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Molecular Excited States: **Time-Dependent Density Functional Theory**

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Objectives

Part 1:
- Basics of geometry optimization
- Geometry optimization of the DFT ground state

Part 2:
- Introduction to TDDFT
- The vertical absorption spectrum
- Excited-state analysis using the ground state MOs
- Excited-state geometry optimizations and PES
- TDDFT challenges

Part 4:
- Spin-flip TDDFT
- Mixed-reference SF-TDDFT (MRSF-TDDFT)

ORCA 6.0

PyOpenQP

Geometry Optimization – The Ground State –

The potential energy surface (PES)

$$\hat{H}\Psi(\{\mathbf{R}_I\},\{\mathbf{r}_i\}) = E\Psi(\{\mathbf{R}_I\},\{\mathbf{r}_i\})$$

$$\downarrow$$

Born-Oppenheimer approximation

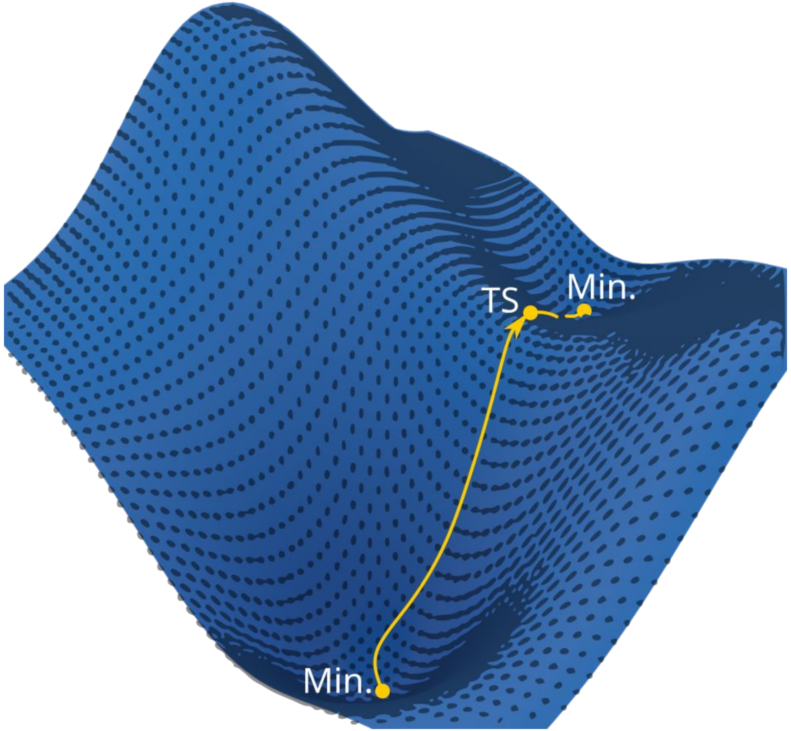
$$\Psi(\{\mathbf{R}_I\},\{\mathbf{r}_i\}) = \psi_{\mathrm{N}}(\{\mathbf{R}_I\})\,\psi_{\mathrm{e}}(\{\mathbf{r}_i\})$$

$$\downarrow$$

The electronic problem:

$$\hat{H}\Psi(\{\mathbf{R}_I\},\{\mathbf{r}_i\}) = E\Psi(\{\mathbf{R}_I\},\{\mathbf{r}_i\})$$

@ fixed $\{\mathbf{R}_\mathrm{I}\}$

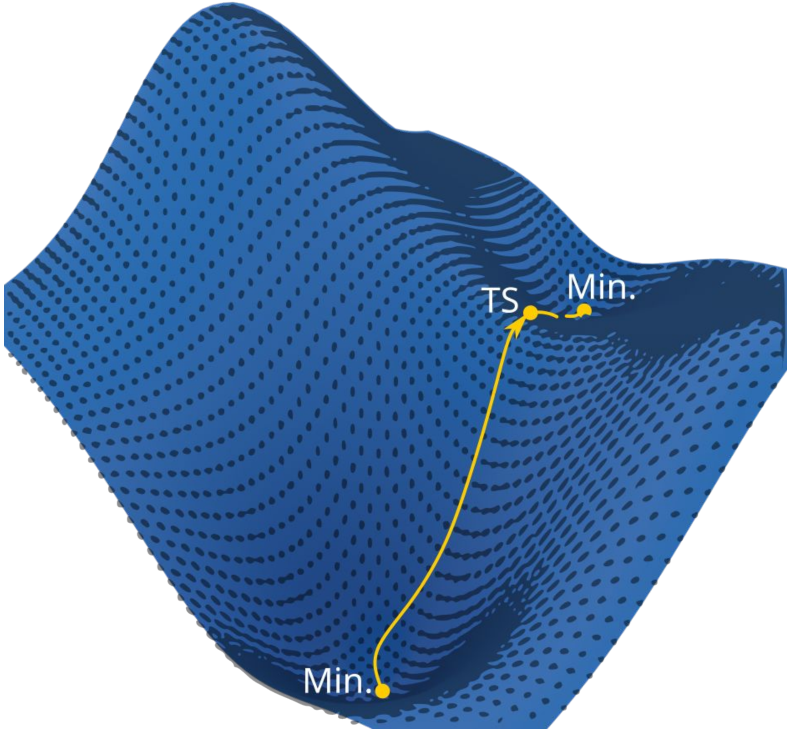


Special points on the PES

- Local minima,
- Global minimum,
- Saddle points (transition states),

For a function $f(\mathbf{x})$, find $\mathbf{x'}$ such that the gradient is zero, $\nabla f(\mathbf{x'})=0$.

The Hessian, $\mathbf{H}_f(x')$, will reveal the nature of the point.

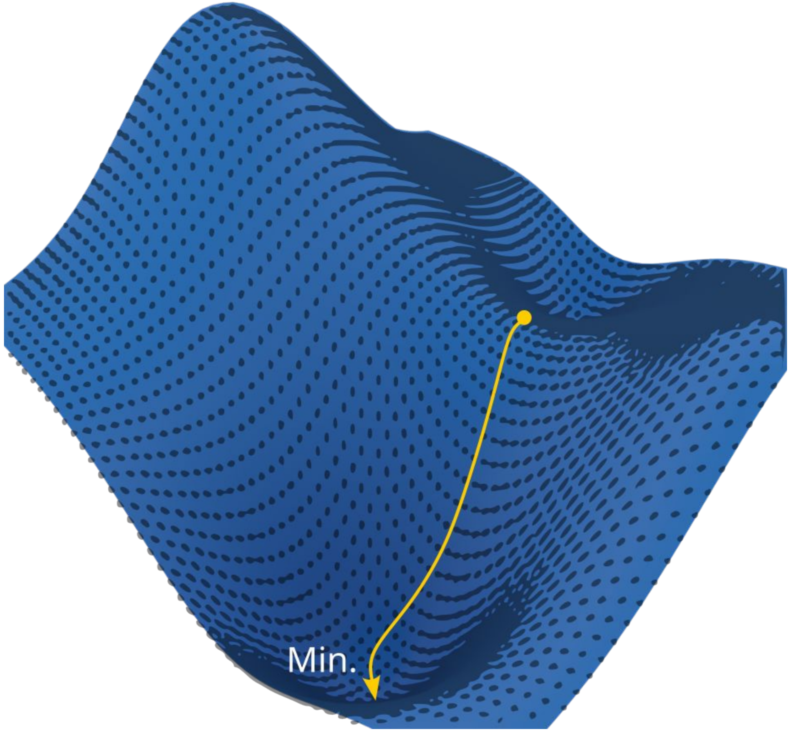


Geometry optimization

Procedure of finding local minima on the PES.

Ingredients:

- Initial molecular coordinates,
- Energy, gradient, and sometimes Hessian,
- Procedure/algorithm to update the molecular coordinates and move on the PES towards lower energies.



Gradient descent

One of the simplest optimization algorithms. It updates the coordinates by taking a step in the direction opposite to the gradient ($\mathbf{g}_i$).

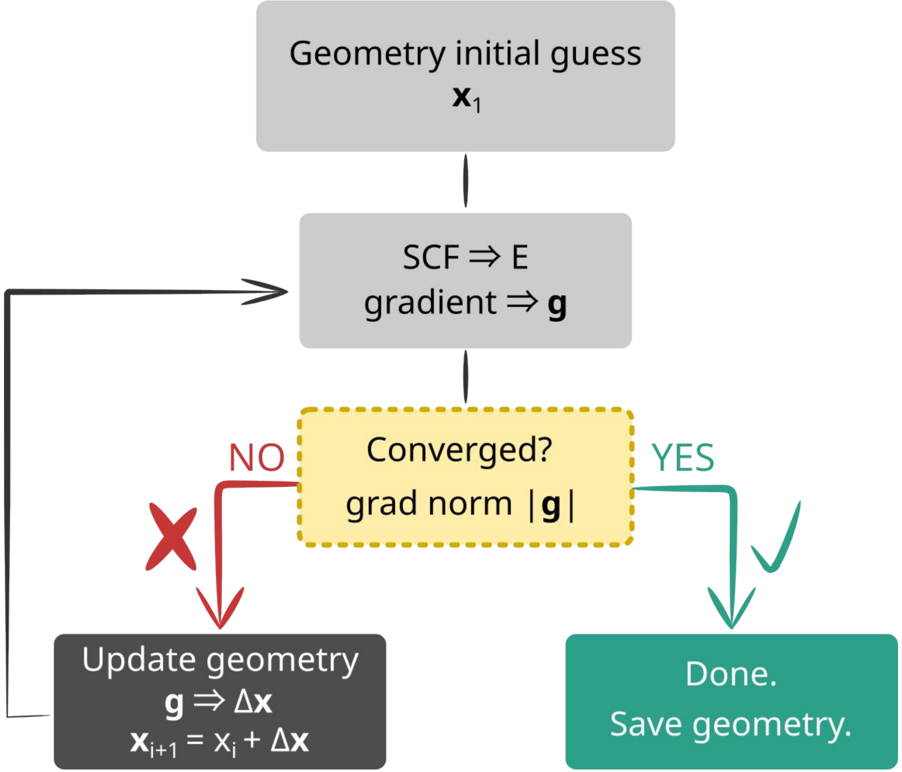
$$\mathbf{x}_{i+1} = \mathbf{x}_i - k\mathbf{g}_i$$

gradient @ old coords.

new coords.

old coords.

step size param.



Geometry initial guess $\mathbf{x}_1$

SCF ⇒ E
gradient ⇒ **g**

Converged?
grad norm |**g**|

NO

YES

Update geometry
$\mathbf{g} \Rightarrow \Delta\mathbf{x}$
$\mathbf{x}_{i+1} = x_i + \Delta\mathbf{x}$

Done.
Save geometry.

The energy gradient and molecular Hessian

$$\frac{\mathrm{d}E_\mathrm{e}}{\mathrm{d}\mathbf{R}} = \left(\frac{\mathrm{d}E_\mathrm{e}}{\mathrm{d}x_1}, \frac{\mathrm{d}E_\mathrm{e}}{\mathrm{d}y_1}, \frac{\mathrm{d}E_\mathrm{e}}{\mathrm{d}z_1}, \dots, \frac{\mathrm{d}E_\mathrm{e}}{\mathrm{d}x_n}, \frac{\mathrm{d}E_\mathrm{e}}{\mathrm{d}y_n}, \frac{\mathrm{d}E_\mathrm{e}}{\mathrm{d}z_n}\right)$$

Gradient

$$\frac{\mathrm{d}^2 E_\mathrm{e}}{\mathrm{d}\mathbf{R}^2} = \begin{array}{cc}
\begin{array}{ccccccc}
 & \text{Atom 1} & & \dots & & \text{Atom n} & \\
\mathrm{x}_1 & \mathrm{y}_1 & \mathrm{z}_1 & \dots & \mathrm{x}_n & \mathrm{y}_n & \mathrm{z}_n
\end{array} & \\
\begin{pmatrix}
\frac{\mathrm{d}^2 E_\mathrm{e}}{\mathrm{d}{x_1}^2} & \frac{\mathrm{d}^2 E_\mathrm{e}}{\mathrm{d}x_1\mathrm{d}y_1} & \frac{\mathrm{d}^2 E_\mathrm{e}}{\mathrm{d}x_1\mathrm{d}z_1} & \cdots & \frac{\mathrm{d}^2 E_\mathrm{e}}{\mathrm{d}x_1\mathrm{d}x_n} & \frac{\mathrm{d}^2 E_\mathrm{e}}{\mathrm{d}x_1\mathrm{d}y_n} & \frac{\mathrm{d}^2 E_\mathrm{e}}{\mathrm{d}x_1\mathrm{d}z_n} \\
 & & & & & & \\
\frac{\mathrm{d}^2 E_\mathrm{e}}{\mathrm{d}z_n\mathrm{d}x_1} & \frac{\mathrm{d}^2 E_\mathrm{e}}{\mathrm{d}z_n\mathrm{d}y_1} & \frac{\mathrm{d}^2 E_\mathrm{e}}{\mathrm{d}z_n\mathrm{d}z_1} & \cdots & \frac{\mathrm{d}^2 E_\mathrm{e}}{\mathrm{d}z_n\mathrm{d}x_n} & \frac{\mathrm{d}^2 E_\mathrm{e}}{\mathrm{d}z_n\mathrm{d}y_n} & \frac{\mathrm{d}^2 E_\mathrm{e}}{\mathrm{d}{z_n}^2}
\end{pmatrix} &
\begin{array}{c} \mathrm{x}_1 \\ \vdots \\ \mathrm{z}_n \end{array}
\end{array}$$

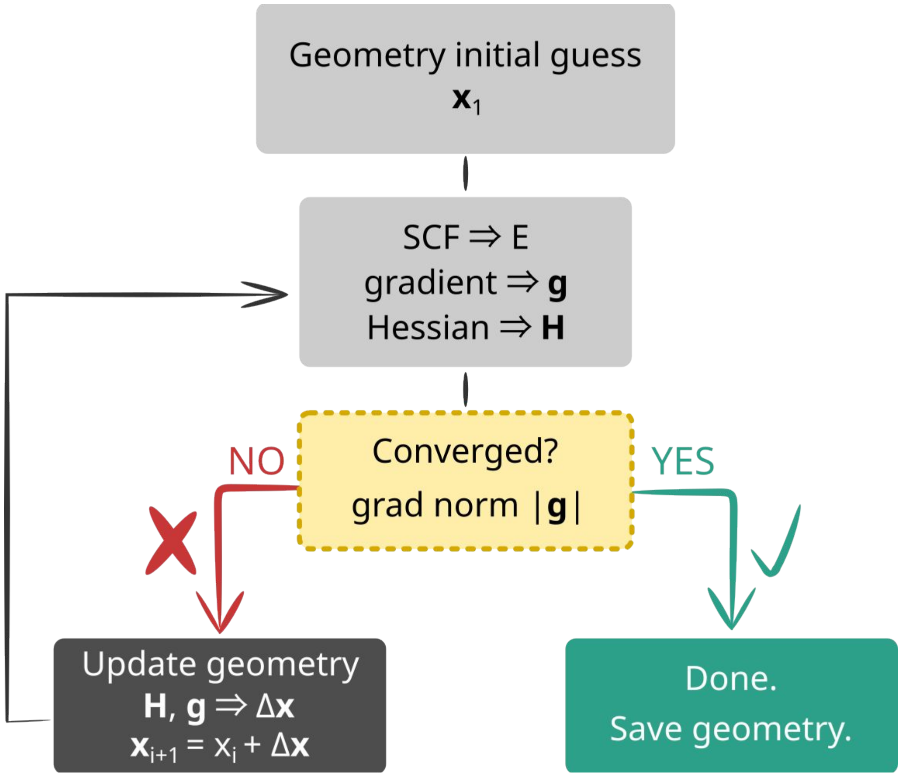
Hessian

Newton–Raphson

Procedure which updates the coordinates based on the quadratic approximation of the PES. Both the gradient ($\mathbf{g}_i$) and the Hessian ($\mathbf{H}_i$) are used to determine the next set of coordinates.

$$\Delta \mathbf{x}_i = -\mathbf{H}_i^{-1} \mathbf{g}_i,$$

$$\mathbf{x}_{i+1} = \mathbf{x}_i + \Delta \mathbf{x}_i.$$



Geometry initial guess
$\mathbf{x}_1$

SCF ⇒ E
gradient ⇒ $\mathbf{g}$
Hessian ⇒ $\mathbf{H}$

Converged?
grad norm $|\mathbf{g}|$

NO ✗

Update geometry
$\mathbf{H}, \mathbf{g} \Rightarrow \Delta\mathbf{x}$
$\mathbf{x}_{i+1} = x_i + \Delta\mathbf{x}$

YES ✓

Done.
Save geometry.

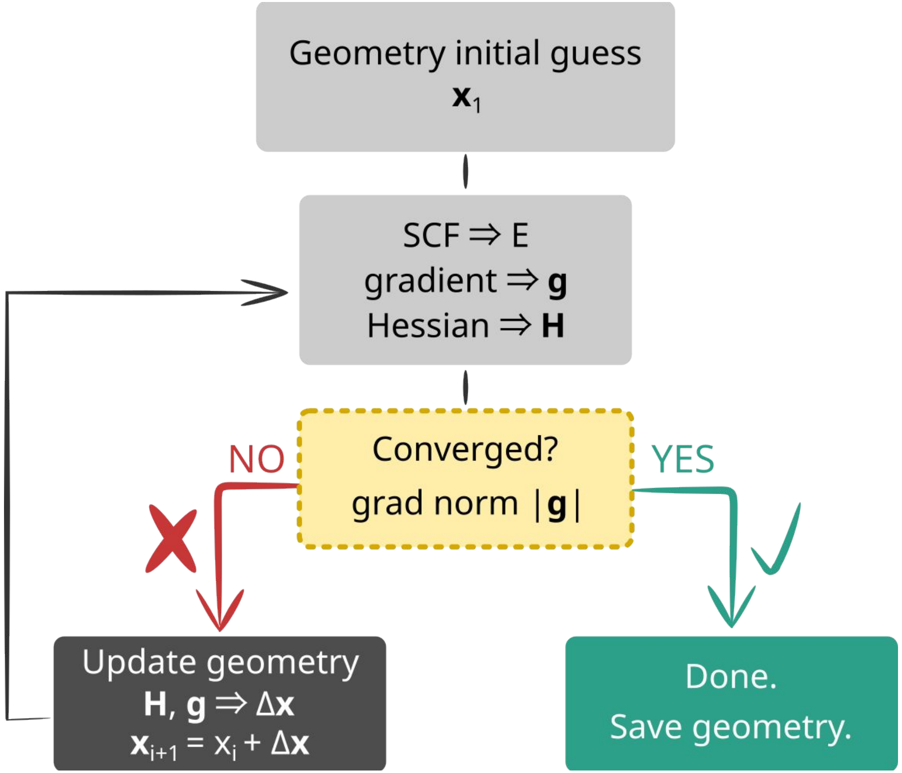
Quasi-Newton

Procedure which updates the coordinates based on the quadratic approximation of the PES. Both the gradient (**g**$_i$) and the Hessian (**H**$_i$) are used to determine the next set of coordinates.

$$\Delta \mathbf{x}_i = -\mathbf{H}_i^{-1}\mathbf{g}_i,$$

$$\mathbf{x}_{i+1} = \mathbf{x}_i + \Delta \mathbf{x}_i.$$

The Hessian is approximated based on the gradient history, e.g. in the (BFGS) Broyden-Fletcher-Goldfarb-Shanno approach.



Geometry initial guess
$\mathbf{x}_1$

SCF ⇒ E
gradient ⇒ **g**
Hessian ⇒ **H**

Converged?
grad norm |**g**|

NO ✗

YES ✓

Update geometry
H, **g** ⇒ $\Delta\mathbf{x}$
$\mathbf{x}_{i+1} = x_i + \Delta\mathbf{x}$

Done.
Save geometry.

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The potential energy surface (PES)

$$\hat{H}\Psi(\{\mathbf{R}_I\},\{\mathbf{r}_i\}) = E\Psi(\{\mathbf{R}_I\},\{\mathbf{r}_i\})$$

↓

Born-Oppenheimer approximation

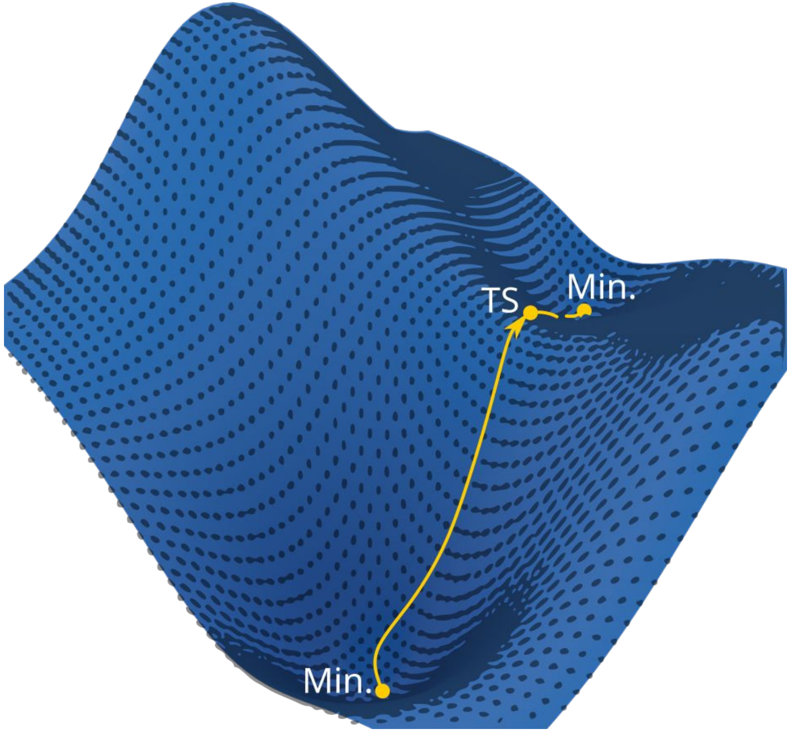
$$\Psi(\{\mathbf{R}_I\},\{\mathbf{r}_i\}) = \psi_\mathrm{N}(\{\mathbf{R}_I\})\,\psi_\mathrm{e}(\{\mathbf{r}_i\})$$

↓

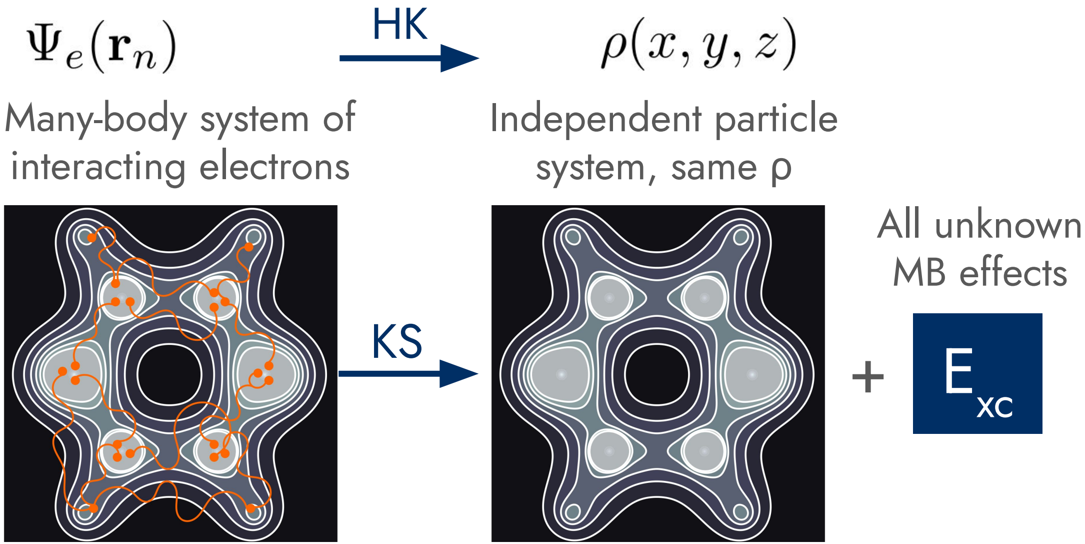
The electronic problem:

$$\hat{H}\Psi(\{\mathbf{R}_I\},\{\mathbf{r}_i\}) = E\Psi(\{\mathbf{R}_I\},\{\mathbf{r}_i\})$$

@ fixed $\{\mathbf{R}_\mathrm{I}\}$



Density Functional Theory – Basic concepts



$$\Psi_e(\mathbf{r}_n) \xrightarrow{\text{HK}} \rho(x,y,z)$$

Many-body system of interacting electrons

Independent particle system, same ρ

KS

All unknown MB effects

$+ \ E_{xc}$

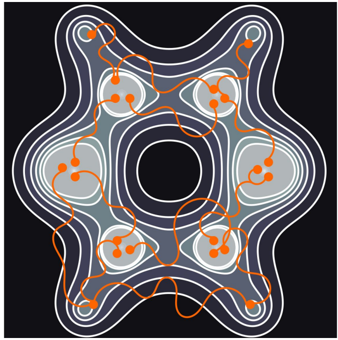
R. Martin, *Electronic Structure Basic Theory and Practical Methods*, Cambridge University Press, 2013.

Density Functional Theory – Basic concepts

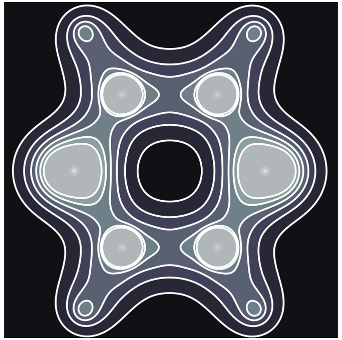
$\Psi_e(\mathbf{r}_n) \xrightarrow{\text{HK}} \rho(x, y, z)$

Many-body system of interacting electrons

Independent particle system, same ρ

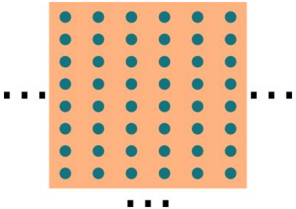


$\xrightarrow{\text{KS}}$



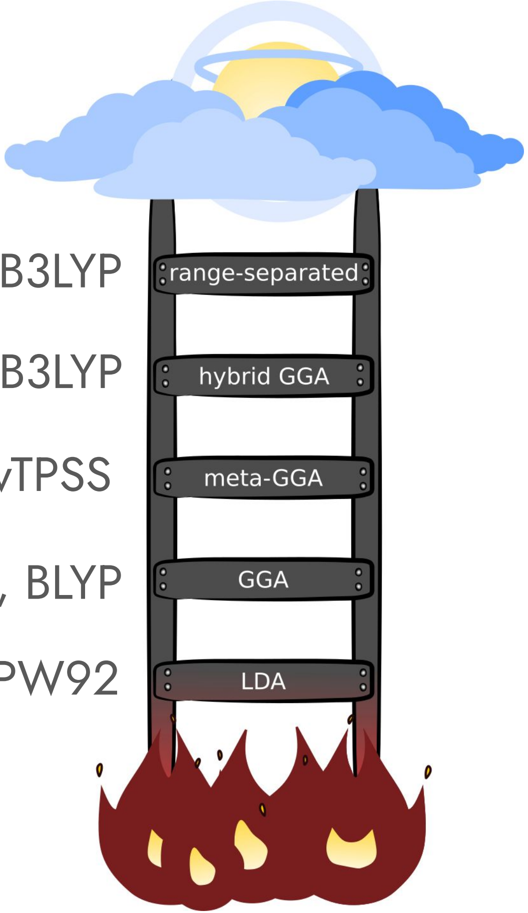
All unknown MB effects

$+ \boxed{E_{xc}}$



Uniform electron gas

$\longrightarrow \boxed{E_{xc}}$



CAM-B3LYP	range-separated
B3LYP	hybrid GGA
RevTPSS	meta-GGA
PBE, BLYP	GGA
PW92	LDA

Pyrazine: DFT ground state

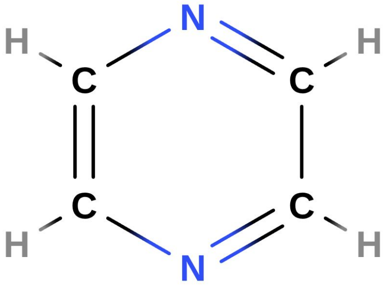
- Geometry optimization with ORCA.

Login to the HPC cluster:

```
ssh -X username@ui.wcss.pl
```

Copy tutorial to your home directory:

```
cp -r TUTORIAL_1 ./
```

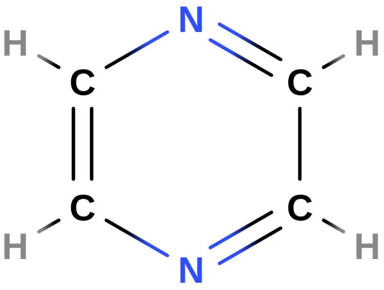


```
! B3LYP def2-SVP TIGHTSCF OPT
%pal nprocs 6
    end
%MaxCore 1000

*xyz 0 1
    N … … …
    N …
    …
*
```

Pyrazine: DFT ground state

- Geometry optimization with ORCA,
- Hessian and frequencies.

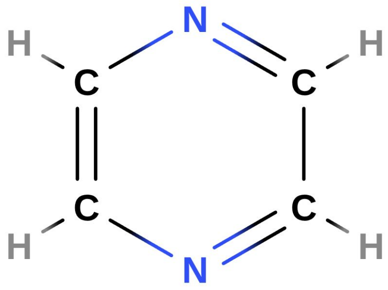
```
! B3LYP def2-SVP TIGHTSCF FREQ
%pal nprocs 6
    end
%MaxCore 1000

*xyz 0 1
    !OPTIMIZED GEOMETRY HERE!
*
```



Pyrazine: DFT ground state

- Geometry optimization with ORCA,
- Hessian and frequencies,
- Single point electronic structure for the optimized geometry with CAM-B3LYP.

```
! CAM-B3LYP def2-SVP TIGHTSCF
%pal nprocs 6
    end
%MaxCore 1000

*xyz 0 1
    !OPTIMIZED GEOMETRY HERE!
*
```



Pyrazine: DFT ground state

- Geometry optimization with ORCA,
- Hessian and frequencies,
- Single point electronic structure for the optimized geometry with CAM-B3LYP → visualize the orbitals and identify the N lone pairs, π, π*.

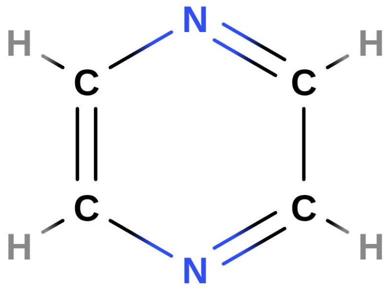
```
sub-interactive -x
source enable-jmol
```

Analyze in Jmol:

```
jmol file.molden
```

Jmol Console commands:

```
mo homo
mo color yellow cyan
mo mesh fill translucent 0.4
mo lumo
mo 18
```



Note: MO indexing starts at <u>**0**</u> in the ORCA output, but at <u>**1**</u> in the molden file!

Introduction to TDDFT
– Vertical Absorption Spectra –

Introduction to TDDFT

$$\hat{H} = \hat{H}_0 + \sum\nolimits_{\pm\omega} V^{\omega} e^{-i\omega t}$$

$i\hbar \frac{\partial \Psi(t)}{\partial t} = \hat{H}\Psi(t)$ → Real-time methods (e.g. RT-TDDFT)

Response methods:

$$\langle \hat{O} \rangle_t = \langle 0|\hat{O}|0\rangle + \hat{V}(t)\underline{\langle\langle \hat{O}; \hat{V}^{\pm\omega} \rangle\rangle} + \frac{1}{2}\hat{V}^2(t)\langle\langle \hat{O}; \hat{V}^{\pm\omega}, \hat{V}^{\pm\omega} \rangle\rangle + \dots$$

$$\langle\langle \hat{O}; \hat{V}^{\omega} \rangle\rangle = -\frac{1}{\hbar}\sum\nolimits_n \left(\frac{\langle 0|\hat{O}|n\rangle\langle n|\hat{V}^{\omega}|0\rangle}{\omega_{n0}-\omega-i\gamma_n} + \frac{\langle 0|\hat{V}^{\omega}|n\rangle\langle n|\hat{O}|0\rangle}{\omega_{n0}+\omega+i\gamma_n} \right)$$

Linear response
(e.g. LR-TDDFT)

P. Norman, K. Ruud, T. Saue, *Principles and Practices of Molecular Properties*, John Wiley & Sons, 2018.

TDDFT response equation

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} \begin{matrix} \text{Excitation} \\ \text{De-excitation} \end{matrix}$$

$$A_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + (ia|jb) - \alpha(ij|ab) + (1-\alpha)(ia|\hat{f}_{\mathrm{xc}}|jb)$$

$$B_{ia,jb} = (ia|bj) - \alpha(ib|aj) + (1-\alpha)(ia|\hat{f}_{\mathrm{xc}}|bj)$$

Tamm–Dancoff approximation(TDA): keep only block A. $\boxed{A\,X = \omega\,X}$

A. Dreuw, M. Head-Gordon, *Chem. Rev.* **105**, 4009–4037 (2005).

Pyrazine, vertical absorption spectrum

- TDDFT/CAM-B3LYP vertical excitation at the optimized geometry

```
! CAM-B3LYP def2-SVP TIGHTSCF
%tddft
    TDA false
    nroots 10
    end
%pal nprocs 6
    end
%MaxCore 1000

*xyz 0 1
    !OPTIMIZED GEOM. HERE!
*
```

Pyrazine, vertical absorption spectrum

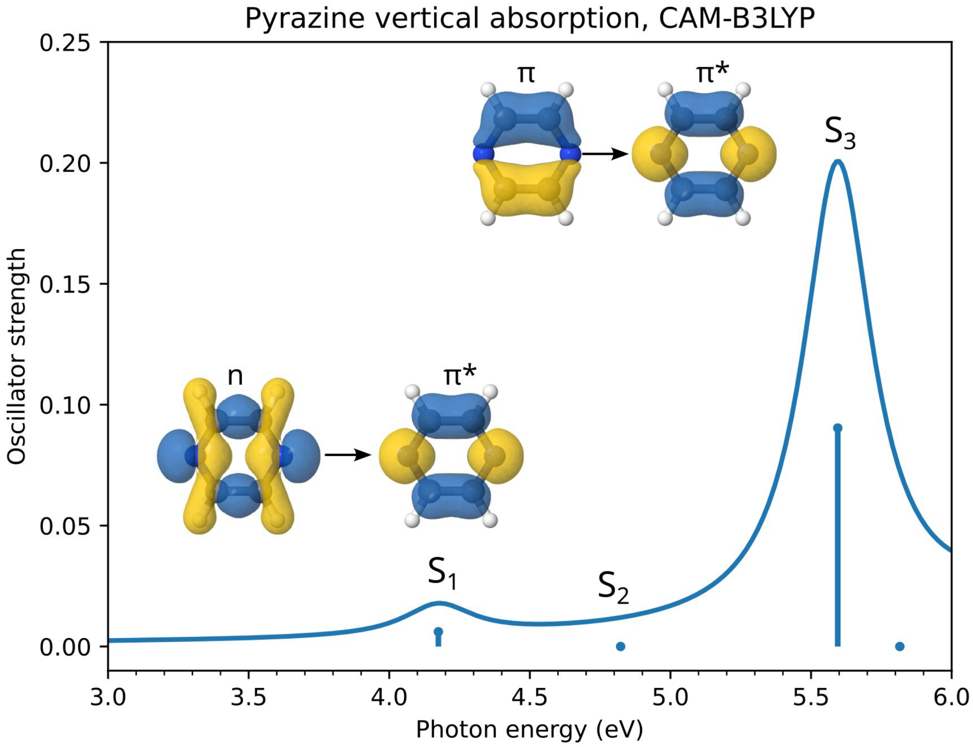
- TDDFT/CAM-B3LYP vertical excitation at the optimized geometry
- What is the nature of the first three excited states (π→π*, n→π*)?
- Which orbitals are involved in these transitions?

Remember: MO indexing starts at **0** in the ORCA output, but at **1** in the molden file!

Note

More sophisticated excited state analysis can be performed using **natural transition orbitals** (NTOs), **detachment/attachment** densities, or **particle/hole** densities.

Pyrazine, vertical absorption spectrum



- S_1 – mainly attributed to a transition from the N lone pair orbital to LUMO (π*)
- S_2 – N lone pair to LUMO+1 (π*)
- S_3 – assigned mainly to a HOMO-1 (π) to LUMO (π*) transition.

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Excited-State Geometry Optimizations and the Excited-State PES

TDDFT optimization of S_1

- TDDFT/CAM-B3LYP optimization of S_1.
- True minimum? Hessian and frequencies.

```
! CAM-B3LYP def2-SVP TIGHTSCF OPT FREQ
%tddft
   TDA false
   nroots 10
   iroot 1
   end
%pal nprocs 6
   end
%MaxCore 1000

*xyz 0 1
…  …  …
*
```

TDDFT optimization of S_1

- Visualize the normal mode with imaginary frequency.
- Displace the molecule along this mode.
- Restart the geometry optimization starting with this new geometry.

```
sub-interactive -x
source enable-jmol
```

Analyze in Jmol:

```
jmol filename.out.v0xx
```

(xx – index of mode with img. freq)

Jmol Console commands:

```
animation on
vector on
```

TDDFT optimization of S_1

- Restart the TDDFT/CAM-B3LYP optimization of S_1 from the distorted geometry along the imaginary mode.

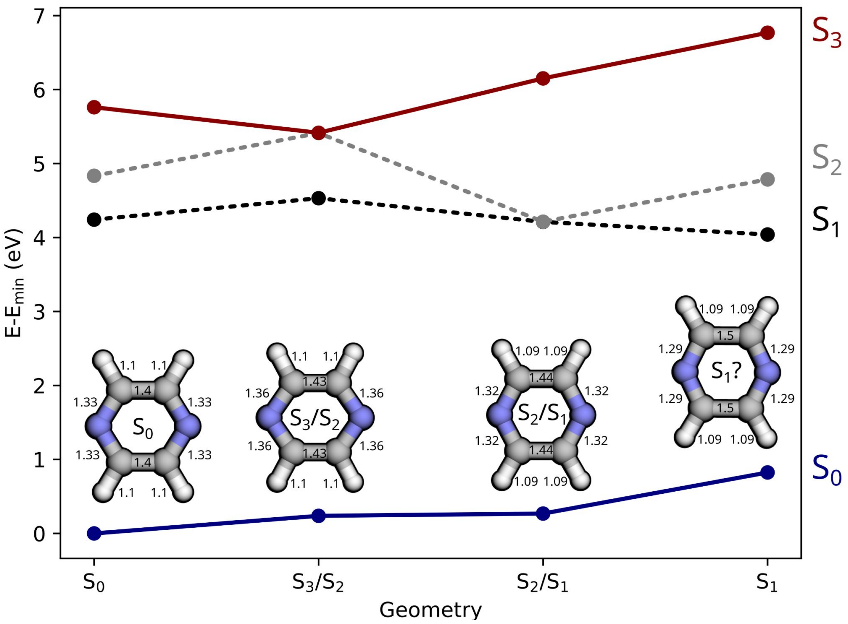
```
! CAM-B3LYP def2-SVP TIGHTSCF OPT
%tddft
    TDA false
    nroots 10
    iroot 1
    end
%pal nprocs 6
    end
%MaxCore 1000

*xyz 0 1
    !DISTORTED GEOM HERE!
*
```

TDDFT optimization of the S_2/S_1 CI

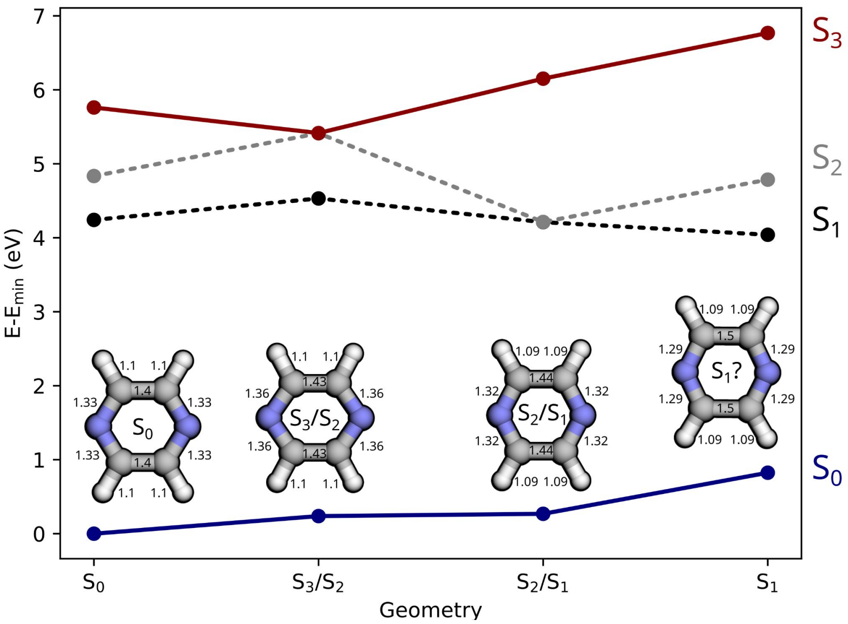
- TDDFT/CAM-B3LYP optimization of the S_2/S_1 CI.

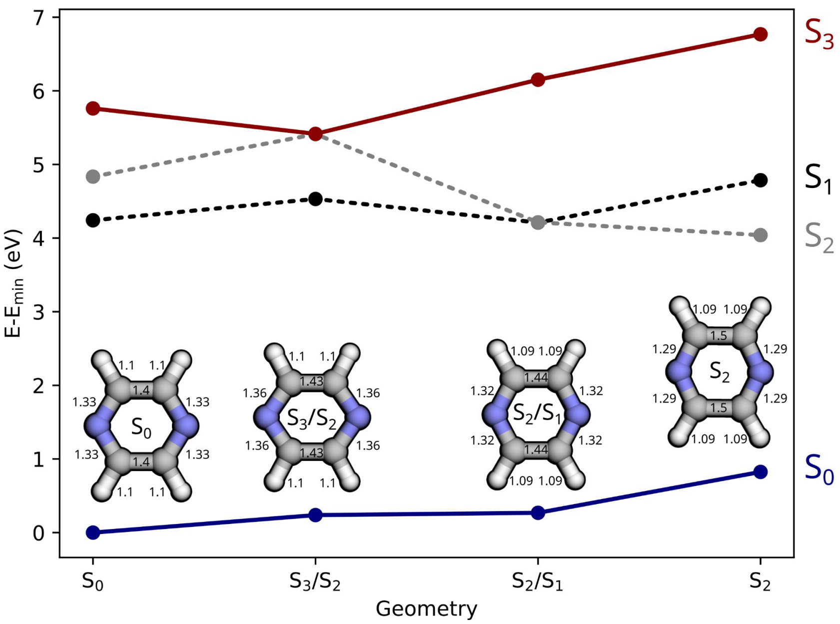
```
! CAM-B3LYP def2-SVP TIGHTSCF CI-OPT
%tddft
    TDA false
    nroots 10
    iroot 2
    jroot 1
    end
%pal nprocs 6
    end
%MaxCore 1000

*xyz 0 1
…  …  …
*
```

S_0—S_3—S_2—S_1 PES of pyrazine



S_0–S_3–S_2–S_1 PES of pyrazine



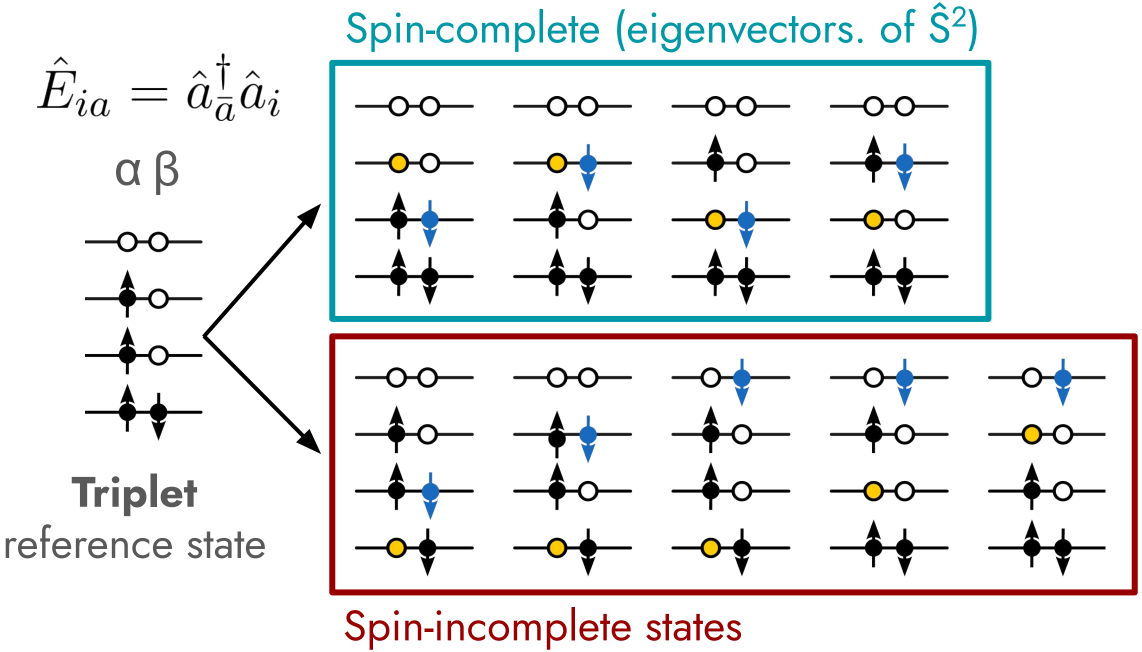


Challenges for TDDFT

- Cannot capture double-excitation character.
- The **topology** of **conical intersections** involving the **reference state** (the ground state in LR-TDDFT) is **fundamentally flawed**.
- Often, the **DFT** electronic structure is **difficult**/impossible **to converge** for molecular configurations where **S_0** is **quasi-degenerate** with **S_1** (e.g. ethylene with the CH_2 groups rotated to 90° with respect to each other.)

Mixed-reference spin-flip TDDFT

Spin-Flip TDDFT – Basic idea

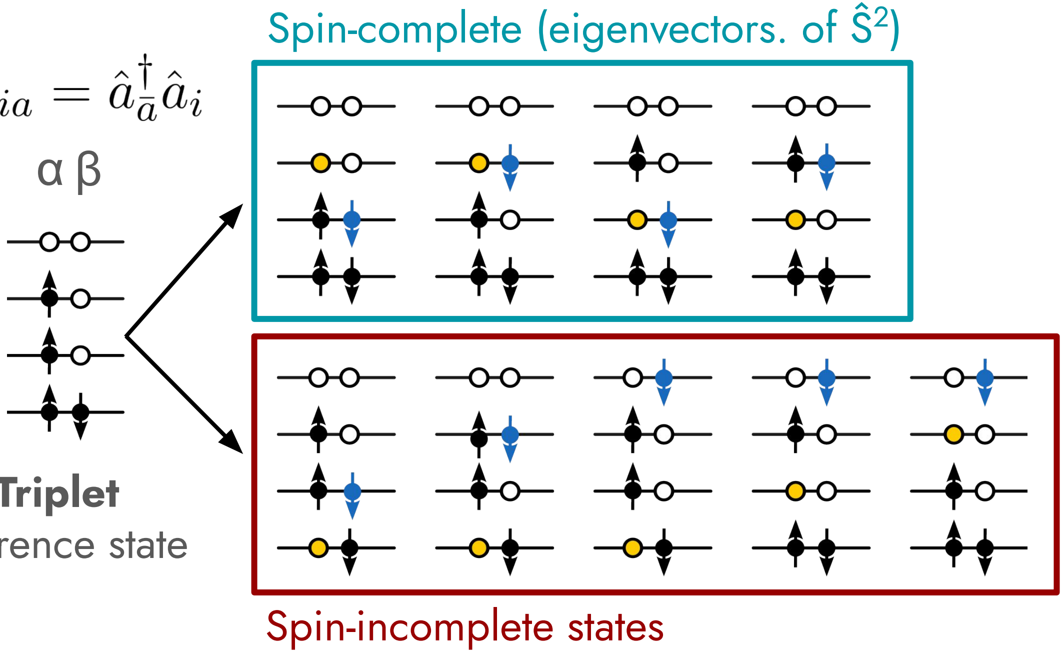


- Solves the topology issue of TDDFT.
- Captures double-excitation character.
- Introduces **spin contamination**!

J. M. Herbert, A. Mandal, *Spin-Flip TDDFT for Photochemistry*, Jenny Stanford Publishing Pte. Ltd. 2023.

Spin-Flip TDDFT – Basic idea

$$\hat{E}_{ia} = \hat{a}^{\dagger}_{\bar{a}}\hat{a}_i$$

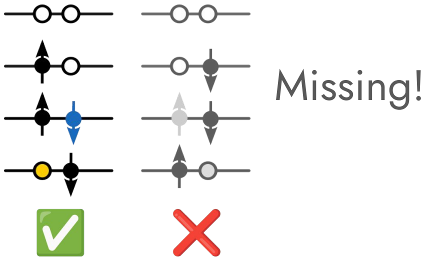


Spin-complete (eigenvectors. of $\hat{S}^2$)

Triplet
reference state

Spin-incomplete states

- Solves the topology issue of TDDFT.
- Captures double-excitation character.
- Introduces **spin contamination**!



J. M. Herbert, A. Mandal, *Spin-Flip TDDFT for Photochemistry*, Jenny Stanford Publishing Pte. Ltd. 2023.

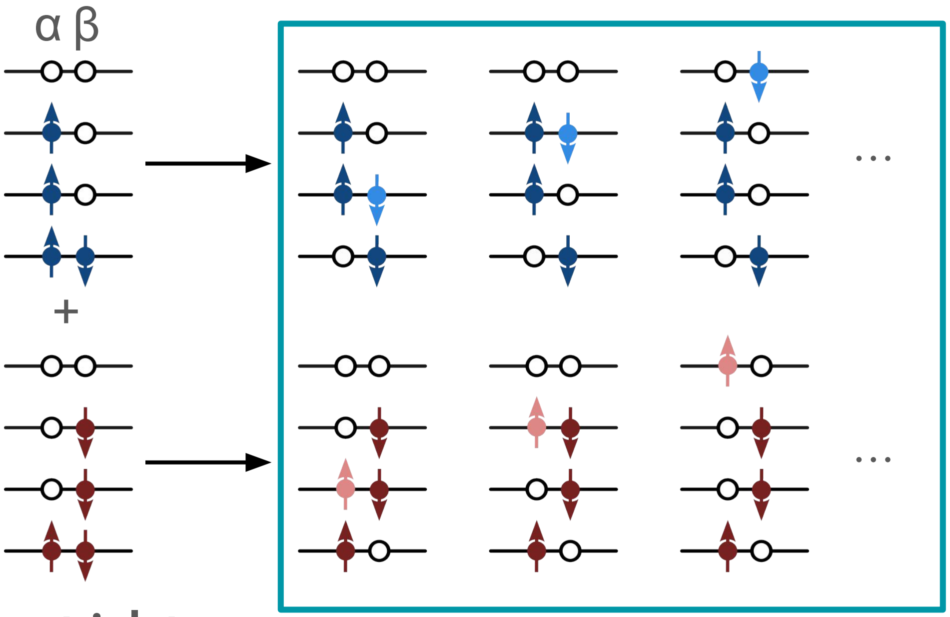
SF-TDDFT vertical absorption

```
! CAM-B3LYP def2-SVP TIGHTSCF
%tddft
    TDA true
    SF true
    nroots 10
    end
%pal nprocs 6
    end
%MaxCore 1000

*xyz 0 3
    ...    ...    ...
*
```

Mixed-reference SF-TDDFT – Basic idea

$$\hat{E}_{i\bar{a}} = \hat{a}^{\dagger}_{\bar{a}}\hat{a}_{i}$$

$$\hat{E}_{\bar{i}a} = \hat{a}^{\dagger}_{a}\hat{a}_{\bar{i}}$$



Two triplet ref. states

Spin-complete (eigenvectors. of $\hat{S}^2$)

- Solves the topology issue of TDDFT.
- Captures double-excitation character.
- Removes spin contamination (to a large extent).

S. Lee, W. Park, C. H. Choi, *Acc. Chem. Res.* **58**, 208–217 (2025).

MRSF-TDDFT vertical absorption: PyOpenQP

```
[input]
system = opt_gs.xyz
charge = 0
functional = cam-b3lyp
basis = def2-svp
runtype = energy
method = tdhf

[scf]
type = rohf
maxit = 200
multiplicity = 3

[tdhf]
type = mrsf
nstate = 10
```

- MRSF-TDDFT/CAM-B3LYP vertical absorption at the S_0 geometry.

MRSF-TDDFT optimization of S_1: PyOpenQP

```
[input]
system = opt_gs.xyz
charge = 0
functional = cam-b3lyp
basis = def2-svp
runtype = optimize
method = tdhf

[scf]
type = rohf
maxit = 200
multiplicity = 3

[tdhf]
type = mrsf
nstate = 10

[optimize]
maxit = 100
istate = 2
```

- MRSF-TDDFT/CAM-B3LYP optimization of S_1.

Remember: the first state in MRSF-TDDFT is the singlet ground state S_0!

MRSF-TDDFT optimization of S_1: PyOpenQP

```
[input]
system = opt.xyz
charge = 0
functional = cam-b3lyp
basis = def2-svp
runtype = hess
method = tdhf

[scf]
type = rohf
maxit = 200
multiplicity = 3

[tdhf]
type = mrsf
nstate = 10

[hess]
istate = 2
```

- MRSF-TDDFT/CAM-B3LYP optimization of S_1.
- Hessian and frequencies.

Remember: the first state in MRSF-TDDFT is the singlet ground state S_0!

MRSF-TDDFT optimization of the S_2/S_1 CI: PyOpenQP

```
[input]
system = opt_gs.xyz
charge = 0
functional = cam-b3lyp
basis = def2-svp
runtype = meci
method = tdhf

[scf]
type = rohf
maxit = 200
multiplicity = 3

[tdhf]
type = mrsf
nstate = 10

[optimize]
maxit = 100
istate = 2
jstate = 3
```

- MRSF-TDDFT/CAM-B3LYP optimization of the S_2/S_1 conical intersection.

Remember: the first state in MRSF-TDDFT is the singlet ground state S_0!

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MRSF-TDDFT optimization of the S_2/S_1 CI: PyOpenQP

```
[input]
system = opt.xyz
charge = 0
functional = cam-b3lyp
basis = def2-svp
runtype = hess
method = tdhf

[scf]
type = rohf
maxit = 200
multiplicity = 3

[tdhf]
type = mrsf
nstate = 10

[hess]
istate = 2
```

- MRSF-TDDFT/CAM-B3LYP optimization of the S_2/S_1 conical intersection.
- Hessian and frequencies: 2 imaginary modes indicate a CI. These are the two coordinates along which the potential energy surfaces are degenerate.

Remember: the first state in MRSF-TDDFT is the singlet ground state S_0!

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MRSF-TDDFT optimization of the S_2/S_1 CI: PyOpenQP

- Hessian and frequencies: 2 imaginary modes indicate a CI.
- These are the two coords. along which the potential energy surfaces are degenerate.

```
sub-interactive -x
source enable-jmol
```

```
jmol filename.freq.molden
```

(all 3N-6 normal modes)

Jmol Console commands:

```
vibration 1
frame first
frame next
frame last
```

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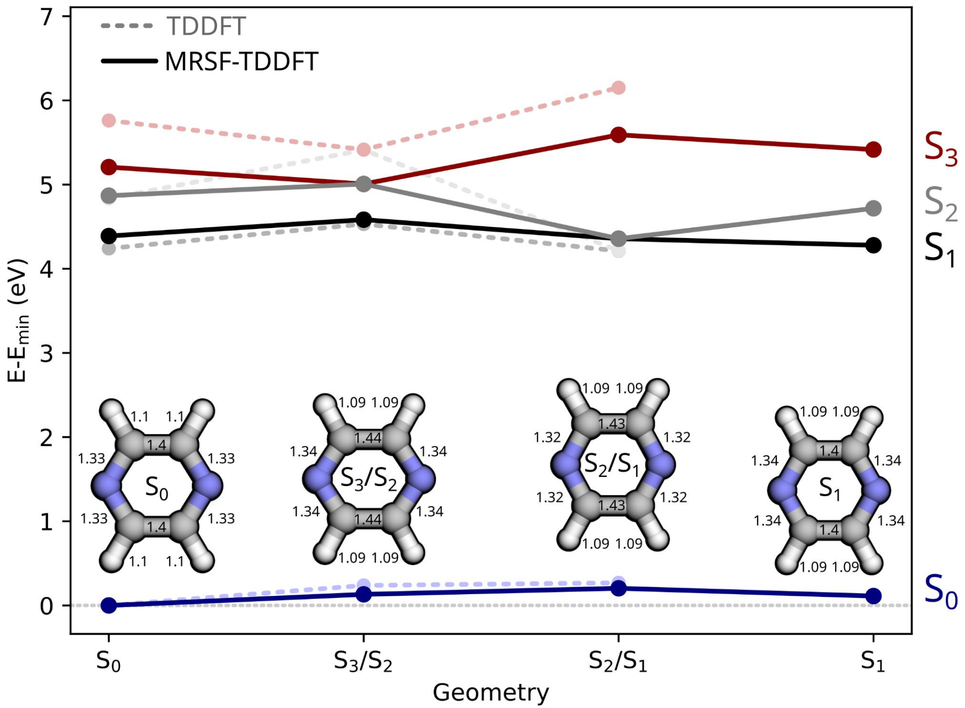
S_0–S_3–S_2–S_1 MRSF-TDDFT PES



Summary

- **Workflow** to construct the PES of a molecule:
  - Ground state geometry optimization,
  - Vertical absorption spectrum,
  - Excited-state and CI geometry optimizations,
  - Vertical excitation energies at these different geometries ⇒PES.
- **Some issues of LR-TDDFT** in its original formulation:
  - Flawed topology of CIs involving the reference state,
  - Cannot capture double excitation character,
  - Convergence issues around CIs involving reference state.
- **New TD-TDDFT approaches** which solve some of these issues:
  - SF-TDDFT: affected by spin-contamination.
  - MRSF-TDDFT.

Coming up next: Wavefunction-based multi-reference methods!

Questions?

Enjoy the rest of the week!