Nonadiabatic molecular dynamics with Libra/CP2K interface

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WELCOME! ☺

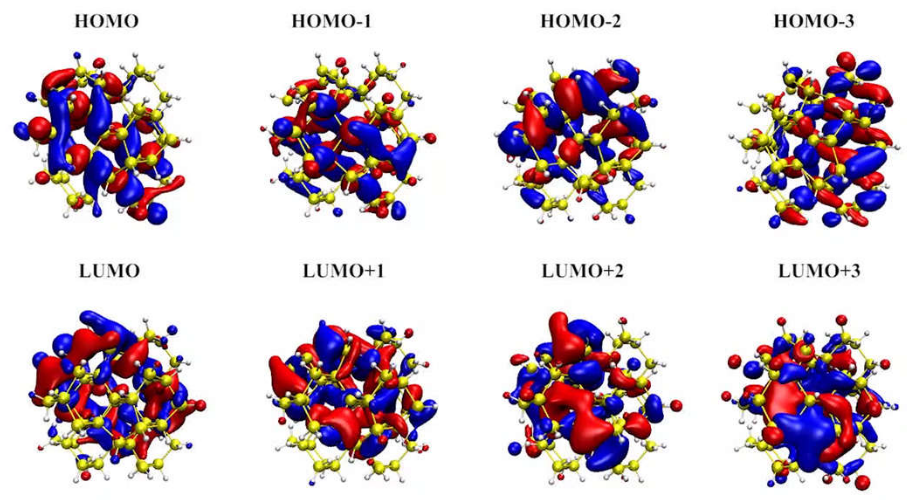
Let’s get started!

What is CP2K?

- CP2K is a quantum chemistry and solid state physics software package that can perform atomistic simulations of solid state, liquid, molecular, periodic, material, crystal, and biological systems.
- CP2K provides a general framework for different modeling methods such as DFT using the mixed Gaussian and plane waves approaches GPW and GAPW.
- Supported theory levels include xTB, DFTB, LDA, GGA, MP2, RPA, semi-empirical methods (AM1, PM3, PM6, RM1, MNDO, …), and classical force fields (AMBER, CHARMM, …).
- CP2K can do simulations of molecular dynamics, metadynamics, Monte Carlo, Ehrenfest dynamics, vibrational analysis, core level spectroscopy, energy minimization, and transition state optimization using NEB or dimer method.

What are the main steps for doing NA-MD with Libra/CP2K interface?

- Step 1:
  - Run a molecular dynamics simulation
- Step 2:
  - Compute the molecular orbitals and their time-overlaps
- Step 3:
  - Form the excited states basis and compute nonadiabatic couplings
- Step 4:
  - Run NA-MD simulations



Smith, Shakiba, Akimov, J. Chem. Theory Comp. 2021

How a molecular orbital is defined?

- A molecular orbital (MO) is defined as a linear combination of atomic orbitals:

$$|\Psi_n> = \sum_i c_i |\phi_i>$$

- The MO overlap:

$$S_{nm} = <\Psi_n|\Psi_m> = \sum_{i,j} c_i^* c_j <\phi_i|\phi_j>$$

the $<\phi_i|\phi_j>$ is the atomic orbital overlap. So the MO overlap matrix ($\boldsymbol{S^{MO}}$) can be written as follows where $\boldsymbol{c}$ is the matrix of molecular orbital coefficients and $\boldsymbol{S^{AO}}$ is the atomic orbital overlap matrix:

$$\boldsymbol{S^{MO}} = \boldsymbol{c^T S^{AO} c}$$

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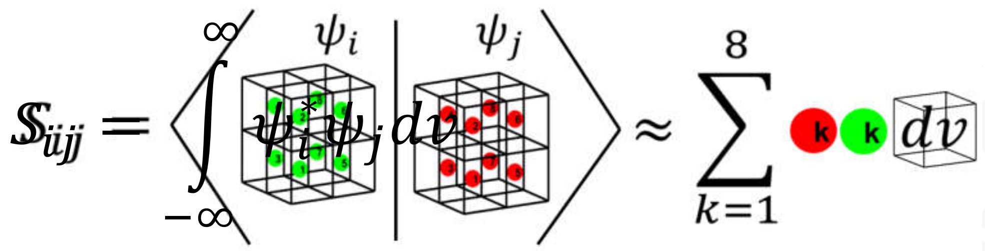
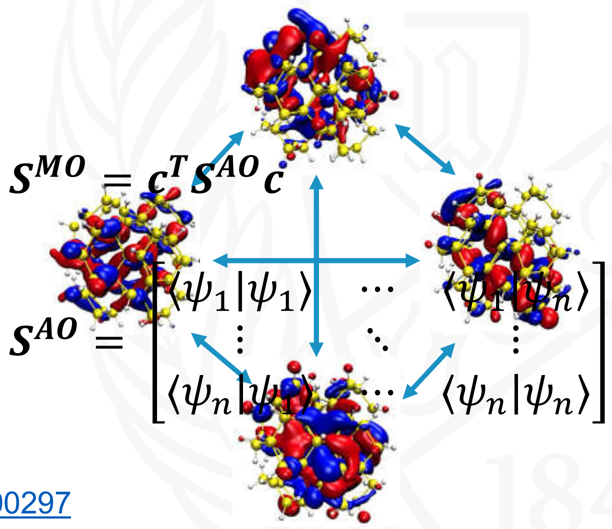
Molecular orbital integrals

- Grid-based approach using *.cube* files
  - Easy to implement
  - Most codes can output these file
  - Not suitable for large structures with large number of states
- Double-molecule approach
  - Easy to use and can be used in different codes
  - Very time-consuming for large structures
  - Not suitable for periodic structures
- Analytical approach
  - Suitable for large systems and large number of states (uses recurrence relations)



$$S_{ij} = \int_{-\infty}^{\infty} \psi_i^* \psi_j \, dv \approx \sum_{k=1}^{8} \, dv$$



$$S^{MO} = c^T S^{AO} c$$

$$S^{AO} = \begin{bmatrix} \langle \psi_1 | \psi_1 \rangle & \cdots & \langle \psi_1 | \psi_n \rangle \\ \vdots & \ddots & \vdots \\ \langle \psi_n | \psi_1 \rangle & \cdots & \langle \psi_n | \psi_n \rangle \end{bmatrix}$$

Smith, Shakiba, Akimov, J. Chem. Theory Comp. 2021, 17, 678–693
Shakiba, Stippel, Akimov, J. Chem. Theory Comp. 2022, DOI: 10.1021/acs.jctc.2c00297

Gaussian type orbitals (GTO)

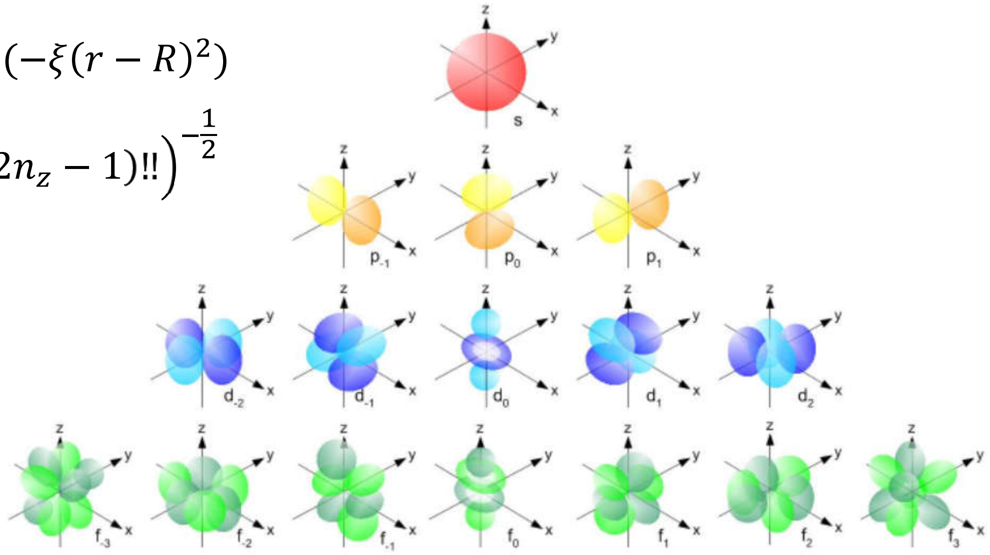
- Atom centered basis sets

$$\varphi(r-R;n,\xi) = N(x-R_x)^{n_x}(y-R_y)^{n_y}(z-R_z)^{n_z} \times \exp(-\xi(r-R)^2)$$

$$N = \left(\frac{2\xi}{\pi}\right)^{\frac{3}{4}} (4\xi)^{(n_x+n_y+n_z)/2} \times \left((2n_x-1)!!\,(2n_y-1)!!\,(2n_z-1)!!\right)^{-\frac{1}{2}}$$

$$\Phi_i(\vec{r}) = \varphi(r;n_i,\xi).Y_{n_i,m_i}(\theta,\phi)$$

n shows the angular momentum value:
s-orbital $n = 0$
p-orbital $n = 1$
d-orbital $n = 2$
f-orbital $n = 3$



Recurrence relations between GTOs

$$\langle s|s\rangle = \left(\frac{\pi}{\xi}\right)^{\frac{3}{2}} \exp(-\xi(A-B)^2)$$

$$\langle p_i|s\rangle = (P_i - A_i)\langle s|s\rangle$$

$$\langle p_i|p_j\rangle = \left(P_j - B_j\right)\langle p_i|s\rangle + \frac{\delta_{ij}}{2\xi}\langle s|s\rangle$$

$$\langle d_{ij}|s\rangle = \left(P_j - A_j\right)\langle p_i|s\rangle + \frac{\delta_{ij}}{2\xi}\langle s|s\rangle$$

$$\langle d_{ij}|p_k\rangle = (P_k - B_k)\langle d_{ij}|s\rangle + \frac{\delta_{ik}}{2\xi}\langle p_j|s\rangle + \frac{\delta_{jk}}{2\xi}\langle p_i|s\rangle$$

$$\langle d_{ij}|d_{kl}\rangle = (P_l - B_l)\langle d_{ij}|p_k\rangle + \frac{\delta_{il}}{2\xi}\langle p_j|p_k\rangle + \frac{\delta_{jl}}{2\xi}\langle p_i|p_k\rangle + \frac{\delta_{kl}}{2\xi}\langle d_{ij}|s\rangle$$

$$i, j, k, l = x, y, z$$

Obara, and Saika, J. Chem. Phys. 1986, 84, 3963-3974.
Obara, and Saika, J. Chem. Phys. 1988, 89, 1540-1559.
Libint, Version 2.6.0 Edward F. Valeev, http://libint.valeyev.net.

Extending to periodic structures and K-points

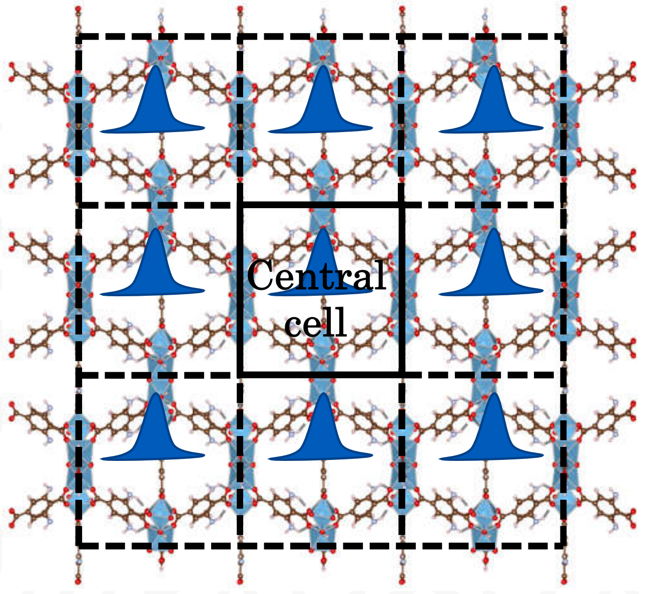
- The Bloch function for K-point in a periodic structure is defined as:

$$\beta_a^k(r) = \frac{1}{\sqrt{N}} \sum_R \varphi_a(r-R) e^{ikR}$$

- Overlaps between Bloch functions of two different K-points:

$$S_{a,b}^k = \langle \beta_a^k \big| \beta_b^{k'} \rangle = \frac{1}{N} \int dr \sum_{R,R'} e^{-ikR} \varphi_a^*(r-R) e^{ik'R'} \varphi_b(r-R')$$

$$= \frac{1}{N} \int dr \sum_{R,R'} e^{i(kR-k'R')} \varphi_a^*(r-R) \varphi_b(r-R')$$



MIL-125-NH_2

Aradi, Hourahine, Frauenheim, J. Phys. Chem. A 2007, 111, 5678–5684

Shakiba, Stippell, Li, Akimov, J. Chem. Theory Compu. 2022, DOI: 10.1021/acs.jctc.2c00297

Step 2: Computing overlap matrices

- Libra uses '*molden*' file formats to read the molecular orbital coefficients, energies, occupation, spin, atomic coordinates, and basis set although it can use other file formats as well including *MOLog* printed out by CP2K.
- Here, we'll show an example of the inner functions that compute the MO overlap matrix for one geometry.
- Note that the workflow is not like this and you only need to specify a couple of variables. The following shows how one can work with the Libra functions, for example, if one intends to write an on-the-fly computation of the NACs.

```python
import os
import numpy as np
import matplotlib.pyplot as plt
from liblibra_core import *
from libra_py import CP2K_methods,molden_methods, data_conv, units
```

```python
# Molden file name
molden_file_name = 'test.molden'
# Number of processors
nprocs = 16
# Spherical or Cartesian coordiantes? Spherical!
is_spherical = True
```

```python
# The integration shells and angular momentum values
shell_1, l_vals =
molden_methods.molden_file_to_libint_shell(molden_file_name,
is_spherical)
```

```python
# All of the eigenvectors and energies of the system
eig_vect_1, energies_1 =
molden_methods.eigenvectors_molden(molden_file_name, nbasis(shell_1),
l_vals)
```

```python
# Resorting the molden indices
new_indices = CP2K_methods.resort_molog_eigenvectors(l_vals)
eigenvectors_1 = []
for j in range(len(eig_vect_1)):
    # the new and sorted eigenvector
    eigenvector_1 = eig_vect_1[j]
    eigenvector_1 = eigenvector_1[new_indices]
    # append it to the eigenvectors list
    eigenvectors_1.append(eigenvector_1)
eigenvectors_1 = np.array(eigenvectors_1)
```

```python
# Alpha and Beta spin eigenvectors
# alpha -> even indices
alpha_eig_vects = eigenvectors_1[0::2]
alpha_eig_vals = energies_1[0::2]
# beta -> odd indices
beta_eig_vects = eigenvectors_1[1::2]
beta_eig_vals = energies_1[1::2]
# Compute AO overlap matrix
AO_S = compute_overlaps(shell_1, shell_1, nprocs)
# Converting to numpy array
AO_S = data_conv.MATRIX2nparray(AO_S)
```

```python
print('The shape of the AO matrix...\n', AO_S.shape)
S_alpha = np.linalg.multi_dot([alpha_eig_vects, AO_S,
alpha_eig_vects.T])
S_beta = np.linalg.multi_dot([beta_eig_vects, AO_S,
beta_eig_vects.T])
```

Overlap calculations input parameters

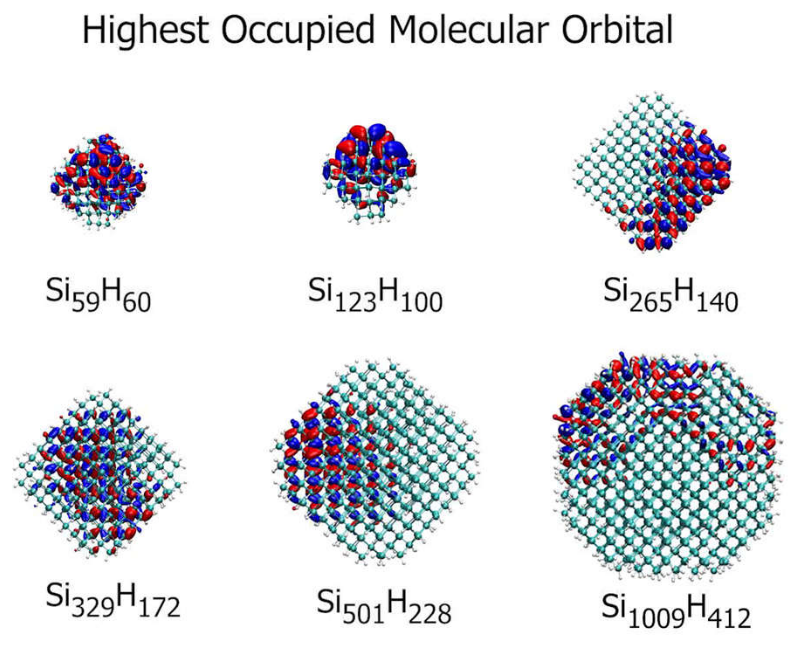
```
params['nprocs']
params['mpi_executable']
params['istep']
params['fstep']
params['lowest_orbital']
params['highest_orbital']
params['isxTB']
params['isUKS']
params['is_periodic']
if params['is_periodic']:
    params['A_cell_vector']
    params['B_cell_vector']
    params['C_cell_vector']
    params['periodicity_type'] # example: 'XYZ'
    origin = [0,0,0]
    params['translational_vectors'] =
    CP2K_methods.generate_translational_vectors(
    origin, [2,2,2], params['periodicity_type'])
params['is_spherical']
params['remove_molden']
params['res_dir']
params['all_pdosfiles']
params['all_logfiles']
```

```
params['cp2k_exe']
params['cp2k_ot_input_template'] # just for xTB
params['cp2k_diag_input_template']
params['trajectory_xyz_filename']

# For cube visualization
params['cube_visualization']
params['vmd_input_template']
params['states_to_plot']
params['plot_phase_corrected']
params['vmd_exe']
params['tachyon_exe']
params['x_pixels']
params['y_pixels']
params['image_format']
params['remove_cube']
params['all_images']


step2.run_cp2k_libint_step2(params)
```

Molecular orbitals visualization



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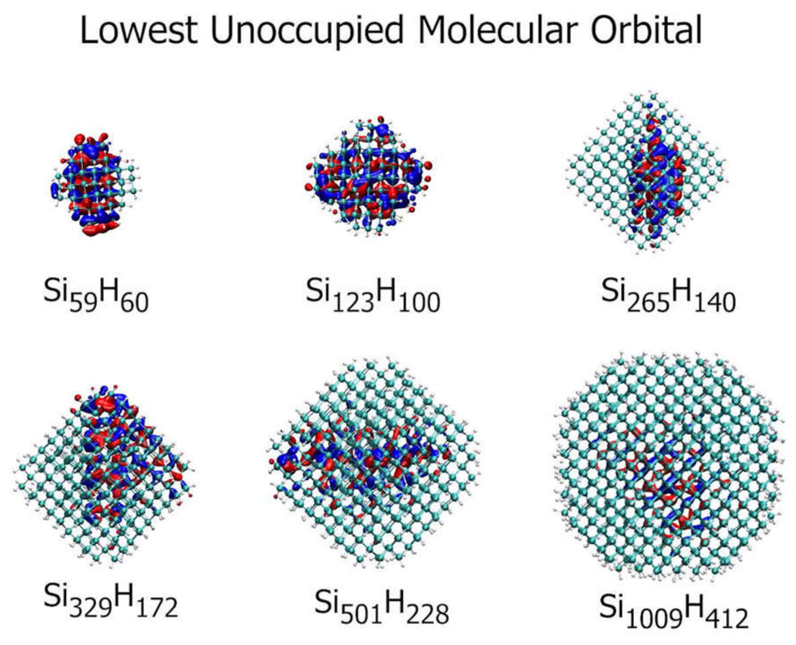

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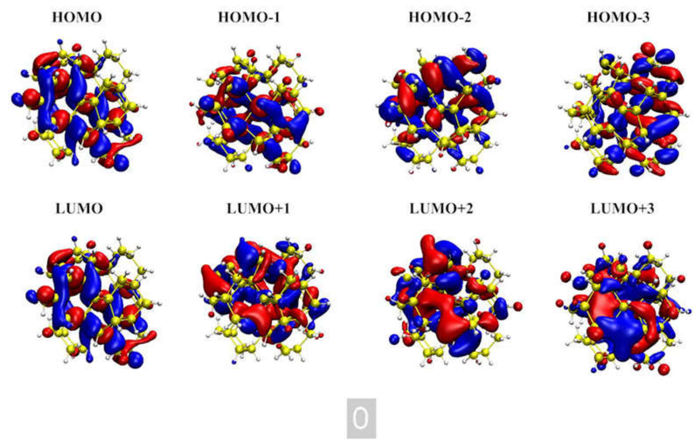
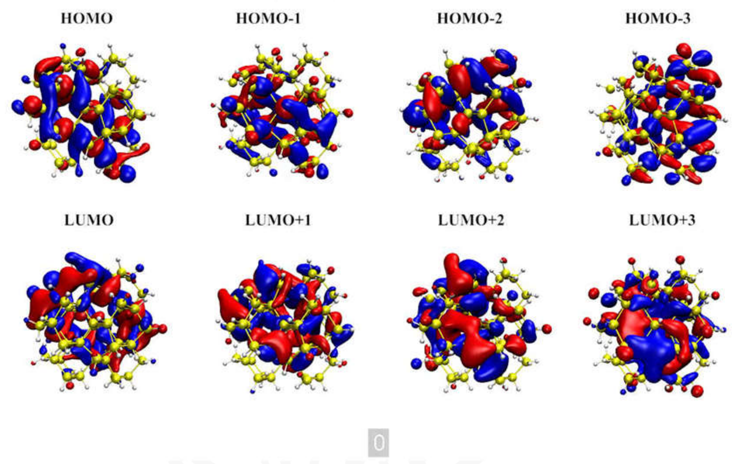
Shakiba, Stippell, Li, Akimov, J. Chem. Theory Compu. 2022, DOI: 10.1021/acs.jctc.2c00297

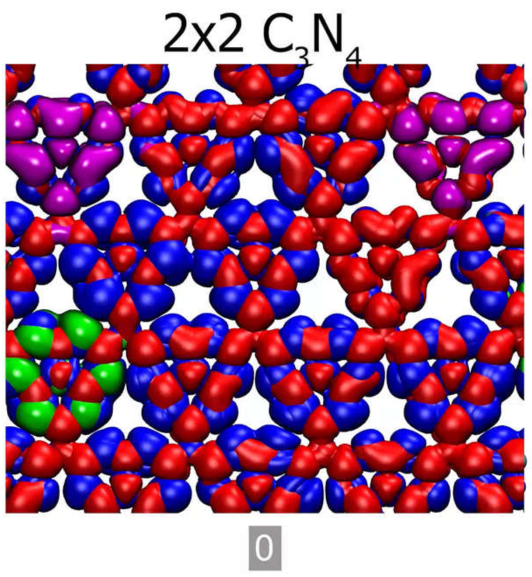
Phase-corrected vs phase-uncorrected

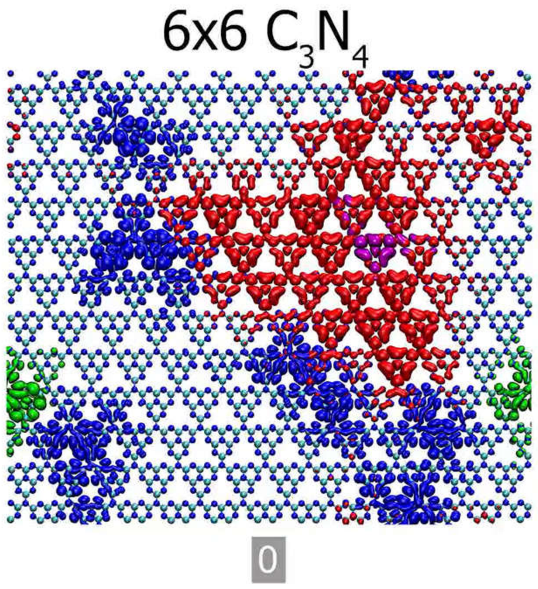
Phase-uncorrected orbitals

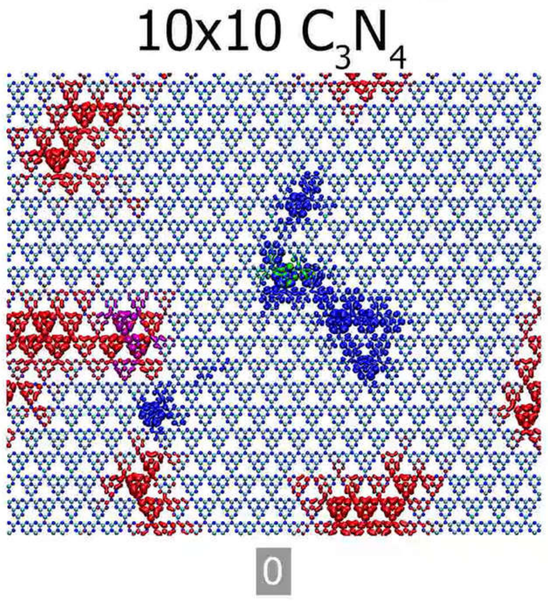


Phase-corrected orbitals







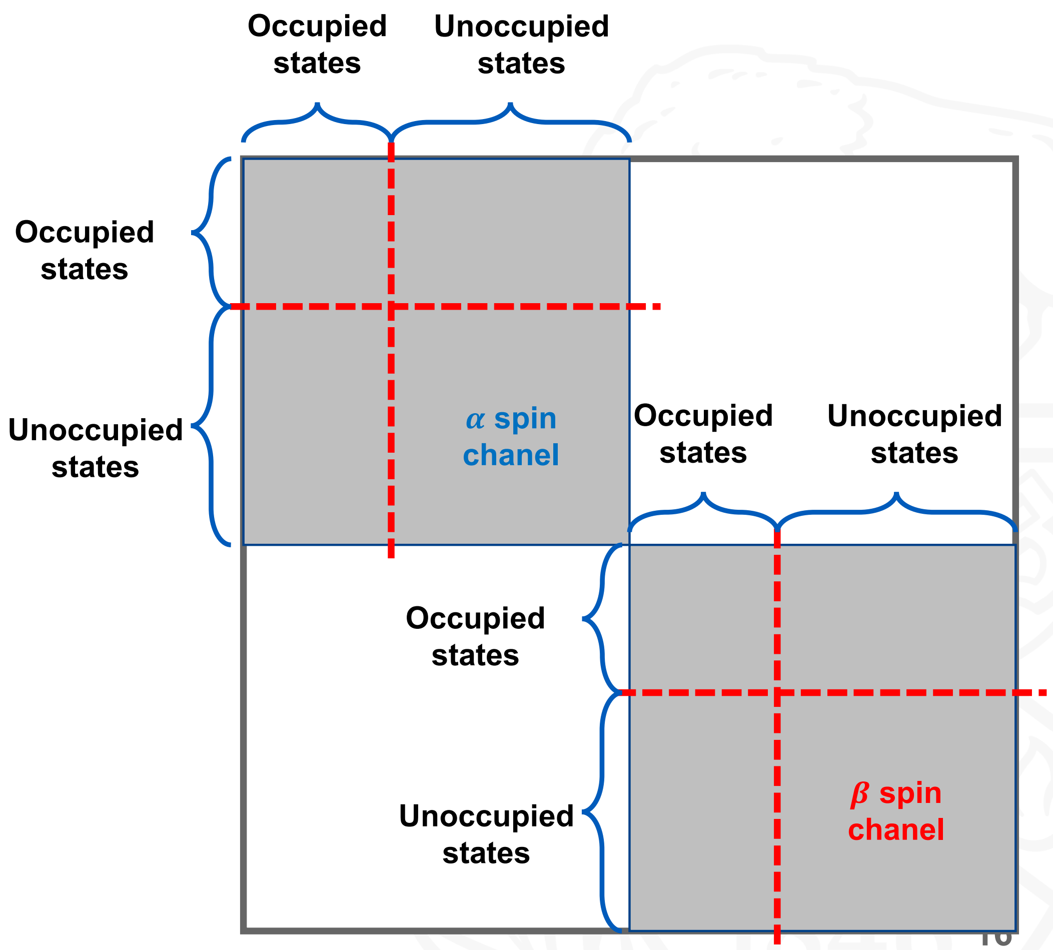


🟦 Occupied
🟥 Unoccupied
🟩 HOMO
🟪 LUMO

Shakiba, Akimov, JPCC 2023, 127, 9083-9096.

Storing data

- Libra saves MO overlaps in 2-spinor format
- With no spin-orbit coupling, the second and third block of the matrix is zero.
- To efficiently storing the data, we use `scipy.sparse` library of Python

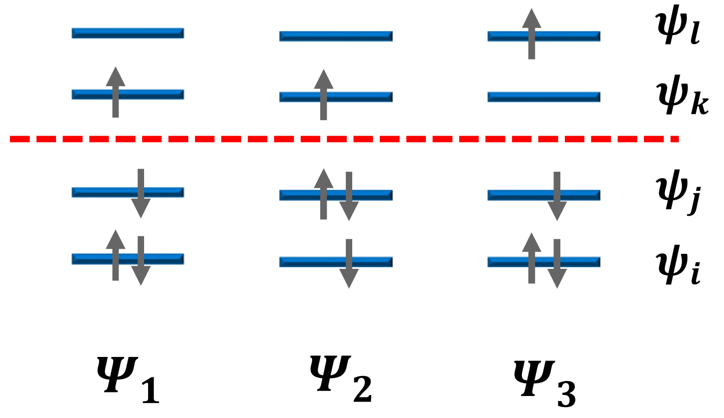


Excited states bases

- In quantum mechanics, electronic wave function has the antisymmetric property which can be expressed in form of Slater determinant.
- For an N-electron system:

$$\Psi(x_1,..,x_N) = \frac{1}{\sqrt{N!}}|\psi_1(x_1)\psi_2(x_2)\ldots\psi_K(x_N)\rangle = \frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(x_1)\cdots\psi_K(x_1)\\ \vdots \quad \ddots \quad \vdots\\ \psi_1(x_N)\cdots\psi_K(x_N)\end{vmatrix}$$

- Single-particle excitations



$$\boldsymbol{\Psi_1} = |\boldsymbol{\psi_i\bar{\psi}_i\psi_k\bar{\psi}_j}\rangle$$

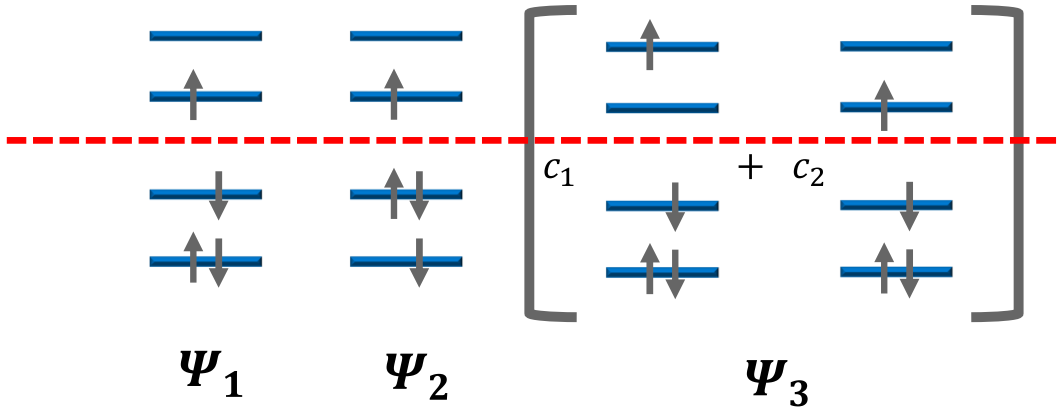
$$\boldsymbol{\Psi_2} = |\boldsymbol{\psi_k\bar{\psi}_i\psi_j\bar{\psi}_j}\rangle$$

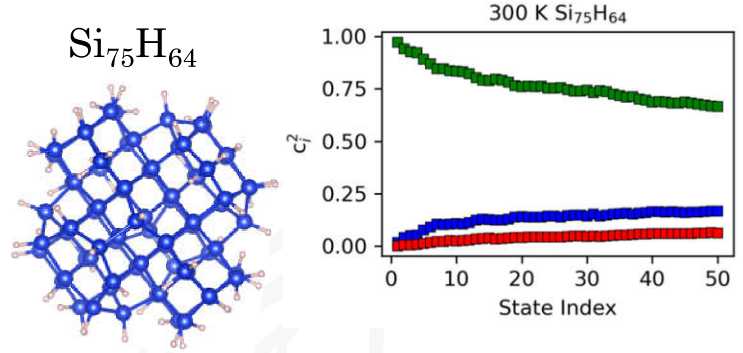
$$\boldsymbol{\Psi_3} = |\boldsymbol{\psi_i\bar{\psi}_i\psi_l\bar{\psi}_j}\rangle$$

$$\langle\boldsymbol{\Psi_1}|\boldsymbol{\Psi_2}\rangle = \det\begin{vmatrix}\langle\psi_i|\psi_k\rangle & \langle\overline{\psi_i}|\psi_k\rangle & \langle\psi_k|\psi_k\rangle & \langle\overline{\psi_j}|\psi_k\rangle\\ \langle\psi_i|\overline{\psi_i}\rangle & \langle\overline{\psi_i}|\overline{\psi_i}\rangle & \langle\psi_k|\overline{\psi_i}\rangle & \langle\overline{\psi_j}|\overline{\psi_i}\rangle\\ \langle\psi_i|\psi_j\rangle & \langle\overline{\psi_i}|\psi_j\rangle & \langle\psi_k|\psi_j\rangle & \langle\overline{\psi_j}|\psi_j\rangle\\ \langle\psi_i|\overline{\psi_j}\rangle & \langle\overline{\psi_i}|\overline{\psi_j}\rangle & \langle\psi_k|\overline{\psi_j}\rangle & \langle\overline{\psi_j}|\overline{\psi_j}\rangle\end{vmatrix}$$

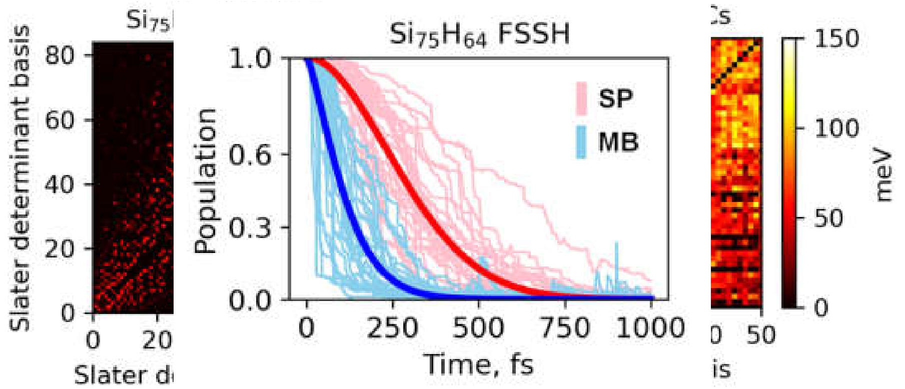
Excited states bases

- Many-body (TD-DFT) excitation





Excitation energy



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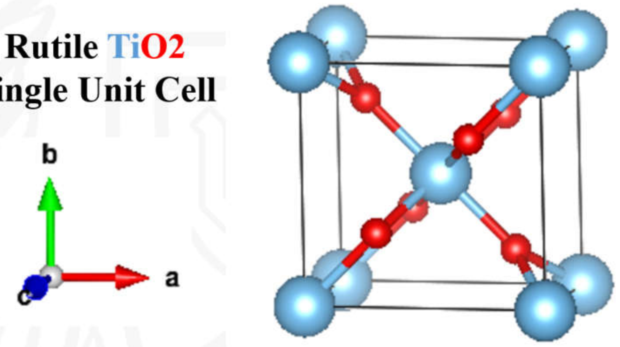
Step 3: Compute nonadiabatic couplings

```
params_ks = { 'lowest_orbital': 24-10,
'highest_orbital': 24+11, 'num_occ_states': 10,
'num_unocc_states': 10, 'use_multiprocessing': True,
'nprocs': 8, 'time_step': 1.0, 'es_software': 'cp2k',
'path_to_npz_files': os.getcwd()+'/res',
'logfile_directory': os.getcwd()+'/all_logfiles',
'path_to_save_ks_Hvibs': os.getcwd()+'/res-ks-DFT',
'start_time': 1200, 'finish_time': 1401,
'apply_phase_correction': True,
'apply_orthonormalization': True,
'do_state_reordering': 2, 'state_reordering_alpha':0,
'nac_algo': 0 }
# For KS states - Applying correction to KS overlaps
and computing the NACs in KS space
step3.run_step3_ks_nacs_libint(params_ks)
```

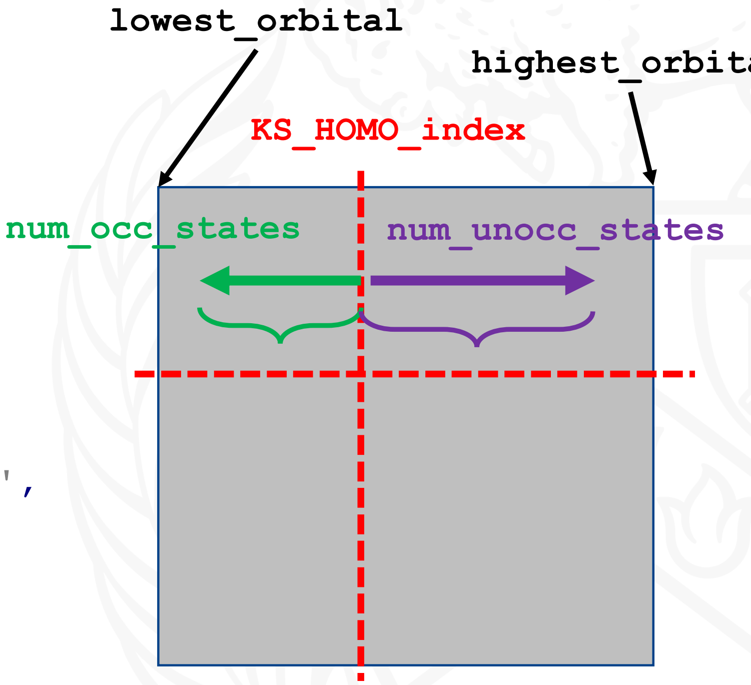
Rutile TiO_2
Single Unit Cell



NAC in excited states basis

```
params_mb_sd = {
   'lowest_orbital': 24-10, 'highest_orbital': 24+11,
   'num_occ_states': 10, 'num_unocc_states': 10,
   'isUKS': 0, 'number_of_states': 10,
   'tolerance': 0.01, 'verbosity': 0,
   'use_multiprocessing': True, 'nprocs': 12,
   'is_many_body': True, 'time_step': 1.0,
   'es_software': 'cp2k',
   ‘path_to_npz_files': os.getcwd()+'/../res’
   'logfile_directory': os.getcwd()+'/../all_logfiles',
   'path_to_save_sd_Hvibs': os.getcwd()+'/res-mb-sd-DFT',
   'outdir': os.getcwd()+'/res-mb-sd-DFT',
   'start_time': 1200, 'finish_time': 1401,
   'sorting_type': 'identity' }

step3.run_step3_sd_nacs_libint(params_mb_sd)
```

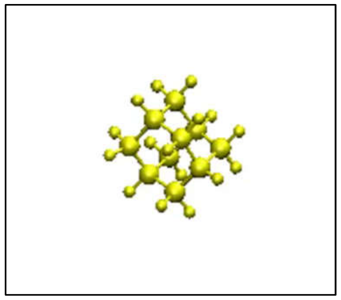


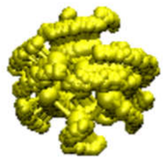
Molecular dynamics trajectory alignment

- Alignment removes the translation and rotation of a molecule

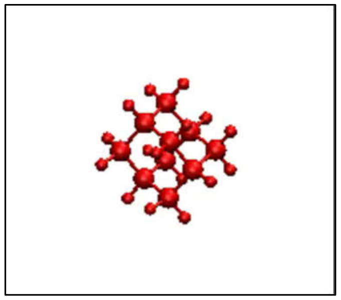
```
from libra_py.md_align import align_trajectory
# Align the MD trajectory by removing the translations and rotations
align_trajectory("step1/adamantane-pos-1.xyz", "step1/aligned-adamantane-pos-1.xyz")
```

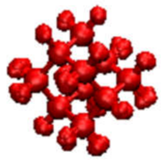
Initial trajectory





Aligned trajectory





Summary

- All these methodologies are implemented and available in Libra software package
  - Open-source code for quantum dynamics methodologies such as trajectory surface hopping
  - The underlying code is written in C++ for faster computation and the functions can be called from Python
  - Libint is used for computation of overlaps between GTOs
  - Sparse representation of the overlap matrices using `scipy.sparse` library in Python
  - High-throughput computation for generating the overlap matrices
  - Applicable to large systems in different electronic structure calculations frameworks.
  - It is interfaced with many quantum chemistry codes such as CP2K, Quantum ESPRESSO, and Gaussian but the Libint interface is only available for CP2K code.

Thank You!

Questions?