SCM
Software for Chemistry & Materials

# ADF Modeling suite

## Overview and spectroscopy with ADF

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DEFNET Workshop
March 24 | Gent

# Dirac in 1929

$$\hat{H}\Psi = E\Psi$$

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus **completely known**, and the difficulty is only that the exact application of these laws leads to **equations much too complicated to be soluble**. It therefore becomes desirable that **approximate practical methods** of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

# Molecular Modeling: A zoo of methods

Fundamental simulation unit: Electrons → Quantum Chemistry (QM)

Atoms → Molecular Mechanics (MM)

Molecular Mechanics (MM): ★★★★ / ★☆☆☆

Quantum Chemistry (QM) → Ab Initio, DFT, Semi-empirical

| | Ab Initio | DFT | Semi-empirical |
|---|---|---|---|
| Speed: | ★☆☆☆ | ★★☆☆ | ★★★☆ |
| Accuracy: | ★★★★ | ★★★☆ | ★★☆☆ |
| | - Configuration Interaction<br>- Coupled Cluster<br>- Quantum Monte Carlo<br>... | - LDA<br>- GGA<br>- Meta-GGA<br>- Hybrids<br>- Meta-Hybrids | - PM7<br>- DFTB<br>- AM1<br>... |

# DFT: Density Functional Theory

$$\cancel{\Psi(r_1, r_2, \ldots r_N)}$$

Wave function

$$\rho(r)$$

Electron density

Kohn-Sham equations

$$(T + V_{\text{nuc\&el}}[\rho] + V_{\text{XC}}[\rho])\phi_i = \epsilon_i \phi_i$$

$$\left\{ \begin{array}{l} \rho = \sum_i |\phi_i|^2 \\ \phi_i = \sum_j c_{ij}\chi_j \end{array} \right.$$

Approximate Exchange-Correlation (XC)

Basis set expansion

# DFT: The Many-Faced Method

Hamiltonians
(e.g. XC functional)

| XC functional family |
|---|
| LDA |
| GGA |
| Meta-GGA |
| Hybrids |

more accurate
&
(computationally)
more expensive

Technical
(e.g. basis sets)

| Basis Set | size | polarization |
|---|---|---|
| SZ | 1x | 0x |
| DZ | 2x | 0x |
| DZP | 2x | 1x |
| TZP | 3x | 1x |
| TZ2P | 3x | 2x |
| QZ4P | 4x | 4x |

Many more Hamiltonians options:

- solvation
- relativistic effects
- dispersion corrections

...

Many more technical parameters:

- numerical integration
- density fitting
- k-space integration (for periodic systems)
- SCF convergence
- linear scaling cut-offs

...

# From Equations to Programs

| Package | License[†] | Language | Basis | Periodic[‡] | Mol. mech. | Semi-emp. | HF | Post-HF | DFT | GPU |
|---|---|---|---|---|---|---|---|---|---|---|
| ABINIT | GPL | Fortran | PW | 3d | Yes | No | No | No | Yes | Yes |
| ACES | GPL | Fortran/C++ | GTO | No | No | No | Yes | Yes | Yes | Yes |
| ADF | Commercial | Fortran | STO | Any | Yes | Yes[4] | Yes | No | Yes | Yes |
| Atomistix ToolKit (ATK) | Commercial | C++/Python | NAO/EHT | 3d[9] | Yes | Yes | No | No | Yes | |
| BigDFT | GPL | Fortran | Wavelet | Any | Yes | No | Yes | No | Yes | Yes |
| CADPAC | Academic | Fortran | GTO | No | No | No | Yes | Yes | Yes | |
| CASTEP | Academic (UK) / Commercial | Fortran 95/Fortran 2003 | PW | 3d | Yes | No | Yes[5] | No | Yes | |
| CONQUEST | Academic | Fortran 90 | NAO/Spline | 3d | Yes | No | Yes[5] | No | Yes | |
| CP2K | GPL | Fortran 95 | Hybrid GTO / PW | 3d | Yes | Yes | Yes | Yes | Yes | Yes |
| CPMD | Academic | Fortran | PW | 3d | Yes | No | Yes | No | Yes | |
| CRYSTAL | Academic (UK) / Commercial | Fortran | GTO | Any | Yes | No | Yes | Yes[10] | Yes | |
| DACAPO | GPL ?[1] | Fortran | PW | 3d | Yes | No | No | No | Yes | |
| DALTON | Academic | Fortran | GTO | No | No | No | Yes | Yes | Yes | |
| deMon2k | Academic / Commercial | Fortran | GTO | No | Yes | No | No | No | Yes | No |
| DFT++ | GPL | C++ | PW / Wavelet | 3d | Yes | No | No | No | Yes | |
| DIRAC | Academic | Fortran 77, Fortran 90, C | GTO | No | No | No | Yes | Yes | Yes | |
| DMol3 | Commercial | Fortran 90 | NAO | Any | No | No | No | No | Yes | |
| ELK | GPL | Fortran 95 | FP-LAPW | 3d | No | No | Yes | No | Yes | |
| ErgoSCF | GPL | C++ | GTO | No | No | No | Yes | No | Yes | |
| ERKALE | GPL | C++ | GTO | No | No | No | Yes | No | Yes | |
| EXCITING | GPL | Fortran 95 | FP-LAPW | 3d | No | No | Yes | No | Yes | |
| FLEUR | Academic | Fortran 95 | FP-(L)APW+lo | 3d, 2d, 1d | No | No | Yes | Yes | Yes | |
| FHI-aims | Commercial | Fortran | NAO | Any | Yes | No | Yes | Yes | Yes | |
| FreeON | GPL | Fortran 95 | GTO | Any | Yes | No | Yes | Yes | Yes | |
| Firefly / PC GAMESS | Academic | Fortran, C, Assembly | GTO | No | Yes[3] | Yes | Yes | Yes | Yes | Yes |
| GAMESS (UK) | Academic (UK) / Commercial | Fortran | GTO | No | No | Yes | Yes | Yes | Yes | Yes |
| GAMESS (US) | Academic | Fortran | GTO | No | Yes[2] | Yes | Yes | Yes | Yes | Yes |
| Gaussian | Commercial | Fortran | GTO | Any | Yes | Yes | Yes | Yes | Yes | |
| GPAW | GPL | Python / C | Grid / NAO / PW | Any | Yes | No | Yes[5] | No | Yes | Yes |
| HLAPW | Unknown | Unknown | FLAPW | 3d | No | No | No | No | Yes | |
| HORTON | GPL | Python / C++ | GTO | No | No | No | Yes | Yes | Yes | No |
| Jaguar | Commercial | Fortran / C | GTO | No | Yes | No[11] | Yes | Yes | Yes | |
| JDFTx | GPL | C++ / CUDA | PW | 3d | No | No | Yes | No | Yes | |
| LOWDIN | Academic | Fortran 95/03 | GTO | No | Yes | No | Yes | Yes | Yes | |
| MADNESS | GPL | C++ | Wavelet | No | No | No | Yes | No | Yes | |
| MISSTEP | GPL | C++ | PW | No | No | No | No | No | Yes | |
| MOLCAS | Academic | Fortran | GTO | No | Yes | Yes | Yes | Yes | Yes | Yes |
| MOLPRO | Commercial | Fortran | GTO | No | No | No | Yes | Yes | Yes | |
| MPQC | LGPL | C++ | GTO | No | No | No | Yes | Yes | Yes | |
| NRLMOL | Unknown | Fortran | GTO | No | No | No | No | No | Yes | |
| NTChem | Unknown | Unknown | GTO | No | No | No | Yes | Yes | Yes | |
| NWChem | ECL v2 | Fortran 77 / C | GTO, PW | Yes(PW) No(GTO) | Yes | No | Yes | Yes | Yes | Yes |
| Octopus | GPL | Fortran 95, C, OpenCL | Grid | Any | Yes | No | Yes | No | Yes | Yes |
| ONETEP | Academic (UK) / Commercial | Fortran | PW | 3d | Yes | No | Yes[5] | No | Yes | Yes |
| OpenAtom | Academic | Charm++ (C++) | PW | Template:3d | Yes | No | No | No | Yes | |
| OpenMX | GPL | C | NAO | 3d | Yes | No | No | No | Yes | |
| ORCA | Academic | C++ | GTO | No | Yes | Yes | Yes | Yes | Yes | |
| PLATO | Academic | Unknown | NAO | Any | Yes | No | No | No | Yes | |
| PQS | Commercial | Unknown | Unknown | Unknown | Yes | Yes | Yes | Yes | Yes | |
| Priroda-06 | Academic | C | GTO | No | No | No | Yes | Yes | Yes | |
| PSI | GPL | C / C++ / Python | GTO | No | No | No | Yes | Yes | Yes | |
| PUPIL | GPL | Fortran / C | GTO, PW | Any | Yes | Yes | Yes | Yes | Yes | Yes |
| PWmat | Commercial | Fortran | PW | 3d | Yes | No | Yes | Yes | Yes | Yes |
| PWscf[6] | GPL | Fortran | PW | 3d | No | No | Yes | No | Yes | |
| PyQuante | BSD | Python | GTO | No | No | Yes | Yes | Yes | Yes | |
| PySCF | BSD | Python | GTO | No | No | No | Yes | Yes | Yes | |
| Q-Chem | Commercial | Fortran / C++ | GTO | No | Yes | Yes | Yes | Yes | Yes | Yes |
| QSite | Unknown | Unknown | GTO | No | Yes | No[11] | Yes | Yes | Yes | |
| Quantum ESPRESSO | GPL | Fortran | PW | 3d | Yes | No | Yes | No | Yes | Yes |
| RMG | GPL | C/C++ | Grid | 3d | Yes | No | No | No | Yes | Yes |
| RSPt | Academic | Fortran / C | FP-LMTO | 3d | No | No | No | No | Yes | |
| SCIGRESS | Commercial | C++, C, Java, Fortran | GTO | Yes | Yes | Yes | No | No | Yes | |
| Spartan | Commercial | Fortran / C / C++ | GTO | No | Yes | Yes | Yes | Yes | Yes | |
| SIESTA | Academic | Fortran | NAO | 3d[12] | Yes | No | No | No | Yes | |
| TB-LMTO | Academic | Fortran | LMTO | 3d | No | No | No | No | Yes | |
| TERACHEM [8] | Commercial | C/CUDA | GTO | No | Yes | No | Yes | No | Yes | Yes |
| TURBOMOLE | Commercial | Fortran | GTO | Yes | Yes | No | Yes | Yes | Yes | |
| VASP | Academic(AT)/ Commercial | Fortran | PW | 3d | Yes | No | Yes | Yes | Yes | Yes |
| WIEN2k | Commercial | Fortran / C | FP-(L)APW+lo | 3d | Yes | No | Yes | No | Yes | |

Kohn-Sham equations

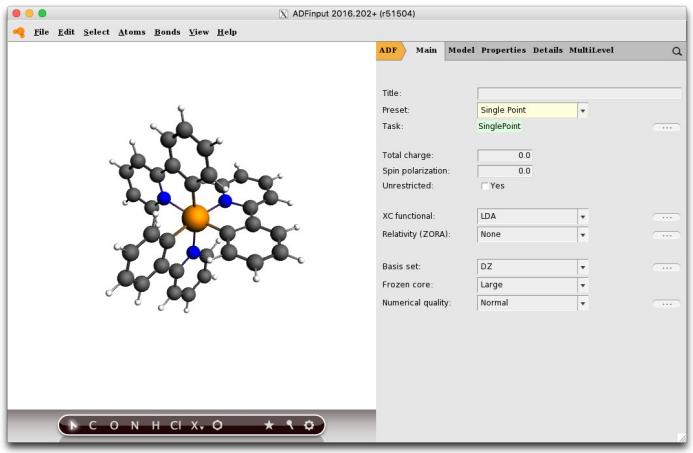
$$(T + V_{\text{nuc\&el}}[\rho] + V_{\text{XC}}[\rho])\phi_i = \epsilon_i \phi_i \qquad \begin{cases} \rho = \sum_i |\phi_i|^2 \\ \phi_i = \sum_j c_{ij}\chi_j \end{cases}$$

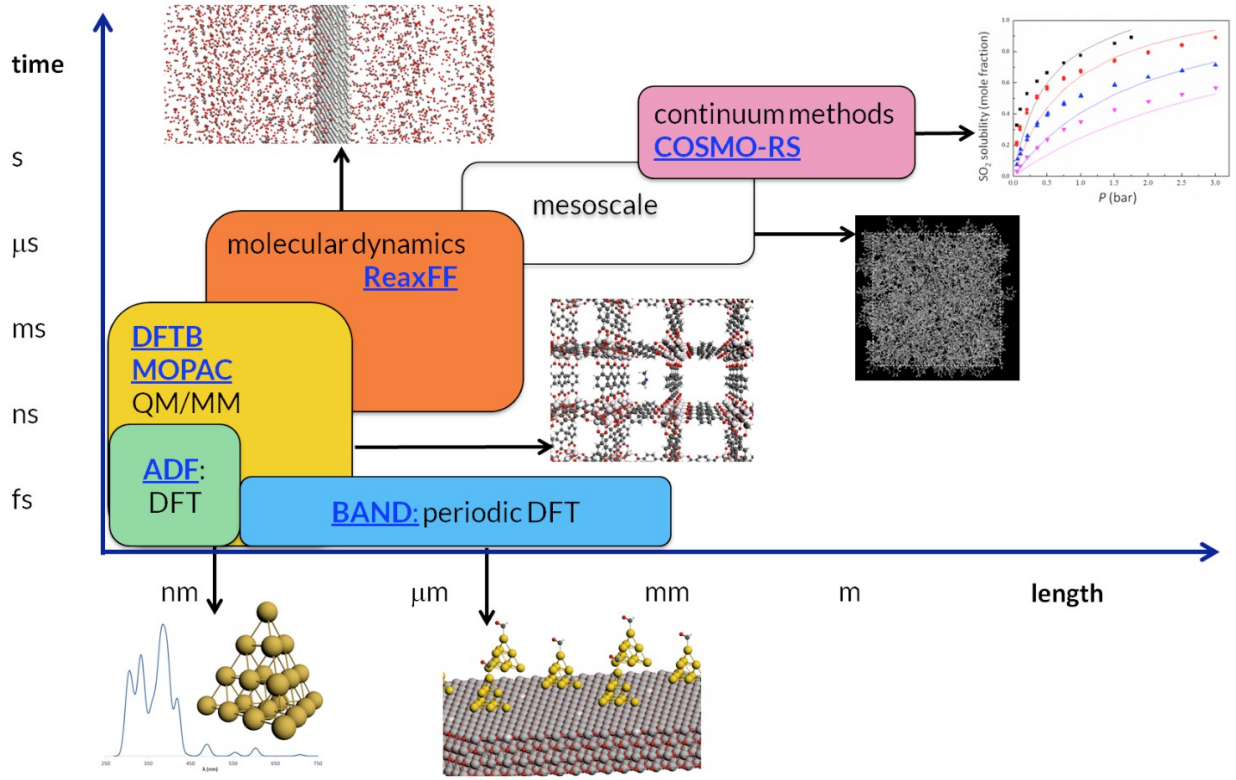
Why so many program?

- Periodic / Molecular
- Orbitals expansion (basis functions)
- Target applications
- Historic / IKB (I know better)

# The ADF Modeling Suite

Graphical User Interface



# ADF: Molecular DFT

## Technical:

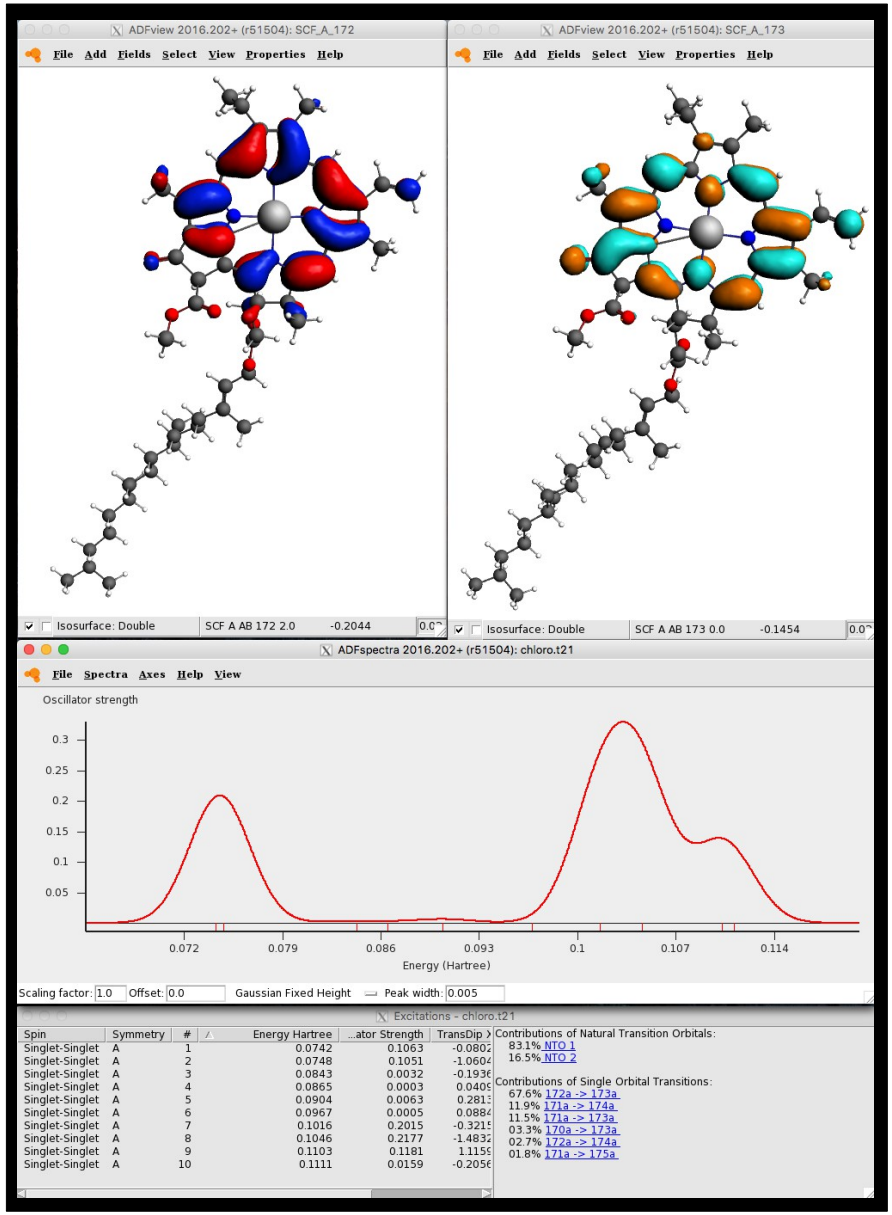
- Slater Type basis functions (all electron, all elements)
- Relativistic effects (ZORA, spin-orbit coupling)
- XC: GGAs, meta-GGAs, Hybrids, RS-hybrids
- Efficiently parallelized, linear scaling techniques

## Miscellaneous Features:

- Geometry optimization, transition state, IR frequencies
- Solvents and environments: COSMO, QM/MM
- Analysis: energy decomposition, bond analysis
- Electronic transport: NEGF, transfer integrals

## Spectroscopy:

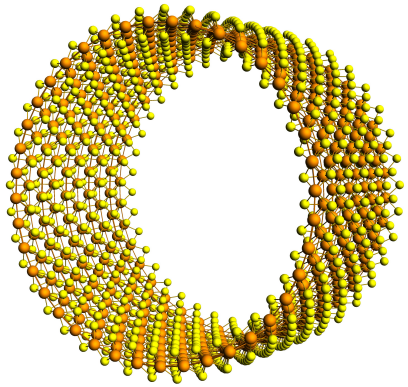
- IR, Raman, VCD, Franck-Condon factors
- UV/Vis spectra (TD-DFT)
- Frequency-dependent (hyper-)polarizability
- NMR chemical shift and spin-spin coupling
- ESR (EPR) g-tensor, hyperfine A-tensor, ZFS
- Mössbauer spectroscopy, NRVS



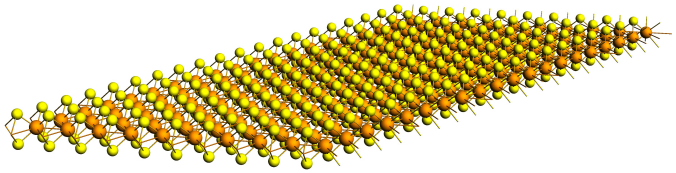
# Band: Periodic DFT

## Technical:
- Numerical Atomic Orbitals (all electron, all elements)
- Any periodicity: 0D, 1D, 2D, 3D
- Relativistic effects (ZORA, spin-orbit coupling)
- XC: GGAs, meta-GGAs, RS-hybrids
- Efficiently parallelized, linear scaling techniques

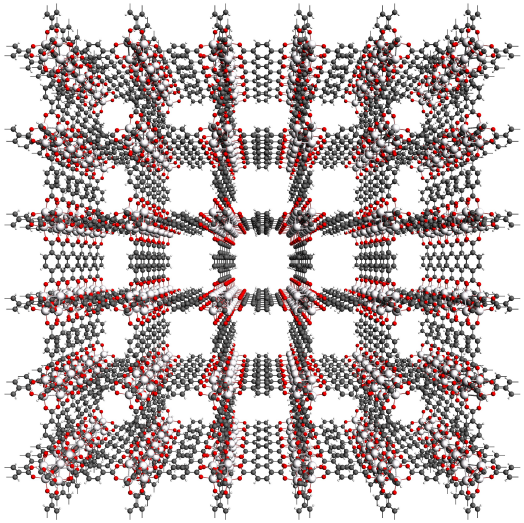
## Miscellaneous Features:
- Geometry optimization, transition state
- Phonons, Thermodynamic Properties
- Solvent effects: COSMO
- Static electric fields
- Analysis: Energy Decomposition, partial DOS
- Electronic transport: NEGF
- Spectroscopy: TD-DFT/TD-CDFT, ESR, EFG



1D



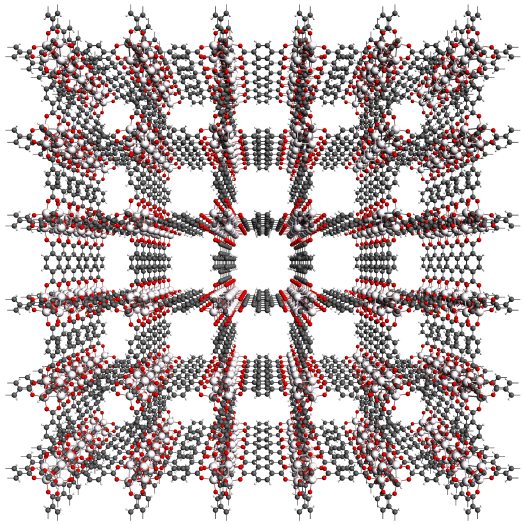
2D



3D

# DFTB: Fast, approximate DFT

DFBT: Density-Functional based Tight-Binding

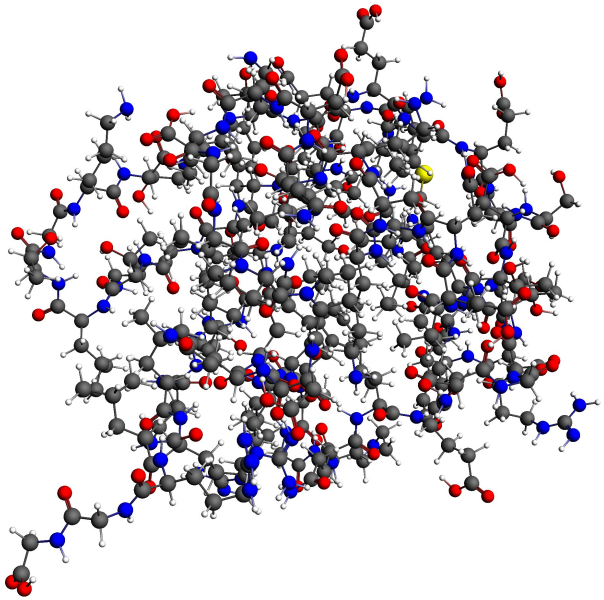


## Technical:

- Any periodicity: 0D, 1D, 2D, 3D
- Efficiently parallelized, linear scaling techniques

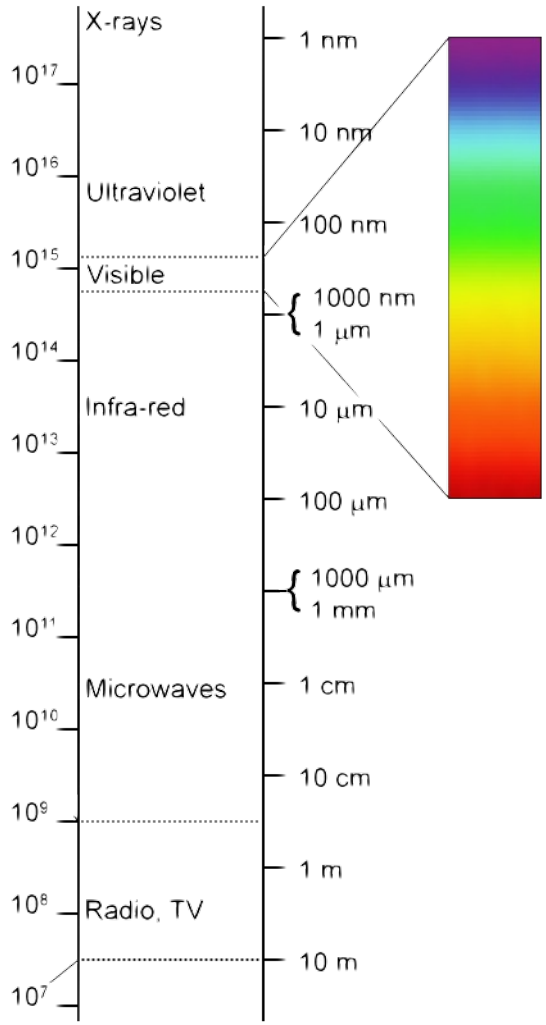
## Miscellaneous Features:

- Geometry optimization, transition state, IR frequencies
- UV/VIS, IR spectra, phonons, pDOS
- Band structures and Density of States
- Molecular dynamics



# ADF: Spectroscopy

Interaction between matter and electromagnetic radiation




- Mössbauer spectroscopy, NRVS
- Core excitations

- UV/Vis spectra
  oscillator strength, (hyper-)polarizability
  circular dichroism, optical rotation, ...

Electronic Spectroscopy

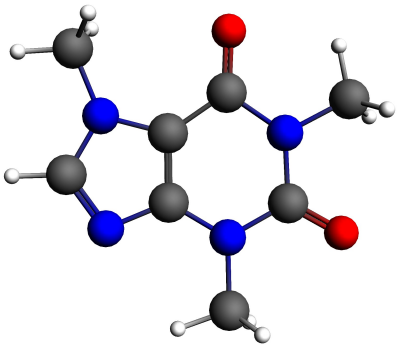
- IR frequencies
  VCD, Raman, Frank-Condon, VROA

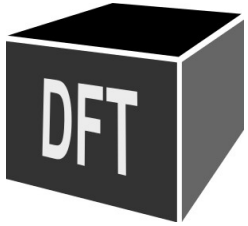
- EPR
  g-tensor and hyperfine interaction (A-tensor)

- NMR
  chemical shift, spin-spin coupling

# Electronic excitations

Caffeine

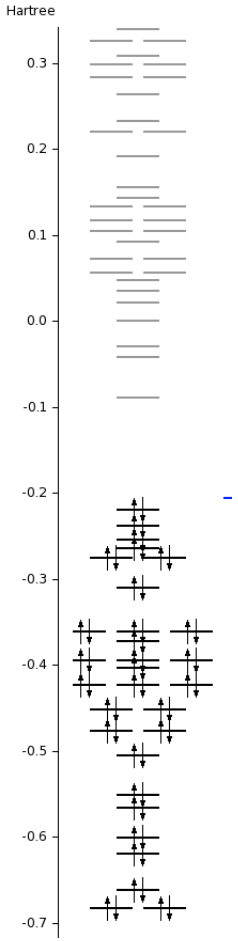





Kohn-Sham equations

$$(T + V_{\mathrm{nuc\&el}}[\rho] + V_{\mathrm{XC}}[\rho])\phi_i = \epsilon_i \phi_i$$

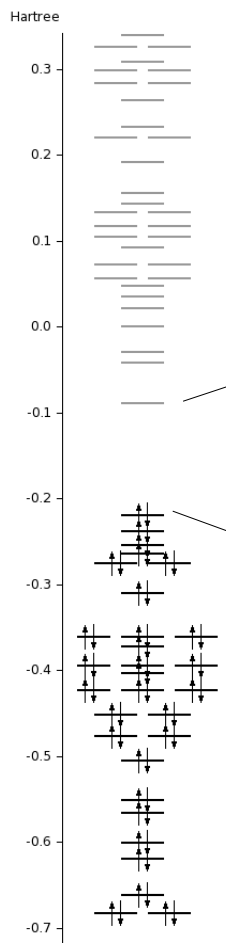
Orbitals



# Electronic excitations: a simple approach

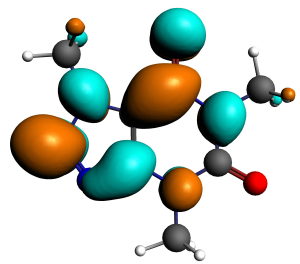
Kohn-Sham equations

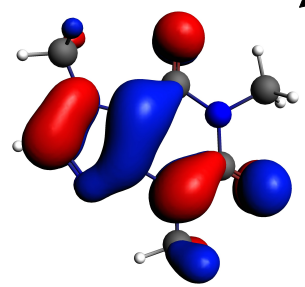
$$(T + V_{\text{nuc\&el}}[\rho] + V_{\text{XC}}[\rho])\phi_i = \epsilon_i \phi_i$$




Orbitals

LUMO: E=-0.09 Hartree





HOMO: E=-0.22 Hartree

excitation energy

$$\epsilon_j - \epsilon_i$$

transition dipole moment

$$\mu_{ij} = \langle \phi_i | \vec{\mu} | \phi_j \rangle = e \int \phi_i \mathbf{r} \phi_j d\mathbf{r}$$

- DFT: ground state theory
- Very approximate...

# Electronic excitations: Time-dependent DFT (TD-DFT)

Kohn-Sham equations
(ground state)

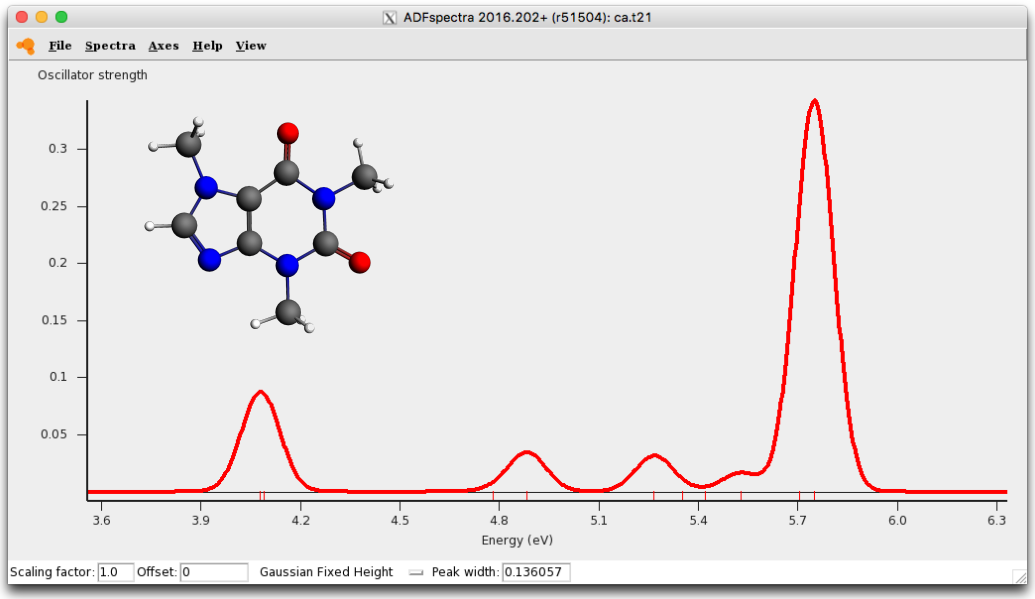
$$(T + V_{\text{nuc\&el}}[\rho] + V_{\text{XC}}[\rho])\phi_i = \epsilon_i \phi_i$$

Time dependent Kohn-Sham equations
(excited states)

$$i\frac{\partial \phi_i}{\partial t} = (T + V_{\text{el-el\&nuc}} + V_{\text{ext}}(t))\phi_i$$

Linear response:
- excitations energies
- oscillator strength

(Line width: gaussian convolution)



# DFT: The Many-Faced Method

Hamiltonians
(e.g. XC functional)

| XC functional family |
| --- |
| LDA |
| GGA |
| Meta-GGA |
| Hybrids |

more accurate
&
(computationally)
more expensive

Technical
(e.g. basis sets)

| Basis Set | size | polarization |
| --- | --- | --- |
| SZ | 1x | 0x |
| DZ | 2x | 0x |
| DZP | 2x | 1x |
| TZP | 3x | 1x |
| TZ2P | 3x | 2x |
| QZ4P | 4x | 4x |

Many more Hamiltonians options:

- solvation
- relativistic effects
- dispersion corrections

...

Many more technical parameters:

- numerical integration
- density fitting
- k-space integration (for periodic systems)
- SCF convergence
- linear scaling cut-offs

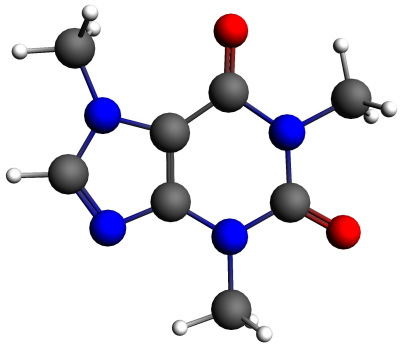
...

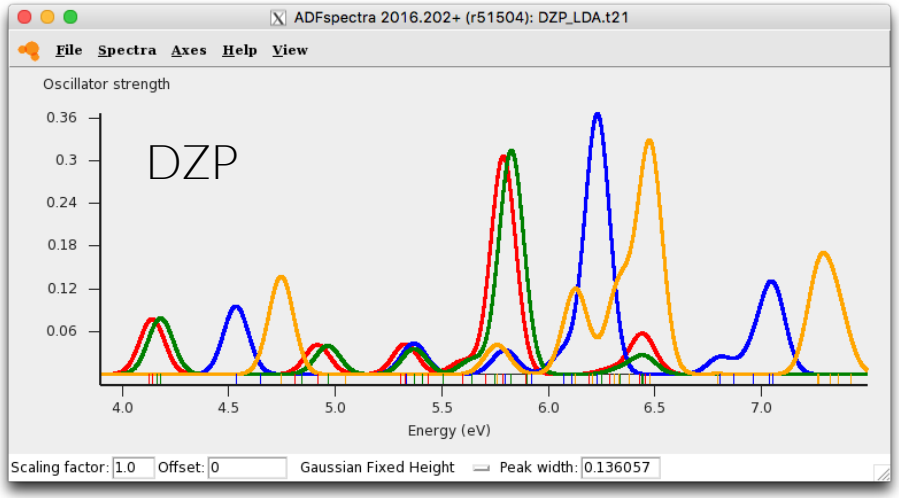
# Excitations with TDDFT: computation time v.s. accuracy

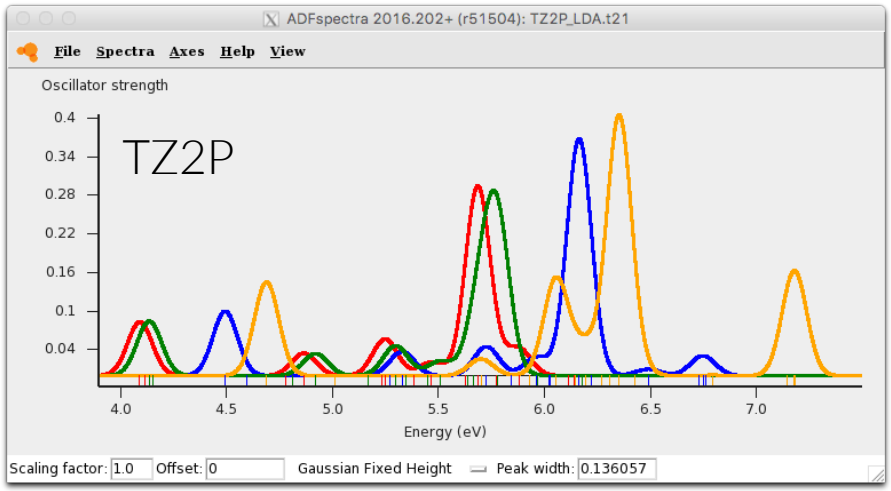
Simulation time in minutes (on one node)

XC functional

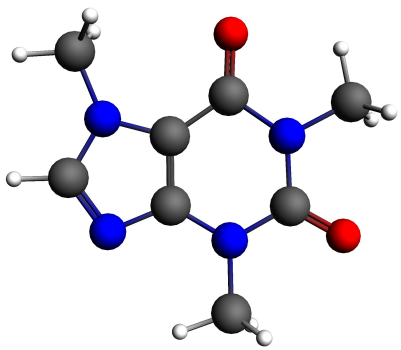
| Basis set | LDA | GGA (PBE) | Meta-GGA (M06L) | Hybrid (PBE0) |
|---|---|---|---|---|
| DZP | < 1 | 1.5 | 2.5 | 26 |
| TZ2P | 3 | 4 | 9 | 90 |



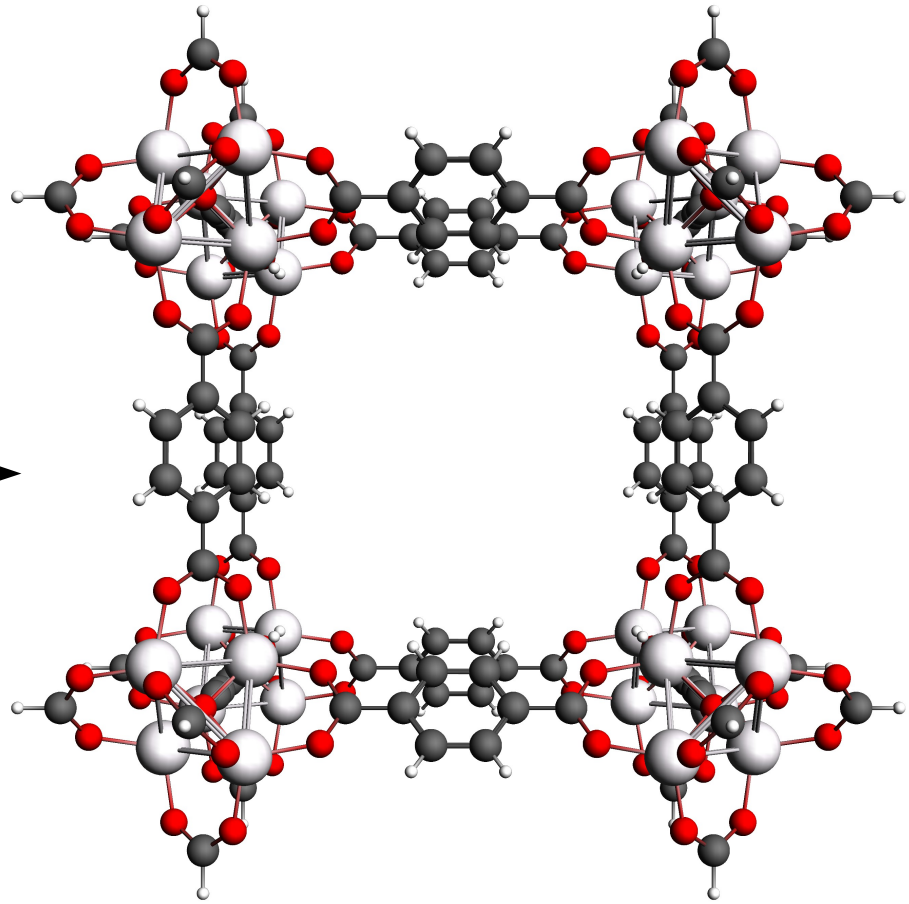


# From Caffeine to MOFs



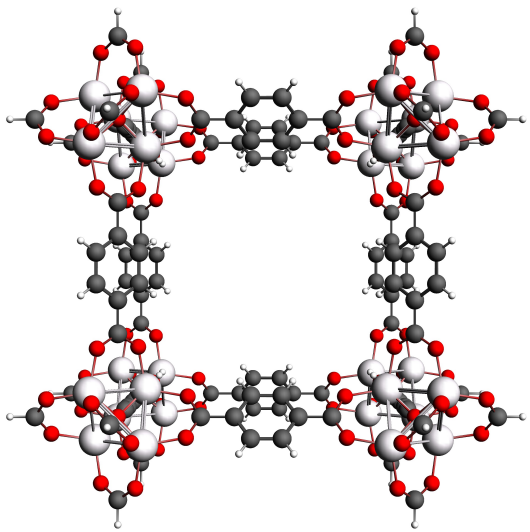
24 Atoms

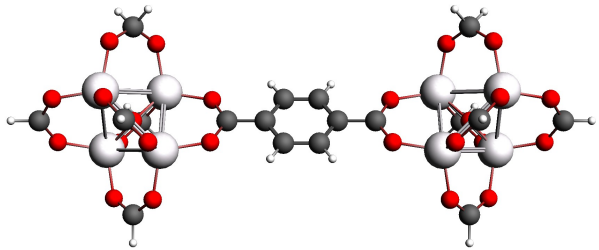


328 Atoms

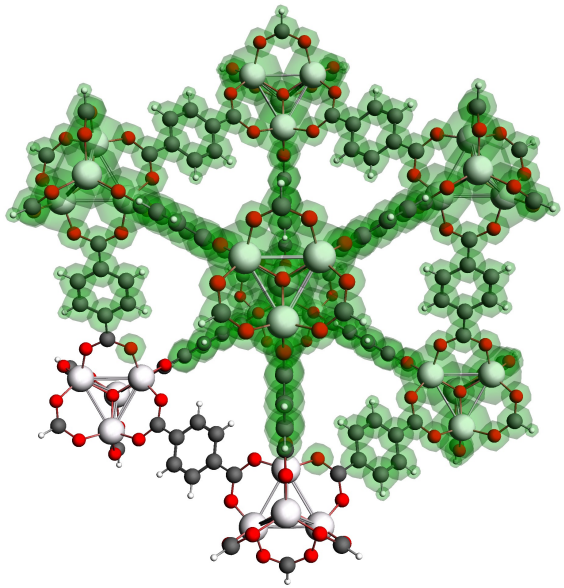
# From Caffeine to MOFs: 1) Model systems

Model systems





Small model



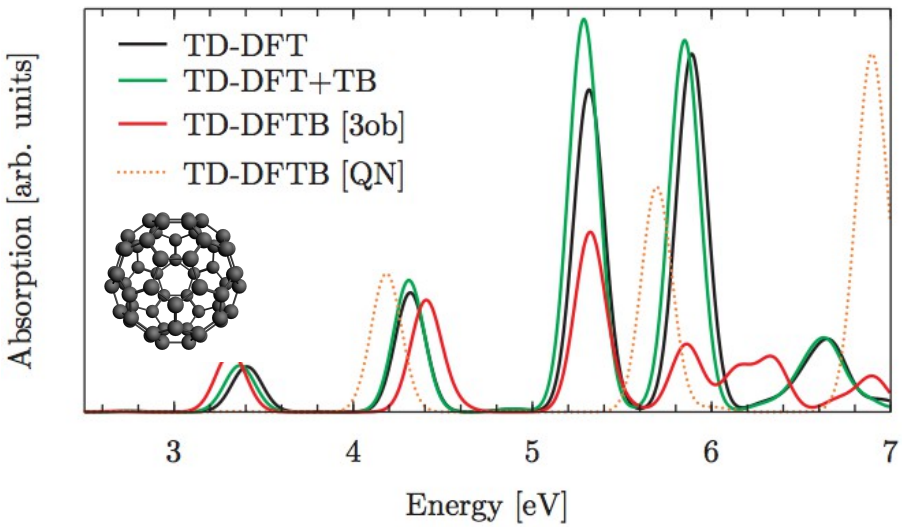
QM/MM

FDE

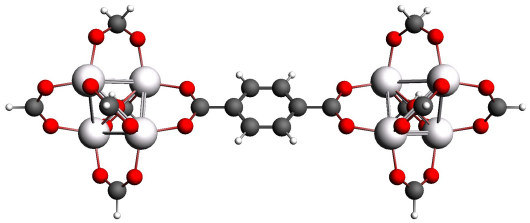
# From Caffeine to MOFs: 2) Approximate methods

TD-DFT-TB: Approximate TD-DFT

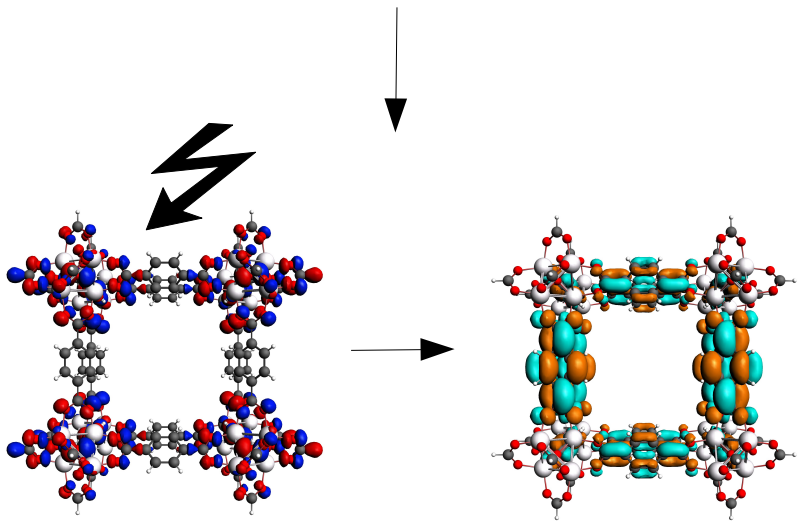
| | TD-DFT | TD-DFT+TB | TD-DFTB |
|---|---|---|---|
| ground state | 4min 38s | 4min 33s | < 1s |
| excited states | 19h 37min | 11min 35s | 1min 26s |



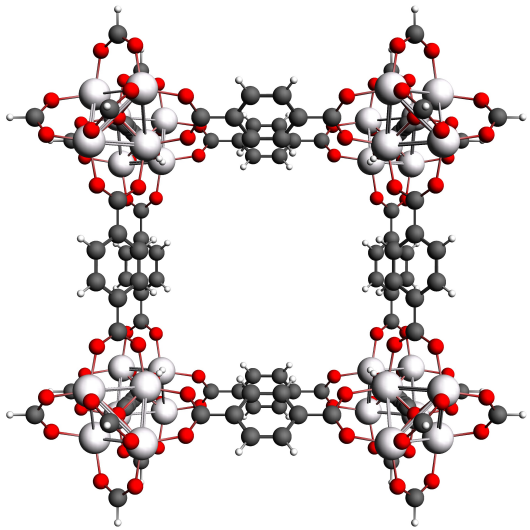

Rüger et. al. http://arxiv.org/abs/1603.02571

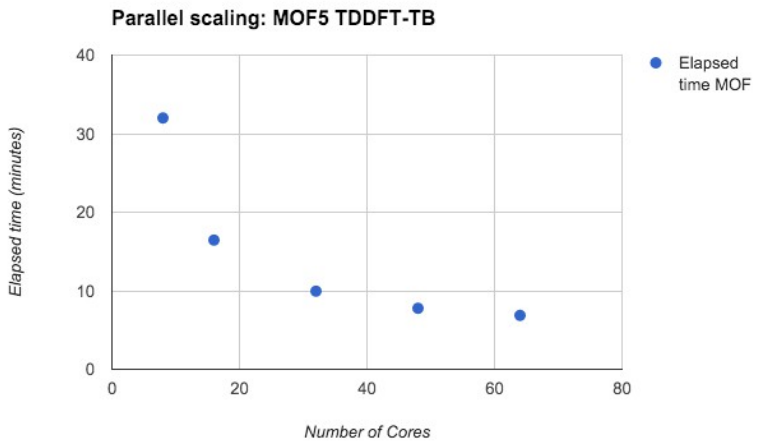


- validate the method on model systems
- understand limitation of approximation



# From Caffeine to MOFs: 3) Parallel Computing





# Summary

- DFT
    - workhorse of molecular modeling
    - be aware of approximations and applicability

- ADF Modeling suite:
    - ADF: molecular DFT
    - BAND: periodic DFT
    - DFTB: fast approximate DFT
    - ReaxFF: Reactive molecular mechanics

- Spectroscopy:
    - Electronic excitations → TD-DFT

- Modeling MOFs:
    - Model systems
    - Approximate methods

# Hands-on session

www.scm.com/documentation/Tutorials (Note: capital 'T')

1) GUI overview tutorials / Getting started: Geometry optimization of ethanol

2) ADF-GUI tutorials / Excitation energies and UV/Vis spectrum of ethene

3) ADF-GUI tutorials / Vibrational frequencies and IR spectrum of ethane

# Vibrational spectroscopy

Infra red (IR) spectroscopy: absorption of light to excite molecular vibrations

Molecular vibration → Newtonian mechanics

Harmonic approximation (at the optimized geometry):
- parabolic potential wrt nuclear displacements

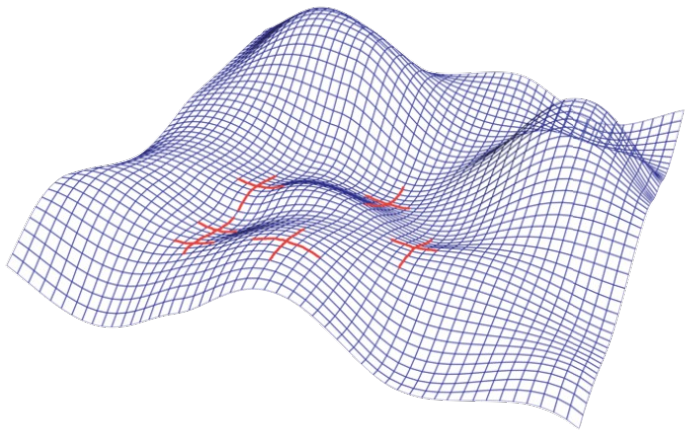
Normal modes 'Q': from Hessian

$$H_{ij} = \frac{\partial^2 E}{\partial x_i \partial x_j}$$

Absorption intensity:

$$I_{IR} \propto \left( \frac{d\mu}{dQ} \right)^2$$

# Geometry Optimization



How to find the minimum of the Potential Energy Surface (PES)?

Follow the gradients: $(\nabla E)_i = \dfrac{\partial E}{\partial x_i}$

Hessian: $H_{ij} = \dfrac{\partial^2 E}{\partial x_i \partial x_j}$