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Calculation of
Intersystem
Crossing and
Reverse
Intersystem
Crossing Rate
▷ Constants

Qualitative Rules

Static Approach:
Fermi's Golden Rule

Calculation of Intersystem Crossing and Reverse Intersystem Crossing Rate Constants

Calculation of
Intersystem Crossing
and Reverse
Intersystem Crossing
Rate Constants

▷ Qualitative Rules

El-Sayed Rule

Energy gap law

Summary

Static Approach:
Fermi's Golden Rule

Qualitative Rules

Qualitative Rules

- **Electronic coupling strength**
- **El-Sayed Rule:**
The rate of ISC is relatively large if the radiationless transition involves a change of orbital type.
- Application to locally excited (LE) states of organic chromophores with singlet ground state (GS)

ISC is expected to be fast for

- $1,3(\pi\pi^*) \rightsquigarrow 3,1(n\pi^*)$
- $1,3(n\pi^*) \rightsquigarrow 3,1(\pi\pi^*)$
- $3(n\pi^*) \rightsquigarrow \text{GS}$
- $1,3(\pi\sigma^*) \rightsquigarrow 3,1(\pi\pi^*)$

ISC is expected to be slow for

- $1,3(\pi\pi^*) \rightsquigarrow 3,1(\pi\pi^*)$
- $3(\pi\pi^*) \rightsquigarrow \text{GS}$
- $1,3(n\pi^*) \rightsquigarrow 3,1(n\pi^*)$
- $1,3(\pi\sigma^*) \rightsquigarrow 3,1(\pi\sigma^*)$

- Can these rules be understood?
- What can we say about charge transfer (CT) states?

Qualitative Rules

- To derive qualitative rules, it is sufficient to consider two-particle wavefunctions and the one-electron terms of $\hat{\mathcal{H}}_{\text{SO}}$.

$$\hat{\mathcal{H}}_{\text{SO}} \propto \sum_I \frac{Z_I}{r_{1I}^3} \vec{\ell}(1) \vec{s}(1) + \sum_I \frac{Z_I}{r_{2I}^3} \vec{\ell}(2) \vec{s}(2) \quad (77)$$

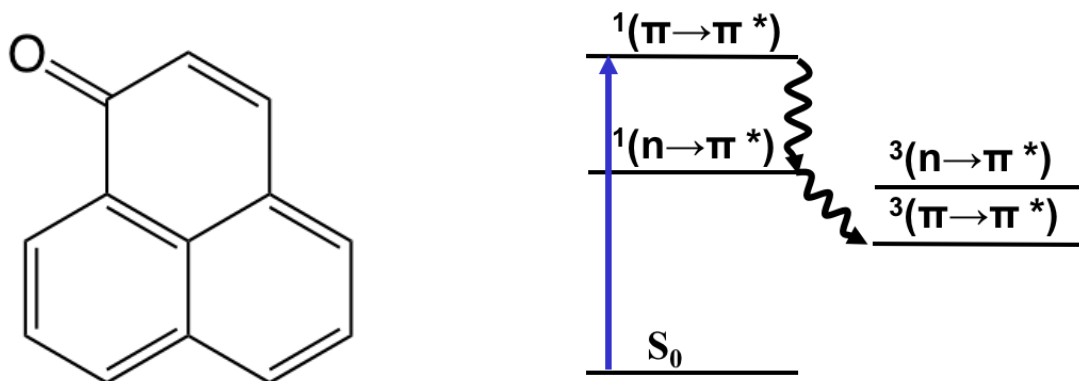
where, e.g.,

$$\vec{\ell}(1) \vec{s}(1) = \hat{\ell}_x(1) \hat{s}_x(1) + \hat{\ell}_y(1) \hat{s}_y(1) + \hat{\ell}_z(1) \hat{s}_z(1) \quad (78)$$

- Note that
 1. The inherent angular momentum operators are purely imaginary and thus do not have diagonal matrix elements (MEs) in a basis of real functions.
 2. Due to its r^{-3} dependence, the SOC operator is fairly local, i.e., the largest contributions stem from single excitations on the same center.
- For both reasons, $\langle {}^1\text{CT} | \hat{\mathcal{H}}_{\text{SO}} | {}^3\text{CT} \rangle \approx 0$, if the two CT states originate from the same orbital transition.

Qualitative Rules

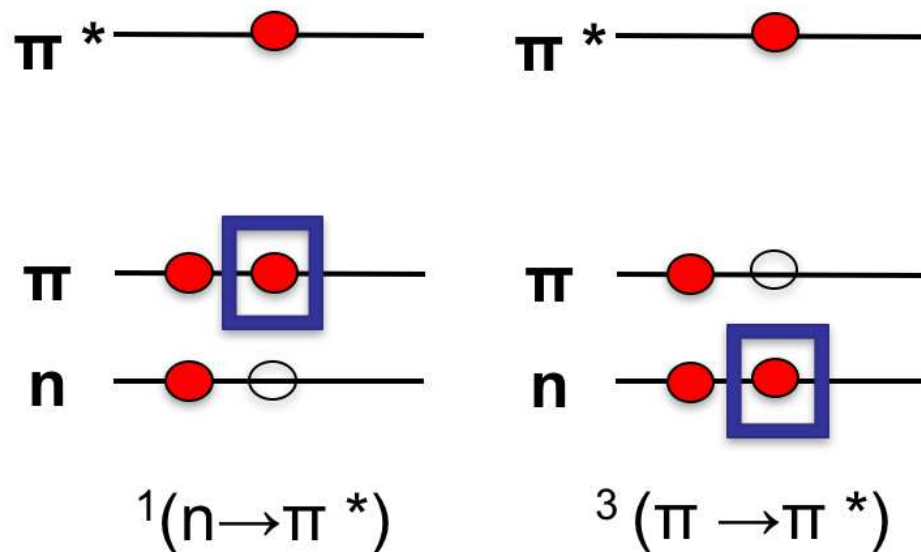
- Consider an organic molecule (here phenalenone) lying in the yz plane.



- Absorption of light takes the molecule to the $^1(\pi\pi^*)$ state from which it rapidly decays via internal conversion (IC) to the $^1(n\pi^*)$ state.
- Energetically close-by is the $^3(n\pi^*)$ state. The lowest excited triplet state is the $^3(\pi\pi^*)$ state.
- There is no change of orbital type upon the $^1(n\pi^*) \rightsquigarrow ^3(n\pi^*)$ transition. El-Sayed rules predict this ISC to be slow.
- The spatial wavefunctions of $^1(n\pi^*)$ and $^3(n\pi^*)$ are (nearly) identical and real-valued. Because $\vec{\ell}$ does not have diagonal MEs, their SOME is close to zero. ✓

Qualitative Rules

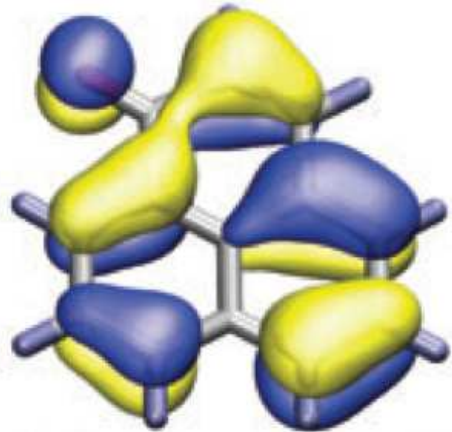
- Now look at $^1(n\pi^*) \rightsquigarrow ^3(\pi\pi^*)$.
- There is a change of orbital type upon this transition. El-Sayed rules predict ISC to proceed fast in this case.
- The $^1(n\pi^*)$ and $^3(\pi\pi^*)$ states are singly excited with respect to each other.



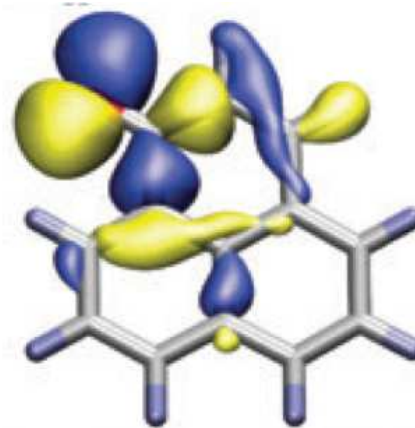
- To evaluate the spatial part of the SOME, consider $\langle \pi(1)\pi^*(2) | \vec{\ell}(1) | n(1)\pi^*(2) \rangle = \langle \pi(1) | \vec{\ell}(1) | n(1) \rangle$.

Qualitative Rules

- The π and n orbitals both exhibit electron density at the oxygen center.



π

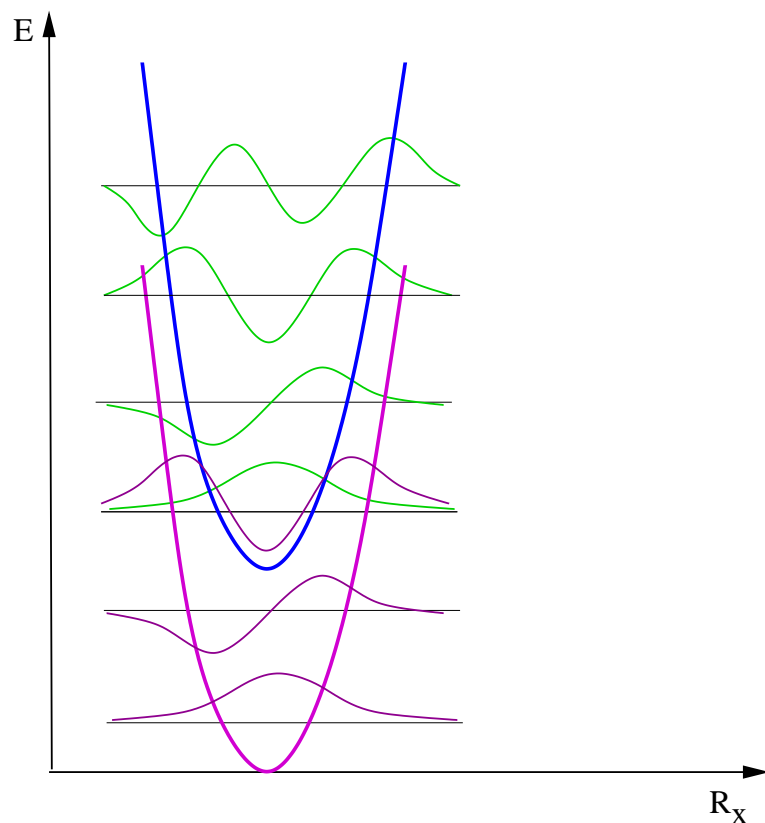


n

- The $\hat{\ell}_z$ operator couples the out-of-plane p_x orbital at oxygen with the in-plane p_y (n) orbital at the same center, i.e., $\langle \pi(1) | \hat{\ell}_z(1) | n(1) \rangle \neq 0$.
- The $\hat{\ell}_z$ component of $\vec{\hat{\ell}}$ has to be combined with \hat{s}_z .
- \hat{s}_z changes the sign of a β spin function, thus transforming the $M_s = 0$ component of a triplet into a singlet and vice versa, i.e., $\langle \alpha(1)\beta(2) - \beta(1)\alpha(2) | \hat{s}_z(1) | \alpha(1)\beta(2) + \beta(1)\alpha(2) \rangle \neq 0$
- The SOME is sizeable. ✓

Qualitative Rules

- **Vibrational contributions**
- Two limiting cases
 - In the **weak coupling limit**, the coordinate displacement for each normal mode is assumed to be relatively small (nested states).



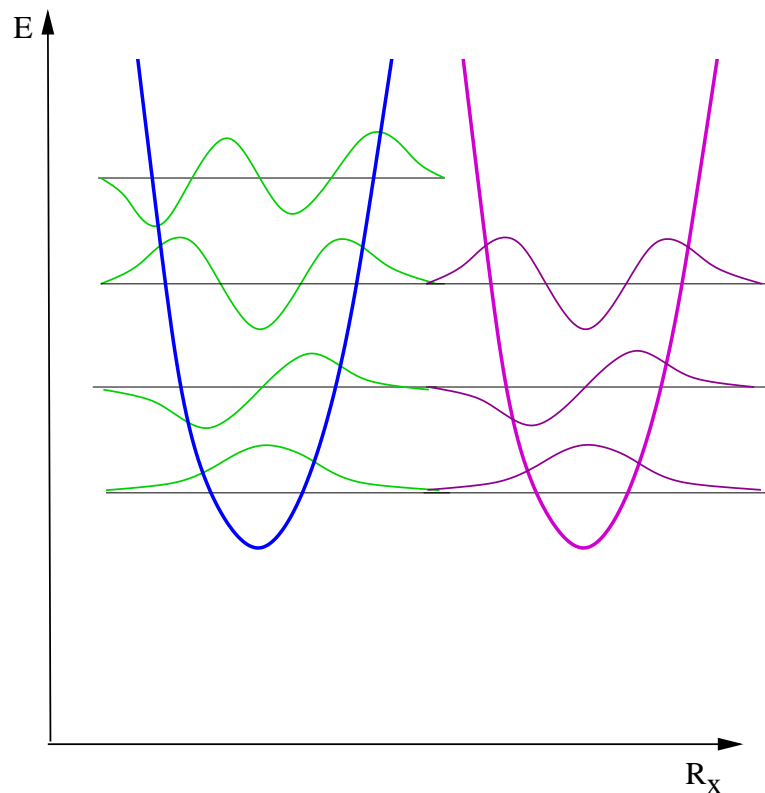
The probability for a radiationless transition decreases **exponentially** with increasing adiabatic energy difference ΔE , i.e., the smaller the energy gap the larger the transition probability.

This exponential dependence of the transition probability on ΔE is usually dubbed the **Energy Gap Law**.

Qualitative Rules

- But beware!

This energy gap law applies only to nested states!

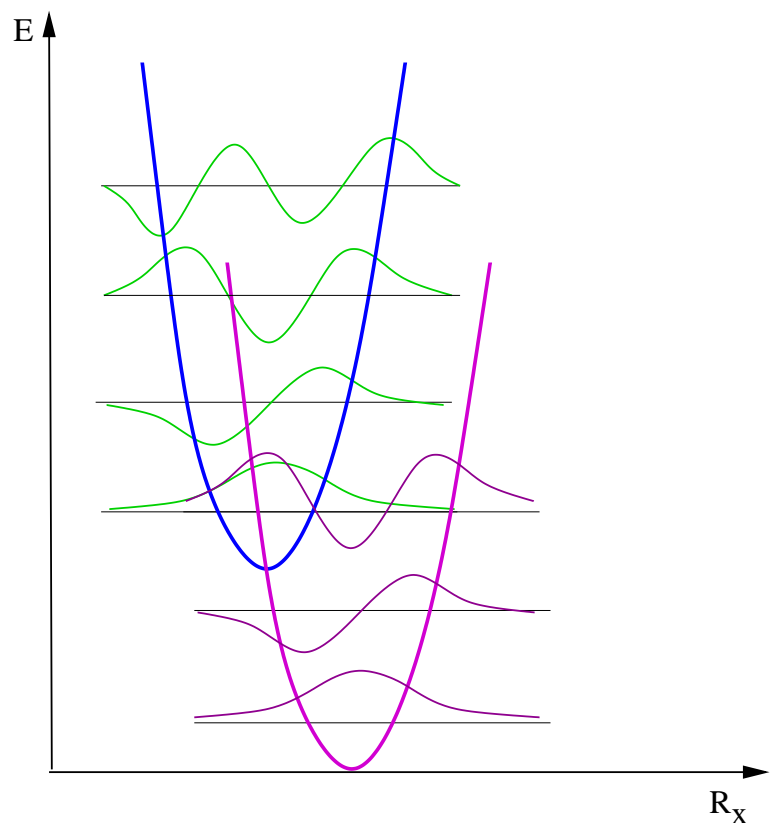


In particular, it does not apply to potentials with nearly degenerate adiabatic excitation energies but large relative displacements in some coordinates.

Due to the small overlap of the vibrational wavefunctions, the transition probability is typically very small in this case.

Qualitative Rules

- The **strong coupling limit** is characterized by large relative displacements in some coordinates so that an intersection of the potential energy surfaces can be expected.



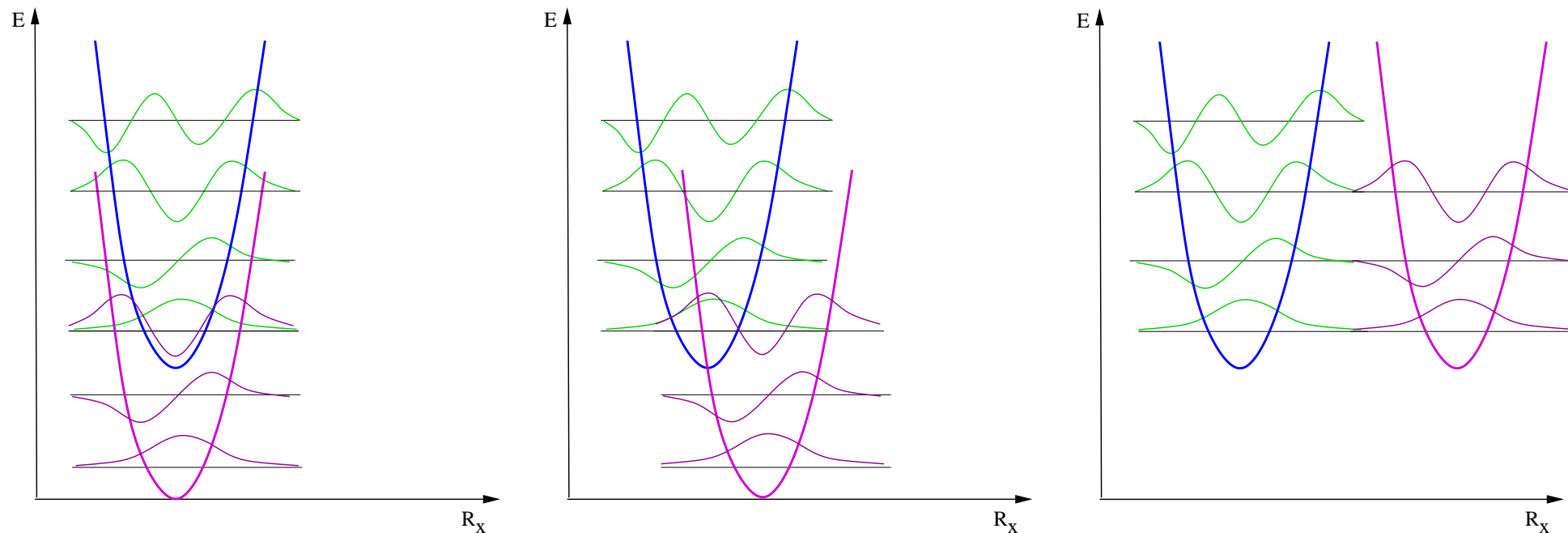
The probability of the radiationless transition exhibits a **Gaussian** dependence on the energy parameter $\Delta E - E_M$, where E_M is the molecular rearrangement energy for the two electronic states under consideration.

Occasionally an inverse relationship between the transition probability and ΔE is observed, i.e., there exist cases where the probability increases with increasing energy gap.

General Considerations and Size of ISC Rate Constants

- The ISC rate constant depends on the size of the
 - **electronic SOC** *and*
 - **vibrational overlap** *and* on the
 - **density of accepting states**

- Excited-state ISC rate constants in heteronuclear organic molecules
 - Fast $10^{11} - 10^{12} \text{ s}^{-1}$
 - Typical $10^8 - 10^9 \text{ s}^{-1}$
 - Slow $10^5 - 10^6 \text{ s}^{-1}$



- Ultrafast transitions: \Rightarrow Nonadiabatic wavepacket dynamics
- Fast - slow transitions: \Rightarrow Static approach, Fermi's Golden Rule

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Static Approach:
Fermi's Golden
▷ Rule

Golden Rule

Example

Condon

Approximation

Energy Domain

Time Domain

Temperature

Example

Vibronic Effects

Example

Summary

Literature

Static Approach: Fermi's Golden Rule

The Fermi Golden Rule Approximation

- Within the **Fermi golden rule approximation**, the rate k for the irreversible decay of an initial state $|i\rangle$, coupled by a perturbation $\hat{\mathcal{H}}^{(1)}$ to a set of final states $\langle f|$, is given by

$$k = \frac{2\pi}{\hbar} \sum_f |\hat{\mathcal{H}}_{if}^{(1)}|^2 \delta(E_i - E_f) \quad (79)$$

- The δ distribution ensures the conservation of the molecular energy for the nonradiative transition.
- Preconditions for the applicability of the golden rule approximation:
 - The interaction of the two states is small compared to their adiabatic energy difference.
 - The density of final vibrational states (VDOS) at the energy of the initial state is high.

Partitioning of the Molecular Hamiltonian

- There are several ways of partitioning the molecular Hamiltonian into a zeroth-order Hamiltonian $\hat{\mathcal{H}}^{(0)}$ and a perturbation $\hat{\mathcal{H}}^{(1)}$.
 1. $\hat{\mathcal{H}}_{\text{SO}}$ is included in the electronic Hamiltonian
⇒ Basis states are **spin-orbit coupled Born-Oppenheimer states**:
 $\hat{\mathcal{H}}^{(1)}$ is given by the nuclear kinetic energy operator $\hat{\mathcal{T}}_{\text{N}}$.
 2. $\hat{\mathcal{H}}_{\text{SO}}$ is not included in the electronic Hamiltonian
⇒ Basis states are **pure-spin Born-Oppenheimer states**:
 $\hat{\mathcal{H}}^{(1)}$ is given by the sum of $\hat{\mathcal{T}}_{\text{N}}$ and $\hat{\mathcal{H}}_{\text{SO}}$.
The action of $\hat{\mathcal{T}}_{\text{N}}$ on the wavefunction may lead to vibronic interaction terms that modulate the ISC process.
- Here, we concentrate on the latter approach.

ISC Rate Constants Pure-Spin BO states

- In a two-state process, nonadiabatic coupling matrix elements (NACMEs) between the initial and final electronic states of an ISC vanish because of their different multiplicities.
- Up to second order in Rayleigh-Schrödinger perturbation theory, the coupling between vibrational state v_{aj} of a singlet state Ψ_{S_a} and the fine-structure component α of a vibrational level v_{bk} of a triplet state Ψ_{T_b} is given by

$$\hat{\mathcal{H}}_{aj,bk}^{(1)\alpha} \approx \langle \Psi_{S_a}, v_{aj} | \hat{\mathcal{H}}_{\text{SO}} | \Psi_{T_b}^\alpha, v_{bk} \rangle \quad (80)$$

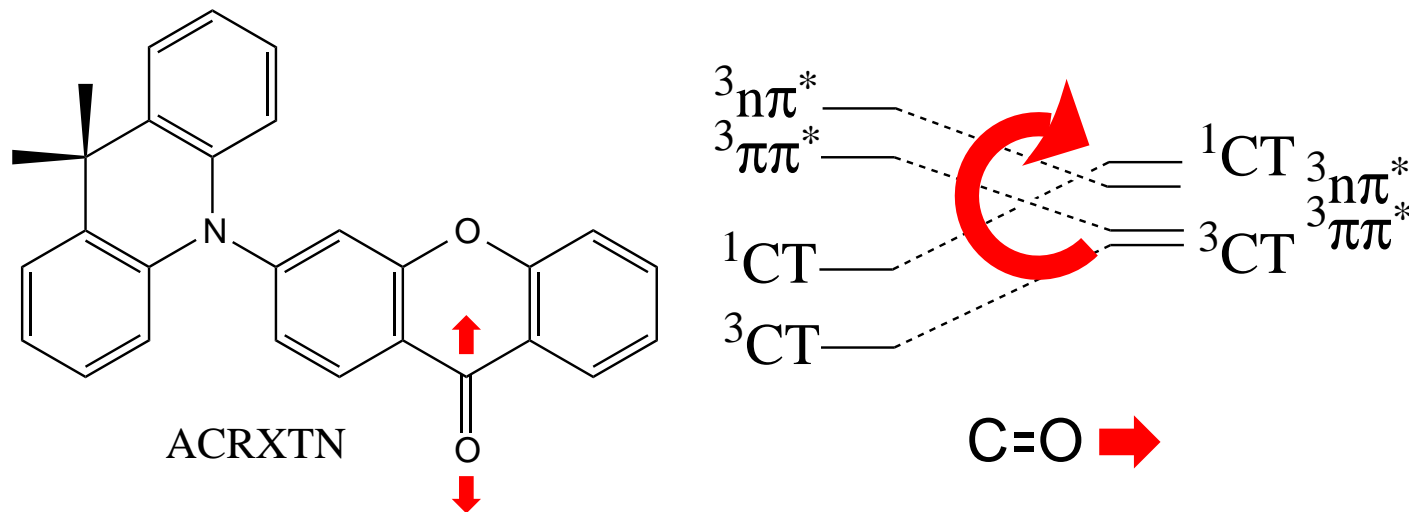
$$+ \sum_{d \neq b} \sum_m \frac{\langle \Psi_{S_a}, v_{aj} | \hat{\mathcal{H}}_{\text{SO}} | \Psi_{T_d}^\alpha, v_{dm} \rangle \langle \Psi_{T_d}^\alpha, v_{dm} | \hat{\mathcal{T}}_{\text{N}} | \Psi_{T_b}^\alpha, v_{bj} \rangle}{E_{dm} - E_{bk}} \quad (81)$$

$$+ \sum_{c \neq a} \sum_l \frac{\langle \Psi_{S_a}, v_{aj} | \hat{\mathcal{T}}_{\text{N}} | \Psi_{S_c}, v_{cl} \rangle \langle \Psi_{S_c}, v_{cl} | \hat{\mathcal{H}}_{\text{SO}} | \Psi_{T_b}^\alpha, v_{bk} \rangle}{E_{cl} - E_{bk}} \quad (82)$$

- The spin-vibronic interaction terms (81) and (82) are often neglected. They can become decisive in TADF emitters with close-lying CT and LE states!

Example: Spin-vibronic interaction in a TADF emitter

- ^1CT and ^3CT are nested states, 0.06 eV apart \Rightarrow weak coupling limit
- Direct SOC is tiny, $|\langle ^1\text{CT} | \hat{\mathcal{H}}_{\text{SO}} | ^3\text{CT} \rangle|^2 < 10^{-3} \text{ cm}^{-2}$.



(C. M. Marian, *J. Phys. Chem. C* 120 (2016) 3715.)

- Strong nonadiabatic coupling of
 - $^1n\pi^*$ and ^1CT
 - $^3n\pi^*$ and ^3CT
- Decent SOC between
 - $^1n\pi^*$ and $^3\pi\pi^*$
 - $^3n\pi^*$ and $^3\pi\pi^*$

ISC Rates of Pure-Spin Born-Oppenheimer States

- If we neglect the spin-vibronic interaction terms (81) and (82), the decay rate of an initially populated $\Psi_{S_a, v_{aj}}$ vibronic state via ISC to a quasicontinuum of final vibronic states $\Psi_{T_b}^\alpha, \{v_{bk}\}$ is given by

$$k_{\text{ISC}} = \frac{2\pi}{\hbar} \sum_{\alpha} \sum_k |\langle \Psi_{S_a, v_{aj}} | \hat{\mathcal{H}}_{\text{SO}} | \Psi_{T_b}^\alpha, v_{bk} \rangle|^2 \delta(E_{aj} - E_{bk}) \quad (83)$$

- Taylor expansion in the vibrational coordinates Q series about an appropriately chosen reference point q_0 yields

$$\langle \Psi_{S_a, v_{aj}} | \hat{\mathcal{H}}_{\text{SO}} | \Psi_{T_b}^\alpha, v_{bk} \rangle \approx \langle \Psi_{S_a} | \hat{\mathcal{H}}_{\text{SO}} | \Psi_{T_b}^\alpha \rangle \Big|_{q_0} \langle v_{aj} | v_{bk} \rangle \quad (84)$$

$$+ \sum_K \frac{\partial \langle \Psi_{S_a} | \hat{\mathcal{H}}_{\text{SO}} | \Psi_{T_b}^\alpha \rangle}{\partial Q_K} \Big|_{q_0} \langle v_{aj} | Q_K | v_{bk} \rangle \quad (85)$$

$$+ \dots$$

Condon Approximation

- The expansion is usually truncated at the constant term (84) (“**direct spin–orbit coupling**”) or at the term (85) linear in Q_K (“**vibronic spin–orbit interaction**”).
- In the Condon approximation, i.e., assuming only direct SOC, the electronic and vibrational contributions to the ISC rate can be separated.

$$k_{\text{ISC}}^{\text{FC}} \approx \frac{2\pi}{\hbar} \sum_{\alpha} \left| \langle \Psi_{S_a} | \hat{\mathcal{H}}_{\text{SO}} | \Psi_{T_b}^{\alpha} \rangle \right|_{q_0}^2 \sum_k |\langle v_{aj} | v_{bk} \rangle|^2 \delta(E_{aj} - E_{bk}) \quad (86)$$

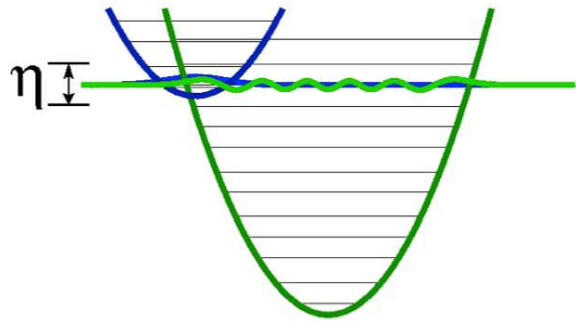
$$= \frac{2\pi}{\hbar} \sum_{\alpha} \left| \langle \Psi_{S_a} | \hat{\mathcal{H}}_{\text{SO}} | \Psi_{T_b}^{\alpha} \rangle \right|_{q_0}^2 \rho(E_{aj}) \quad (87)$$

where $\rho(E_{aj})$ is the VDOS at the energy of the initial state.

- Instead of determining the VDOS at the energy of the initial state explicitly, it is more convenient to replace the delta distribution in Eq. (86) by an appropriate expression in the energy or time regimes.

Determining Vibrational Contributions in the Energy Domain

- In this approach, the delta function in Eq. (86) is replaced by a step function of finite width.



- In Condon approximation, the vibrational part of the rate is obtained by explicitly summing over the Franck-Condon factors of all states in the interval η .

$$k_{\text{ISC}} = \frac{2\pi}{\hbar\eta} \sum_{\alpha} \left| \langle \Psi_{S_a} | \hat{\mathcal{H}}_{\text{SO}} | \Psi_{T_b}^{\alpha} \rangle \right|_{q_0}^2 \sum_{\{k | \eta > |(E_{aj} - E_{bk})|\}} |\langle v_{aj} | v_{bk} \rangle|^2 \quad (88)$$

- The sensitivity of the calculated rate with respect to the interval width η has to be tested carefully in each case.
- The approach is straight forward, but too time-consuming for large molecules and large energy gaps.
- It is not easily extended to include temperature effects (RISC).

Determining Vibrational Contributions in the Time Domain

- The time-dependent approach employs a Fourier transform representation of delta function in Eq. (86).

$$\delta(E_{aj} - E_{bk}) = \int_{-\infty}^{+\infty} e^{it(E_{aj} - E_{bk})} dt \quad (89)$$

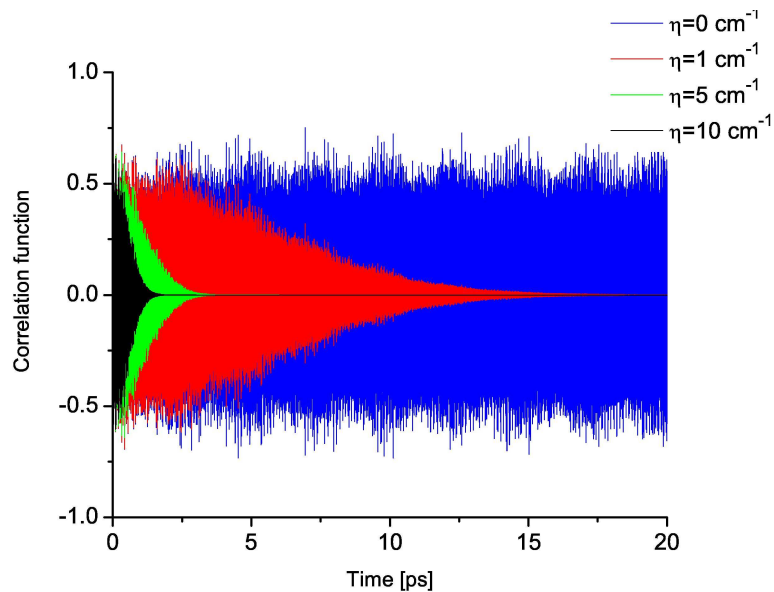
- In the harmonic oscillator model and making use of the Condon approximation, the ISC rate can be determined by numerical integration of

$$k_{ISC}^{corr} = |\langle \Psi_S | \hat{\mathcal{H}}_{SO} | \Psi_T \rangle|^2 \int_{-\infty}^{\infty} dt G(t) e^{it(\Delta E_{ST}^0 + \frac{1}{2} Tr \Omega_S)} \quad (90)$$

where Ω_S is a diagonal matrix containing the harmonic frequencies of the initial state and the correlation function $G(t)$ depends on the normal coordinates and harmonic frequencies of the initial and final states.

Determining Vibrational Contributions in the Time Domain

- To ensure convergence of the time integration, a Gaussian (or Lorentzian) damping function is introduced.



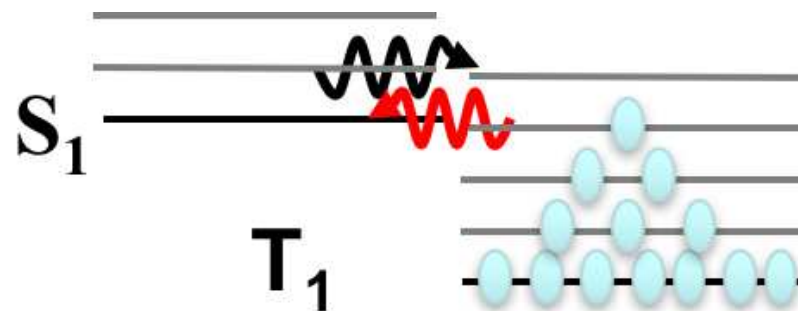
- From a physical point of view, this damping is consistent with a dephasing of the correlation function due to the interaction with a bath (solution) or the redistribution of vibrational energy (gas phase).

- The sensitivity of the calculated rate with respect to the width of the damping function has to be tested carefully in each case.

Adding Temperature in the Time Domain

- So far, all rates were calculated for vibrationally cold molecules.
- For RISC, thermal population of higher vibrational levels is needed.
- Assume a Boltzmann population of vibrational states.

$$Z = \sum_k e^{-\beta E_k} \quad (91)$$



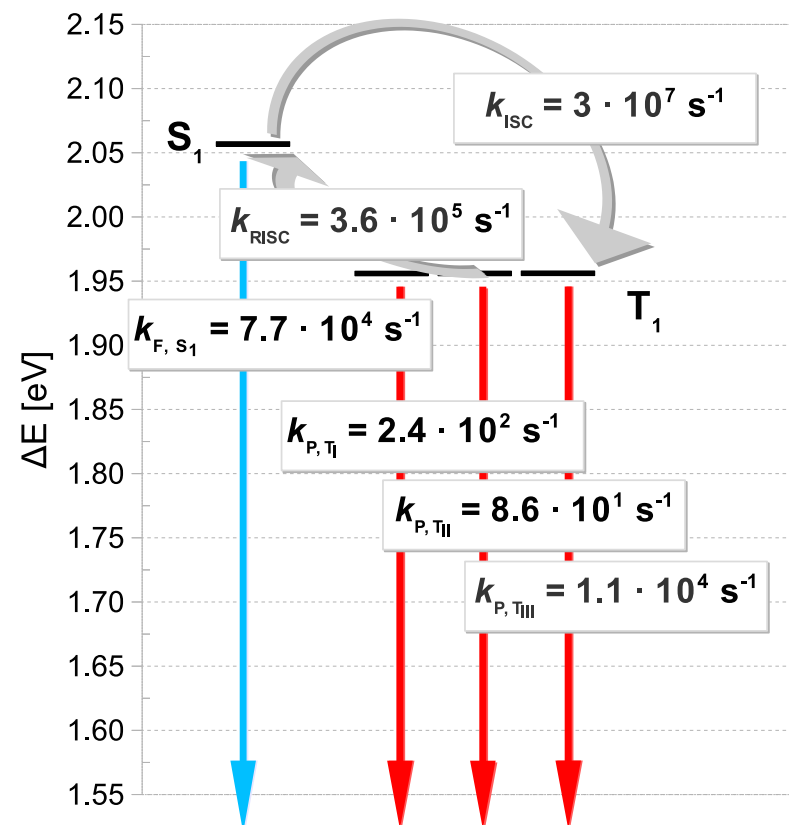
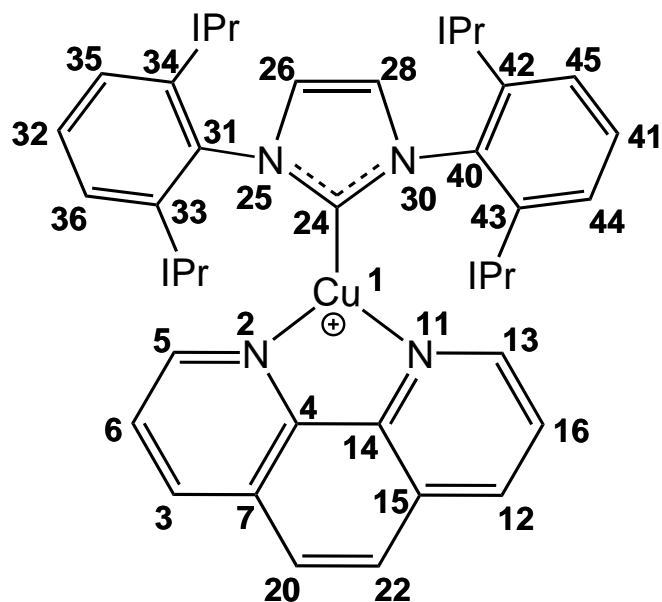
is the canonical partition function for vibrational motion in the initial state and β the inverse temperature.

- The rate constant for RISC from a manifold of thermally populated initial vibronic states k then is

$$k_{\text{RISC}}(T) = \frac{2\pi}{Z} \sum_{j,k} e^{-\beta E_k} |\langle \Psi_{S_a}, \{v_{aj}\} | \hat{\mathcal{H}}_{\text{SO}} | \Psi_{T_b}, \{v_{bk}\} \rangle|^2 \delta(E_{aj} - E_{bk}) \quad (92)$$

Example: Thermal ISC and RISC in NHC-Copper(I)-Phen Complex

- First excited states have mixed MLCT and L'LCT character.
- At 298K, ISC is about $100\times$ faster than RISC.



- Radiative decay via thermally activated delayed fluorescence and phosphorescence can compete.
(J. Föllner et al., *Inorg. Chem.* 55 (2016) 7508.)

Beyond the Condon Approximation

- When direct SOC is very small, it is often meaningful to include vibronic spin-orbit effects.
- In addition to the Condon term (86), two contributions to the ISC rate are obtained from the derivative coupling terms.
- 1. A cross term that contains Franck-Condon- and Herzberg-Teller-like expressions

$$k_{\text{ISC}}^{\text{FC/HT}} = \frac{4\pi}{\hbar} \Re \left(\left. \langle \Psi_{S_a} | \hat{\mathcal{H}}_{\text{SO}} | \Psi_{T_b} \rangle \right|_{q_0} \sum_k \langle v_{aj} | v_{bk} \rangle \delta(E_{aj} - E_{bk}) \right. \\ \left. \sum_K \frac{\partial \langle \Psi_{S_a} | \hat{\mathcal{H}}_{\text{SO}} | \Psi_{T_b} \rangle}{\partial Q_K} \right|_{q_0} \sum_l \langle v_{aj} | Q_K | v_{bl} \rangle \delta(E_{aj} - E_{bl}) \right) \quad (93)$$

Beyond the Condon Approximation

2. A term that stems exclusively from the derivative couplings.

$$k_{\text{ISC}}^{\text{HT}} = \frac{2\pi}{\hbar} \Re \left(\sum_K \frac{\partial \langle \Psi_{S_a} | \hat{\mathcal{H}}_{\text{SO}} | \Psi_{T_b} \rangle}{\partial Q_K} \Big|_{q_0} \sum_k \langle v_{aj} | Q_K | v_{bk} \rangle \delta(E_{aj} - E_{bk}) \right. \\ \left. \sum_L \frac{\partial \langle \Psi_{S_a} | \hat{\mathcal{H}}_{\text{SO}} | \Psi_{T_b} \rangle}{\partial Q_L} \Big|_{q_0} \sum_l \langle v_{aj} | Q_L | v_{bl} \rangle \delta(E_{aj} - E_{bl}) \right) \quad (94)$$

Herein \Re denotes the real part of the expression.

- Vibronic interactions can substantially increase the ISC rates, making ${}^1(\pi\pi^*) \rightsquigarrow {}^3(\pi\pi^*)$ transitions nearly as allowed as ${}^1(\pi\pi^*) \rightsquigarrow {}^3(n\pi^*)$ or ${}^1(n\pi^*) \rightsquigarrow {}^3(\pi\pi^*)$ transitions.
- Important mechanism if $(n\pi^*)$ states are not accessible for mediating an El-Sayed-forbidden ISC between a singlet and a triplet $(\pi\pi^*)$ state.

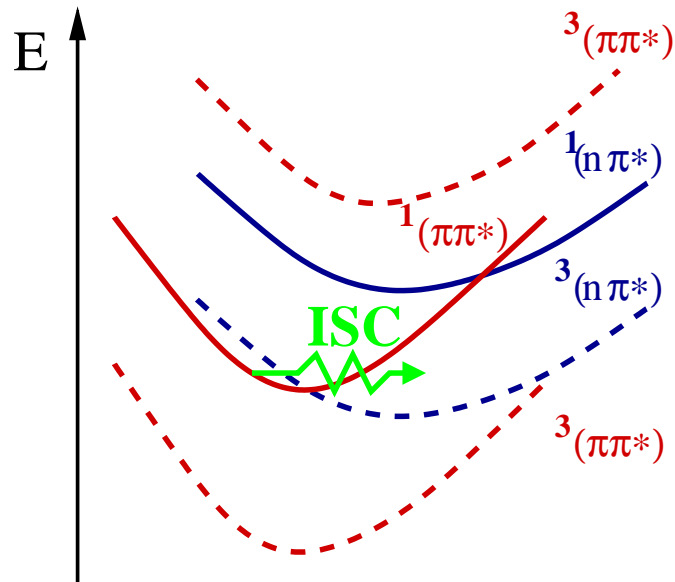
Example: Effect of Aqueous Solution on ISC in Flavin

□ Apolar solution

- ISC channel



- Direct ISC $k_{\text{ISC}} \approx 10^9 \text{ s}^{-1}$

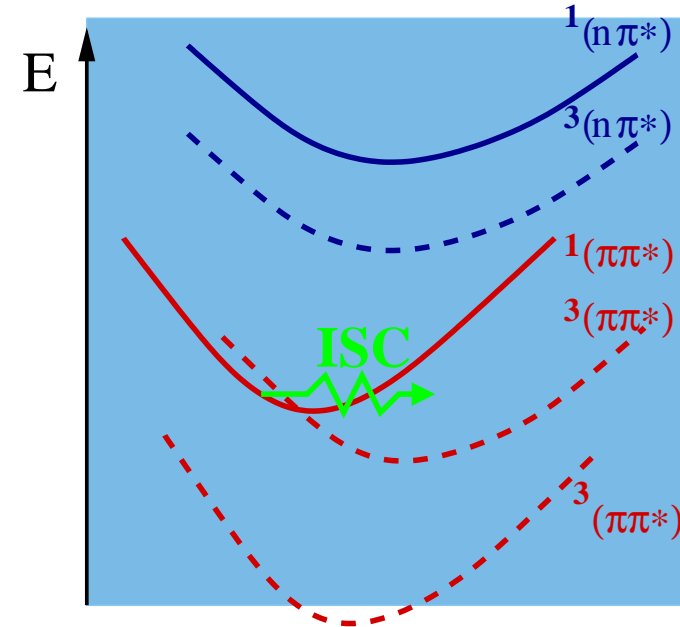


□ Aqueous solution

- ISC channel



- Vibronic SOC $k_{\text{ISC}} \approx 10^8 \text{ s}^{-1}$



□ Environment changes size *and* mechanism of ISC!

(S. Salzmann et al., *J. Photochem. Photobio. A: Chemistry* 198 (2008) 221.)

Example: Vibronic SOC and ISC in Porphyrin

□ All low-lying states are of ($\pi\pi^*$) type; first ($n\pi^*$) ca. 3 eV above T_1

□ Direct SOC

– S_1/T_1 $SOCME \approx 0.05 \text{ cm}^{-1}$

– S_1/T_1 $k_{ISC} \approx 10^5 \text{ s}^{-1}$

□ Vibronic SOC

– Out-of-plane modes mix in ($n\pi^*$) character

– S_1/T_1 $k_{ISC} \approx 10^7 \text{ s}^{-1}$



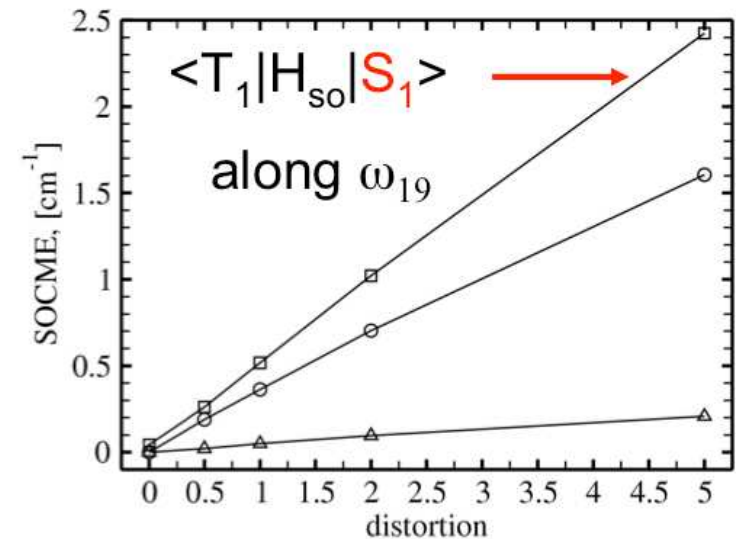
$\omega_{19} = 401.9 \text{ cm}^{-1}$

b_{2g}



$\omega_{30} = 708.7 \text{ cm}^{-1}$

b_{3g}



(S. Perun et al., *ChemPhysChem* 9 (2008) 282.)

Summary

- Qualitative rules may be used to estimate the size of electronic spin–orbit coupling between two states.
- The energy gap law is applicable only for nested states!
- Electronic SOE between ^1CT and ^3CT is usually very small.
- Nonadiabatic interactions with close-by LE states can markedly increase the SOC.
- This is also true for symmetry-breaking vibrational displacements.
- Static approaches can be used to compute rate constants for ISC and RISC between two states.
- If more than two electronic states are involved, dynamic approaches are required (but also much more expensive).

Summary

- In my view, the most critical ingredients for the computation of ISC and RISC rate constants are the potential energy surfaces.
- DFT/MRCI and DFT/MRSOCI appear to do a good job in this respect.
- So far, I did not come across a single density functional which yields a balanced description of CT and LE states in organic TADF emitters of the donor–acceptor type.
- Interstate SOMEs can be obtained from TDDFT amplitudes via approximate many-electron wavefunctions.
- SOMEs are much less sensitive to the quality of the wavefunctions than energies.
- It is in general not sufficient to calculate ISC rate constants for isolated molecules. A solvent environment can change probability and mechanism of ISC.

Related Literature

- For further details, such as the derivation of equations, and for supplementary literature see:
 1. Christel M. Marian, *Spin-orbit coupling in molecules*, Reviews In Computational Chemistry, K. Lipkowitz and D. Boyd, Eds., Wiley VCH, Weinheim, 17 (2001) 99-204
 2. Christel M. Marian, *Spin-orbit coupling and intersystem crossing in molecules*, Wiley Interdisciplinary Reviews: Computational Molecular Science (2011) 1880-1888; DOI 10.1002/wcms.83
 3. Mihajlo Etinski, Vidisha Rai-Constapel, Christel M. Marian, *Time-dependent approach to spin-vibronic: Implementation and assessment*, 140 (2014) 114104; DOI 10.1063/1.4868484
 4. Christel M. Marian, Jelena Föllner, Martin Kleinschmidt, Mihajlo Etinski, *Intersystem Crossing Processes in TADF Emitters*, in: Yersin (Ed.), Highly Efficient OLEDs, Materials Based on Thermally Activated Delayed Fluorescence. Wiley VCH (2018); ISBN: 978-3-527-33900-6