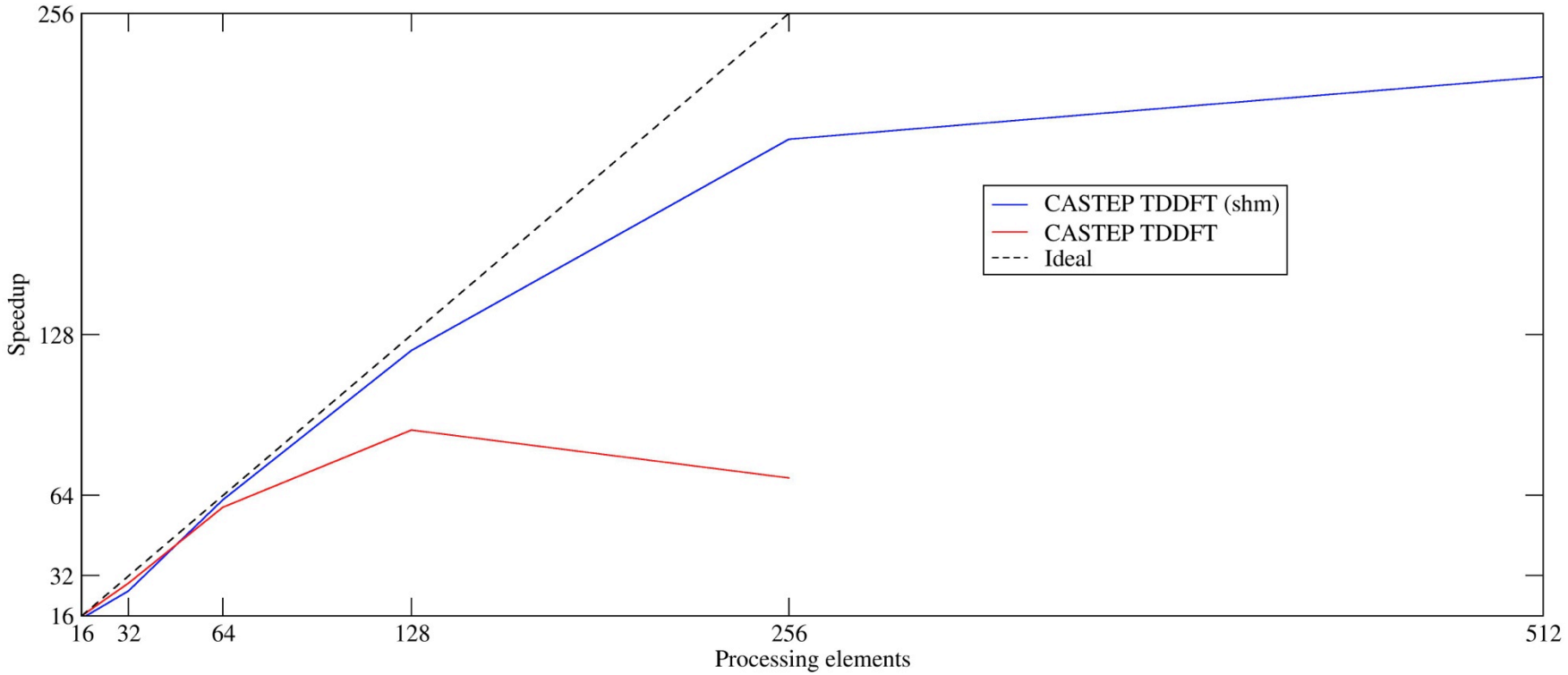
C_{60}



Science & Technology Facilities Council

Parallel Scaling

- Performance on HECToR (Phase 2b)



TD-DFT Forces

- Three contributions:

$$F^{\mathrm{I}}_{\mathrm{GS}} = \sum_{i}^{\mathrm{occ}} \left\langle \Phi_i^{(0)} \left| \frac{\partial H^{(0)}}{\partial \mathrm{R_I}} \right| \Phi_i^{(0)} \right\rangle$$

$$F^{\mathrm{I}}_{X} = \sum_{i}^{\mathrm{occ}} \left\langle \Phi_i^{(1)} \left| \frac{\partial H^{(0)}}{\partial \mathrm{R_I}} \right| \Phi_i^{(1)} \right\rangle - \sum_{i}^{\mathrm{occ}} \left\langle \Phi_i^{(0)} \left| \frac{\partial H^{(0)}}{\partial \mathrm{R_I}} \right| \left(\sum_{j}^{\mathrm{occ}} \left\langle \Phi_i^{(1)} \middle| \Phi_j^{(1)} \right\rangle \middle| \Phi_j^{(0)} \right\rangle \right)$$

$$F^{\mathrm{I}}_{Z} = \sum_{i}^{\mathrm{occ}} \left\langle Z_i \left| \frac{\partial H^{(0)}}{\partial \mathrm{R_I}} \right| \Phi_i^{(1)} \right\rangle + \left\langle \Phi_i^{(1)} \left| \frac{\partial H^{(0)}}{\partial \mathrm{R_I}} \right| Z_i \right\rangle$$

Science & Technology Facilities Council

Handy-Schaefer Z vector

- Need to take into account the how the TDDFT response wavefunction changes as the ground state is perturbed
- Requires the solution of a self-consistent Sternheimer equation to obtain the Handy-Schaefer Z vector

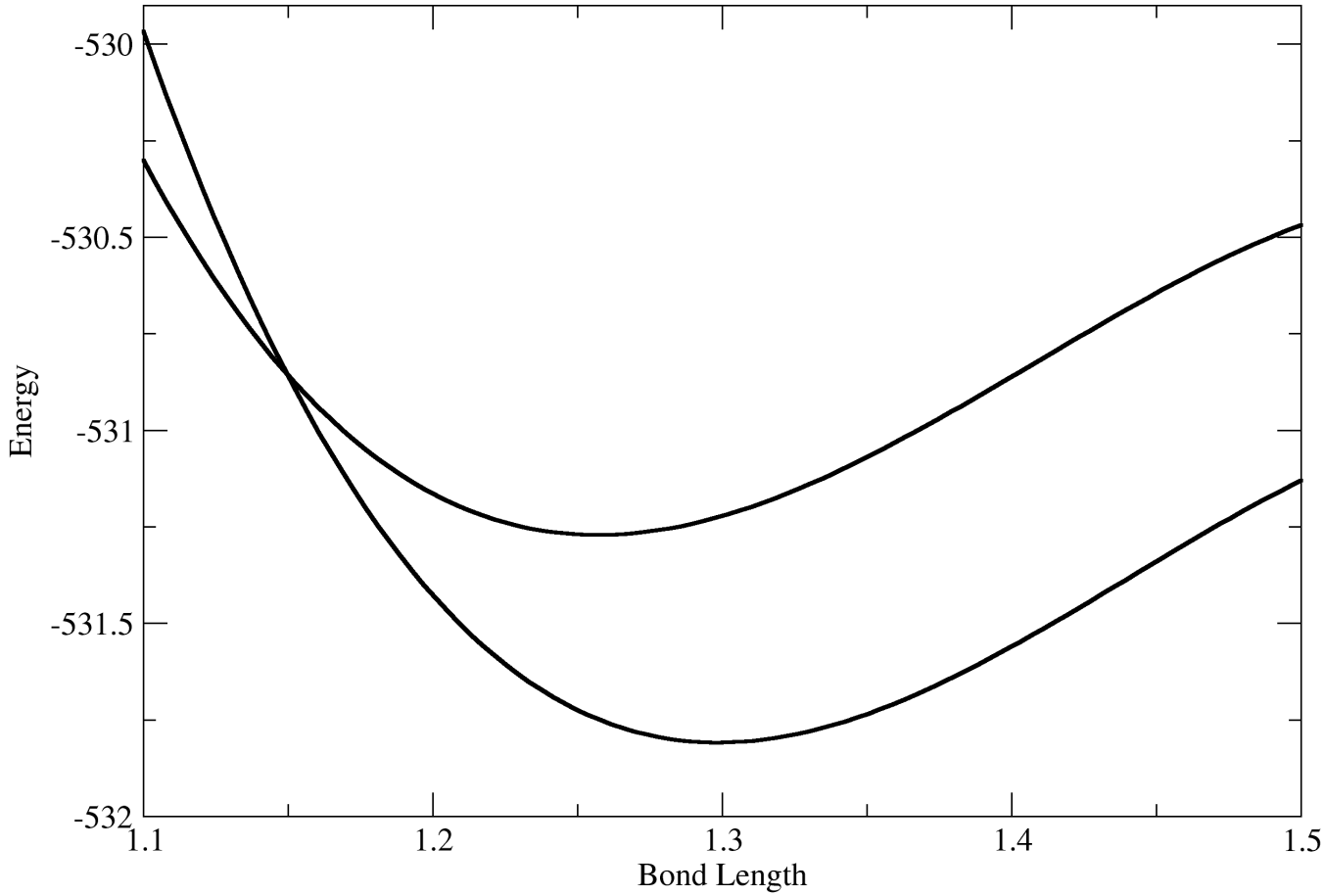
$$\left(H^{(0)} - \varepsilon_i\right)\left|Z_i^*\right\rangle + P_c \delta V_{\mathrm{SCF}}\left[n^{(z)}\right]\left|\Phi_i^{(0)}\right\rangle = \left|u_i\right\rangle$$

$$n^{(z)}(\mathbf{r}) = \sum_i^{\mathrm{occ}} Z_i(\mathbf{r})\Phi_i^{(0)}(\mathbf{r})$$

- http://www.hector.ac.uk/cse/distributedcse/reports/castep03/

Science & Technology Facilities Council

State Crossings



Science & Technology Facilities Council

Summary

- TDDFT in CASTEP
  - Electronic excitation energies
  - Characterisation of TDDFT states as KS orbitals
  - Optical matrix elements (transition intensities)
  - Compatible with OptaDOS
  - For a selected TDDFT state - Forces
    - Structure optimisation
    - Molecular dynamics
    - (Phonons)
- **Available in CASTEP 7.0**