

Time-dependent density functional theory (TD-DFT)

Stewart Clark

University of Durham

Outline

- Why go beyond DFT?
- What is TD-DFT?
- Computational approaches
- Approach in Castep
- Examples and features

Beyond DFT

- What do we mean by a band gap?
- What is the excitation?
- Sometimes want to describe excited states of electronic systems:
 - Optical properties
 - Excitons
 - Charge transfer
 - Structure
 - Dynamics

Going Beyond DFT

$$F[n(\mathbf{r})]$$

- DFT

$$F[n(\mathbf{r}), V(\mathbf{r}, \mathbf{r}')]]$$

- Hybrid-DFT

$$F[n(\mathbf{r}, \omega), V(\mathbf{r}, \mathbf{r}')]]$$

- Time-Dependent DFT

$$G(\mathbf{r}_1, \mathbf{r}_2, \omega)$$

- GW

$$G(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \omega)$$

- Bethe-Salpeter

Time-dependent DFT

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

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

- Time dependent Kohn-Sham equations

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

Why TD-DFT

- Formally exact and improvements of the xc-functionals is still possible.
- Improvement of wavefunction based methods can only be done at huge costs in computational time.
- Computationally more efficient and scales better than ab-initio methods.
- Can be easily combined with MD – you get forces

Approaches to TD-DFT

- Real-time propagation
- Sternheimer frequency scan
- Linear Response (Casida)
- Solution of the response equation
- Lanczos chains

Some formalities

TDDFT in the linear response formulation

The basic quantity in LR-TDDFT is the density-density response function

$$\chi(\mathbf{r}, t, \mathbf{r}', t') = \left. \frac{\delta\rho(\mathbf{r}, t)}{\delta v_{ext}(\mathbf{r}', t')} \right|_{v_0}$$

which relates the first order density response to the applied perturbation

$$\delta\rho(\mathbf{r}, t) = \int d^3\mathbf{r}' dt' \chi(\mathbf{r}, t, \mathbf{r}', t') \delta v(\mathbf{r}', t'),$$

Response function

The physical response function is related to the non-interacting KS response function via the Dyson-like equation

$$\chi(\mathbf{r}, t, \mathbf{r}', t') = \chi_s(\mathbf{r}, t, \mathbf{r}', t') + \int d^3\mathbf{r}_1 dt_1 \int d^3\mathbf{r}_2 dt_2 \chi_s(\mathbf{r}, t, \mathbf{r}_1, t_1) \left(\frac{\delta(t_1 - t_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{\delta v_{xc}(\mathbf{r}_1, t_1)}{\delta \rho(\mathbf{r}_2, t_2)} \right) \chi(\mathbf{r}_2, t_2, \mathbf{r}, t_1),$$

or in Fourier space $\chi^{-1}(\mathbf{r}, \mathbf{r}', \omega) = \chi_s^{-1}(\mathbf{r}, \mathbf{r}', \omega) - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - f_{xc}(\mathbf{r}_1, \mathbf{r}_2, \omega)$

The KS response function can be computed (non-interacting system)

$$\chi_s(\mathbf{r}, \mathbf{r}', \omega) = \sum_{k,j} (f_k - f_j) \frac{\psi_k^*(r) \psi_j(r) \psi_j(r') \psi_k^*(r')}{\omega - (\epsilon_j - \epsilon_k) + i\eta}$$

TD-DFT in practice

After writing the dynamic polarizability in KS basis one gets

$$\begin{bmatrix} \mathbf{A}(\omega) & \mathbf{B}(\omega) \\ \mathbf{B}^*(\omega) & \mathbf{A}^*(\omega) \end{bmatrix} \begin{bmatrix} \vec{X}_I \\ \vec{Y}_I \end{bmatrix} = \omega_I \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{bmatrix} \vec{X}_I \\ \vec{Y}_I \end{bmatrix}.$$

with

$$A_{ia\sigma,jb\tau}(\omega) = \delta_{\sigma\tau}\delta_{ij}\delta_{ab}(\epsilon_{a\sigma} - \epsilon_{i\sigma}) + (ia|f_H + f_{xc}^{\sigma\tau}(\omega)|jb)$$

$$B_{ia\sigma,jb\tau}(\omega) = (ia|f_H + f_{xc}^{\sigma\tau}(\omega)|jb),$$

and

$$f_{xc}^{\sigma\tau}(\mathbf{r}_1, \mathbf{r}_2; \omega) = \int_{-\infty}^{+\infty} e^{i\omega(t_1-t_2)} \frac{\delta^2 A_{xc}[\rho_\uparrow, \rho_\downarrow]}{\delta\rho_\sigma(\mathbf{r}_1, t_1)\delta\rho_\tau(\mathbf{r}_2, t_2)} d(t_1 - t_2).$$

In the adiabatic approximation the TDDFT kernel is time-independent (and its Fourier transform is independent from ω) and therefore the number of solutions of Casida's equations is equal to the dimensionality of the matrices.

Simplify notation

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

- Tamm-Dancoff approximation

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

where

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

TD-DFT in Castep

- Based on Hutter's formulation

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

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

- Self-consistent response

$$\delta V_{\text{SCF}}[n^{(1)}] = \int d\mathbf{r}' \left\{ \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{\text{XC}}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \Big|_{n=n^{(0)}} \right\} n^{(1)}(\mathbf{r}')$$

- Response density

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

Hartree-Fock Contribution

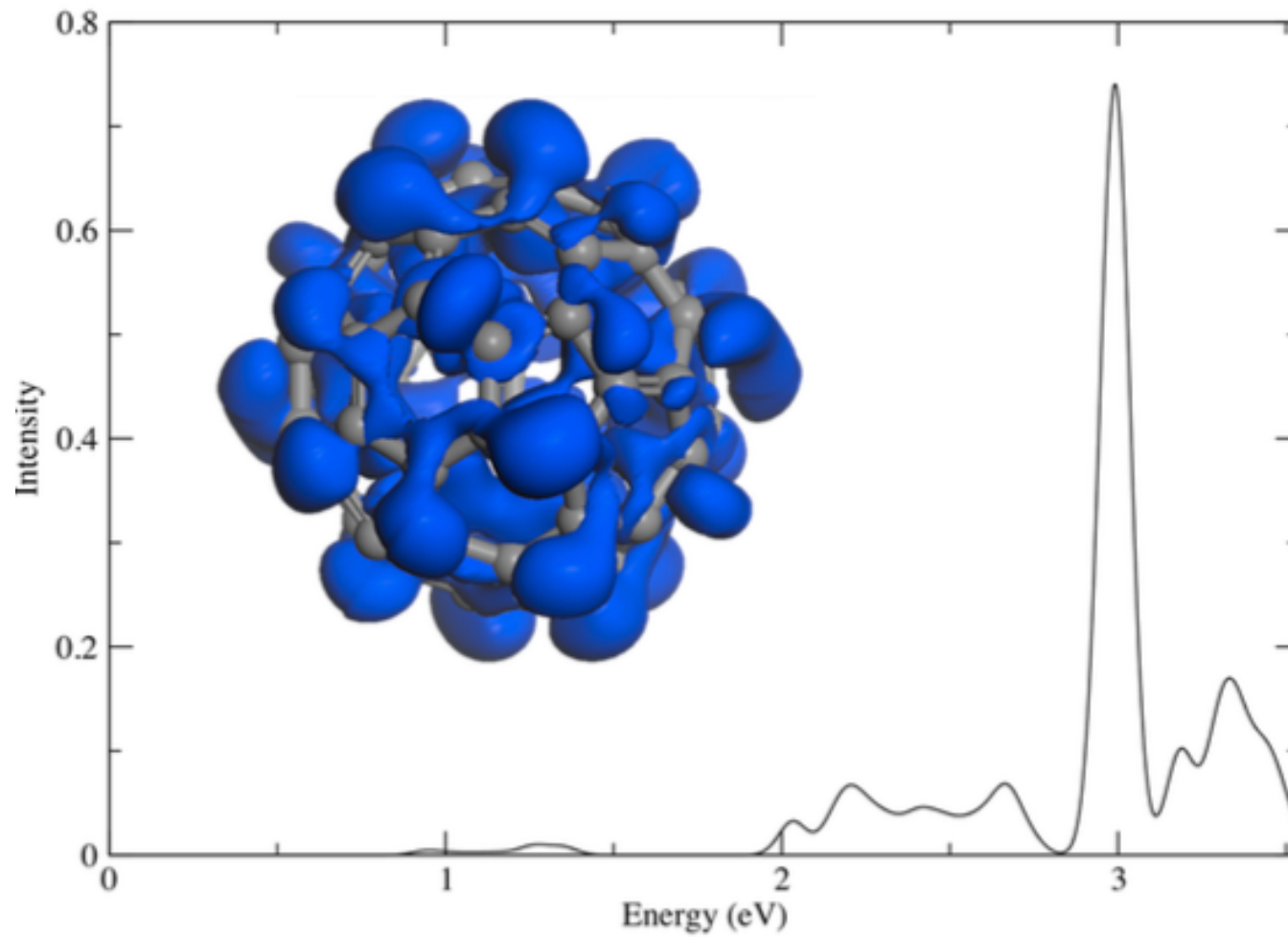
- Contribution to excitation energy

$$-C_{\text{HF}} \sum_i^{\text{occ}} \sum_j^{\text{occ}} \iint d\mathbf{r} d\mathbf{r}' \frac{\Phi_i^{(1)*}(\mathbf{r}) \Phi_j^{(1)}(\mathbf{r}) \Phi_j^{(0)*}(\mathbf{r}') \Phi_i^{(0)*}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

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

Example

C_{60}



Example: N₂

```
%BLOCK lattice_abc  
  6.0  6.0  6.0  
 90.0 90.0 90.0  
%ENDBLOCK lattice_abc
```

```
%BLOCK species_pot  
N N_00.recpot  
%ENDBLOCK species_pot
```

```
%BLOCK positions_abs  
N  0.6893  0.0  0.0  
N -0.6893  0.0  0.0  
%ENDBLOCK positions_abs
```

```
kpoints_mp_grid 1 1 1
```

```
FIX_ALL_CELL true
```

```
symmetry_generate
```

```
task : spectral  
spectral_theory : tddft  
xc_functional : lda  
fix_occupancy : true  
opt_strategy : speed  
tddft_nextra_states : 4  
tddft_num_states : 10  
tddft_eigenvalue_method : davidson
```



```

+ ===== +TDDFT
+           TDDFT excitation energies +TDDFT
+           ----- +TDDFT
+ State number      Energy in eV      Estimated error +TDDFT
+ ===== +TDDFT
+           +TDDFT
+           1      5.389370934360212      6.9753711408E-07      spurious +TDDFT
+           2      6.037881253610007      9.0568954265E-07      Singlet +TDDFT
+           3      6.038887862713620      8.2371540215E-07      Singlet +TDDFT
+           4      6.296051105997545      9.2209779744E-07      Singlet +TDDFT
+           5      6.296051934448821      8.8907697662E-07      Singlet +TDDFT
+           6      9.114970608091221      7.7091845361E-07      Singlet +TDDFT
+           7      9.114970919633304      9.8733193863E-07      Singlet +TDDFT
+           8      9.423086373661569      9.1482768917E-07      Singlet +TDDFT
+           9      11.480297881574630      7.8964451155E-07      Singlet +TDDFT
+           10     12.284357054899688      9.6666531863E-07      Singlet +TDDFT
+           +TDDFT
+ ===== +TDDFT
+ TDDFT calculation time:      57.39 +TDDFT
+ ===== +TDDFT

```

Writing analysis data to N2-LDA.castep_bin

Writing model to N2-LDA.check

Note: One or more states have been marked as spurious.

These states may not be true TDDFT states, yet are valid solutions to the equations being solved. A geometry optimisation, MD or phonon calculation where the selected state is spurious may have limited physical meaning.

Optical matrix elements / oscillator strengths should be negligible for spurious states.

N2.tddft and .bands files

State	Occ.	Unocc.	Overlap	
1	4 -->	6	0.470016	
1	4 -->	7	0.029984	
1	5 -->	6	0.029983	
1	5 -->	7	0.470017	
Total overlap for state		1 = 1.000000		
2	4 -->	6	0.322229	
2	4 -->	7	0.177367	
2	5 -->	6	0.177368	
2	5 -->	7	0.322229	
Total overlap for state		2 = 0.999253		
3	4 -->	6	0.177366	
3	4 -->	7	0.322218	
3	5 -->	6	0.322241	
3	5 -->	7	0.177369	
Total overlap for state		3 = 0.999248		
4	1 -->	6	0.001341	
4	1 -->	7	0.001664	
4	3 -->	6	0.443194	
4	3 -->	7	0.550940	
Total overlap for state		4 = 0.998041		
5	1 -->	6	0.001665	
5	1 -->	7	0.001336	
5	3 -->	6	0.550938	
5	3 -->	7	0.443197	
Total overlap for state		5 = 0.998041		
				10 electron, 5 bands
				1 -23.6634
				2 -14.3753
				3 -9.25816
				4 -9.14942
				5 -9.14942
				6 -3.76005
				7 -3.76005
				8 0.000881377
				9 3.31035
				10 3.35238
				11 3.85511
				12 3.85511
				13 3.88802
				14 5.23154
				15 5.34276
				16 6.45266
				17 7.38200
				18 7.38200
				19 7.59524
				20 7.67846
				21 7.68771

Another example: phosphorous

```
%BLOCK LATTICE_CART
  4.196884689078602    0.000000000000000    0.000000000000000
  0.000000000000000    15.000000000000002    0.000000000000001
  0.000000000000000   -0.000000000000000    4.563427984024002
%ENDBLOCK LATTICE_CART
```

```
%BLOCK POSITIONS_FRAC
  P -0.5000000000000002  1.9048791258879185  0.9107624444447524
  P  1.0000000000000002 -1.9048791258879185  1.4107624444447526
  P -0.0000000000000005  1.9125190256942162  0.4980918164309386
  P  0.5000000000000003 -1.9125190256942162  0.9980918164309384
%ENDBLOCK POSITIONS_FRAC
```

```
kpoints_mp_grid 1 1 1
```

```
symmetry_generate
```

```
%BLOCK SPECIES_POT
  P P_00PBE_OP.recpot
%ENDBLOCK SPECIES_POT
```

```
task : spectral
xc_functional : PBE
fix_occupancy : true
spectral_theory : tddft
tddft_num_states : 12
spin_polarised : true
opt_strategy : speed
elec_energy_tol : 1.0e-12 eV
```

Excitation Energies

TDDFT excitation energies				State	Occ.	Unocc.	Overlap
State number	Energy in eV	Estimated error					
1	0.783442128062892	4.3491749946E-07	Triplet	1	5 -->	16	0.001524 spin channel 1
2	1.364692207056864	7.9884918922E-07	Triplet	1	10 -->	11	0.631881 spin channel 1
3	1.719504901920373	7.9228211278E-07	Triplet	1	5 -->	16	0.004060 spin channel 2
4	1.751885263778976	8.0642059869E-07	Triplet	1	8 -->	12	0.001710 spin channel 2
5	2.077954759586475	8.6286667012E-07	Triplet	1	9 -->	13	0.001859 spin channel 2
6	2.097696876062901	8.9205214095E-07	Triplet	1	10 -->	11	0.354534 spin channel 2
7	2.285070941990853	7.7473654913E-07	Triplet	Total overlap for state 1 = 0.999058			
8	2.521388110380361	8.7691194996E-07	Triplet	2	5 -->	16	0.002678 spin channel 1
9	2.569385820640139	7.4534855252E-07	Triplet	2	6 -->	14	0.001526 spin channel 1
10	2.656291097881030	9.0939675695E-07	Triplet	2	7 -->	15	0.001824 spin channel 1
11	2.662265767168658	9.3858554114E-07	Triplet	2	8 -->	12	0.006650 spin channel 1
12	2.716517634327477	9.8533575488E-07	Triplet	2	9 -->	13	0.006345 spin channel 1
				2	10 -->	11	0.337583 spin channel 1
				Total overlap for state 2 = 0.999056			
				3	9 -->	11	0.629691 spin channel 1
				3	10 -->	13	0.013514 spin channel 1
				3	9 -->	11	0.335751 spin channel 2
				3	10 -->	13	0.018442 spin channel 2
				Total overlap for state 3 = 0.998717			
				4	8 -->	11	0.601638 spin channel 1
				4	10 -->	12	0.029184 spin channel 1
				4	8 -->	11	0.331015 spin channel 2
				4	10 -->	12	0.033164 spin channel 2
				4	10 -->	16	0.001230 spin channel 2
				Total overlap for state 4 = 0.998674			
				5	9 -->	11	0.341329 spin channel 1
				5	10 -->	13	0.028207 spin channel 1
				5	9 -->	11	0.619382 spin channel 2
				5	10 -->	13	0.008010 spin channel 2
				Total overlap for state 5 = 0.999409			

TDDFT calculation time: 341.76

Forces

- Contributions from TDDFT response wavefunction
- Also need to take into account 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
- Essentially computing a 3rd-order energy derivative, so need 3rd derivative of XC functional
- <http://www.hector.ac.uk/cse/distributedcse/reports/castep03/>

Castep TD-DFT Features

- Calculation of singlet and triplet states in Tamm-Dancoff approximation for both open and closed-shell systems
- 'Pure' and hybrid-DFT adiabatic XC kernels
- Solvers: Conjugate gradient and block Davidson (both with preconditioning)
- G-vector parallel
- Optimisations for Γ -point
- Calculation checkpointing and restart
- Oscillator strengths (for computing spectra)
- Characterisation of eigenvectors by decomposing into KS orbitals
- Calculation of atomic forces using the Handy-Schaefer Z-vector method
- Structure optimisation of a chosen excited state Born-Oppenheimer molecular dynamics of a chosen excited state