Nonadiabatic Molecular Dynamics for $Ir(C_3H_4N)_3$ and $Ir(ppy)_3$ Complexes

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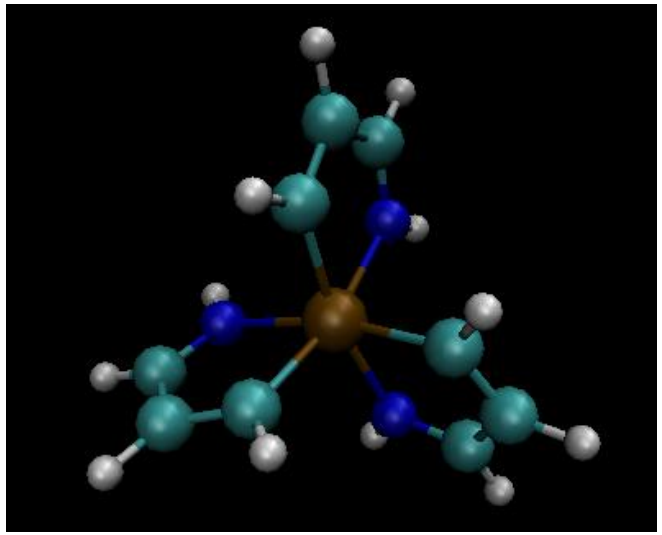
The State University of New York

Outline

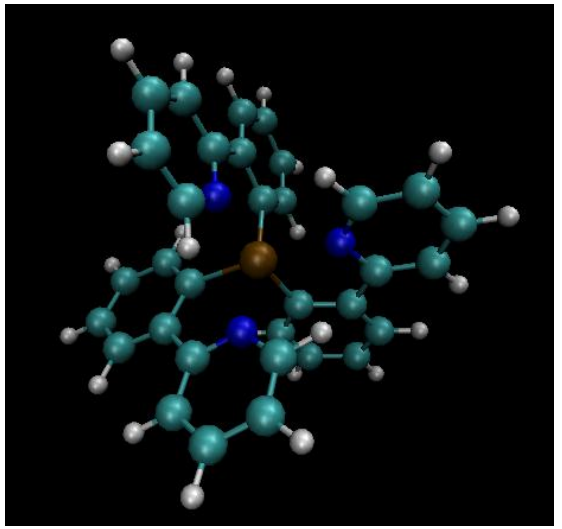
- Review
- Tutorials vs Project
- Workflow
- Results
- Conclusions
- Prospective

Review

- Organic Iridium Complexes



Complex-1: $Ir(C_3H_4N)_3$



Complex-2: $Ir(Pyy)_3$

Study the excited State and charge transfer using XCDFT and CDFT

XCDFT

Provide nonlocal potential pulling electrons into the virtual space

$$P_o^g = \sum_{i_g=1}^{occ} |i_g\rangle\langle i_g|$$

Projector onto occupied space of a reference ground state.

Lagrangian formalism

$$\mathcal{L}_{XCDFT}[D] = E_{HK}[D] \int v_{ext}(\boldsymbol{r})\rho[D](\boldsymbol{r})\,d\boldsymbol{r} + V_c[Tr[W_c D] - N_c] - \mu[Tr[D] - N_e]$$

Interaction with a external potential

Constraint on the electronic transition

Fock matrix for the excited State

$$F = F_{bare} + V_c W_c,$$

F_{bare} unmodified Fock matrix

$$E_{HK}[D] \equiv E_{HK}[\rho] = T_s[\rho] + E_H[\rho] + E_{xc}[\rho]$$

$$(W_c)_{\mu\nu} = \langle\mu|1 - P_o^g|\nu\rangle$$

Atomic orbitals functions (AOs) are defined by μ , ν , σ , and τ

$$\frac{\delta E[\rho]}{\delta N_c} = -V_c$$

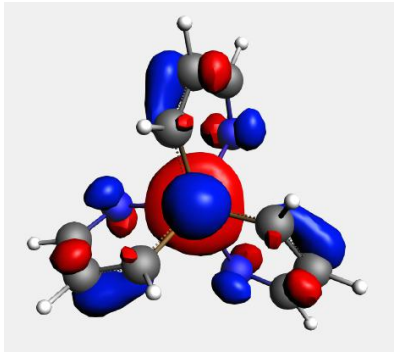
$$1 = \sum_{j=1}^{occ} \langle j_e|1 - P_o^g|j_e\rangle \equiv Tr[W_c D] = N_e - \sum_{ij=1}^{occ} \langle j_e|i_g\rangle\langle i_g|j_e\rangle$$

pull one electron from the occupied orbital space of the reference G.S to the first virtual orbital

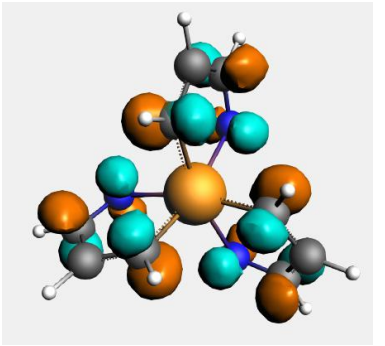
D is the density matrix

Ramos, P., & Pavanello, M. (2018). Low-lying excited states by constrained DFT. The Journal of chemical physics, 148(14), 144103.

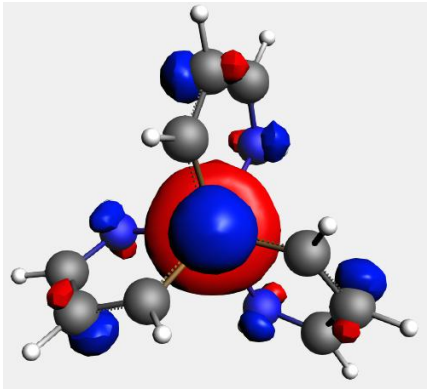
G.S



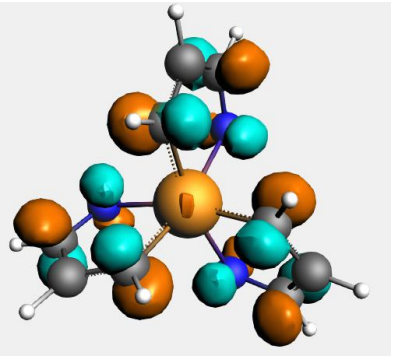
Homo-Lumo Gap
2.5852 eV



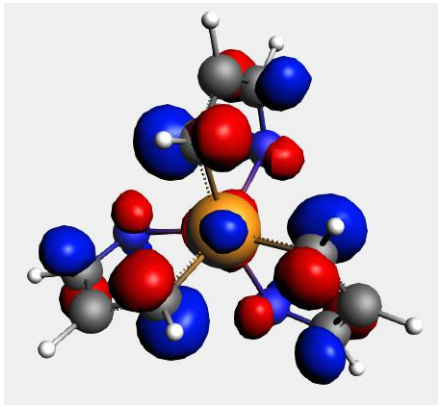
Diabat 1



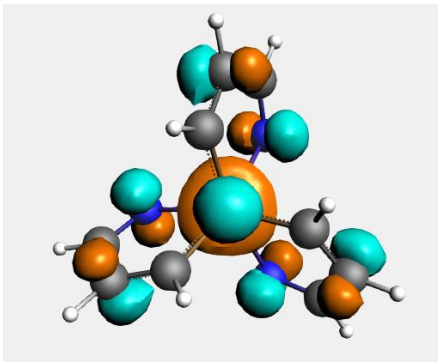
Homo-Lumo Gap
1.3507 eV



Diabat 2



Homo-Lumo Gap
0.2627 eV



Article ref Excitation Energy from the singlet ^1E (LC-MLCT) $d_a \rightarrow \pi_e^*$ = 3.862 eV

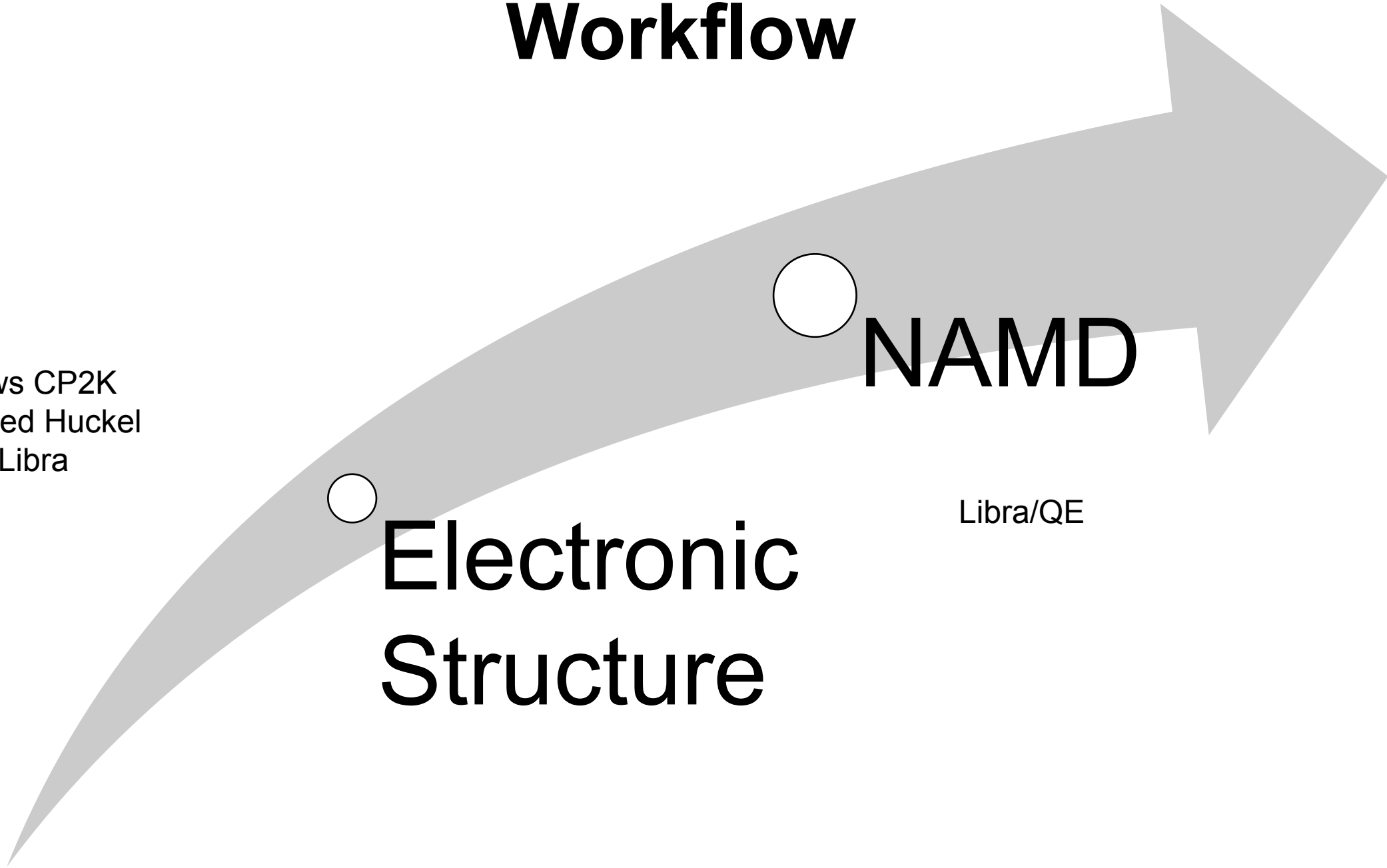
Charge transfer between (CT1-EX3) = 3.819 eV

Plasser, F., & Dreuw, A. (2015). High-level ab initio computations of the absorption spectra of organic iridium complexes. The Journal of Physical Chemistry A, 119(6), 1023-1036.

Tutorials vs Project

Qmflows CP2K	• Single Point
Extended Huckel Theory Libra	• Electronic Structure
Libra/QE	• NAMD
NEXMD	QMMM: Atom number: 1 has atomic number 77. QMMM: There are no AM1 parameters for this element. Sorry. SANDER BOMB in subroutine qm2_load_params_and_allocate UNSUPPORTED ELEMENT QM AM1 NOT AVAILABLE FOR THIS ATOM

Workflow



-Qmflows CP2K
-Extended Huckel Theory Libra

Libra/QE

CP2K-Input file

```
workflow:
  single_points

project_name: iridium-1
active_space: [82, 18]
compute_orbitals: True
path_hdf5: "iridium-1.hdf5"
path_traj_xyz: "iridium-1.xyz"
scratch_path: "/panasas/scratch/grp-cyberwksp21/ub2050/single_point_iridium"

cp2k_general_settings:
  basis:  "DZVP-MOLOPT-SR-GTH"
  potential: "GTH-PBE"
  cell_parameters: 10
  periodic: none
  executable: cp2k.popt

  cp2k_settings_main:
    specific:
      template: pbe_main

  cp2k_settings_guess:
    specific:
      template:
        pbe_guess
```

```
workflow:
  single_points

project_name: irpyy
active_space: [160, 80]
compute_orbitals: True
path_hdf5: "Ir-ppy-3.hdf5"
path_traj_xyz: "Ir-ppy-3.xyz"
scratch_path: "/panasas/scratch/grp-cyberwksp21/ub2050/single_point_irppy"

cp2k_general_settings:
  basis:  "DZVP-MOLOPT-SR-GTH"
  potential: "GTH-PBE"
  cell_parameters: 15.0
  periodic: none
  executable: cp2k.popt

  cp2k_settings_main:
    specific:
      template: pbe_main

  cp2k_settings_guess:
    specific:
      template:
        pbe_guess
```

Extended Huckel Theory (EHT)

```
possible_systems = [
    {"input_file":"ir-c3h4n3.xyz", "input_format":"xyz", "out_prefix":"_res_ir-c3h4n3"},
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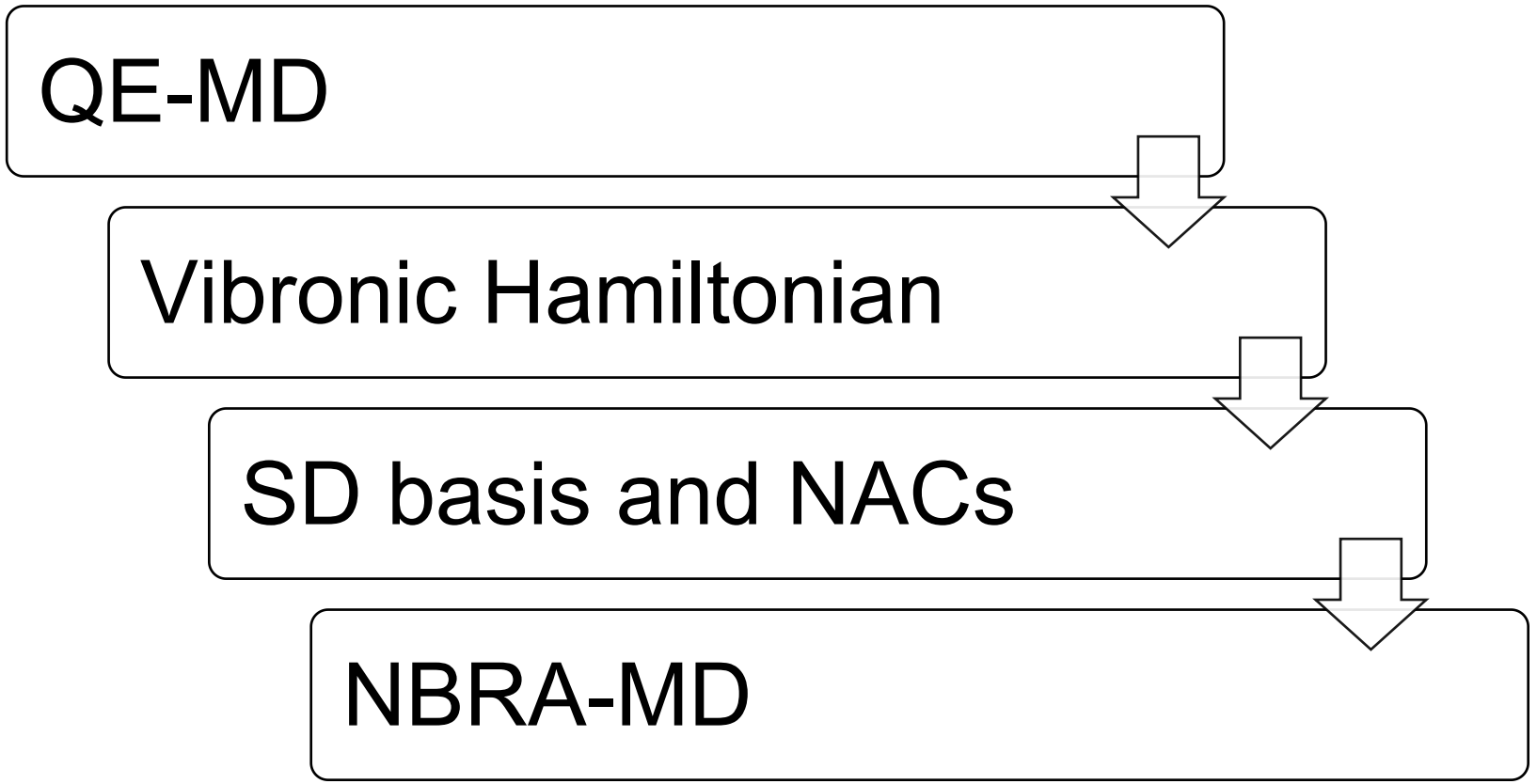
```

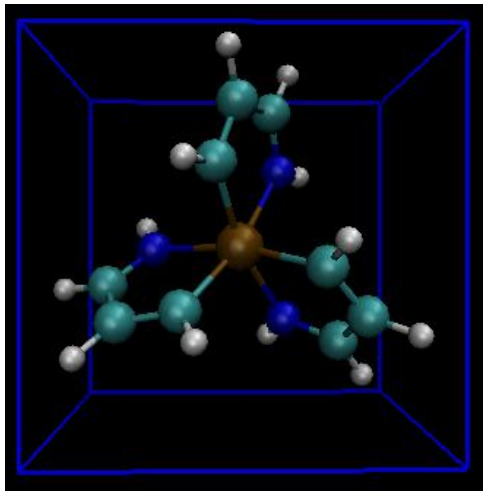
NAMD Libra/QE

- Tutorials-Libra/6_dynamics/2_nbra_workflows



Smith, B., & Akimov, A. V. (2019). A comparative analysis of surface hopping acceptance and decoherence algorithms within the neglect of back-reaction approximation. The Journal of chemical physics, 151(12), 124107.

Complex-1: $Ir(C_3H_4N)_3$



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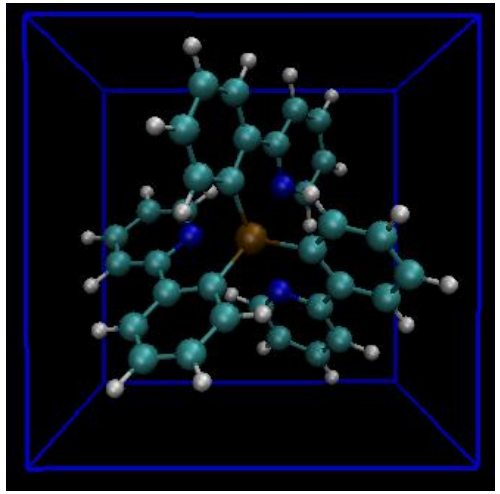
  ion_temperature   = 'andersen',
  tempw             = 300,
  nraise            = 10,
  pot_extrapolation = 'second-order',
  wfc_extrapolation = 'second-order',
/

ATOMIC_SPECIES
C  12.010     C.pbe-n-rrkjus_psl.0.1.UPF
H  1.007      H.pbe-rrkjus_psl.0.1.UPF
Ir 192.217    Ir.pbe-n-rrkjus_psl.0.2.3.UPF
N  14.006     N.pbe-n-rrkjus_psl.0.1.UPF
```

100 fs: dt:1 fs

Complex-2: $Ir(Pyy)_3$



```
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       0.0000000000        7.0652699470        0.0000000000
       0.0000000000        0.0000000000        7.0652699470
```

```
CELL_PARAMETERS  angstrom
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       0.0000000000       10.394909858703      0.0000000000
       0.0000000000        0.0000000000       10.394909858703
```

Vibronic Hamiltonian and NBRA-MD

Complex-1: $Ir(C_3H_4N)_3$

```
bravais-lattice index     =            0
lattice parameter (alat)  =      13.3514  a.u.
unit-cell volume          =    2380.0325 (a.u.)^3
number of atoms/cell      =           25
number of atomic types    =            4
number of electrons       =        72.00
number of Kohn-Sham states=           43
kinetic-energy cutoff     =      30.0000  Ry
charge density cutoff     =     300.0000  Ry
convergence threshold     =      1.0E-04
mixing beta               =       0.3000
number of iterations used =            8  plain     mixing
Exchange-correlation      = PBE ( 1  4  3  4 0 0)
nstep                     =          100
```

```
nbnd        = 50
```

```
params[\\"minband\\"]=20
params[\\"maxband\\"]=50
params[\\"minband_soc\\"]=20
params[\\"maxband_soc\\"]=50
```

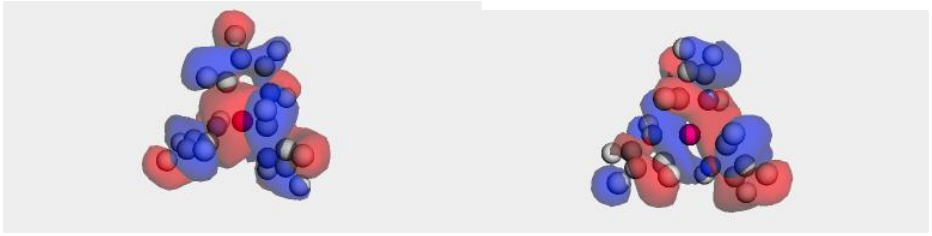
Complex-2: $Ir(Pyy)_3$

```
bravais-lattice index     =            0
lattice parameter (alat)  =      19.6435  a.u.
unit-cell volume          =    7579.8182 (a.u.)^3
number of atoms/cell      =           61
number of atomic types    =            4
number of electrons       =       180.00
number of Kohn-Sham states=          108
kinetic-energy cutoff     =      30.0000  Ry
charge density cutoff     =     300.0000  Ry
convergence threshold     =      1.0E-04
mixing beta               =       0.3000
number of iterations used =            8  plain     mixing
Exchange-correlation      = PBE ( 1  4  3  4 0 0)
nstep                     =          100
```

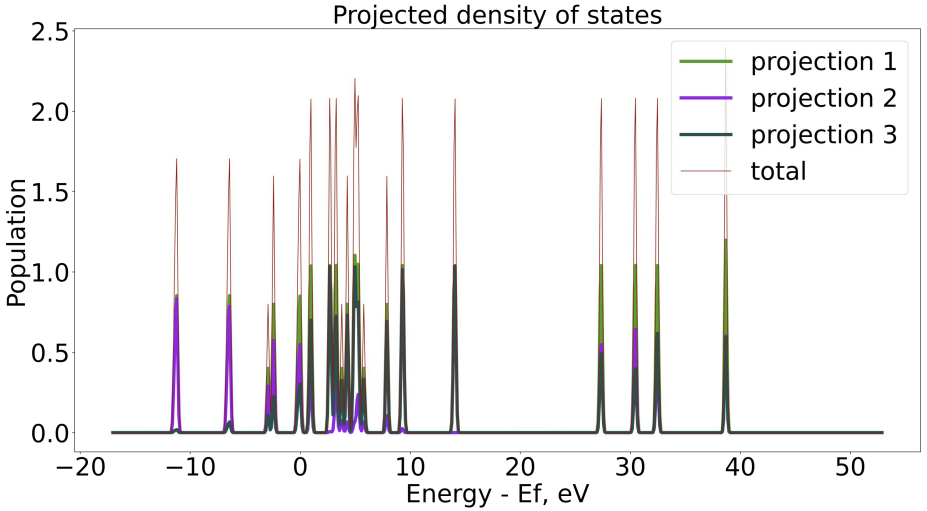
```
nbnd        = 150
```

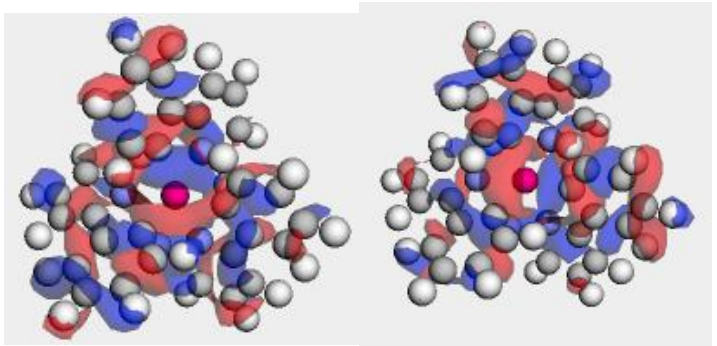
```
params[\\"minband\\"]=65
params[\\"maxband\\"]=150
params[\\"minband_soc\\"]=65
params[\\"maxband_soc\\"]=150
```

Electronic structure Calculations

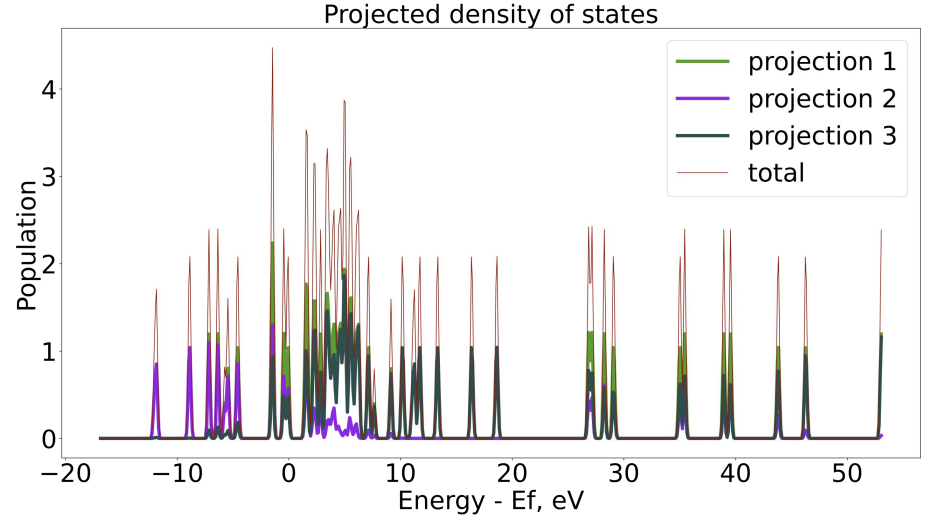


HOMO LUMO





HOMO LUMO



A.O Energies

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       -0.5215552 , -0.50810146, -0.5073219 , -0.43353802, -0.4297624 ,
       -0.428949  , -0.40929046, -0.4083463 , -0.4068004 , -0.34337506,
       -0.32789007, -0.3271614 , -0.3041484 , -0.2980505 , -0.2980287 ,
       -0.28129858, -0.2807471 , -0.26622343, -0.26047915, -0.2600243 ,
       -0.25225043, -0.19527523, -0.19508521, -0.18566789, -0.18191506,
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        0.15318327,  0.18715519,  0.21155082,  0.21257448,  0.21603735,
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        0.        ,  0.        ,  0.        ,  0.        ,  0.        ,
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        0.        ,  0.        ,  0.        ,  0.        ,  0.        ],
```

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       -0.6784103 , -0.61975807, -0.6170882 , -0.6166154 , -0.6155282 ,
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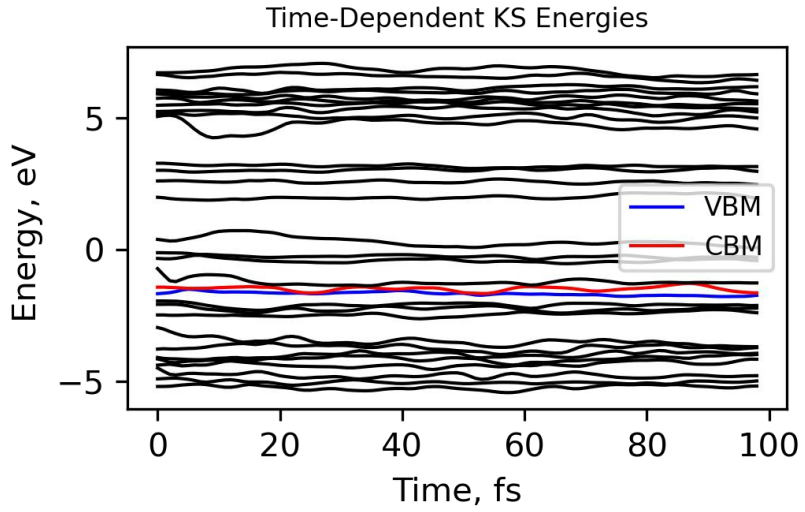
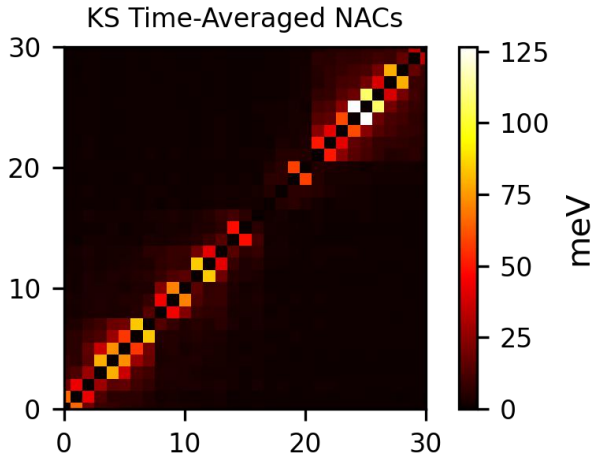
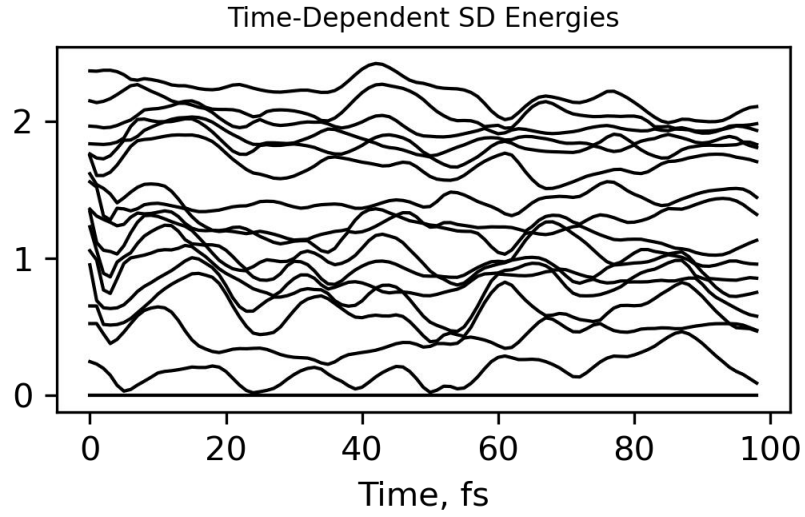
```

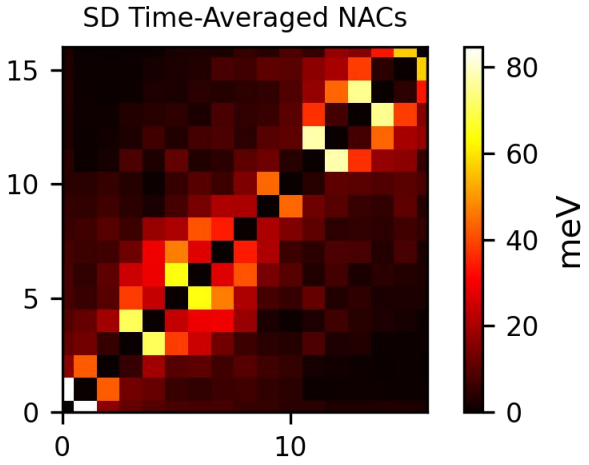
MD-Libra/QE

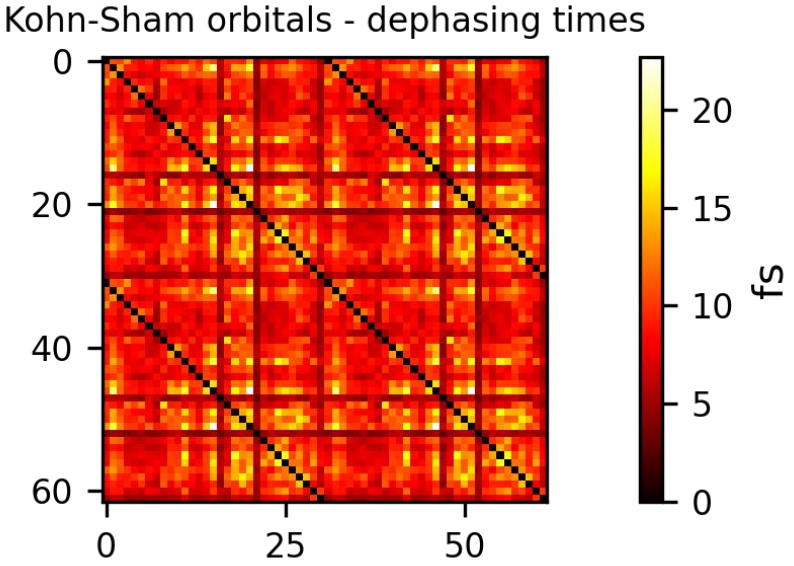
Complex-1: $Ir(C_3H_4N)_3$



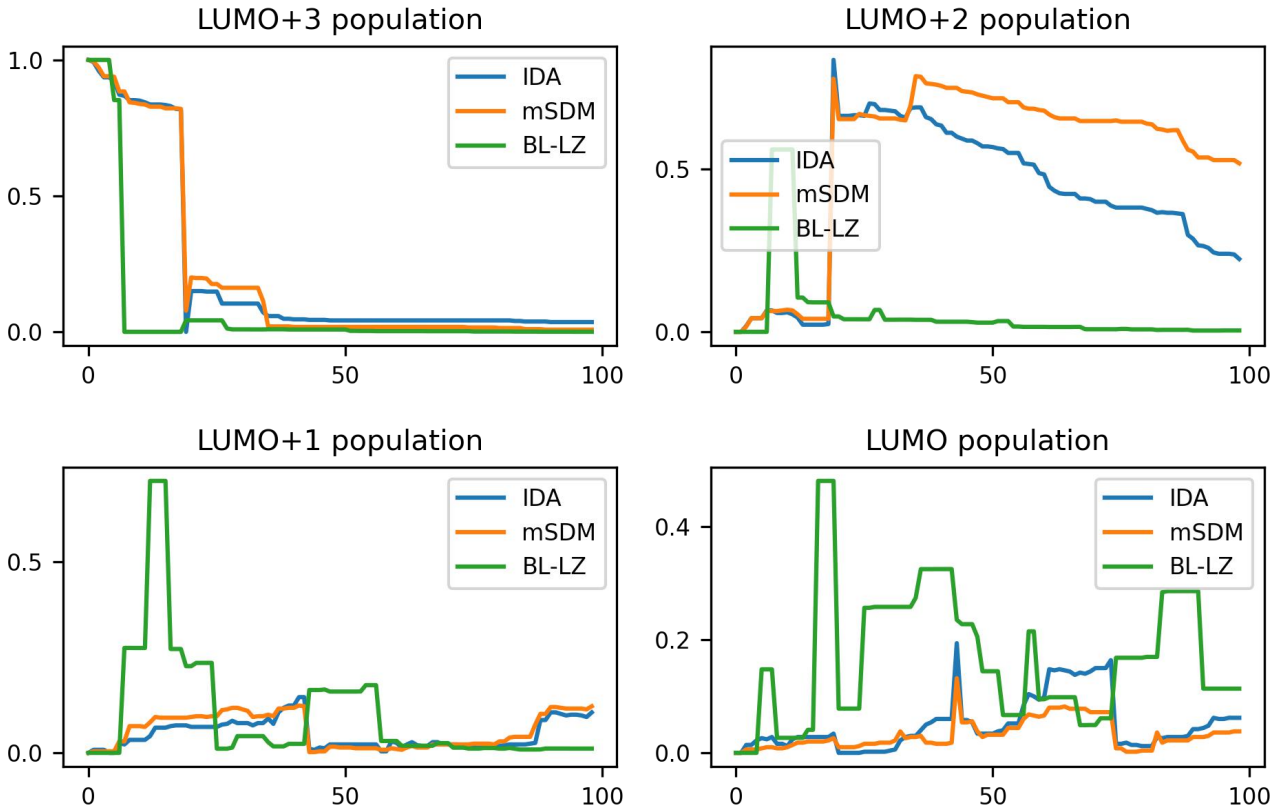




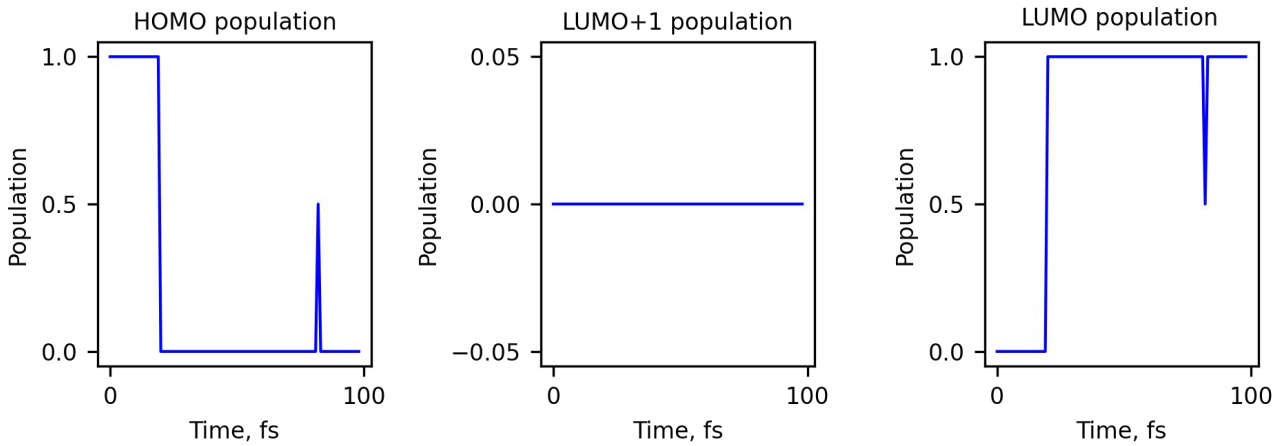




NBRA-MD

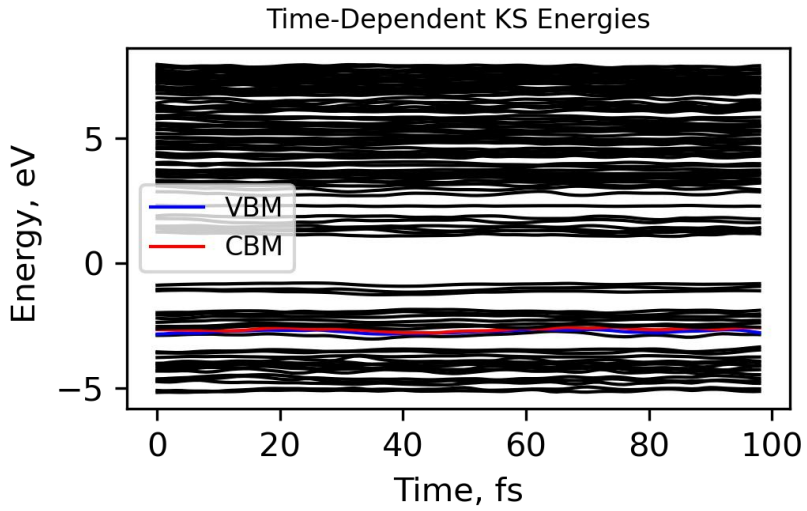


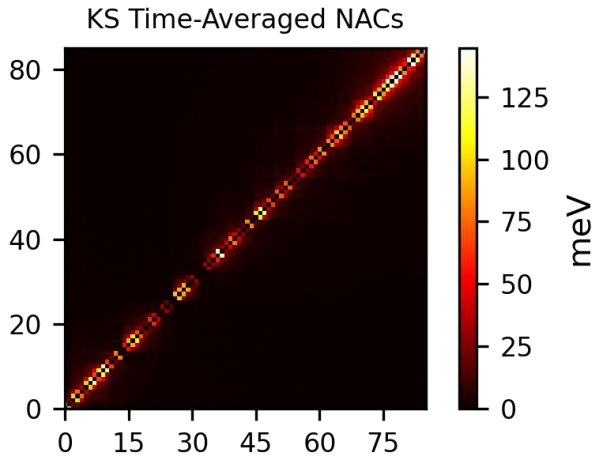
HOMO-LUMO Transition

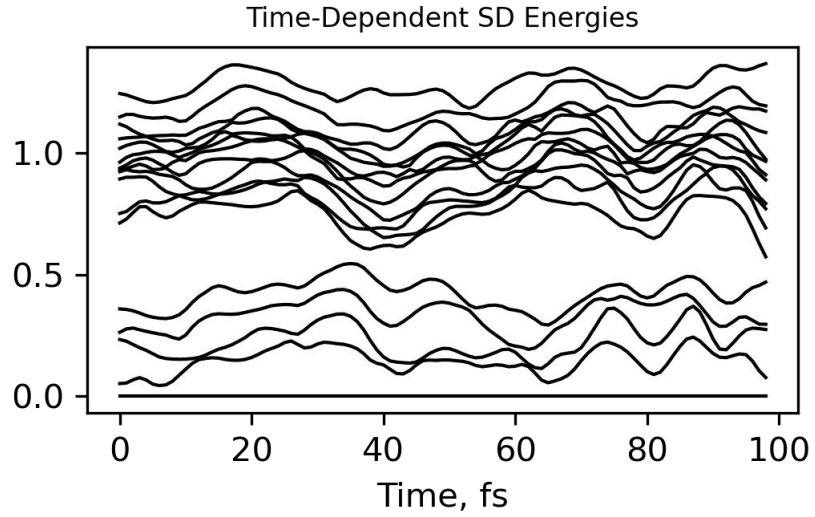


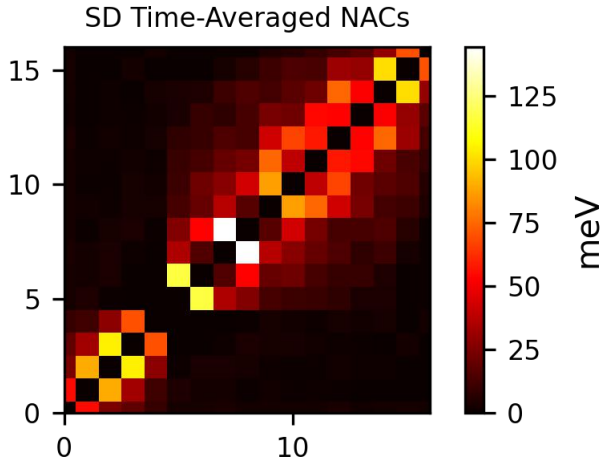
MD-Libra/QE

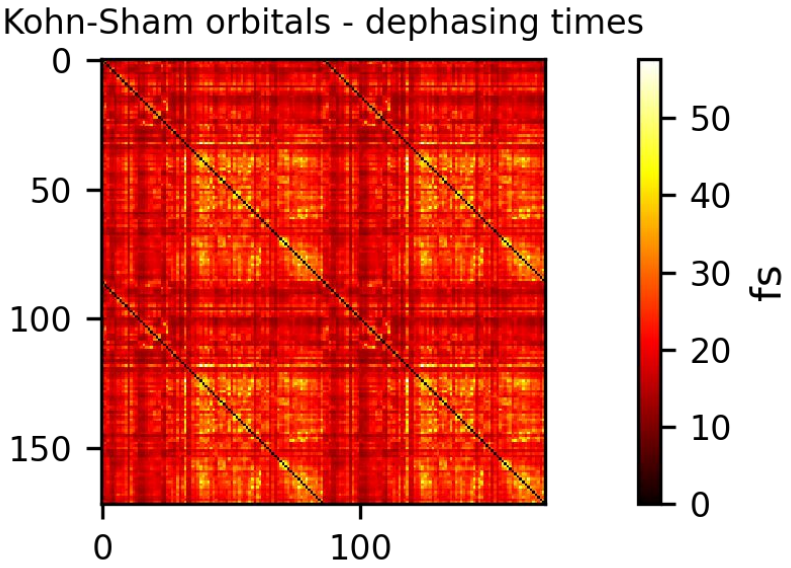
Complex-2: $Ir(C_3H_4N)_3$



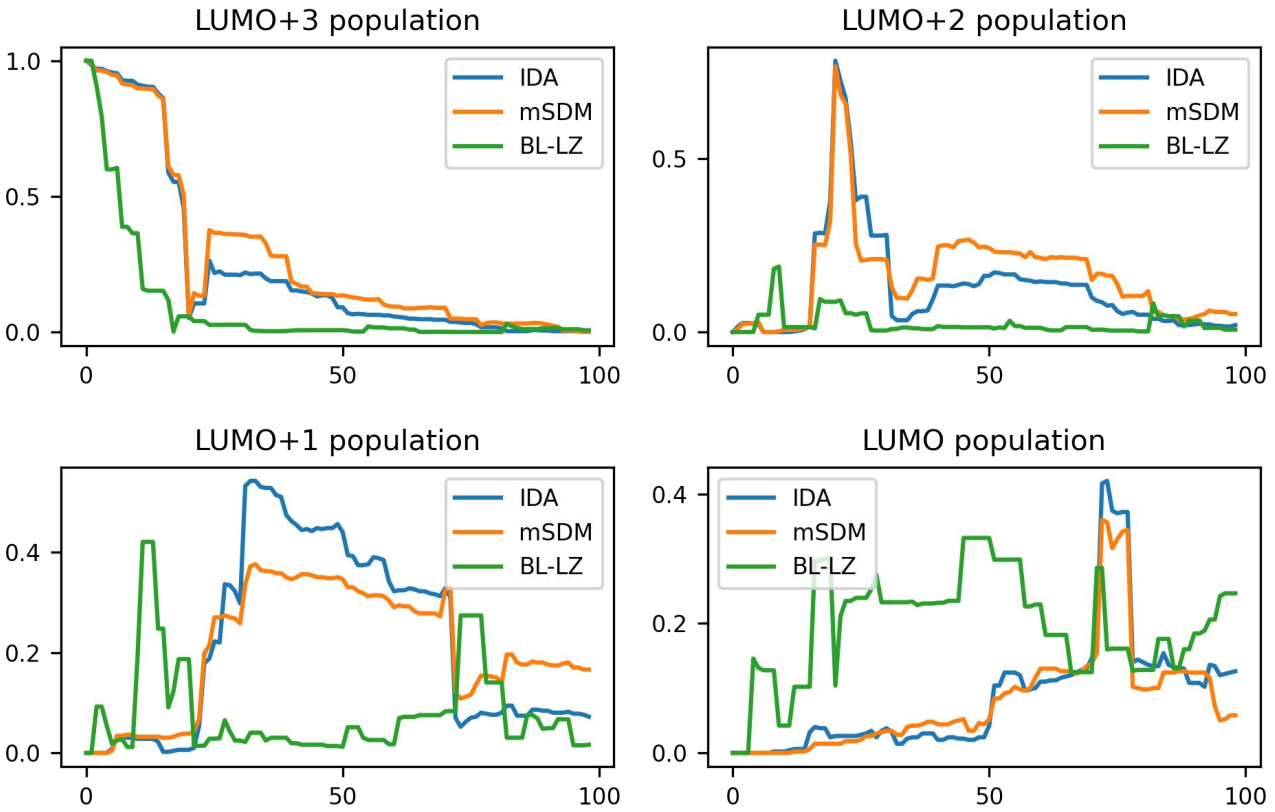




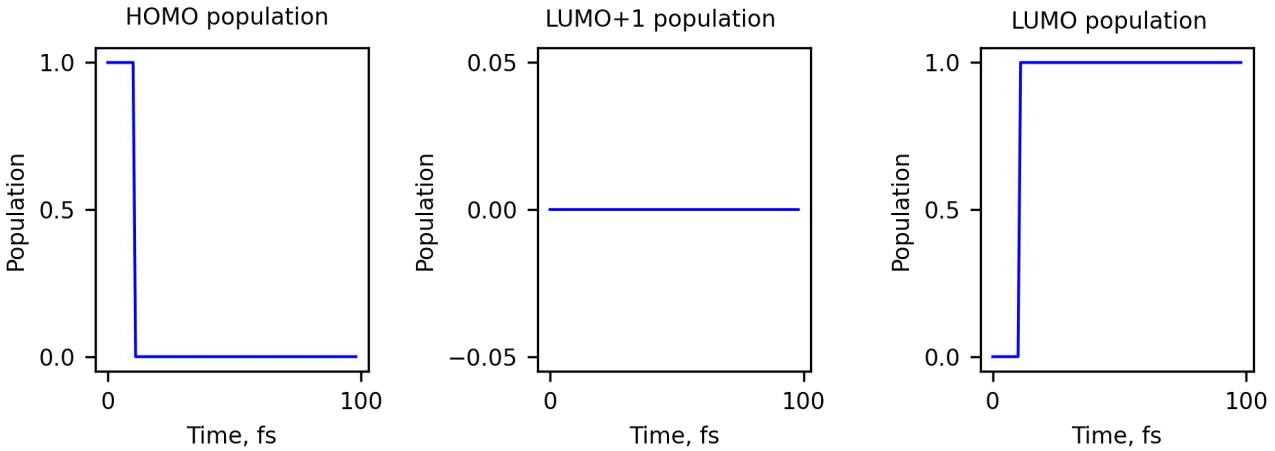




NBRA-MD



HOMO-LUMO Transition



Conclusions

For both complexes, the HOMO-LUMO transition took place in the initial part of the MD, where we can observe that the complex-1 (smallest one) had a change over 100 fs. While for the complex-2, this transition was not observed.

In general terms, these packages allow us to describe the excited states through nonadiabatic Molecular dynamics. These results could be compared with future works using the code of XCDFT.

Prospective

- Multireference Calculation
- Excited States Dynamics
- Nexmd


thank you
danke
謝謝
ngiyabonga
teşekkür ederim
gracias
merci
obrigado
спасибо
dziękuję
bedankt
go raibh maith agat
mochchakkeram
sukriya
kop khun krap
terima kasih
감사합니다
ありがとう
ευχαριστώ
arigatô
dakujem
grazie
tapadh leat
dank je
мерси
рахмат
Баярлалаа
mersi
kia ora
barka
welalin
tack
spas
mahalo
paldies
grazzi
misaotra
matondo
vinaka
благодарам
blagodaram
faafetai lava
kiitos
dankie
nanni
nandri
dhanyavad
hvala
maururu
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gràcie
bayarlalaa
enkosi
dankon
akun
aciu
хвала
asante
manana
obrigada
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sulpáy
taiku
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sobodi
dėkuji
sagolun
mèsi
didi madloba
najis tuke
kam sah hamnida
rahmat
tanemirt
rahmet
diolch
dhanyavadagalu
shukriya
merce
trugarez
xièxie
তোমাকে ধন্যবাদ

Apendix-Charge transfer

$$D + A \rightarrow D^+ + A^-$$

$$D^- + A \rightarrow D + A^-,$$

$$D^+ + A \rightarrow D + A^+,$$

$$\mathbf{H} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \qquad \begin{vmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{21} - ES_{12} & H_{22} - E \end{vmatrix} = 0. \qquad \Delta E = \sqrt{\frac{(H_{11} - H_{22})^2}{1 - S_{12}^2} + 4V_{12}^2}$$

Excitation Energy

$$\mathbf{S} = \begin{pmatrix} 1 & S_{12} \\ S_{12} & 1 \end{pmatrix}. \qquad V_{12} = \frac{1}{1-S_{12}^2}\left[H_{12} - S_{12}\frac{H_{11}+H_{22}}{2}\right]$$

Electronic Coupling

Pavanello, M., Van Voorhis, T., Visscher, L., & Neugebauer, J. (2013). An accurate and linear-scaling method for calculating charge-transfer excitation energies and diabatic couplings. The Journal of chemical physics, 138(5), 054101.