Spin-orbit coupling with relativistic MRSF-TDDFT as the first step for developing applications for studying intersystem crossings

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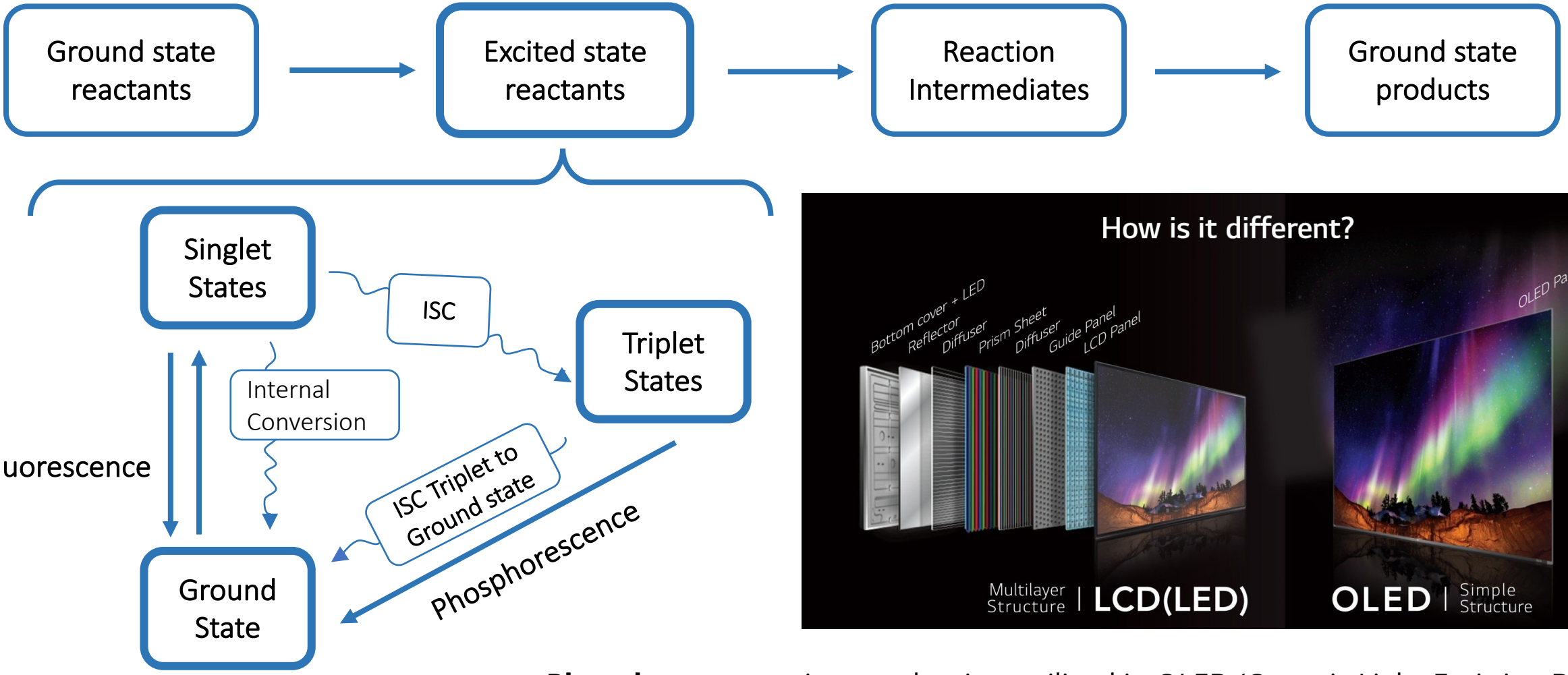
Intersystem crossings (ISC), spin-orbit coupling



Phosphorescence is a mechanism utilized in OLED (Organic Light-Emitting Diode)

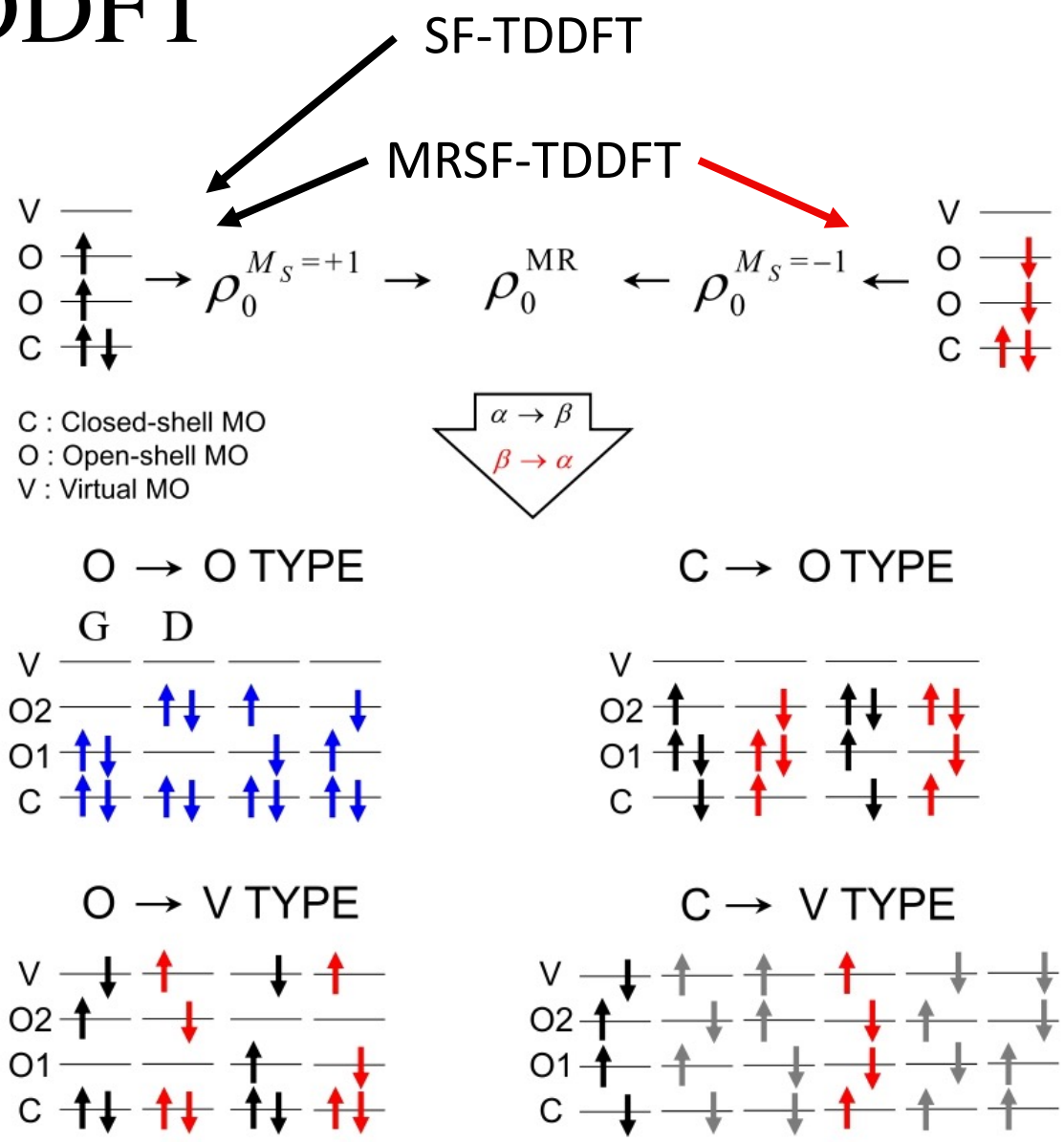
Thermally Activated Delayed Fluorescence (TADF) also involves ISC and can be employed in OLED

MRSF vs TDDFT, SF-TDDFT

- TDDFT: no doubles, incorrect topology of Conical Intersection CI_{10}
- SF-TDDFT has spin contamination.

Resolved by:

- MRSF-TDDFT[1-3]: no spin contamination.



[1] S Lee, M Filatov, S Lee, CH Choi,
Journal of chemical phys. 2018, 149, 104101
[2] W Park et al, J. Phys. Chem. Lett. 2021, 39, 9720
[3] S Lee et al, J. Phys. Chem. A 2019, 123, 6455

Spin-orbit coupling of Relativistic MRSF-TDDFT

Relativistic two-component Hamiltonian:

$$H = H_0 + H_{\mathrm{SOC}}$$

MRSF unperturbed wavefunctions for singlet and triplet states:

Singlets $|\Psi_I^{00}\rangle$

Triplets $|\Psi_I^{10}\rangle$

$$|\Psi_I^{1\bar{1}}\rangle = \frac{1}{\sqrt{2}}\hat{S}_-|\Psi_I^{10}\rangle$$

$$|\Psi_I^{11}\rangle = \frac{1}{\sqrt{2}}\hat{S}_+|\Psi_I^{10}\rangle$$

The final SOC states and energies are obtained by diagonalization of the matrix

$$\langle \Psi_I^{SM_S}|\hat{H}_0 + \hat{H}_{\mathrm{SOC}}|\Psi_J^{S'M'_S}\rangle$$

Matrix elements of spin-orbit coupling operator (H_{SOC})

$$H_{\mathrm{SOC}} = H_{\mathrm{en}} + H_{\mathrm{ee}} = \frac{\alpha^2}{2}\sum_{aA}\frac{Z_A}{r_{aA}^3}\mathbf{l}_{aA}\cdot\mathbf{s}_a - \frac{\alpha^2}{2}\sum_{a}\sum_{b\neq a}\frac{1}{r_{ab}^3}\mathbf{l}_{ab}\cdot(\mathbf{s}_a + 2\mathbf{s}_b)$$

Electron-nuclea Electron-electron

where $\mathbf{l}_{aA} = \mathbf{r}_{aA}\times\mathbf{p}_a$ is the angular momentum of the electron *a* relative to the nucleus *A*, the second – to the electron *b*. The $\mathbf{r}_a, \mathbf{p}_a,$ and $\mathbf{s}_a$ are position, momentum and spin operators.

$$\hat{H}_{\mathrm{SOMF}}|j\rangle = \langle i|\hat{H}_{\mathrm{en}}|j\rangle + \sum_{kl} D_{kl}\left(\langle ik|\hat{H}_{\mathrm{ee}}|jl\rangle - \frac{3}{2}\langle ik|\hat{H}_{\mathrm{ee}}|lj\rangle - \frac{3}{2}\langle ki|\hat{H}_{\mathrm{ee}}|jl\rangle\right)$$

where D_{kl} is the single-particle spin-dependent transition density matrix elements:

$$D_{ij}^{IJ}(1,1) = \langle\Psi_I^{SM_S}|T^{1,1}|\Psi_J^{S'M'_S}\rangle\delta_{M_S,M'_S+1},$$

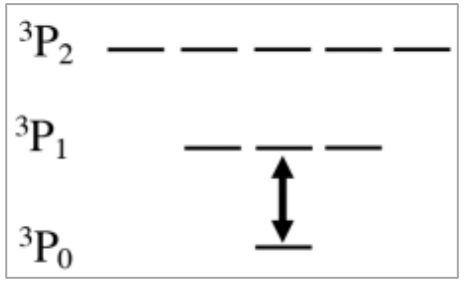
$$D_{ij}^{IJ}(1,-1) = \langle\Psi_I^{SM_S}|T^{1,-1}|\Psi_J^{S'M'_S}\rangle\delta_{M_S,M'_S-1},$$

$$D_{ij}^{IJ}(1,0) = \langle\Psi_I^{SM_S}|T^{1,0}|\Psi_J^{S'M'_S}\rangle\delta_{M_S,M'_S}.$$

$^3P_1 - ^3P_0$ Gap of Tin (Sn)

The absolute value of the gap of C, Si, Ge, and Sn in cm^{-1} as calculated by SOC-MRSF with the effective core potential of SBJKC basis set[1].

	C	Si	Ge	Sn
SOC-MRSF/SBKJC/PBE0	16.5 (1%)	75.7 (-2%)	587.6 (5%)	2051.5 (21%)
Effective nuclear charges[1]	3.9	168	1312	5500
Experiment	16.4	77.1	557.1	1691.8



The effects of all-electron scalar relativity treatment. The absolute value of the gap of Sn in cm^{-1}

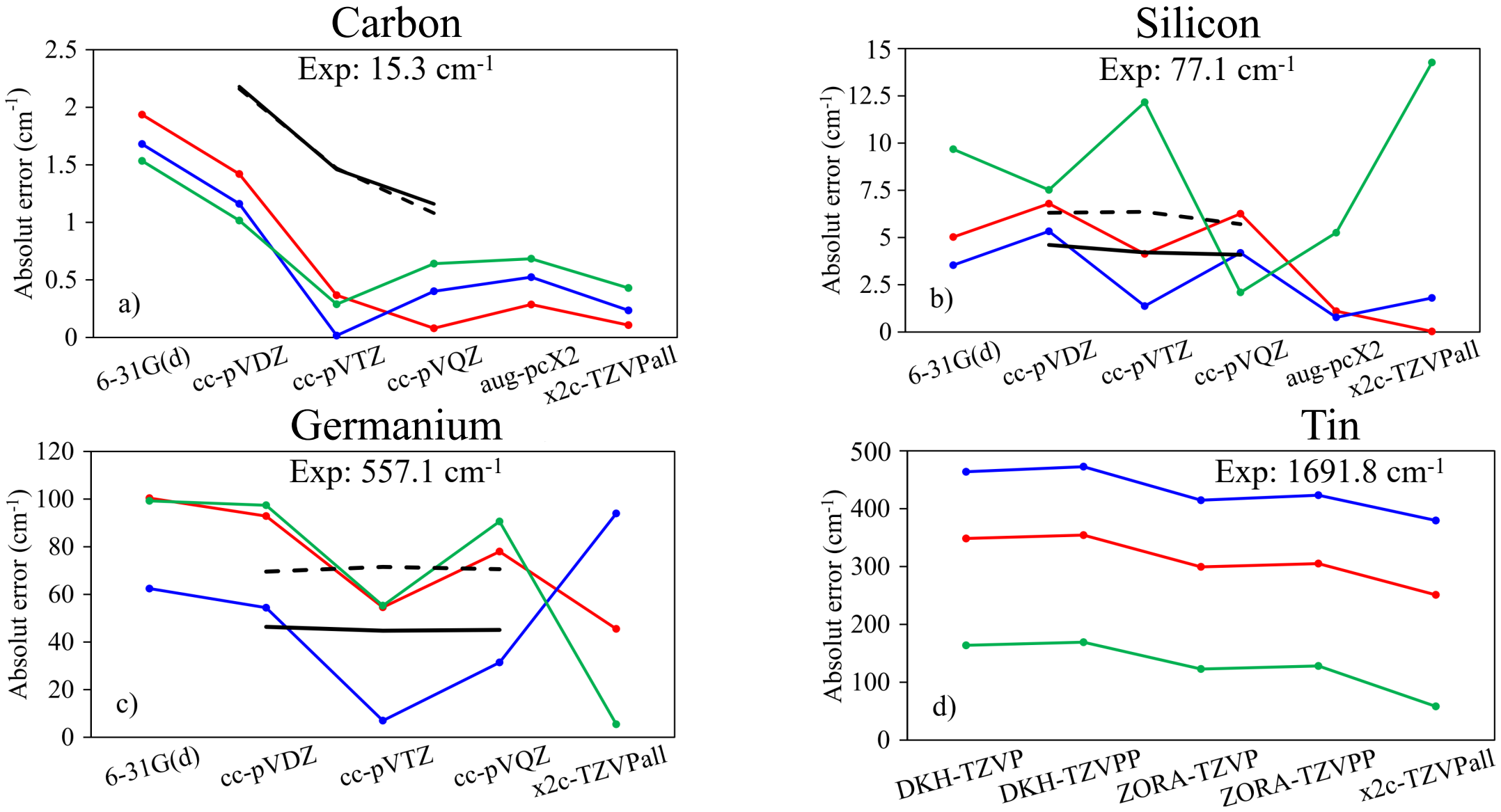
	DK	
	1st	2nd
M06-2X/x2c-TZVPall	1757 (4%)	1750 (3%)

Employed 1st and 2nd order Duglas-Kroll relativistic corrections for non-SOC MRSF.

SOC-MRSF includes only 1st order DK correction to one-electron spin-orbit integrals.

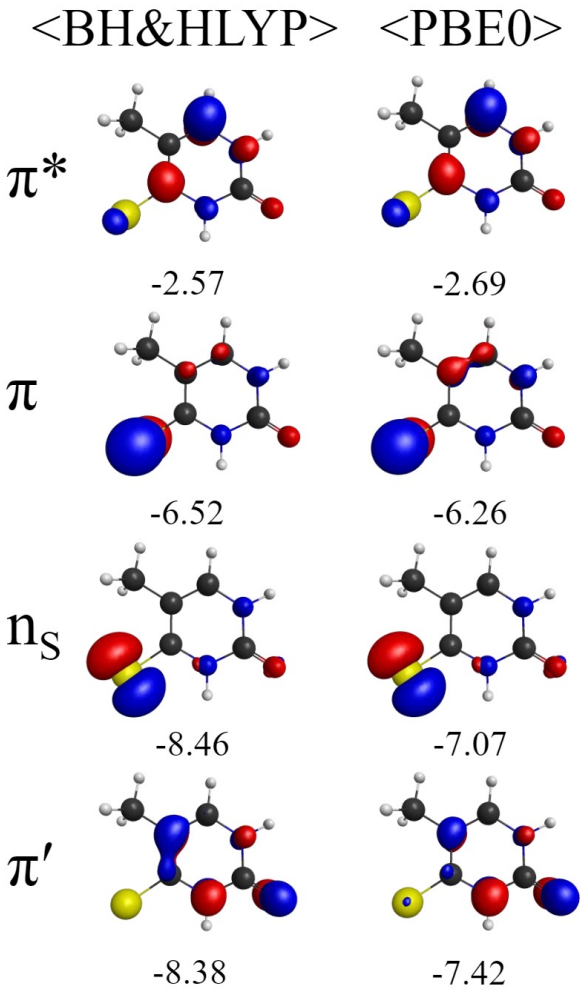
[1] D. Fedorov, et al,
Int. Rev. Phys. Chem. 2003, 22, 551

$^3P_1 - ^3P_0$ Gap of Group IV Elements



[4c-CASSCF, 4c-CASPT2] B. Zhang et al, J. Chem. Theory Comput. 2018, 14,

Spin-Orbit Couplings of 4-Thiothymine



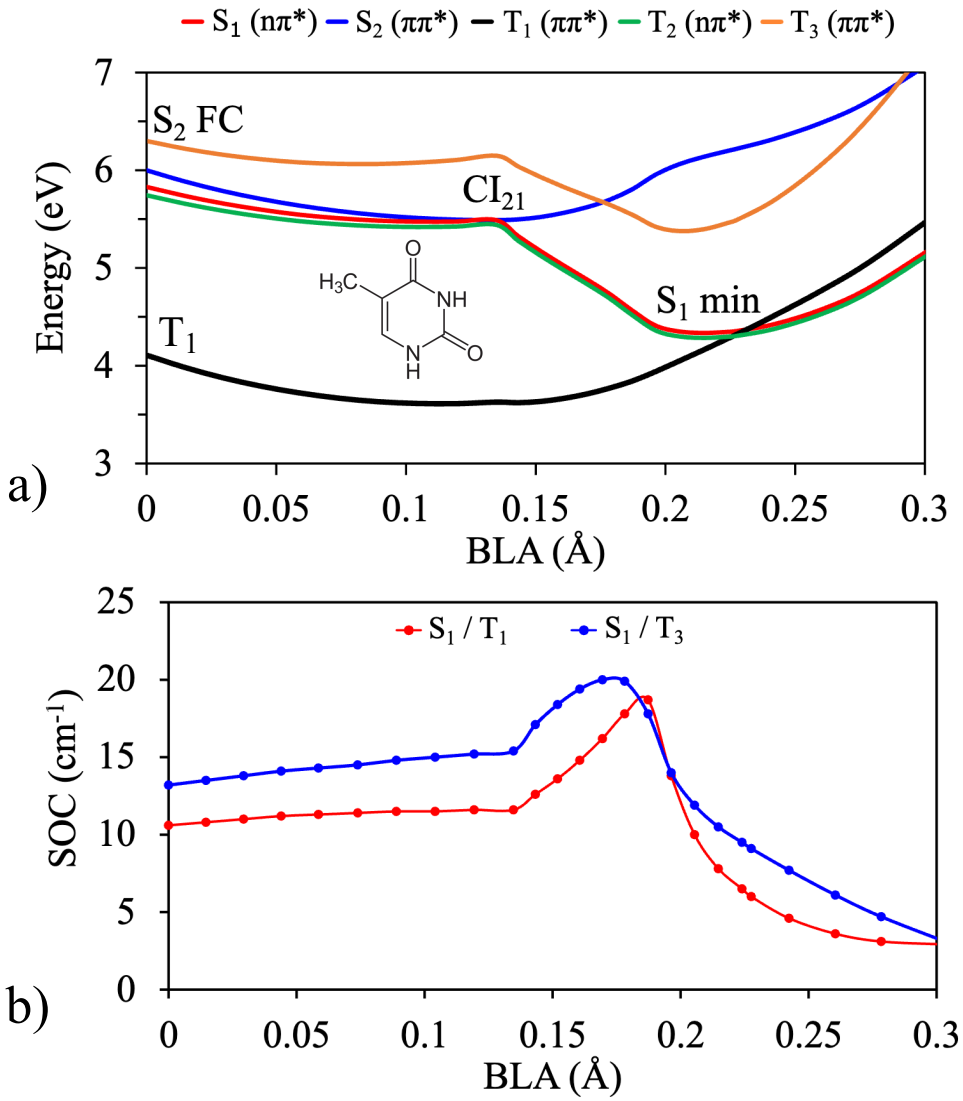
S_0	π^2 (0.90)	π^2 (0.98)
S_1	$n_S\pi^*$ (0.96)	$n_S\pi^*$ (0.98)
T_1	$n_S\pi^*$ (0.96)	$n_S\pi^*$ (0.98)
T_2	$\pi'\pi^*$ (0.98)	$\pi'\pi^*$ (0.94)

Table 1. Spin-orbit couplings of 4-thiothymine

	MRSF/**PBE0**/6-31G(d) geometry ($S_{1\ min}$)		MRSF/**BH&HLYP**/6-31G(d) geometry ($S_{1\ min}$)	
cc-pVTZ with	GMC-QDTP2	SOC-MRSF	GMC-QDTP2	SOC-MRSF
	cm^{-1}			
GS / $^3\pi\pi^*$	1/1	0/0	1/1	0/0
GS / $^3n\pi^*$	98/13	82/9	108/12	97/10
$^1n\pi^*$ / $^3\pi\pi^*$	113/14	109/13	116/13	116/13
$^1n\pi^*$ / $^3n\pi^*$	0/0	0/0	2/0	1/0

The values separated by slash means $M_S = \pm 1$ / $M_S = 0$.
GMC-QDPT2 is General Multi-Configurational second-order quasidegenerate perturbation theory.

The intersystem crossing probability of Thymine



Magnitude of transition probability by Landau Zerner is P_{ab}=0.0018

[1]CASSCF NAMD simulation predict
ISC in **0.9 ps** for $S_1(^1n\pi^*) \rightarrow T_2(^3\pi\pi^*)$ and ultrafast $T_2 \rightarrow T_1$

[2]Extreme Ultraviolet Time-Resolved Photoelectron Spectroscopy studies predict
IC S2 → S1 within **80 fs** and
ISC in **3.5 ps** for $S_1(^1n\pi^*) \rightarrow T_1(^3\pi\pi^*)$

[3]Out previous study predict
IC S2 → S1 within **30 fs** and
IC S1 → S0 within **6 ps**

[1] S. Mai at al, Chem. Phys. 2017, 482, 9
[2] T. J. A. Wolf at al, J. Phys. Chem. A 2019, 123, 6897
[3] W. Pack et al, J. Phys. Chem. Lett. 2021, 12, 4339

Feature plans:

- NAMD with IC and ISC together
- Optimizing XC for MRSF-TDDFT
- Improving MRSF

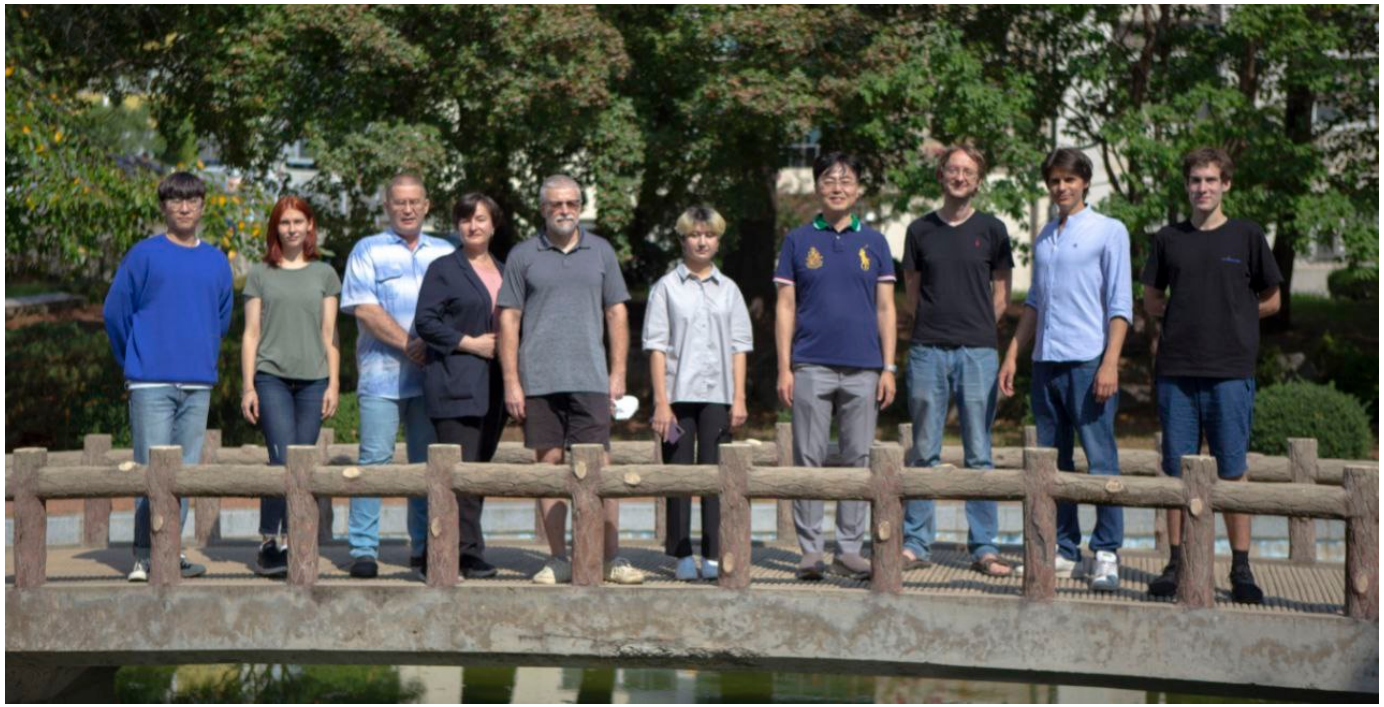
Conclusion

- We have developed SOC-MRSF-TDDFT.
- SOC-MRSF calculations of the $^3P_1$–$^3P_0$ gap and of 4-thiothymine both yielded accurate and consistent results with experimental data and high-level theories.
- In the study of Thymine, the majority of excited state populations remain near $S_{1\ min}$, increasing the chance of intersystem crossing due to the proximity to the S_1/T_1 crossing and existing spin-orbit coupling.
- SOC-MRSF can be a promising protocol for SOC-involved nonadiabatic molecular dynamics (NAMD), especially for large molecules.

The team

Thank you for your attention!

Michael Filatov Cheol Ho Choi



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