
TADF OLED Krutyn Summer School 2017

Prof. Dr. Christel M. Marian

Institute of Theoretical and Computational Chemistry
Heinrich-Heine-University Düsseldorf

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Spin–Orbit
Coupling in
▷ Molecules

OLEDs

Introduction

Spin–Orbit Coupling
Hamiltonians

Symmetry
Considerations

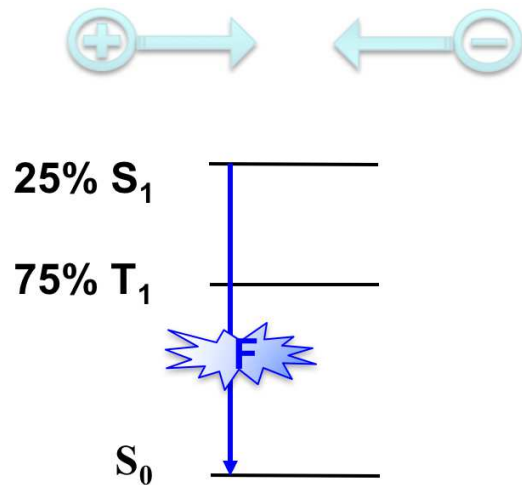
Practical Evaluation
of SOMEs

Spin–Orbit Coupling in Molecules

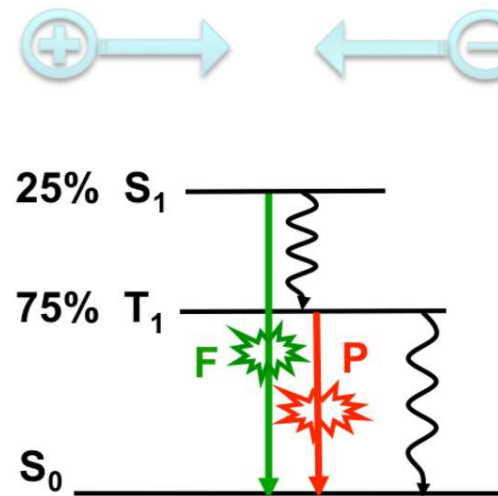
Triplet Harvesting in Organic Light-Emitting Diodes (OLEDs)

- Photoluminescence: Initial population (100%) in an excited singlet state.
- Electroluminescence: Recombination of electron and hole creates statistically 25% singlet and 75% triplet population.

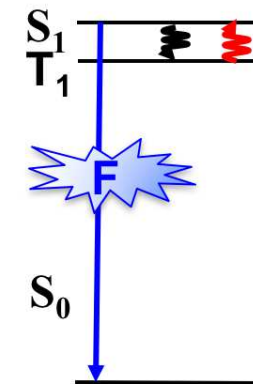
Fluorescent OLED emitter



Phosphorescent OLED emitter



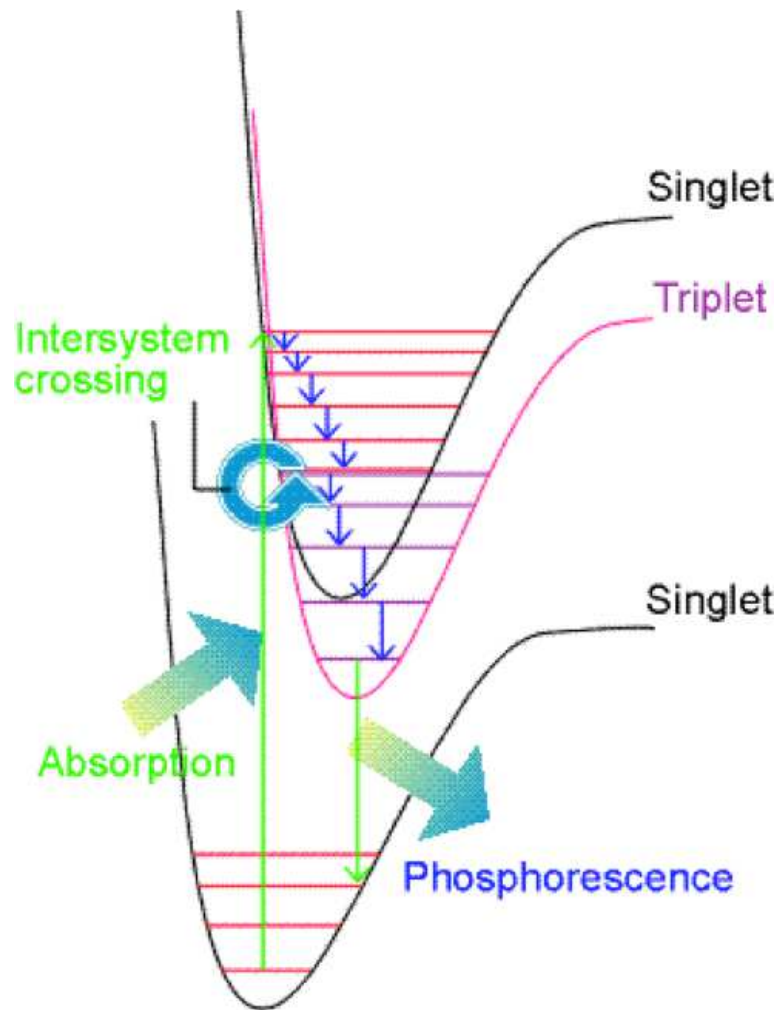
OLED emitter using TADF



- To reach internal quantum yields of 100% in OLEDs it is necessary to harvest the triplet population for emission. \Rightarrow Spin-forbidden processes are essential.

Spin-Forbidden Processes in Molecules

- Many excited-state processes involve a change in (electron) spin state.



- The most important ones are
 - Intersystem crossing (ISC)
 - Phosphorescence (P)
- Change of spin state requires
 - Spin-orbit coupling (SOC)
 - Spin-spin coupling (SSC)
- Typically, SOC by far exceeds SSC.
⇒ **Focus on SOC.**
⇒ Unlike SOC, SSC may couple singlets and triplets with equal spatial configuration.

Spin–Orbit Coupling
in Molecules

Spin–Orbit
Coupling

▷ Hamiltonians

Semiclassical
Picture of SOC

SOC Hamiltonians

Breit–Pauli
Mean–Field
Operators

AMFI
 Z^{eff}

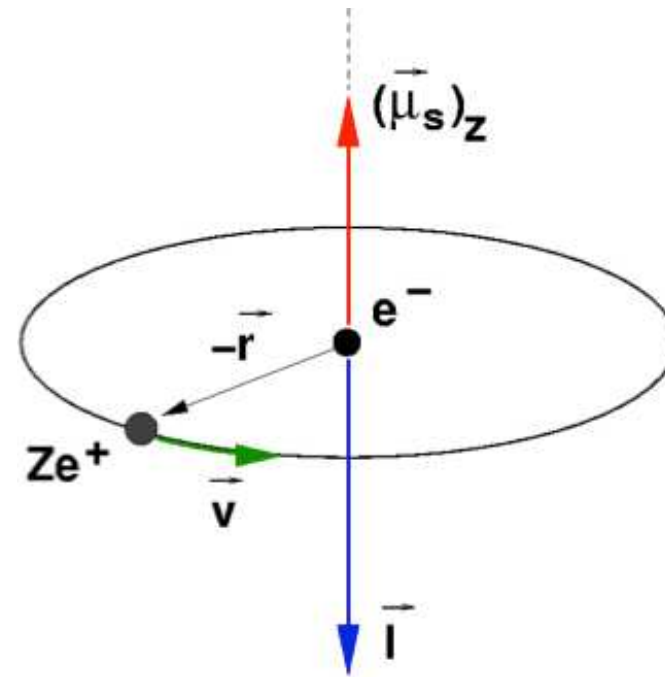
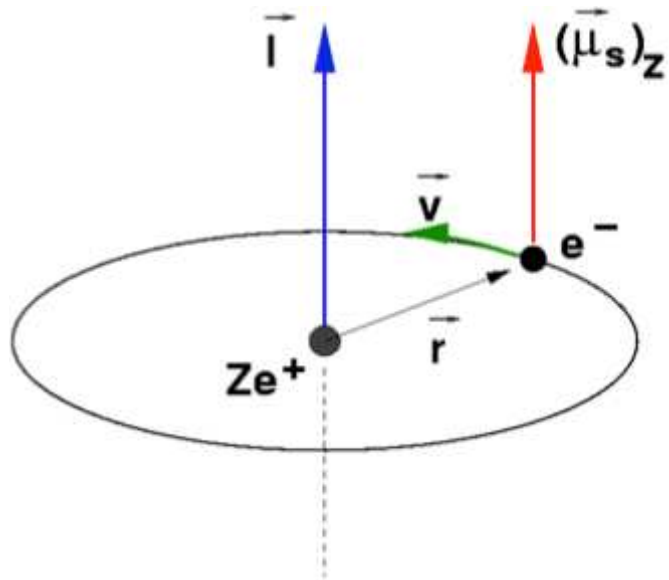
SO ECP

Symmetry
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Spin–Orbit Coupling Hamiltonians

Semiclassical Picture of Spin–Orbit Coupling



The motion of the electron relative to the nucleus (left) corresponds to a motion of the nucleus relative to the electron (right)

Semiclassical spin–orbit interaction energy:

$$\Delta E_{ls} \approx \frac{\mu_0 Z e^2}{8\pi m_e^2 r^3} (\vec{\ell} \cdot \vec{s}) \quad (53)$$

Microscopic Spin–Orbit Coupling Hamiltonians

- General form of the spin–orbit coupling term in the Schrödinger equation

$$\hat{\mathcal{H}}_{\text{SO}} = -\frac{e\hbar}{2m_e^2 c^2} \left(\vec{\nabla}\phi \times \vec{p} \right) \cdot \vec{s} \quad (54)$$

where ϕ is the electrostatic potential.

- In the absence of external fields (non-relativistic regime): ϕ consists of
 - Electron-nuclear Coulomb attraction (one-electron) terms
 - Electron-electron Coulomb repulsion (two-electron) terms
- Consider, e.g., the interaction of a nucleus and an electron at distance r . Then

$$\phi = \frac{Ze}{r} \quad \text{and thus} \quad \vec{\nabla}\phi = \frac{d\phi}{dr} \frac{\vec{r}}{r} = -\frac{Ze}{r^2} \frac{\vec{r}}{r} = -\frac{Ze}{r^3} \vec{r} \quad (55)$$

and therefore

$$\vec{\nabla}\phi \times \vec{p} = -\frac{Ze}{r^3} (\vec{r} \times \vec{p}) = -\frac{Ze\hbar}{r^3} \vec{\ell} \quad (56)$$

Breit-Pauli Spin–Orbit Coupling Hamiltonian

- Complete one- and two-electron Breit-Pauli spin-orbit Hamiltonian

$$\hat{\mathcal{H}}_{\text{SO}}^{\text{BP}} = \frac{e^2 \hbar}{2m_e^2 c^2} \left\{ \sum_i \left(\vec{\nabla}_i \left(\sum_I \frac{-Z_I}{r_{iI}} \right) \times \vec{p}_i \right) \cdot \vec{s}_i \right. \quad (57)$$

$$+ \sum_i \sum_{j \neq i} \left(\vec{\nabla}_i \left(\frac{1}{r_{ij}} \right) \times \vec{p}_i \right) \cdot \vec{s}_i \quad (58)$$

$$+ \sum_i \sum_{j \neq i} \left(\vec{\nabla}_j \left(\frac{1}{r_{ij}} \right) \times \vec{p}_j \right) \cdot \vec{s}_i \quad (59)$$

$$+ \left. \sum_j \sum_{i \neq j} \left(\vec{\nabla}_i \left(\frac{1}{r_{ji}} \right) \times \vec{p}_i \right) \cdot \vec{s}_j \right\} \quad (60)$$

- SOC Hamiltonian is symmetric in particle indices: one-electron term (57), two-electron terms: spin-same-orbit (58), spin-other-orbit (59)-(60)

Breit-Pauli Spin–Orbit Coupling Hamiltonian

- Short form where spin-same– and spin-other–orbit parts of the two-electron Hamiltonian have been contracted to a single term

$$\hat{\mathcal{H}}_{\text{SO}}^{\text{BP}} = \frac{e^2 \hbar}{2m_e^2 c^2} \left\{ \sum_i \sum_I Z_I \left(\frac{\vec{r}_{iI}}{r_{iI}^3} \times \vec{p}_i \right) \cdot \vec{s}_i - \sum_{i \neq j} \left(\frac{\vec{r}_{ij}}{r_{ij}^3} \times \vec{p}_i \right) \cdot (\vec{s}_i + 2\vec{s}_j) \right\} \quad (61)$$

- In heavy-element compounds, the one-electron SOC term is dominant. The two-electron terms screen the one-electron contributions by about
 - 5% in Pb
 - 10% in Pt
 - 50% in O
 - >100% in He
- Two-electron SOC contributions cannot be neglected in molecular calculations, but they can in good approximation be treated in a mean-field manner.

Mean-Field Spin–Orbit Coupling Operators

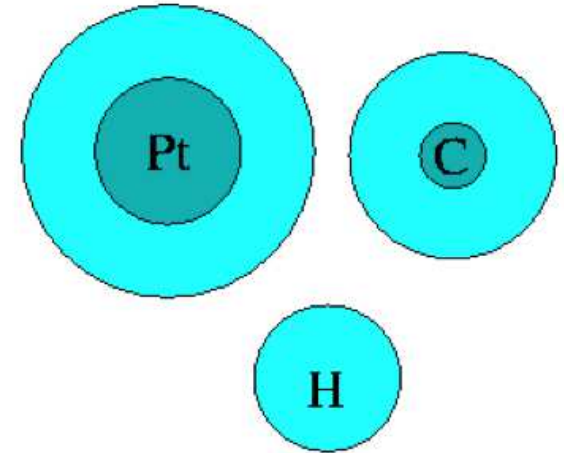
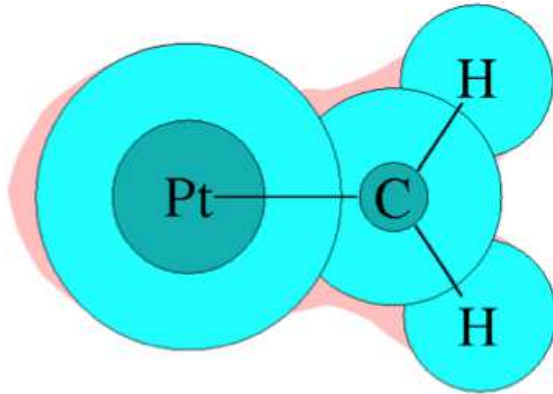
- Matrix element (ME) of the effective one-electron SOMF Hamiltonian:

$$\begin{aligned} \langle i(1) | \hat{\mathcal{H}}_{\text{SO}}^{\text{mf}} | j(1) \rangle &= \langle i(1) | \hat{h}_{\text{SO}}(1) | j(1) \rangle \\ &+ \frac{1}{2} \sum_k n_k \left\{ 2 \langle i(1)k(2) | \hat{\mathcal{H}}_{\text{SO}}(1, 2) | j(1)k(2) \rangle \right. \\ &\quad - 3 \langle k(1)i(2) | \hat{\mathcal{H}}_{\text{SO}}(1, 2) | j(1)k(2) \rangle \\ &\quad \left. - 3 \langle i(1)k(2) | \hat{\mathcal{H}}_{\text{SO}}(1, 2) | k(1)j(2) \rangle \right\} \quad (62) \end{aligned}$$

Herein, k represents (partially filled) molecular orbitals (MOs) with occupation numbers n_k .

- Observations:
 - The largest screening terms stem from the inner shells.
 - Two-center one-electron terms and two-center two-electron contributions to the mean-field integrals cancel partially.

The Atomic Mean-Field Integral (AMFI) Approximation



- ⇒ Neglect all multi-center terms.
- Use atomic orbitals instead of molecular orbitals for k in Eq. (62).
 - Exploit atomic symmetry to speed up calculation of mean-field integrals.
- Errors introduced by the AMFI approximation
- amount up to about 10% for light-element compounds,
 - are considerably smaller for heavy-element compounds.

Spin–Orbit Operators with Effective Nuclear Charges

- In this SOC Hamiltonian, the two-electron contributions are approximated by screening the nuclear potential.

$$\hat{\mathcal{H}}_{\text{SO}}^{\text{eff}} = \frac{e^2 \hbar^2}{2m_e^2 c^2} \sum_I \sum_i \frac{Z_{I,\ell}^{\text{eff}}}{\hat{r}_{Ii}^3} \vec{\ell}_{Ii} \vec{\hat{s}}_i \quad (63)$$

Herein, i denotes an electron occupying an orbital at center I . The effective nuclear charge $Z_{I,\ell}^{\text{eff}}$ is fitted to experimental atomic spin–orbit splittings.

- This is a very crude approximation, not recommended for metal-free emitters: $Z_{I,\ell}^{\text{eff}}$ depends on the particular electronic state.
- Be careful when combining the operator in Eq. (63) with pseudopotentials: Z^{eff} may adopt very large values. Preferably, use spin–orbit pseudopotentials in these cases.

Spin–Orbit Operators for Effective Core Potentials

- In most spin–orbit pseudopotentials the original $1/r^3$ -dependence has been dropped and the action of the SOC operator has been relocated to the valence region.

- Spin–orbit pseudopotentials may be written as

$$\hat{\mathcal{H}}_{\text{SO}}^{\text{REP}}(r) = \sum_{\ell=1}^{\ell_{\text{max}}} \frac{2\Delta V_{\ell}^{\text{REP}}(r)}{2\ell + 1} \vec{\ell} \cdot \vec{s} \sum_{m_{\ell}=-\ell}^{+\ell} |\ell, m_{\ell}\rangle \langle \ell, m_{\ell}| \quad (64)$$

- $\Delta V_{\ell}^{\text{REP}}(r)$ is represented by a linear combination of a few Gaussian functions.
- The parameters are adjusted to fit energies or orbital shapes from two-component or four-component relativistic atomic calculations.
- Different groups use slightly different ℓ dependence of $\hat{\mathcal{H}}_{\text{SO}}^{\text{REP}}$.
(For further details see, e.g., C. Teichteil *et al.* in: P. Schwerdtfeger (Ed.), *Relativistic Electron Structure Theory, Part 2*, pp. 476.)

Spin–Orbit Coupling
in Molecules

Spin–Orbit Coupling
Hamiltonians

Symmetry
▷ Considerations

Simplified Operator

How to?

C_{2v}

Practical Evaluation
of SOMEs

Symmetry Considerations

Phenomenological Spin–Orbit Coupling Operator

- In spite of their different shapes, all SOC Hamiltonians described in the previous section obey the same symmetry selection rules.
- For symmetry considerations, it is useful to define a **phenomenological SOC operator**

$$\hat{\mathcal{H}}_{\text{SO}} = A_{\text{SO}}(r) \vec{\hat{\mathcal{L}}} \cdot \vec{\hat{\mathcal{S}}} \quad (65)$$

- The scalar product of the (axial) vectors $\vec{\hat{\mathcal{L}}}$ and $\vec{\hat{\mathcal{S}}}$ is commonly written in tensorial or Cartesian form

$$\vec{\hat{\mathcal{L}}} \cdot \vec{\hat{\mathcal{S}}} = \hat{\mathcal{L}}_0 \hat{\mathcal{S}}_0 - \hat{\mathcal{L}}_{+1} \hat{\mathcal{S}}_{-1} - \hat{\mathcal{L}}_{-1} \hat{\mathcal{S}}_{+1} \quad (66)$$

$$= \hat{\mathcal{L}}_x \hat{\mathcal{S}}_x + \hat{\mathcal{L}}_y \hat{\mathcal{S}}_y + \hat{\mathcal{L}}_z \hat{\mathcal{S}}_z \quad (67)$$

- The operator (65) can also be utilized for setting up a connection between theoretically and experimentally determined fine-structure splittings via the so-called spin-orbit parameter A_{SO} .
- However, **the operator (65) ought not to be used for computing SOMEs!**

How to Exploit Symmetry?

- Spin–orbit coupling Hamiltonians are **scalar** operators.
- In any molecular point group, they transform like the **totally symmetric** irreducible representation (irrep).
- Magnetic interaction Hamiltonians are **compound tensor operators**. \Rightarrow More specific selection rules (nonrelativistic regime).
- Angular momentum operators are purely imaginary. $\Rightarrow \vec{\hat{\mathcal{L}}}$ **does not have diagonal elements for spatially nondegenerate wavefunctions**.
- For a matrix element (ME) to be different from zero, the **direct products** of the irreps of **space and spin functions** on both sides of the ME must be equal.
- How do **spin functions** transform under the symmetry operations of a **molecular point group**?
- Luckily, TADF molecules have even numbers of electrons:
 \Rightarrow No need for **double groups**

Example: Transformation of Spin Functions and Operators in C_{2v}

C_{2v}	\hat{E}	$\hat{C}_2(z)$	$\hat{\sigma}_{xz}$	$\hat{\sigma}_{yz}$		
A ₁	1	1	1	1	z	S
A ₂	1	1	-1	-1		$\hat{\mathcal{R}}_z, \hat{\mathcal{L}}_z, \hat{\mathcal{S}}_z$ T _z
B ₁	1	-1	1	-1	x	$\hat{\mathcal{R}}_y, \hat{\mathcal{L}}_y, \hat{\mathcal{S}}_y$ T _y
B ₂	1	-1	-1	1	y	$\hat{\mathcal{R}}_x, \hat{\mathcal{L}}_x, \hat{\mathcal{S}}_x$ T _x

where the singlet and symmetry-adapted triplet spin functions are given by

$$S = \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha) \quad (68)$$

$$T_x = \frac{1}{\sqrt{2}}(\beta\beta - \alpha\alpha), \quad T_y = \frac{i}{\sqrt{2}}(\alpha\alpha + \beta\beta) \quad T_z = \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$$

- Singlet spin functions are totally symmetric. (Any point group)
- Triplet spin components transform like rotation operators. (Any point group)
- Note that electronic states with spatial wavefunctions in the same irrep do not directly interact via SOC in molecules with C_{2v} or higher symmetry.

First- and Second-Order Magnetic Interactions

- If a singlet excited state S_1 exhibits exactly the same configuration expansion (apart from spin) as a triplet state T_1 , then

$$\langle S_1 | \hat{\mathcal{H}}_{\text{SO}} | T_1 \rangle = 0. \quad (69)$$

- In case of vanishing first-order SOC, magnetic interaction can arise from
 - vibronic spin-orbit coupling with a near-by state (see next lecture)

$$\langle S_1 | \hat{\mathcal{H}}_{\text{SO}} | T_n \rangle \left\langle T_n \left| \frac{\partial}{\partial Q} \right| T_1 \right\rangle \quad \text{or} \quad \left\langle S_1 \left| \frac{\partial}{\partial Q} \right| S_m \right\rangle \langle S_m | \hat{\mathcal{H}}_{\text{SO}} | T_1 \rangle \quad (70)$$

- higher-order SOC via an intermediate electronic state

$$\propto \langle S_1 | \hat{\mathcal{H}}_{\text{SO}} | T_n \rangle \langle T_n | \hat{\mathcal{H}}_{\text{SO}} | T_1 \rangle \quad (71)$$

- electronic spin-spin coupling, hyperfine interaction, ...
- external electromagnetic fields

Spin–Orbit Coupling
in Molecules

Spin–Orbit Coupling
Hamiltonians

Symmetry
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Practical
Evaluation of
▷ SOMEs

SOMEs from MEWs
Performance

Practical Evaluation of SOMEs

SOMEs from Multielectron Wavefunctions (MEWs)

- MEWs are linear combinations of configurations in a given orbital basis.

$$\langle \Psi_A | = c_0^* \langle \Psi_0 | + \sum_a^{\text{occ}} \sum_r^{\text{virt}} c_a^{r*} \langle \Psi_a^r | + \sum_a^{\text{occ}} \sum_b^{\text{occ}} \sum_r^{\text{virt}} \sum_s^{\text{virt}} c_{ab}^{rs*} \langle \Psi_{ab}^{rs} | + \dots \quad (72)$$

$$|\Psi_B\rangle = d_0 |\Psi_0\rangle + \sum_e^{\text{occ}} \sum_t^{\text{virt}} d_e^t |\Psi_e^t\rangle + \sum_e^{\text{occ}} \sum_f^{\text{occ}} \sum_t^{\text{virt}} \sum_u^{\text{virt}} d_{ef}^{tu} |\Psi_{ef}^{tu}\rangle + \dots \quad (73)$$

- Herein, Ψ_0 symbolizes a reference wavefunction, typically (but not necessarily) a closed-shell Hartree-Fock (HF) determinant.

$$\Psi_0 = |\Phi_a(\vec{x}_1)\Phi_b(\vec{x}_2)\Phi_c(\vec{x}_3)\Phi_d(\vec{x}_4)\dots| \quad (74)$$

- Ψ_a^r stands for a single excitation in which the orbital Φ_a that is occupied in Ψ_0 has been replaced by the previously unoccupied virtual orbital Φ_r

$$\Psi_a^r = |\Phi_r(\vec{x}_1)\Phi_b(\vec{x}_2)\Phi_c(\vec{x}_3)\Phi_d(\vec{x}_4)\dots| \quad (75)$$

- ...

SOMEs from Multielectron Wavefunctions (MEWs)

- Evaluation of SOMEs from such MEWs is straight forward if the employed MO basis is identical.

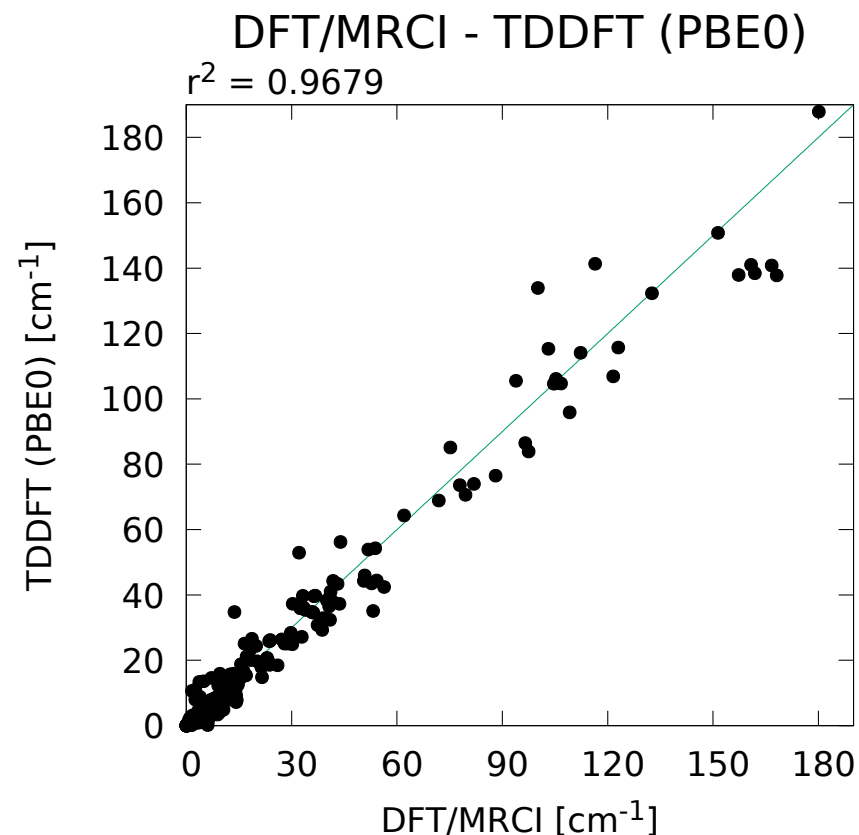
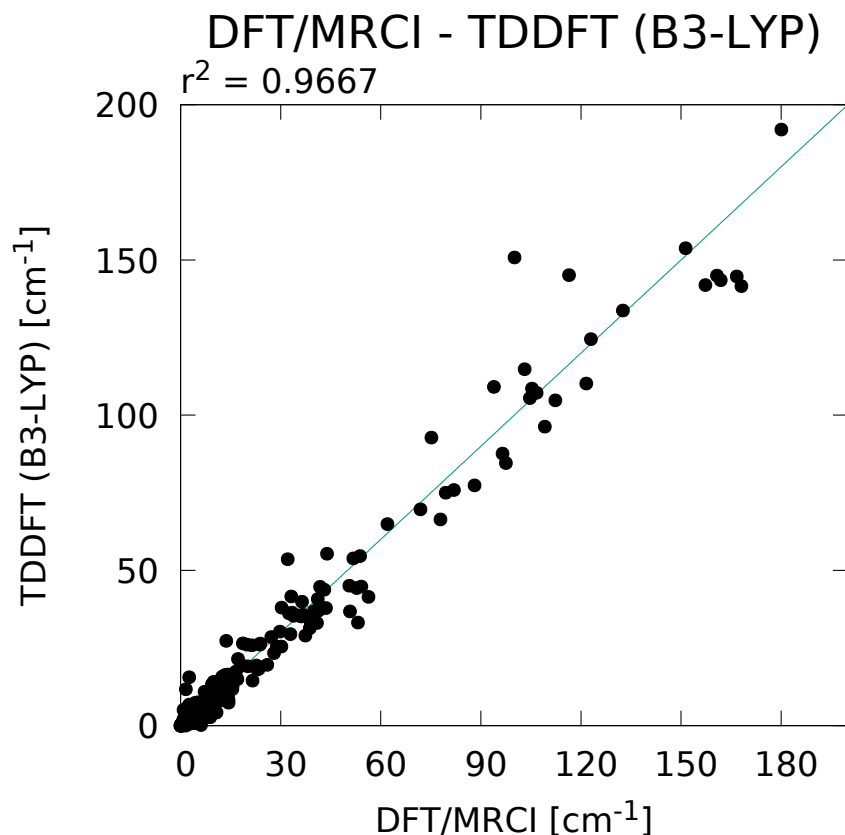
$$\begin{aligned} \langle \Psi_A | \hat{\mathcal{H}}_{\text{SO}} | \Psi_B \rangle &= \sum_e^{\text{occ}} \sum_t^{\text{virt}} c_0^* d_e^t \langle \Psi_0 | \hat{\mathcal{H}}_{\text{SO}} | \Psi_e^t \rangle + \sum_a^{\text{occ}} \sum_r^{\text{virt}} c_a^{r*} d_0 \langle \Psi_a^r | \hat{\mathcal{H}}_{\text{SO}} | \Psi_0 \rangle \\ &+ \sum_a^{\text{occ}} \sum_e^{\text{occ}} \sum_r^{\text{virt}} \sum_t^{\text{virt}} c_a^{r*} d_e^t \langle \Psi_a^r | \hat{\mathcal{H}}_{\text{SO}} | \Psi_e^t \rangle + \dots \end{aligned} \quad (76)$$

- In this sum, MEs between configurations
 - with equal spatial occupation (diagonal terms) vanish,
 - which are singly excited w.r.t. each other may contribute in principle,
 - which are doubly excited w.r.t. each other vanish unless full two-electron SOC Hamiltonian is employed.
- Correlated MEWs of this type are, for example,
 - configuration interaction (CIS, CISD, MRCI, DFT/MRCI ...) MEWs,
 - variational perturbation theory solutions (renormalized MR-MP2).

SOMEs from Multielectron Wavefunctions (MEWs)

- Evaluation of SOMEs from CASSCF or RASSCF MEWs requires orbital transformations, which are easily achieved if the subdivision into
 - inactive
 - active
 - externalorbital spaces is identical for $\langle \Psi_A |$ and $|\Psi_B \rangle$.
- Coupled-cluster expansions have different right and left eigenvectors and require special formulae for the evaluation of SOMEs.
(See, e.g., E. Epifanovsky et al., *J. Chem. Phys.* 143 (2015) 064102.)
- Similar considerations apply to propagator methods such as the algebraic-diagrammatic construction schemes (ADC2 ...).
(See, e.g., C. M. Krauter et al., *Chem. Phys.* 482 (2017) 286.)
- This is even true for TDDFT amplitudes. Approximate MEWs (AMEWs) may be constructed and used for the calculation of interstate SOMEs.
(See, e.g., F. Dinkelbach et al., *J. Chem. Theory Comput.* 13 (2017) 749.)

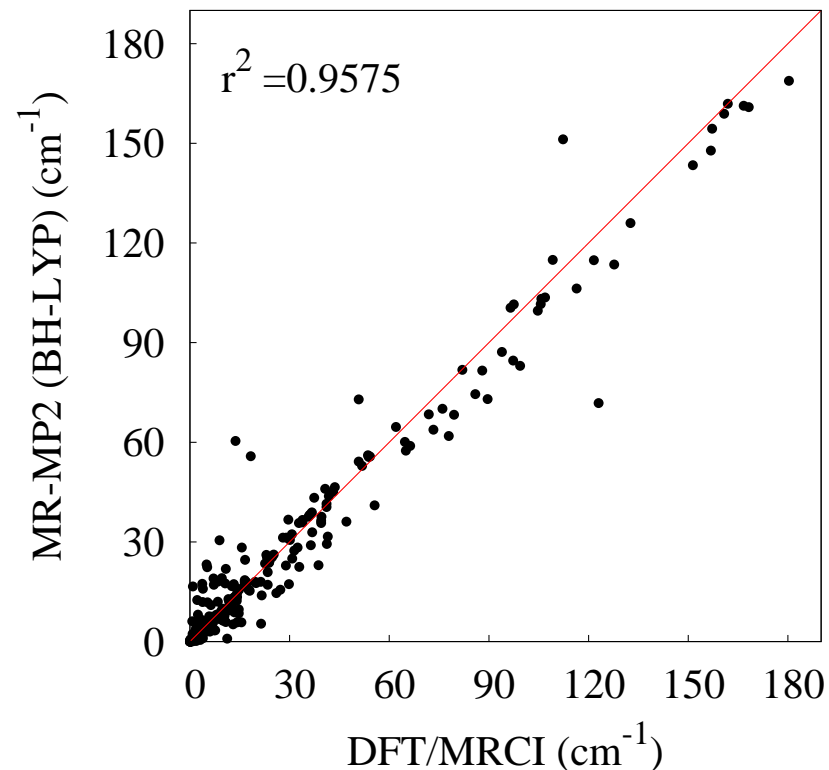
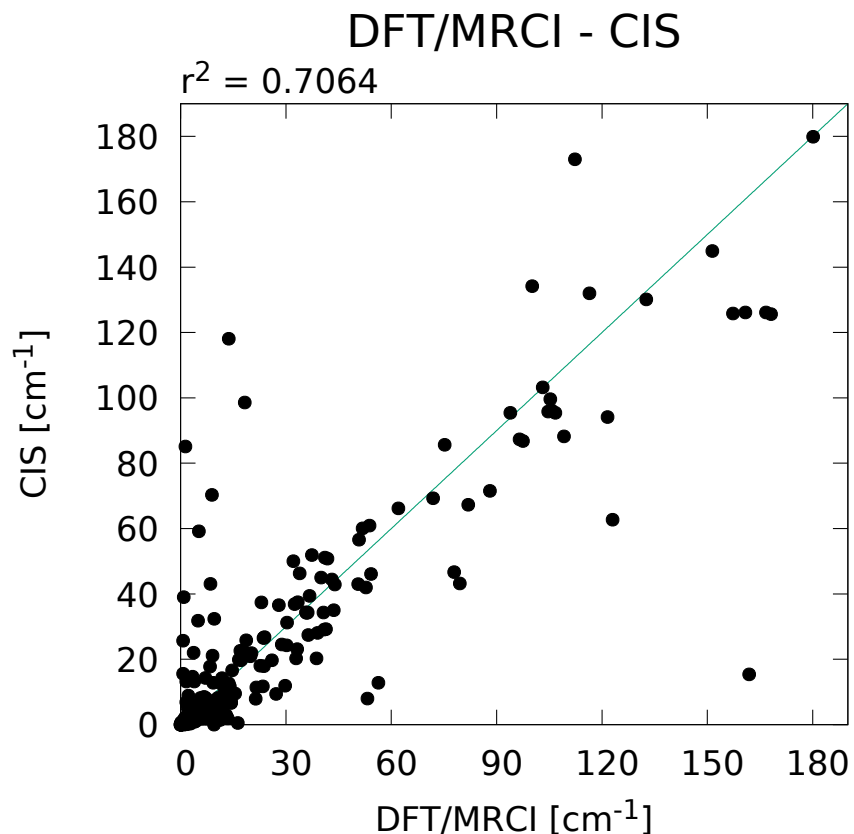
Performance of TDDFT AMEWs for SOMEs



Correlation of SOMEs obtained from DFT/MRCI MEWs and TDDFT AMEWs employing the B3-LYP (left) and PBE0 (right) functionals for a set of valence and Rydberg states of polyatomic organic molecules. CT states are not contained in the test set.

(F. Dinkelbach et al., *J. Chem. Theory Comput.* 13 (2017) 749.)

Performance of CIS and MR-MP2 MEWs for SOMEs



Correlation of SOMEs obtained from DFT/MRCI MEWs and CIS (left) and renormalized first-order MR-MP2 wavefunctions (right) for a set of valence and Rydberg states of polyatomic organic molecules. CT states are not contained in the test set.

(V. Jovanović et al., *Mol. Phys.* 115 (2017) 109.)

Performance of Excited-State Methods for SOMEs

- SOMEs for DFT/MRCI wavefunctions show very good agreement with *ab initio* CASSCF/MRCI results for small molecules.
- For larger molecules, *ab initio* CASSCF/MRCI is practically not feasible.
- We observe good correlation of SOMEs for linear response TDDFT AMEWs of B3-LYP as well as PBE0 functionals with DFT/MRCI results.
- Comparison of SOMEs from TDDFT with or without Tamm-Dancoff approximation (TDA) yields similar correlation coefficients. (Not shown here).
- The SOMEs are less sensitive to the choice of functional than the TDDFT or TDDFT-TDA excitation energies.
- Although CIS MEWs exhibit correct long-range behavior, their (energies and) SOMEs show huge deviations and are practically useless.
- Truncated and renormalized MR-MP2 (and possibly ADC2) expansions may be good alternatives for CT states.