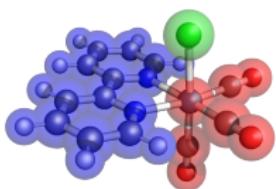


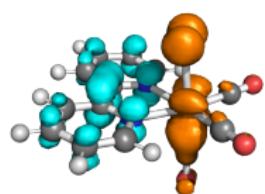
Wavefunction analysis in OpenMolcas: Fragment-based analysis and de-exitations

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Stuttgart / Home, 19 June 2020

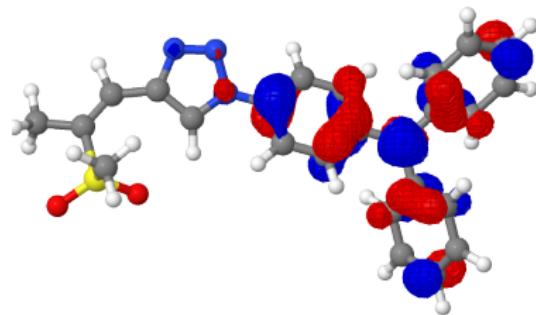


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Introduction

Solving problems using quantum chemistry

- ▶ Accurate numbers
- 😊 *Quantum chemical methods*: CASSCF, GASSCF, CASPT2, DMRG, FCIQMC, CC, ...
- 😊 *Environmental models*: Density embedding, QM/MM, ...
- 😊 *Algorithmic efforts*: GPUs, Cholesky, ...
- ▶ Comparison to experiment
- 😊 *Linear* and *non-linear* optical properties
- 😊 *Static* and *time-resolved* experiments
- ▶ Chemical insight
- 😢 **Look at some blobs of colour**



Introduction

① Why are quantum chemistry methods so complicated

- ▶ Nature is really so **complicated**
 - *Let's analyse the wavefunctions* to learn about nature
- ▶ We are just using an **inefficient description**
 - *Let's analyse the wavefunctions* to find a more efficient description
 - **Correlation** vs **orbital relaxation**^{1,2}

¹FP, A. Dreuw, *JPCA* **2015**, 119, 1023.

²FP, S. Mewes, A. Dreuw, L. González, *JCTC* **2017**, 13,5343.

Motivation

① Why wavefunction analysis

► Practical computations¹

- Rigorous and **quantitative** analysis of trends
- Automatic assignment of excited-state character

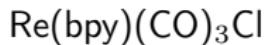
► Chemical theory²

- Learn about nature and/or quantum chemical methods
 - New **qualitative** insight
- De-excitations from a correlated ground state

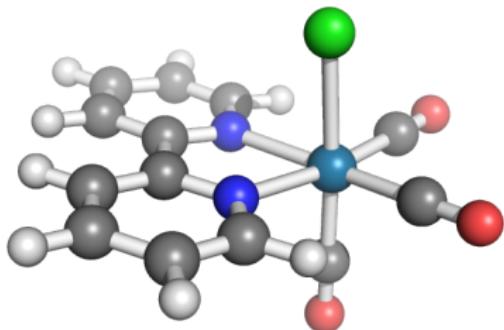
¹FP, *JCP* **2020**, 152, 084108.

²P. Kimber, FP, *PCCP* **2020**, 22, 6058.

Rhenium complex



- ▶ Well-studied complex¹
- Ultrafast intersystem crossing
- ?(?) Which types of states are involved
- ▶ MS-CASPT2 computations
 - CAS(12,12)
 - 19 singlets, 18 triplets
- !(!) How do we characterise so many states



¹J. Eng, C. Gourlaouen, E. Gindensperger, C. Daniel, *Acc. Chem. Res.* **2015**, 48, 809.

Transition Density Matrix

1-Electron transition density matrix (1TDM) - Matrix representation

$$D_{\mu\nu}^{0I} = \langle \Psi_0 | \hat{a}_\mu^\dagger \hat{a}_\nu | \Psi_I \rangle$$

\hat{a}_μ^\dagger Creation operator → **hole**

\hat{a}_ν Annihilation operator → **electron**

1TDM - Real-space representation

$$\gamma^{0I}(\mathbf{r}_h, \mathbf{r}_e) = \sum_{\mu\nu} D_{\mu\nu}^{0I} \chi_\mu(\mathbf{r}_h) \chi_\nu(\mathbf{r}_e)$$

$\mathbf{r}_h, \mathbf{r}_e$ Coordinates of **hole** and **electron**

χ_μ, χ_ν Basis functions

Electron/hole densities

Density for the excited electron / excitation hole

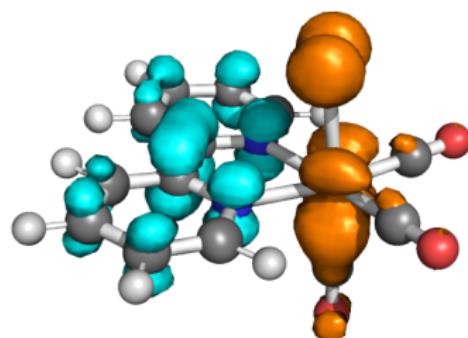
$$\rho_e(\textcolor{teal}{r}_e) = \int \gamma^{0I}(\textcolor{red}{r}_h, \textcolor{teal}{r}_e)^2 d\textcolor{red}{r}_h$$

$$\rho_h(\textcolor{red}{r}_h) = \int \gamma^{0I}(\textcolor{red}{r}_h, r_e)^2 dr_e$$

- ▶ Equivalent to weighted sums over natural transition orbitals

Electron/hole densities

- ▶ Analysis of S_1 state
 - **Hole** on Re and Cl
 - **Electron** on bpy ligand
- 😊 Well-defined and compact description
- 😢 Still looking at blobs of colour



¹I. Fdez. Galván, et al., *JCTC* **2019**, 15, 5925.

Charge Transfer Numbers

- ▶ Summation over **squared 1TDM elements**

Charge transfer numbers

$$\Omega_{AB} = \frac{1}{2} \sum_{\mu \in A} \sum_{\nu \in B} |\tilde{D}_{\mu\nu}^{0I}|^2$$

$\tilde{D}_{\mu\nu}^{0I}$ Element of the 1TDM after Löwdin orthogonalisation

Ω_{AA} Weight of local excitations on fragment A

$\Omega_{AB}, A \neq B$ Amount of charge transfer from A to B

- ▶ **Fragment** definition

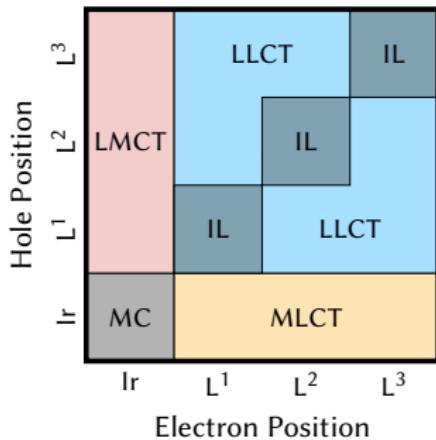
- Central metal + ligands: Re, L^1 , L^2 , L^3

¹FP, H. Lischka, *JCTC* **2012**, 8, 2777.

²FP, M. Wormit, A. Dreuw, *JCP* **2014**, 141, 024106.

Charge Transfer Numbers

- ▶ General classification
 - Different formal state characters correspond to different Ω_{AB} elements
- Automatic **classification** of state character
- Quantification of **state mixing**

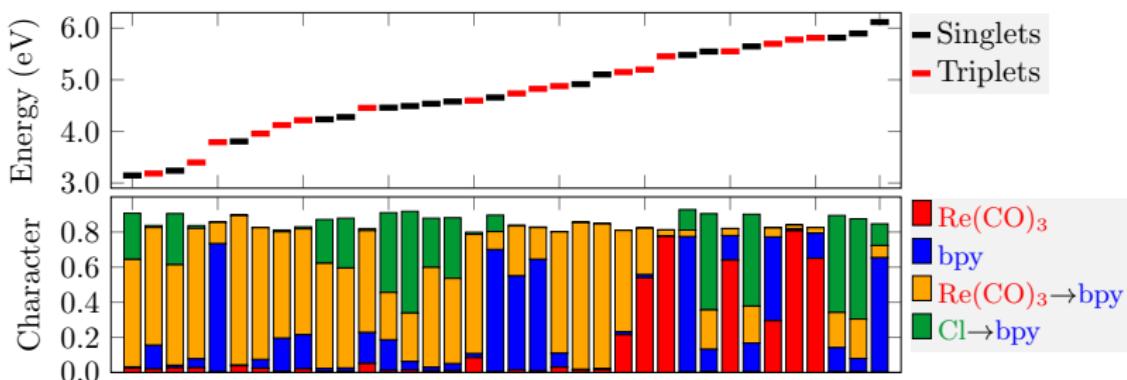
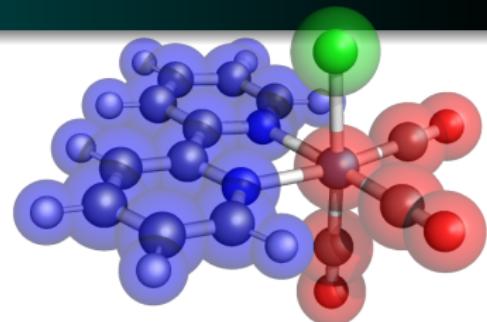


¹FP, A. Dreuw, *JPCA* **2015**, 119,1023.

²S. Mai, FP, J. Dorn, M. Fumanal, C. Daniel, L. González, *CCR* **2018**, 361, 74.

Fragment decomposition

- ▶ Division into three fragments
 - $\text{Re}(\text{CO})_3$, bpy, Cl
- Quantify excitations between them
 - For **singlets** and **triplets**
- ▶ **Discussion**
- More Cl → bpy for **singlets**
- More bpy for **triplets**



Fragment-based analysis

- ▶ Fragment-based analysis
- 😊 State-character assignment by just pressing a button
- 😢 Definition of fragments not always obvious

¹FP, *J. Chem. Phys.* **2020**, 152, 084108.

Exciton Analysis

Exciton analysis

- ▶ Interpret the 1TDM as the wavefunction χ_{exc} of the electron-hole pair
- ▶ Use as a basis for analysis

Exciton wavefunction

$$\chi_{exc}(x_h, x_e) = \sum_{\mu\nu} D_{\mu\nu}^{0I} \chi_\mu(x_h) \chi_\nu(x_e)$$

$D_{\mu\nu}^{0I}$ Matrix representation of the 1TDM

χ_μ Atomic orbital

x_h, x_e Coordinates of the **excitation hole** and the **excited electron**

¹S. A. Bäppler, FP, M. Wormit, A. Dreuw, *Phys. Rev. A* **2014**, 90, 052521.

Exciton Analysis

Operator expectation value

$$\langle \hat{O} \rangle = \frac{\langle \chi_{exc} | \hat{O} | \chi_{exc} \rangle}{\langle \chi_{exc} | \chi_{exc} \rangle}$$

Exciton size

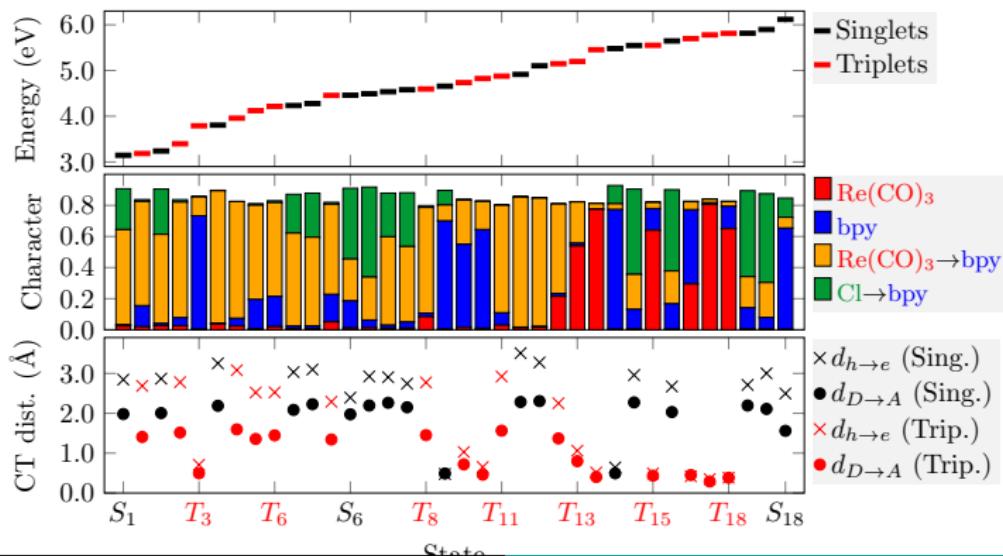
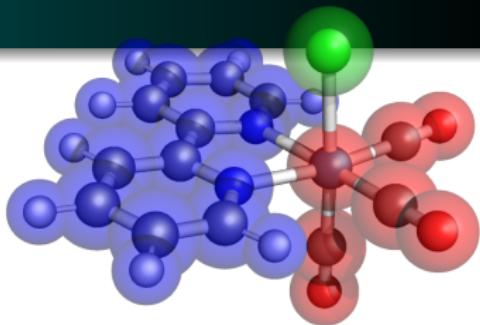
$$d_{h \rightarrow e} = \langle r_e - r_h \rangle$$

- ▶ Average (linear) separation of the electron and hole quasi-particles
 - Evaluated using **analytic integration** techniques
- 😊 No fragment definition
- 😊 No population analysis

¹FP, et al., *J. Comput. Chem.* **2015**, 36, 1609.

Fragment decomposition

- ▶ **Consistent trends** between fragment-based and real-space analysis
- ▶ CT always larger for **singlets** than for **triplets** (×)
- ▶ CT reduced by orbital relaxation (●)



De-excitations

- ① How does the electron-hole picture change if we do not have a single reference determinant
 - No well-defined *Fermi vacuum*



- Validity of the Tamm-Dancoff approximation
- Reason why MR-CC is difficult
- Reason why we need an IPEA shift in CASPT2

¹P. Kimber, FP, *PCCP* **2020**, 22, 6058.

De-excitations

Excitations from a correlated ground state

$$\langle \Psi_0 | = \cos(\eta) \langle h\bar{h} | - \sin(\eta) \langle l\bar{l} |$$

$$|\Psi_{S/T}\rangle = \frac{1}{\sqrt{2}} (|hl\rangle \mp |\bar{h}\bar{l}\rangle)$$

Transition density matrix

$$\sqrt{2}\mathbf{D}^{0I} = \begin{pmatrix} \hat{a}_h & \hat{a}_{\bar{h}} & \hat{a}_l & \hat{a}_{\bar{l}} \\ 0 & 0 & \pm \cos(\eta) & 0 \\ 0 & 0 & 0 & \cos(\eta) \\ -\sin(\eta) & 0 & 0 & 0 \\ 0 & \mp \sin(\eta) & 0 & 0 \end{pmatrix} \begin{matrix} \hat{a}_h^\dagger \\ \hat{a}_{\bar{h}}^\dagger \\ \hat{a}_l^\dagger \\ \hat{a}_{\bar{l}}^\dagger \end{matrix}$$

- ▶ **Excitations** in the **occ-virt** block
- ▶ **De-excitations** in the **virt-occ** block
- ① How to quantify de-excitations

Transition density matrix

$$\sqrt{2}\mathbf{D}_{0I} = \begin{pmatrix} \hat{a}_h & \hat{a}_{\bar{h}} & \hat{a}_l & \hat{a}_{\bar{l}} \\ 0 & 0 & \pm \cos(\eta) & 0 \\ 0 & 0 & 0 & \cos(\eta) \\ -\sin(\eta) & 0 & 0 & 0 \\ 0 & \mp \sin(\eta) & 0 & 0 \end{pmatrix} \begin{matrix} \hat{a}_h^\dagger \\ \hat{a}_{\bar{h}}^\dagger \\ \hat{a}_l^\dagger \\ \hat{a}_{\bar{l}}^\dagger \end{matrix}$$

- ▶ Squared Frobenius norm: $\Omega = \text{tr}(\mathbf{D}_{0I}\mathbf{D}_{0I}^T) = 1$
- Quantifies single-excitation character¹
- ▶ CIS has a **nilpotent** 1TDM²
- ▶ Deviation from nilpotency: $P_{he} = \Omega^{-1} \text{tr}(\mathbf{D}_{0I}\mathbf{D}_{0I}) = \mp \sin(2\eta)$
- Quantifies de-excitations³
 - Related to electron-hole permutation⁴

¹FP, M. Wormit, A. Dreuw, *JCP* **2014**, 141, 024106.

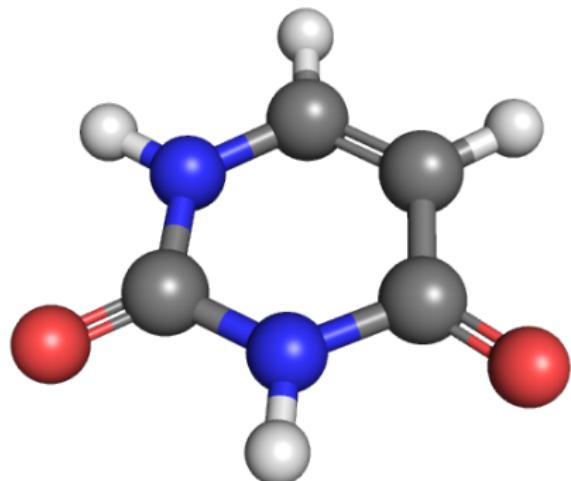
²A. V. Luzanov, O. A. Zhikol, *IJQC* **2009**, 110, 902.

³P. Kimber, FP, *PCCP* **2020**, 22, 6058.

⁴W. Barford, N. Paiboonvorachat, *JCP* **2008**, 129, 164716.

Uracil

- ▶ **Uracil**
- Typical organic molecule with $\pi\pi^*$ and $n\pi^*$ states
- ▶ Singlet and triplet states computed
 - CASSCF
 - ADC(2)
 - RPA-TDDFT/PBE0



¹P. Kimber, FP, *PCCP* **2020**, 22, 6058.

| State | ΔE | f | Configurations | Ω | P_{he} | $d_{h \rightarrow e}$ |
|---------------|------------|------|-------------------------|----------|--------------|-----------------------|
| CASSCF | | | | | | |
| $1^3\pi\pi^*$ | 4.02 | - | $0.85hl - 0.32hl_1$ | 0.97 | 0.35 | 0.25 |
| $1^3n\pi^*$ | 4.70 | - | $0.87h_2l$ | 0.82 | 0.02 | 1.11 |
| $1^1n\pi^*$ | 5.07 | 0.00 | $0.86h_2l$ | 0.78 | -0.02 | 1.18 |
| $2^3\pi\pi^*$ | 5.93 | - | $-0.77h_1l - 0.46hl_1$ | 0.95 | 0.30 | 0.51 |
| $1^1\pi\pi^*$ | 7.27 | 0.49 | $0.83hl - 0.35cs$ | 0.75 | -0.18 | 0.60 |
| ADC(2) | | | | | | |
| $1^3\pi\pi^*$ | 4.07 | - | $0.95hl$ | 0.92 | 0.19 | 0.15 |
| $1^3n\pi^*$ | 4.70 | - | $0.85h_2l + 0.27h_2l_2$ | 0.88 | 0.02 | 1.37 |
| $1^1n\pi^*$ | 4.95 | 0.00 | $0.87h_2l + 0.23h_2l_2$ | 0.87 | -0.01 | 1.44 |
| $2^3\pi\pi^*$ | 5.68 | - | $0.79h_1l - 0.41hl_2$ | 0.89 | 0.13 | 0.78 |
| $1^1\pi\pi^*$ | 5.76 | 0.23 | $0.91hl - 0.17h_4l$ | 0.87 | -0.05 | 0.56 |
| PBE0 | | | | | | |
| $1^3\pi\pi^*$ | 3.47 | - | $0.97hl$ | 1.06 | 0.24 | 0.16 |
| $1^3n\pi^*$ | 4.41 | - | $0.92h_1l - 0.28h_1l_1$ | 1.01 | 0.08 | 1.44 |
| $1^1n\pi^*$ | 4.88 | 0.00 | $0.96h_1l$ | 1.00 | -0.03 | 1.55 |
| $2^3\pi\pi^*$ | 4.92 | - | $0.81h_2l - 0.50hl_1$ | 1.03 | 0.18 | 0.72 |
| $1^1\pi\pi^*$ | 5.56 | 0.14 | $0.95hl$ | 1.03 | -0.01 | 0.71 |

¹P. Kimber, FP, *PCCP* **2020**, 22, 6058.

De-excitations

- ▶ Consistent trends among methods
- Fundamental property of an excited state

▶ Classification scheme

- Double excitation character (Ω)
- Multiconfigurational character (PR_{NTO}, S_{he})
- De-excitations (P_{he})
- Orbital relaxation (p)

¹P. Kimber, FP, *PCCP* **2020**, 22, 6058.

The WFA module

- ▶ The **WFA module** in MOLCAS
- ▶ Analysis of
 - SCF
 - RASSCF
 - RASSI
- MS-CASPT2
- SO-RASSCF ?
- DMRG, FCIQMC ?
- ▶ Communication via HDF5 files

¹FP, S. Mewes, A. Dreuw, L. González, *JCTC* **2017**, 13,5343.

²I. Fdez. Galván, et al., *JCTC* **2019**, 15, 5925.

Input file

```
&RASSI
TRD1

&WFA
H5file = $Project.rassi.h5
ATLISTS
2
1 2 4 *
3 *
```

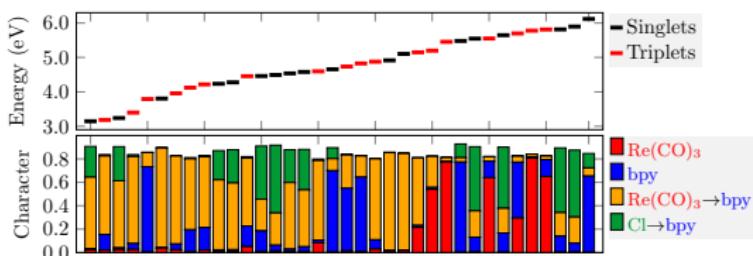
Output

```
===== TheoDORE analysis of CT numbers (Mulliken)=====
| State          dE(eV)      f      0m      POS      CT
| -----
| S1-S0          -4.501891  -0.000000  0.860726  1.820754  0.499137
| S1-T1          -0.571146  0.000000  0.989054  1.657985  0.255970
| S1-T2          2.002148   0.000000  0.494709  1.954089  0.252122
=====
```

Post-processing - TheDORE

TheoDORE - Theoretical Density, Orbital Relaxation and Exciton analysis

- ▶ Post-processing and plotting
- ▶ Copy back OmFrag.txt
 - *Alternative*: *ctnum*.om files
- ▶ `plot_Om_bars.py`



¹<http://theodore-qc.sourceforge.net>

²FP, JCP 2020, 152, 084108.

Orbital/density visualization

- ▶ Orbitals are written to the HDF5 file
- Interface to Pegamoid

- ▶ Export to Molden format via molpy¹

```
penny MOLCAS.rassi.h5 --wfaorbs molden
```

- ▶ Automatic rendering in Jmol
- `jmol_MOs.py`

- ▶ Creation of grid files for densities
- ORBKIT²

- ▶ Automatic rendering in VMD
- `vmd_plots.py`

¹<https://github.com/steabert/molpy>

²<http://orbkit.github.io>

Installation

- ▶ **libwfa** - An open-source wavefunction analysis tool library¹
 - Included as submodule in External
- ▶ Additional libraries
 - Armadillo: C++ linear algebra library
 - HDF5 libraries for C++

Installation

```
cmake -DLINALG=MKL -DWFA=ON -D ARMADILLO_INC=armadillo-x.y/include ...
```

- ▶ Same functionality available in **Q-Chem**
 - ADC, EOM-CC, TDDFT

¹<https://github.com/libwfa/libwfa>

Conclusions

- ▶ **Automatic assignment** of state character¹
 - *Transition metal complexes*
 - *Push-pull molecules* → **Poster by Patrick Kimber**
- ▶ **De-excitations**
 - Measured via *non-nilpotency* of the 1TDM
 - Consistent trends between TDDFT and wavefunction based methods
- (!) Fundamental categorisation of excited states with linear algebra²
- ▶ **Implementation** of the WFA module
 - *Fairly* user friendly
 - Collection of tools

¹FP, *JCP* **2020**, 152, 084108.

²P. Kimber, FP, *PCCP* **2020**, 22, 6058.

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OpenMolcas

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