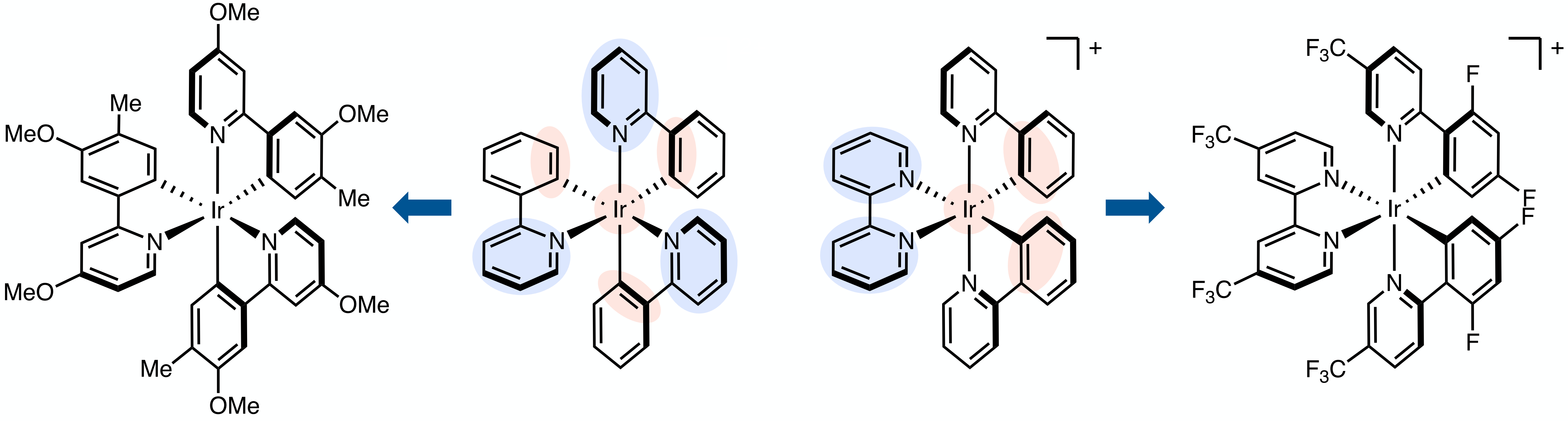
The Excited States of Inorganic Photocatalysts:
(Part of) Why Iridium Polypyridyls are Privileged Structures



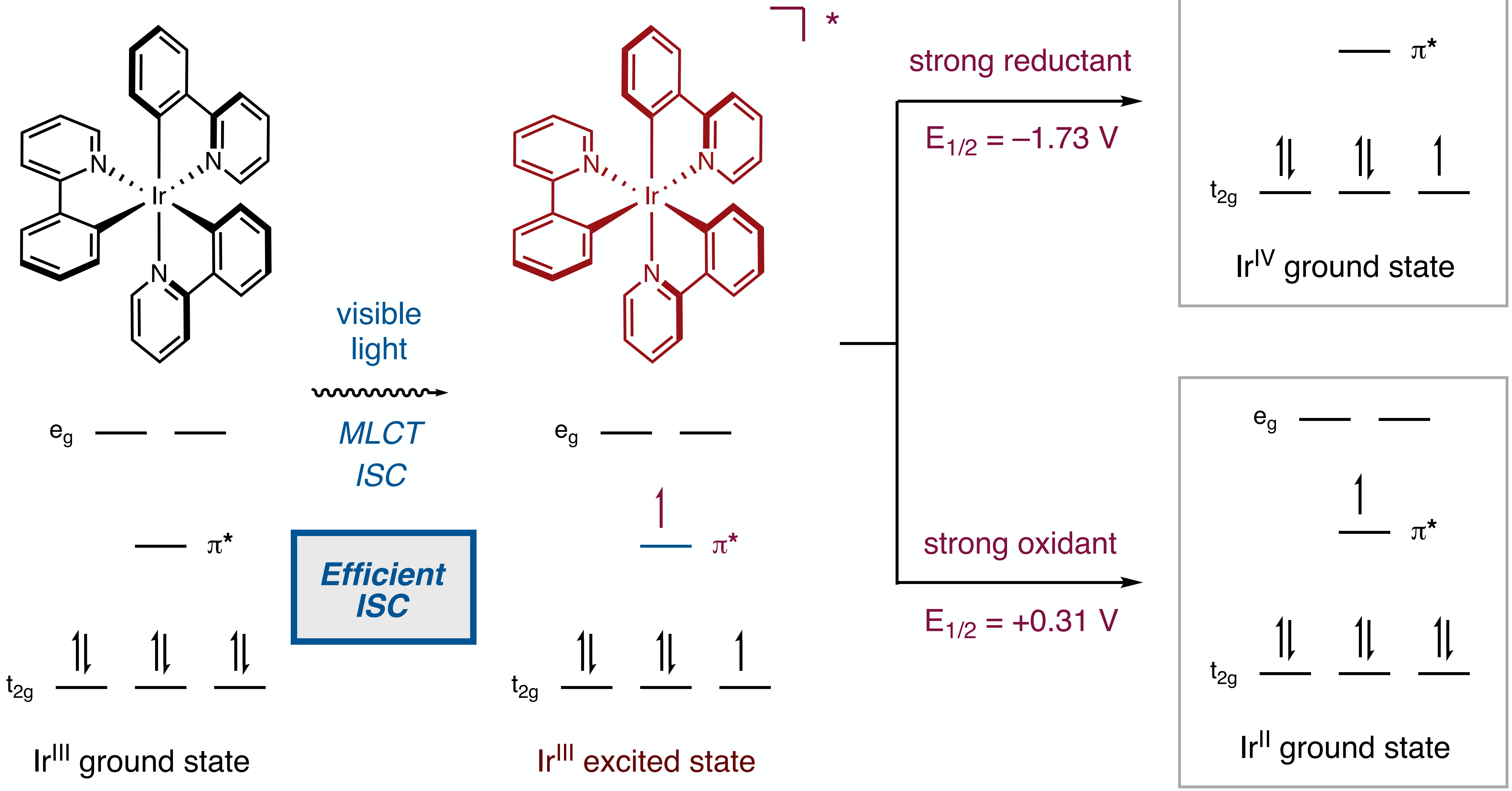
Eric Nacsa
MacMillan Group Meeting

April 10, 2018

What Makes an Effective Photo(redox) Catalyst Class?

Strong absorption in visible region

Long-lived T_1



Efficient ISC

Ir^{III} ground state

Ir^{III} excited state

strong reductant

$E_{1/2} = -1.73$ V

Ir^{IV} ground state

strong oxidant

$E_{1/2} = +0.31$ V

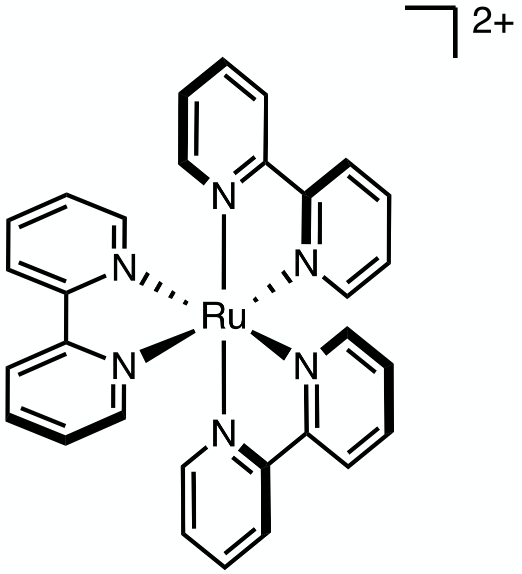
Ir^{II} ground state

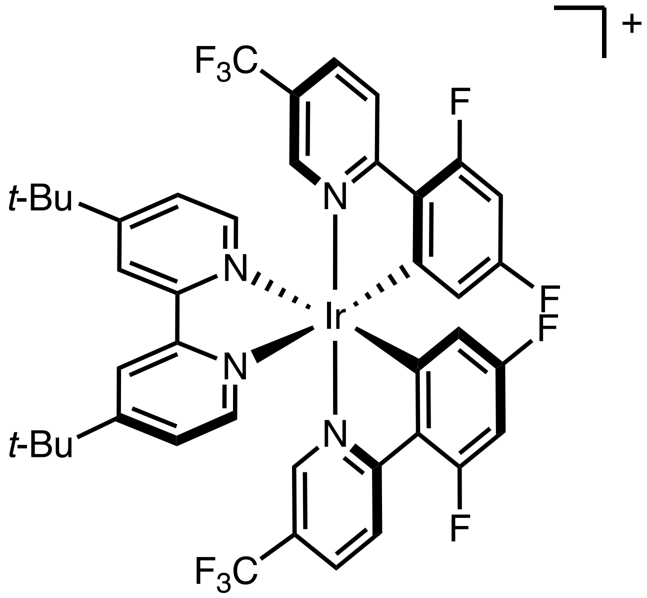
High stability

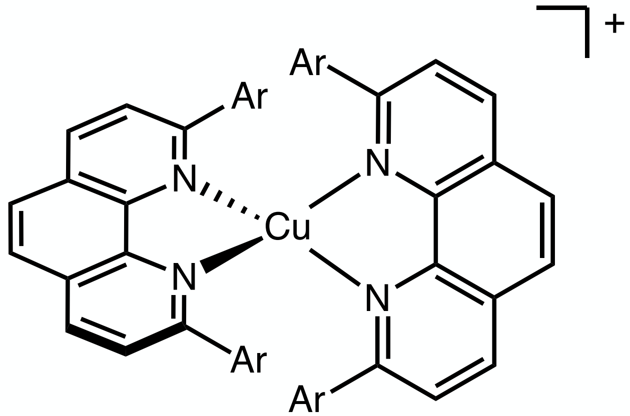
High-energy T_1 → ***Wide & modular redox window***

All properties should remain intact as we move the redox window

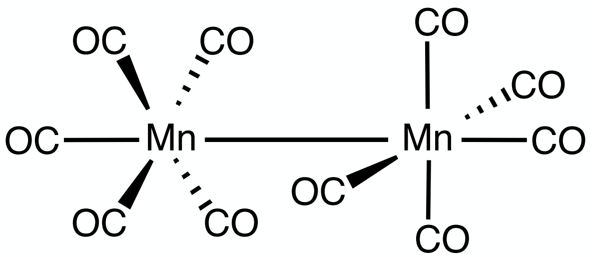
Photo(redox) Catalysis with Inorganic Complexes



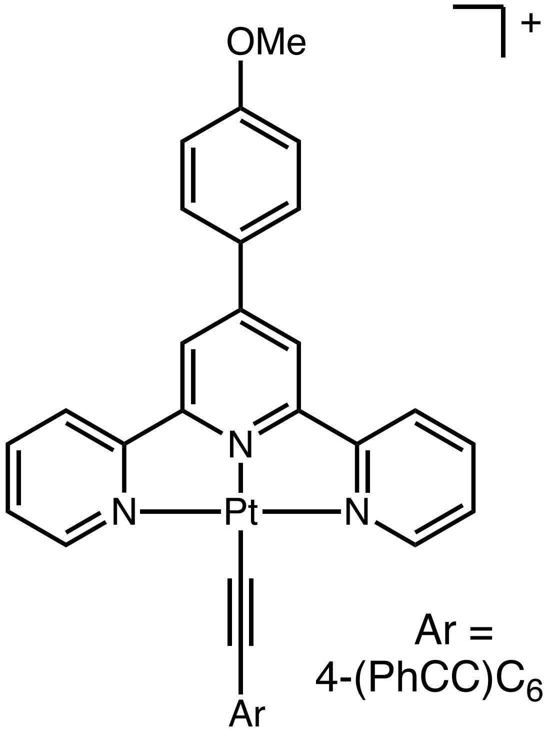




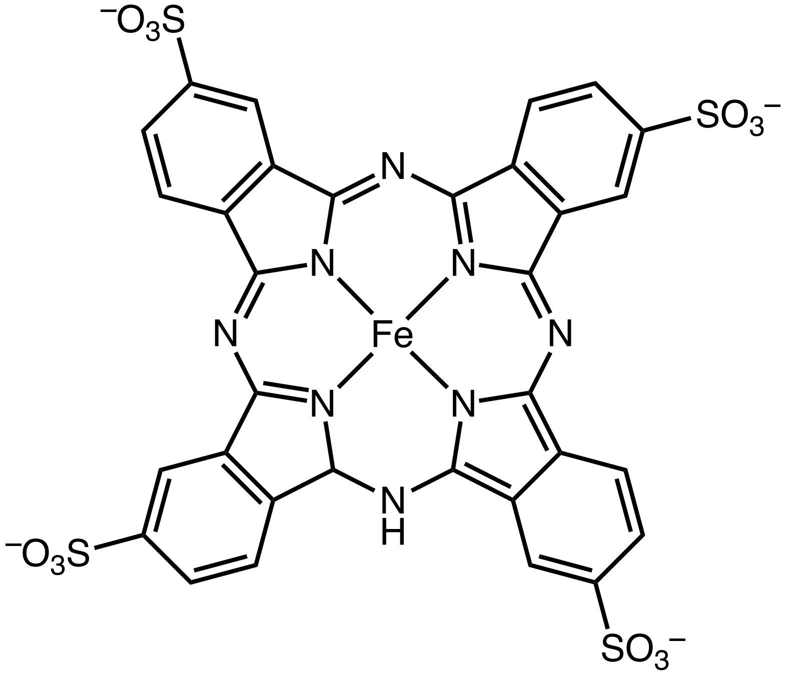
Ar = 4-MeOC$_6$H$_4$

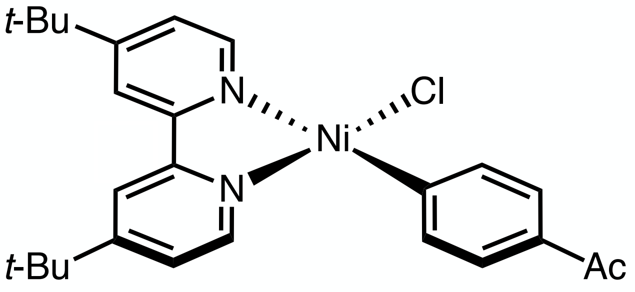


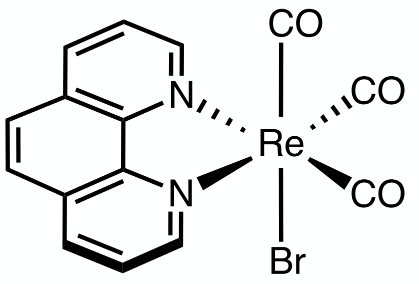
Several metals have been successfully employed



Ar = 4-(PhCC)C$_6$H$_4$

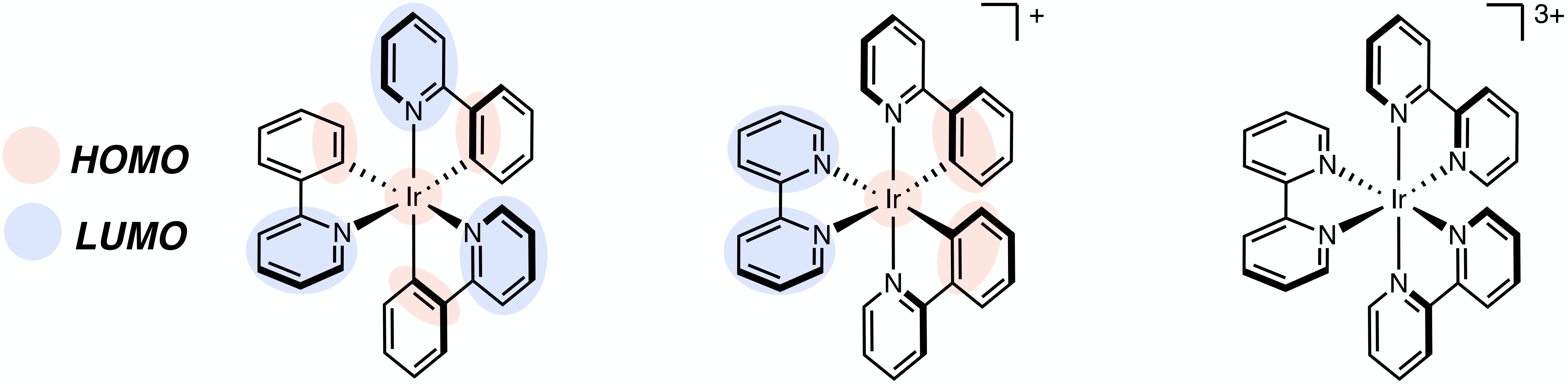






Iridium Provides a General Platform for Photo(redox) Catalysts

Homoleptic ***Heteroleptic*** ***Synthetic challenge***



	$Ir(ppy)_3$	*$Ir(ppy)_2(bpy)^+$*	*$Ir(bpy)_3^{3+}$*
$E(Ir^{IV/III*})$ / V	+0.31	+0.68	+1.81
$E(Ir^{III*/II})$ / V	–1.73	–0.79	–0.88
	■ Strong reductant	■ Intermediate potentials	■ Strong oxidant

- ■ Accommodate bpy-type and ppy-type ligands
- ■ HOMO and LUMO spatially separated – can be modified independently

Highly tunable

Arias-Rotondo, D. M.; McCusker, J. K. *Chem. Soc. Rev.* **2016**, *45*, 5803.

Iridium Provides a General Platform for Photo(redox) Catalysts

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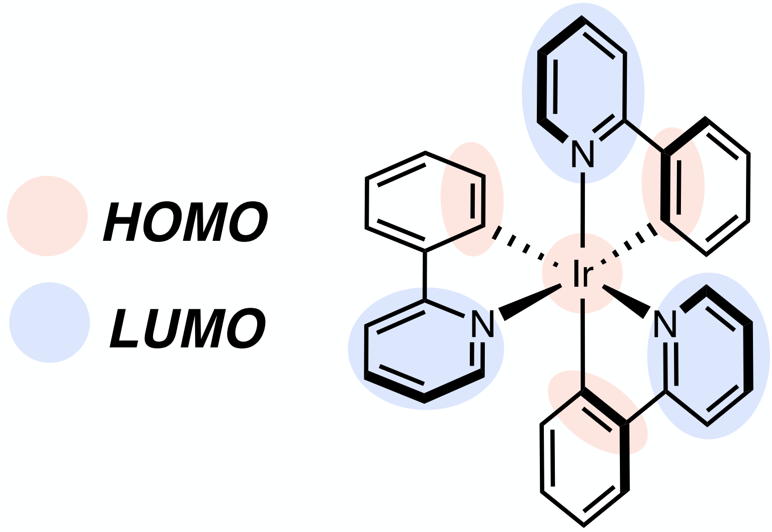
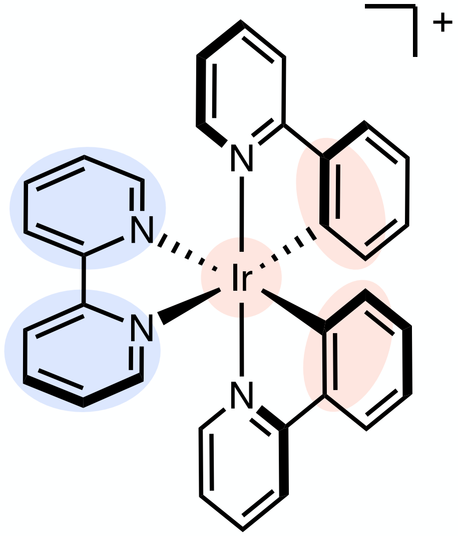
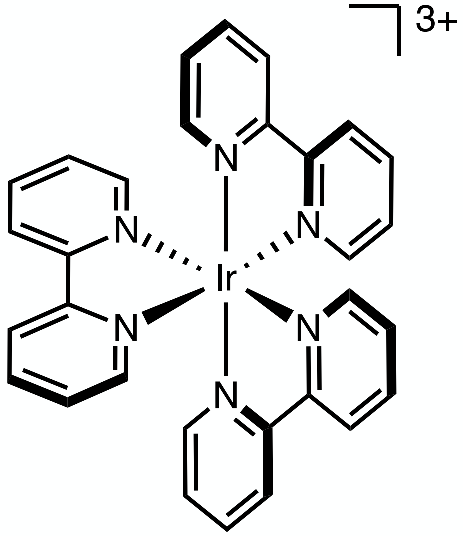
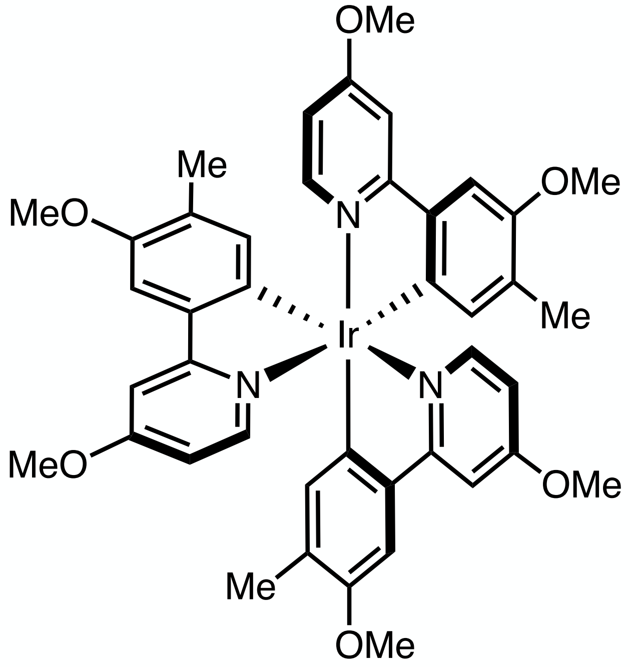
Heteroleptic

Synthetic challenge

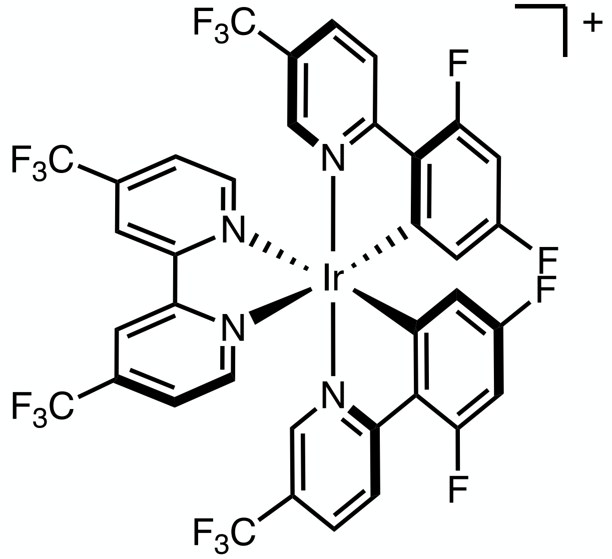








■ 'Super reductant'



■ 'Super oxidant'

Dramatic modifications do not compromise fundamental photo(redox) catalytic properties

Not demonstrated with other metal centers

Outline

- Introduction to spin-orbit coupling
- Role of spin-orbit coupling in intersystem crossing
- The triplet excited state of $Ir(ppy)_3$
- A simple model for photophysical properties of 6-coordinate complexes

Absorption and Emission Spectra

- Atomic/molecular fingerprints allowing the assignment of excited state energies

6 12.01

$[He]2s^2 2p^2$

C

2.55

Emission Spectrum of Carbon

Excited State Energies and Configurations

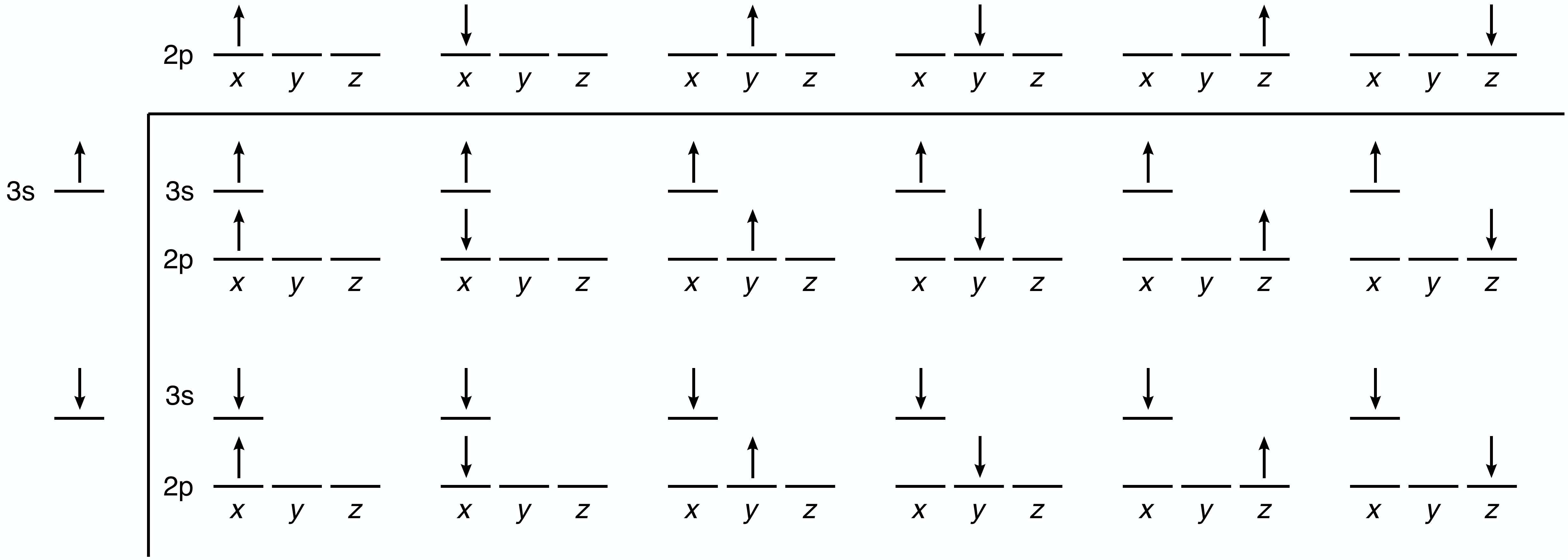
- Sorted first by principal and secondary quantum numbers
  - E ($n = 1$) < E ($n = 2$) < E ($n = 3$) < …
  - E ($l = 0$, *s* orbital) < E ($l = 1$, *p* orbital) < E ($l = 2$, *d* orbital) < …
- Fine structure gives richer information about electronic configuration

Atkins, P.; de Paula, J. *Atkins' Physical Chemistry*, 8th ed. W. H. Freeman: New York, 2006.

An Excited State of Carbon

- Ground state is [He]$2s^2 2p^2$
  - Has further descriptors since it is not closed-shell (we will disregard these here)
- Consider the excited state [He]$2s^2 2p^1 3s^1$
  - It is instructive to work through the associated term symbols and relative energies

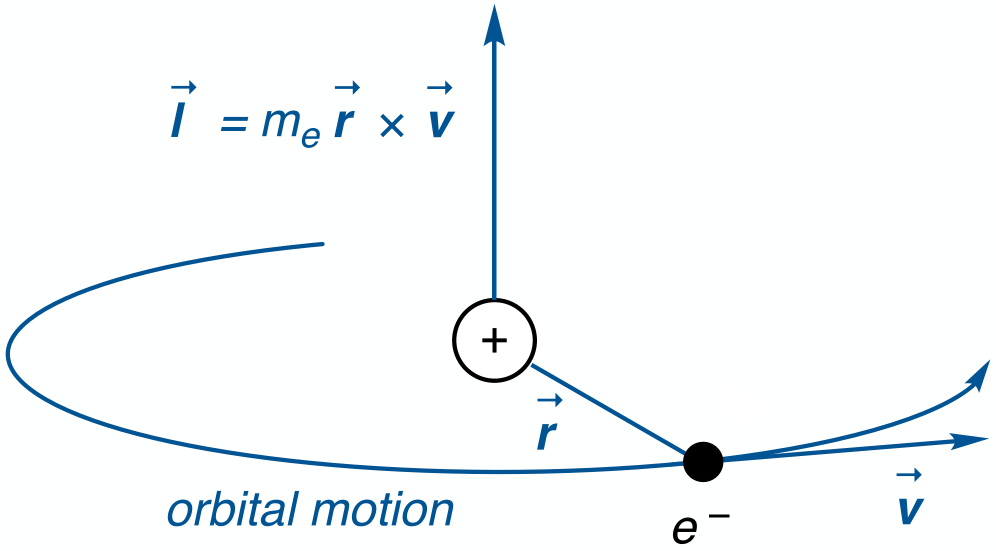
12 possible electron configurations



This strategy indicates there are 12 states but each 'cartoon' descriptor is not a complete state with a unique energy

Quantum Numbers

- Consider the excited state $[\mathrm{He}]2s^2 2p^1 3s^1$
  - Need the quantum numbers of each valence electron
- A quick review of quantum numbers



n – principal quantum number (energy level)

$n = 1, 2, 3, 4, \ldots$

l – orbital quantum number (orbital shape, angular momentum of orbital motion)

$l = 1, 2, 3, \ldots, n - 1$ (s, p, d, …)

$\vec{l}$ is quantized such that its magnitude is given by

$$\| \vec{l} \|^2 = L^2 = \hbar^2 l(l + 1)$$

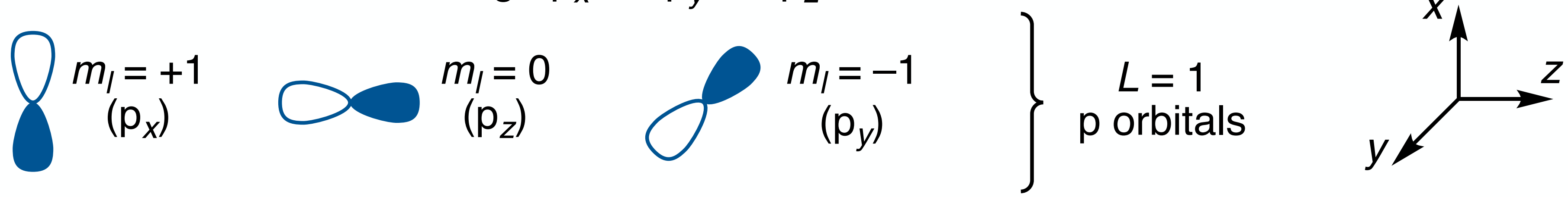
m_l – orbital magnetic quantum number (projection of $\vec{l}$ onto the *z*-axis)

$m_l = -l, -l + 1, \ldots, l - 1, l$

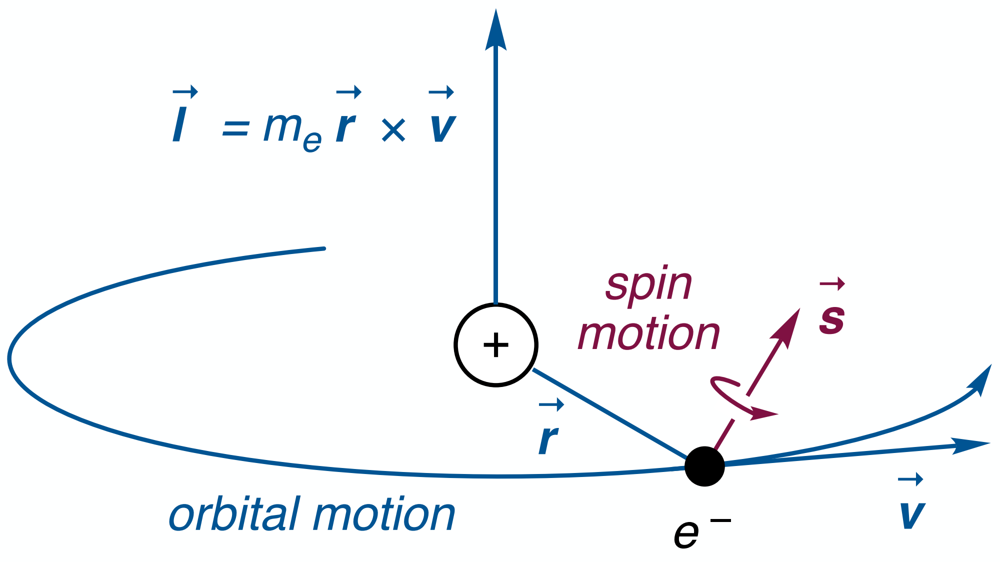
L_z is quantized such that

$$L_z = m_l \hbar$$

for a given *l*, indicates the subshell, e.g., p_x vs. p_y vs. p_z for $l = 1$



Quantum Numbers



- Consider the excited state [He]$2s^2 2p^1 3s^1$
  - Need the quantum numbers of each valence electron
- A quick review of quantum numbers

n – principal quantum number (energy level)

$n = 1, 2, 3, 4, \ldots$

s – spin quantum number (a constant, angular momentum of spin motion)

$s = 1/2$

$\vec{s}$ is quantized such that its magnitude is given by

$$\|\vec{s}\|^2 = S^2 = \hbar^2 s(s+1) = 3/4\hbar^2$$

m_s – spin magnetic quantum number (projection of $\vec{s}$ onto the z-axis)

$m_s = \pm 1/2$

S_z is quantized such that

$$S_z = m_s\hbar = \pm 1/2\hbar$$

indicates spin ‘up’ or ‘down’

Addition of Angular Momentum

- Term symbols for [He]$2s^22p^13s^1$
  - The energies of the various substates will depend on $\vec{l}$ and $\vec{s}$ of the valence electrons
  - These angular momenta can be straightforwardly added in two limiting cases

LS Coupling Hierarchy

- Best applied to lighter elements
- Coupling between electrons of $\vec{l}$ and of $\vec{s}$ is most important
- These quantities are added to give possible values of $\vec{L}$ and $\vec{S}$ for the atom

$$\vec{L} = \vec{l}_1 + \vec{l}_2 \qquad L = |\,l_1 - l_2\,|, |\,l_1 - l_2\,| + 1, \ldots\, l_1 + l_2 - 1, l_1 + l_2$$

$$\vec{S} = \vec{s}_1 + \vec{s}_2 \qquad S = s_1 - s_2, s_1 + s_2 = 1, 0$$

- Interaction between $\vec{L}$ and $\vec{S}$ is relatively small and treated as a perturbation (see later)
- Possible states are assigned a term symbol ${}^{2S+1}L$ (as long as Pauli principle not violated)

Addition of Angular Momentum

- Term symbols for [He]$2s^2 2p^1 3s^1$
  - The energies of the various substates will depend on $\vec{l}$ and $\vec{s}$ of the valence electrons
  - These angular momenta can be straightforwardly added in two limiting cases

LS **Coupling Hierarchy**

- Two valence electrons to consider:

[He]$2s^2\mathbf{2p^1}3s^1$ $l_1 = 1$ [He]$2s^2 2p^1\mathbf{3s^1}$ $l_2 = 0$

- The possible values of *L* and *S* are thus

$$L = | l_1 - l_2 |, | l_1 - l_2 | + 1, \ldots l_1 + l_2 - 1, l_1 + l_2 = 1$$

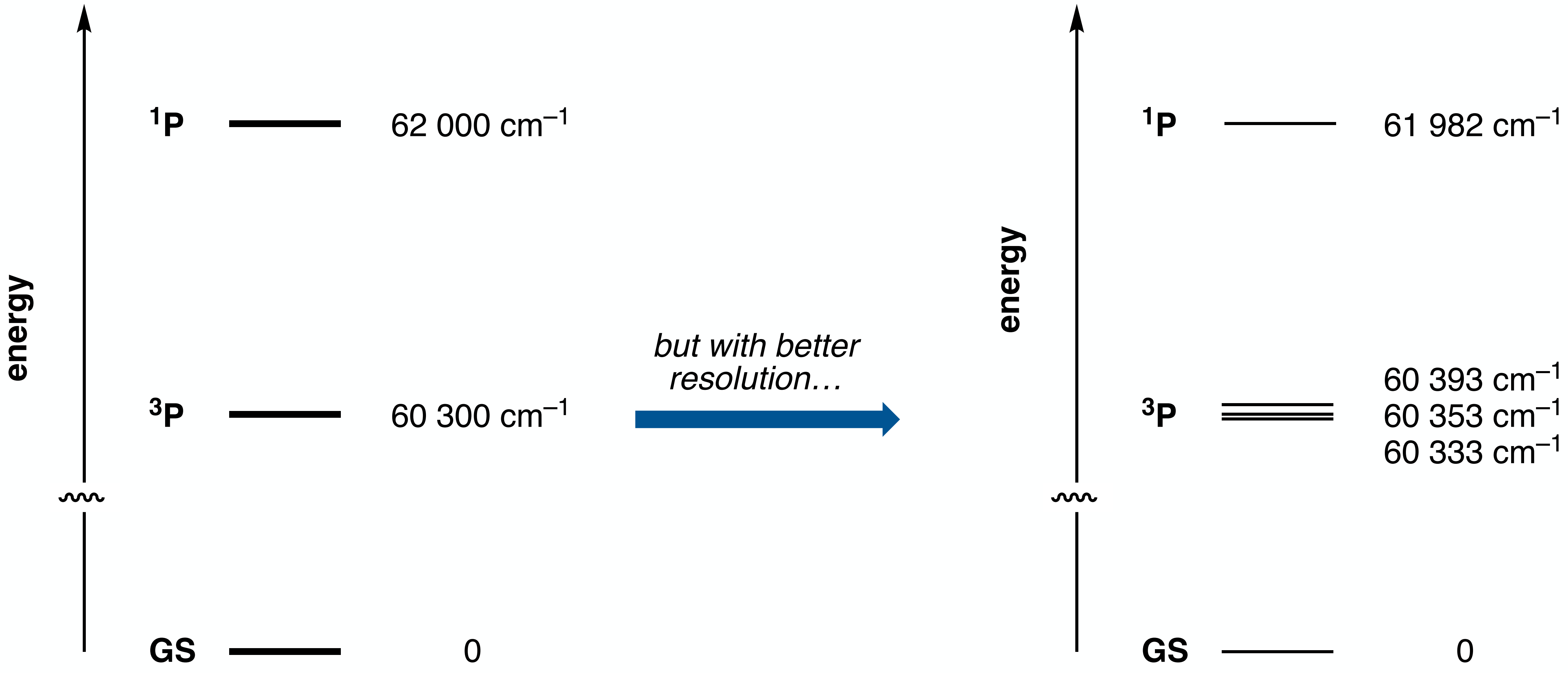
$$S = s_1 - s_2, s_1 + s_2 = 1, 0$$

- The term symbols associated with this excited state of carbon are thus

$\mathbf{^3P}$ and $\mathbf{^1P}$

Excited State Energies of Carbon

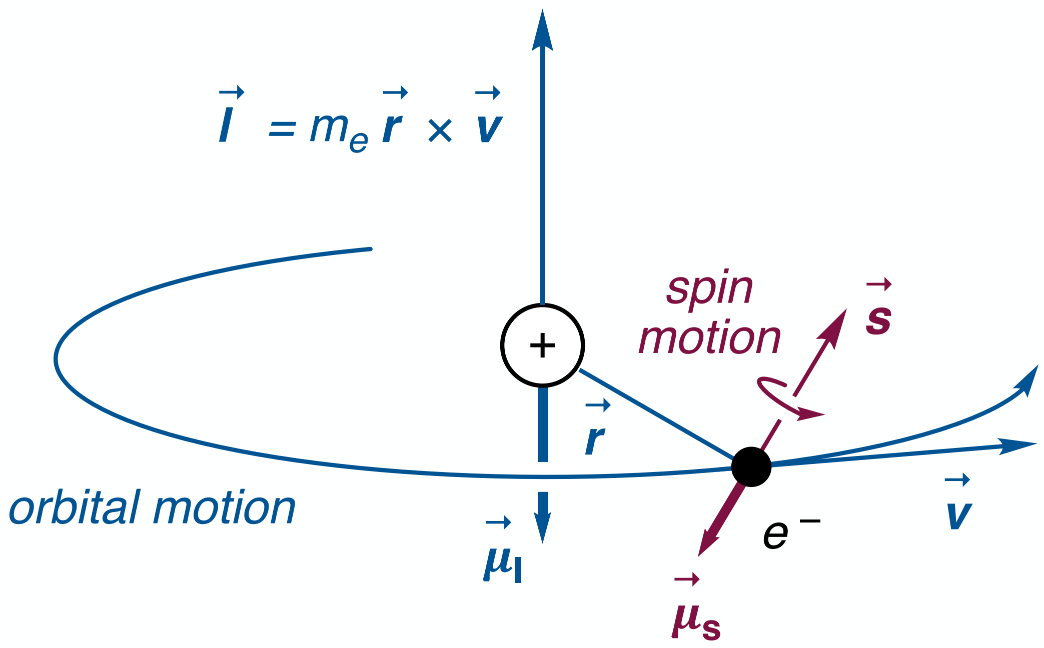
- Energies for $[He]2s^2 2p^1 3s^1$
  - According to Hund's rules, triplets are lower in energy than singlets, so we expect that



What is the origin of this fine structure?

Spin-Orbit Coupling

- There are magnetic moments μ associated with the angular momenta of an electron



The interaction of these magnetic moments gives rise to spin-orbit coupling

- The energy of this interaction is proportional to the scalar product of the angular momenta

$E_{SOC} = k\, \vec{s} \cdot \vec{l}$ which can further be manipulated to obtain the result

$$\mathbf{E_{SOC} = a\,[\,j\,(\,j + 1) - l\,(\,l + 1) - s\,(\,s + 1)\,]}$$

- **An expression for *a* is not important but it is critical to note that $a \propto Z^4$**

Addition of Angular Momentum

- Term symbols for [He]$2s^2 2p^1 3s^1$
  - The energies of the various substates will depend on $\vec{\boldsymbol{l}}$ and $\vec{\boldsymbol{s}}$ of the valence electrons
  - These angular momenta can be straightforwardly added in two limiting cases

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- Best applied to lighter elements
- Coupling between electrons of $\vec{\boldsymbol{l}}$ and of $\vec{\boldsymbol{s}}$ is most important
- These quantities are added to give possible values of $\vec{\boldsymbol{L}}$ and $\vec{\boldsymbol{S}}$ for the atom

$$\vec{\boldsymbol{L}} = \vec{\boldsymbol{l}}_1 + \vec{\boldsymbol{l}}_2 \qquad L = |\, l_1 - l_2 \,|, |\, l_1 - l_2 \,| + 1, \ldots\, l_1 + l_2 - 1, l_1 + l_2$$

$$\vec{\boldsymbol{S}} = \vec{\boldsymbol{s}}_1 + \vec{\boldsymbol{s}}_2 \qquad S = s_1 - s_2, s_1 + s_2 = 1, 0$$

- Interaction between $\vec{\boldsymbol{L}}$ and $\vec{\boldsymbol{S}}$ is accounted for using the total angular momentum, $\vec{\boldsymbol{J}}$

$$\vec{\boldsymbol{J}} = \vec{\boldsymbol{L}} + \vec{\boldsymbol{S}} \qquad J = |\, L - S \,|, |\, L - S \,| + 1, \ldots\, L + S - 1, L + S$$

- Possible states are assigned a term symbol $^{2S+1}L_J$ (as long as Pauli principle not violated)

Addition of Angular Momentum

- Term symbols for [He]$2s^2 2p^1 3s^1$
  - The energies of the various substates will depend on $\vec{l}$ and $\vec{s}$ of the valence electrons
  - These angular momenta can be straightforwardly added in two limiting cases

LS **Coupling Hierarchy**

- Two valence electrons to consider:

[He]$2s^2\mathbf{2p^1}3s^1$ $\quad l_1 = 1$ $\qquad$ [He]$2s^2 2p^1\mathbf{3s^1}$ $\quad l_2 = 0$

- The possible values of L and S are thus

$$L = | l_1 - l_2 |, | l_1 - l_2 | + 1, \ldots l_1 + l_2 - 1, l_1 + l_2 = 1$$

$$S = s_1 - s_2, s_1 + s_2 = 1, 0$$

- The possible values of J are

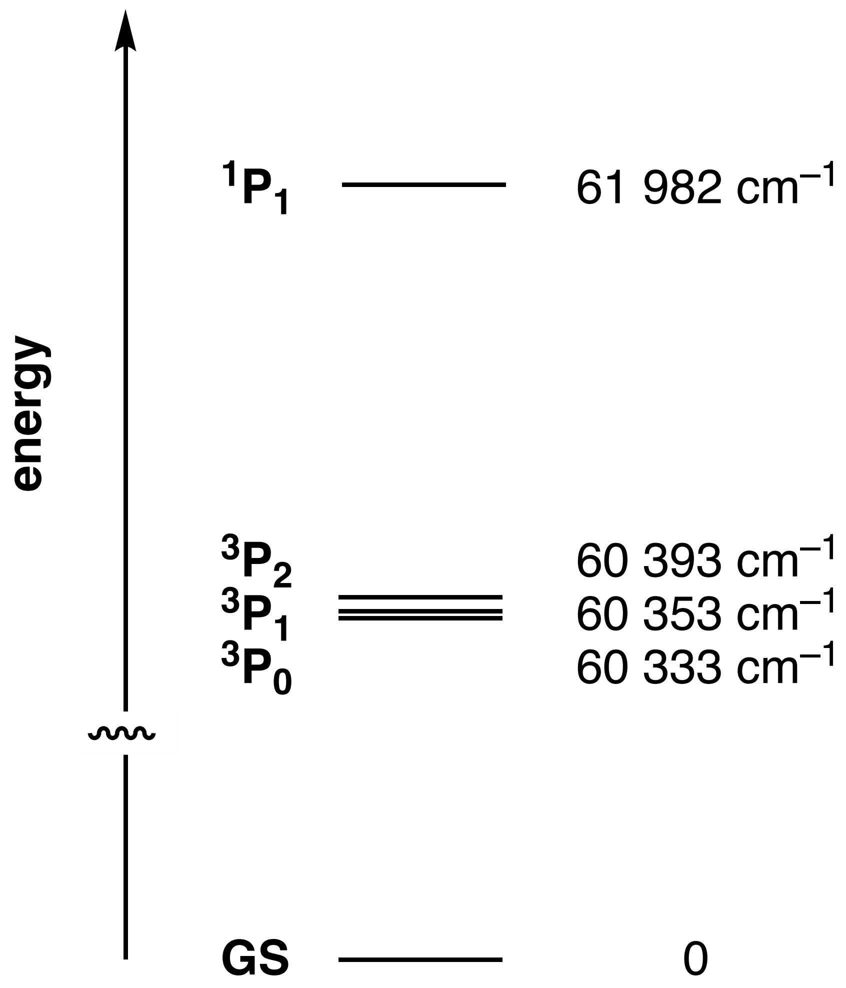
$$J = | L - S |, | L - S | + 1, \ldots L + S - 1, L + S = 2, 1, 0 \quad (\text{for } S = 1) \quad | \quad J = 1 \text{ for } S = 0$$

- The term symbols associated with this excited state of carbon are thus

$\mathbf{{}^3P_2}$ $\quad$ $\mathbf{{}^3P_1}$ $\quad$ $\mathbf{{}^3P_0}$ $\quad$ and $\quad$ $\mathbf{{}^1P_1}$

Fine Structure of Excited State Carbon

- Energies for [He]$2s^2 2p^1 3s^1$
  - Spin-orbit coupling explains the fine structure of the ^3P level



energy

$^1P_1$ 61 982 cm^{-1}

$^3P_2$ 60 393 cm^{-1}

$^3P_1$ 60 353 cm^{-1}

$^3P_0$ 60 333 cm^{-1}

GS 0

applying an external magnetic field reveals all 12 states (Zeeman effect) by lifting the 2J+1 degeneracy

Evaluation of the expression for SOC energy

$$E_{SOC} = a\,[\,J\,(\,J+1) - L\,(\,L+1) - S\,(\,S+1)\,]$$

for the ^3P terms ($L = 1$, $S = 1$, $J = 2, 1, 0$) leads to

$E_{SOC} = +a$ ($J = 2$)

$E_{SOC} = -a$ ($J = 1$)

$E_{SOC} = -2a$ ($J = 0$)

For the [He]$2s^2 2p^1 3s^1$ excited state of carbon, the spin-orbit proportionality constant is $a = 20$ cm^{-1}

An Excited State of Lead

- Term symbols for [Xe]$4f^{14}5d^{10}6s^{2}6p^{1}7s^{1}$
  - The energies of the various substates will depend on $\vec{\boldsymbol{l}}$ and $\vec{\boldsymbol{s}}$ of the valence electrons
  - These angular momenta can be straightforwardly added in two limiting cases

LS Coupling Hierarchy

- Best applied to lighter elements – **not valid for Pb**
- Coupling between electrons of $\vec{\boldsymbol{l}}$ and of $\vec{\boldsymbol{s}}$ is most important
- These quantities are added to give possible values of $\vec{\boldsymbol{L}}$ and $\vec{\boldsymbol{S}}$ for the atom

$$\vec{\boldsymbol{L}} = \vec{\boldsymbol{l}}_1 + \vec{\boldsymbol{l}}_2 \qquad L = |\, l_1 - l_2 \,|, |\, l_1 - l_2 \,| + 1, \ldots\ l_1 + l_2 - 1, l_1 + l_2$$

$$\vec{\boldsymbol{S}} = \vec{\boldsymbol{s}}_1 + \vec{\boldsymbol{s}}_2 \qquad S = s_1 - s_2, s_1 + s_2 = 1, 0$$

- Interaction between $\vec{\boldsymbol{L}}$ and $\vec{\boldsymbol{S}}$ is accounted for using the total angular momentum, $\vec{\boldsymbol{J}}$

$$\vec{\boldsymbol{J}} = \vec{\boldsymbol{L}} + \vec{\boldsymbol{S}} \qquad J = |\, L - S \,|, |\, L - S \,| + 1, \ldots\ L + S - 1, L + S$$

- Possible states are assigned a term symbol $^{2S+1}L_J$ (as long as Pauli principle not violated)

An Excited State of Lead

- Term symbols for [Xe]$4f^{14}5d^{10}6s^{2}6p^{1}7s^{1}$
  - The energies of the various substates will depend on $\vec{\boldsymbol{l}}$ and $\vec{\boldsymbol{s}}$ of the valence electrons
  - These angular momenta can be straightforwardly added in two limiting cases

jj Coupling Hierarchy

- Best applied to heavier elements – valid for Pb
- Coupling between $\vec{\boldsymbol{l}}$ and $\vec{\boldsymbol{s}}$ of each individual electron most important
- These quantities combined first **for each electron** to find its total angular momentum $\vec{\boldsymbol{j}}$

$$\vec{\boldsymbol{j}}_1 = \vec{\boldsymbol{l}}_1 + \vec{\boldsymbol{s}}_1 \qquad j_1 = |\, l_1 - s_1 \,|,\ l_1 + s_1 = |\, l_1 \pm 1/2 \,|$$

$$\vec{\boldsymbol{j}}_2 = \vec{\boldsymbol{l}}_2 + \vec{\boldsymbol{s}}_2 \qquad j_2 = |\, l_2 - s_2 \,|,\ l_2 + s_2 = |\, l_2 \pm 1/2 \,|$$

- Interactions between electrons are less important, accounted for by adding individual $\vec{\boldsymbol{j}}$

$$\vec{\boldsymbol{J}} = \vec{\boldsymbol{j}}_1 + \vec{\boldsymbol{j}}_2 \qquad J = |\, j_1 - j_2 \,|,\ |\, j_1 - j_2 \,| + 1,\ \ldots\ j_1 + j_2 - 1,\ j_1 + j_2$$

- Possible states are assigned a term symbol $(j_1, j_2)_J$

An Excited State of Lead

- Term symbols for [Xe]$4f^{14}5d^{10}6s^{2}6p^{1}7s^{1}$
  - The energies of the various substates will depend on $\vec{l}$ and $\vec{s}$ of the valence electrons
  - These angular momenta can be straightforwardly added in two limiting cases

jj **Coupling Hierarchy**

- Two valence electrons to consider:

[Xe]$4f^{14}5d^{10}6s^{2}\mathbf{6p^{1}}7s^{1}$ $l_1 = 1,\ s_1 = 1/2 \Rightarrow j_1 = 3/2,\ 1/2$

[Xe]$4f^{14}5d^{10}6s^{2}6p^{1}\mathbf{7s^{1}}$ $l_2 = 0,\ s_2 = 1/2 \Rightarrow j_2 = 1/2$

- Evaluating the expression for *J*, possible values are then

$J = 2,\ 1$ (for $j_1 = 3/2,\ j_2 = 1/2$)

$J = 1,\ 0$ (for $j_1 = 1/2,\ j_2 = 1/2$)

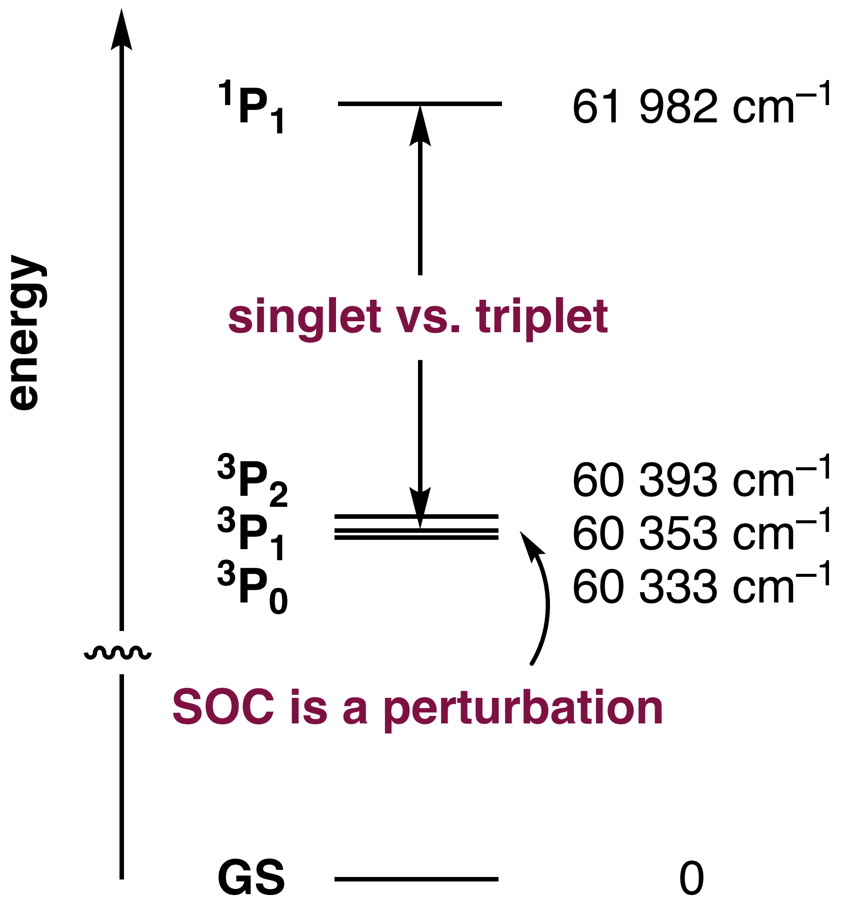
- The term symbols for this excited state of Pb are therefore

$\mathbf{(3/2,\ 1/2)_2}$ $\mathbf{(3/2,\ 1/2)_1}$ $\mathbf{(1/2,\ 1/2)_1}$ $\mathbf{(1/2,\ 1/2)_0}$

Excited States of Carbon and Lead

C*

$[He]2s^2 2p^1 3s^1$



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singlet vs. triplet

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$^3P_1$ 60 353 cm^{-1}

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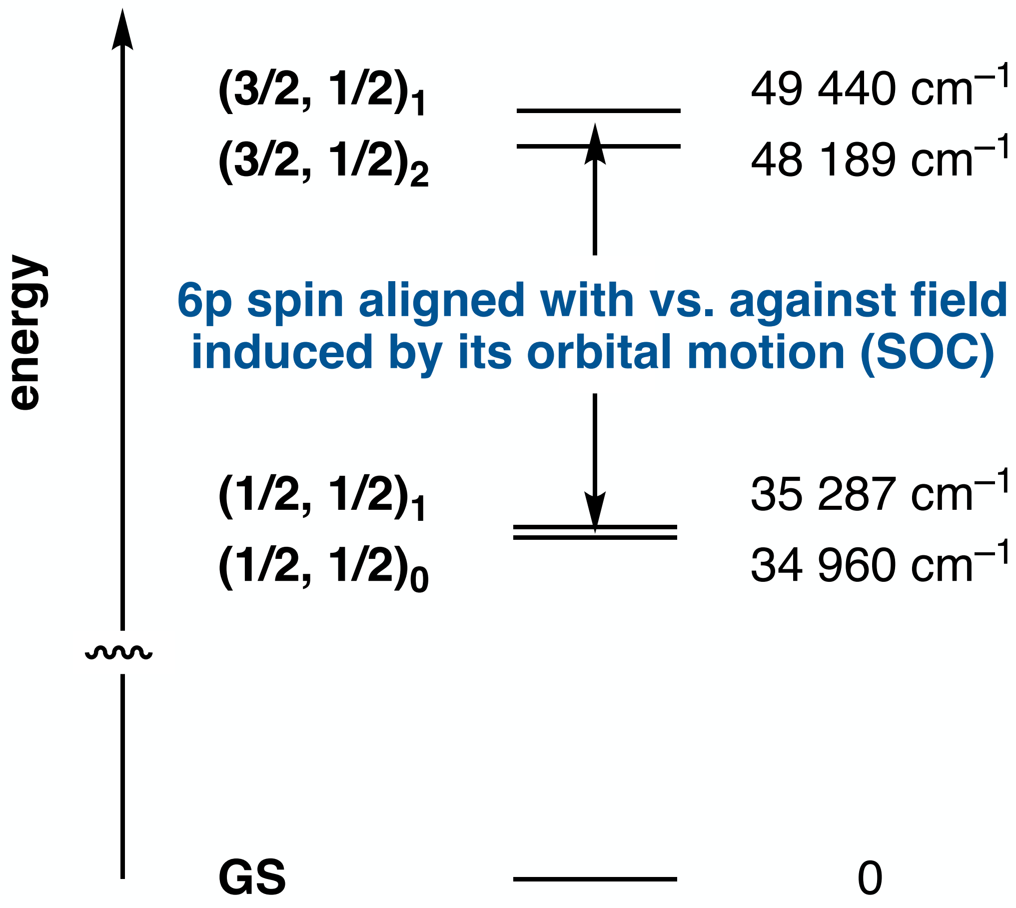
SOC is a perturbation

GS 0

Pb*

$[Xe]4f^{14}5d^{10}6s^2 6p^1 7s^1$



energy

$(3/2, 1/2)_1$ 49 440 cm^{-1}

$(3/2, 1/2)_2$ 48 189 cm^{-1}

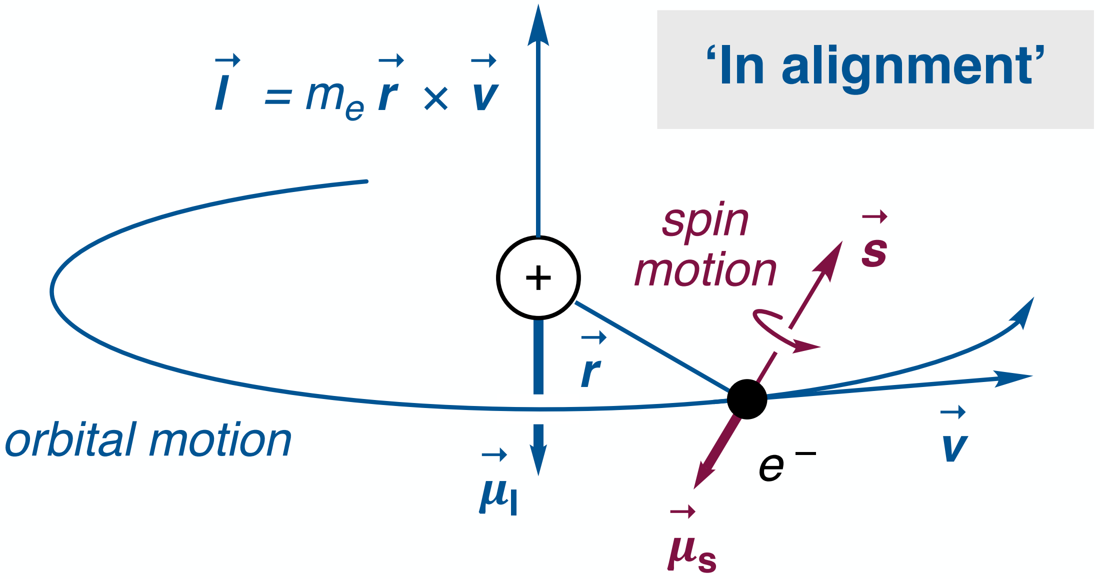
6p spin aligned with vs. against field induced by its orbital motion (SOC)

$(1/2, 1/2)_1$ 35 287 cm^{-1}

$(1/2, 1/2)_0$ 34 960 cm^{-1}

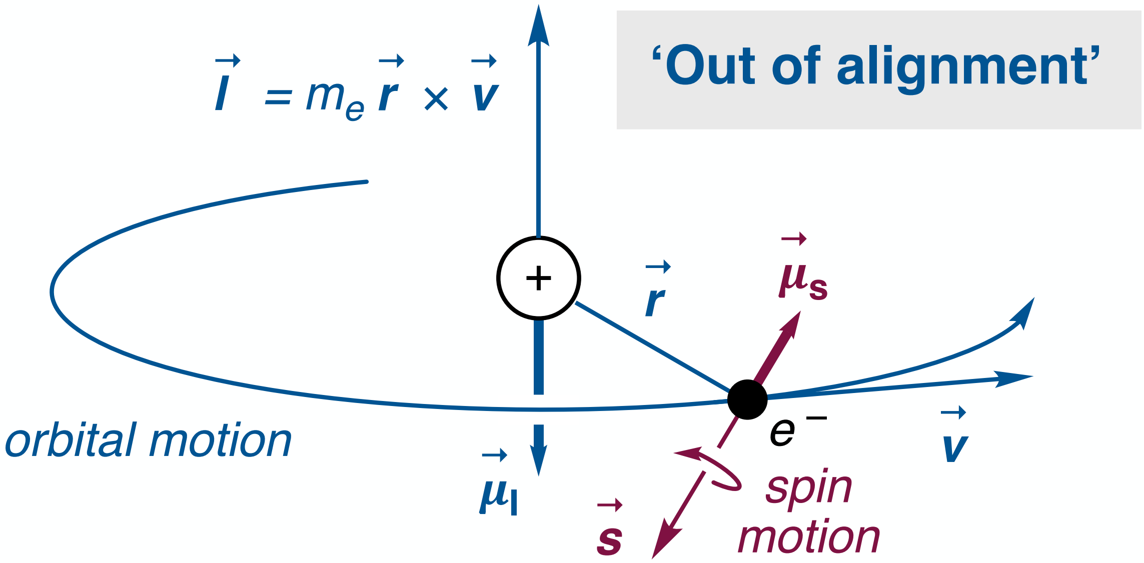
GS 0

Excited States of Carbon and Lead



'In alignment'

$\vec{l} = m_e \vec{r} \times \vec{v}$

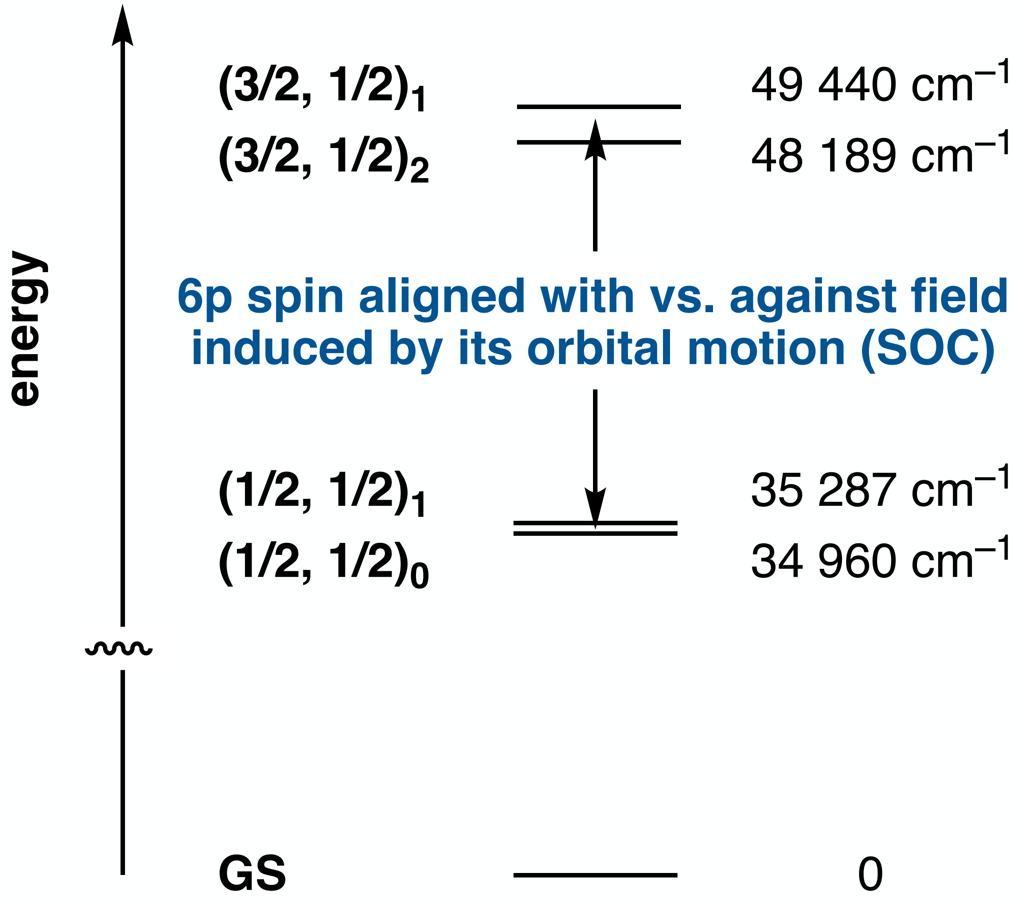


'Out of alignment'

$\vec{l} = m_e \vec{r} \times \vec{v}$

Pb*

[Xe]$4f^{14}5d^{10}6s^{2}6p^{1}7s^{1}$



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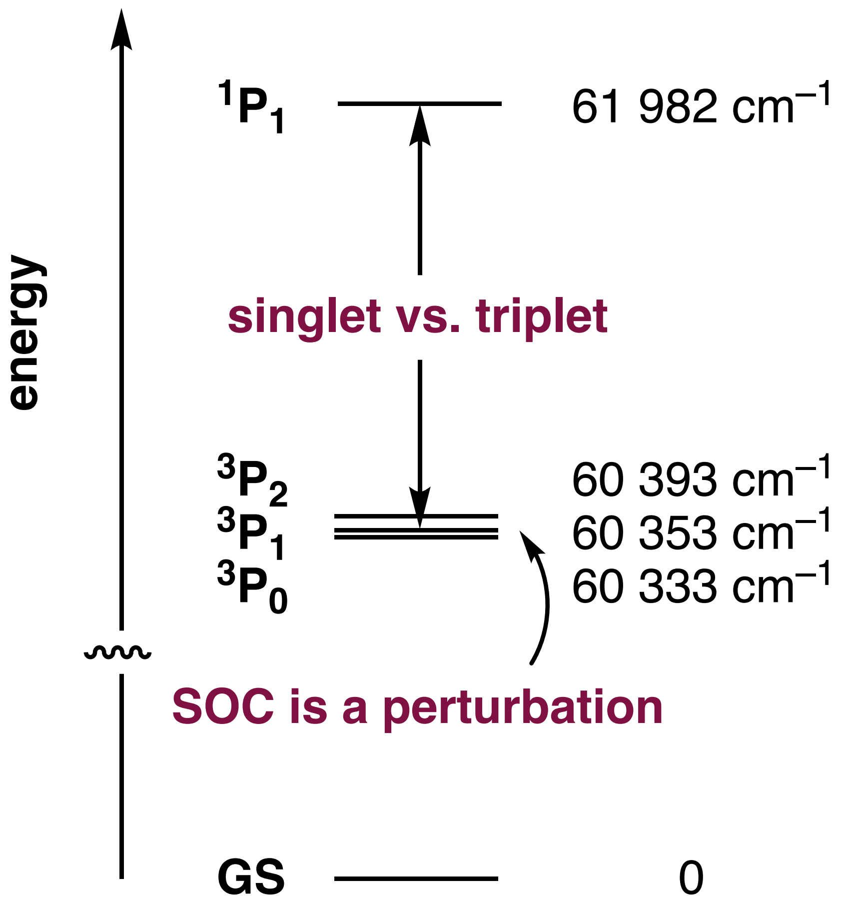
Excited States of Carbon and Lead

C*

[He]$2s^2 2p^1 3s^1$



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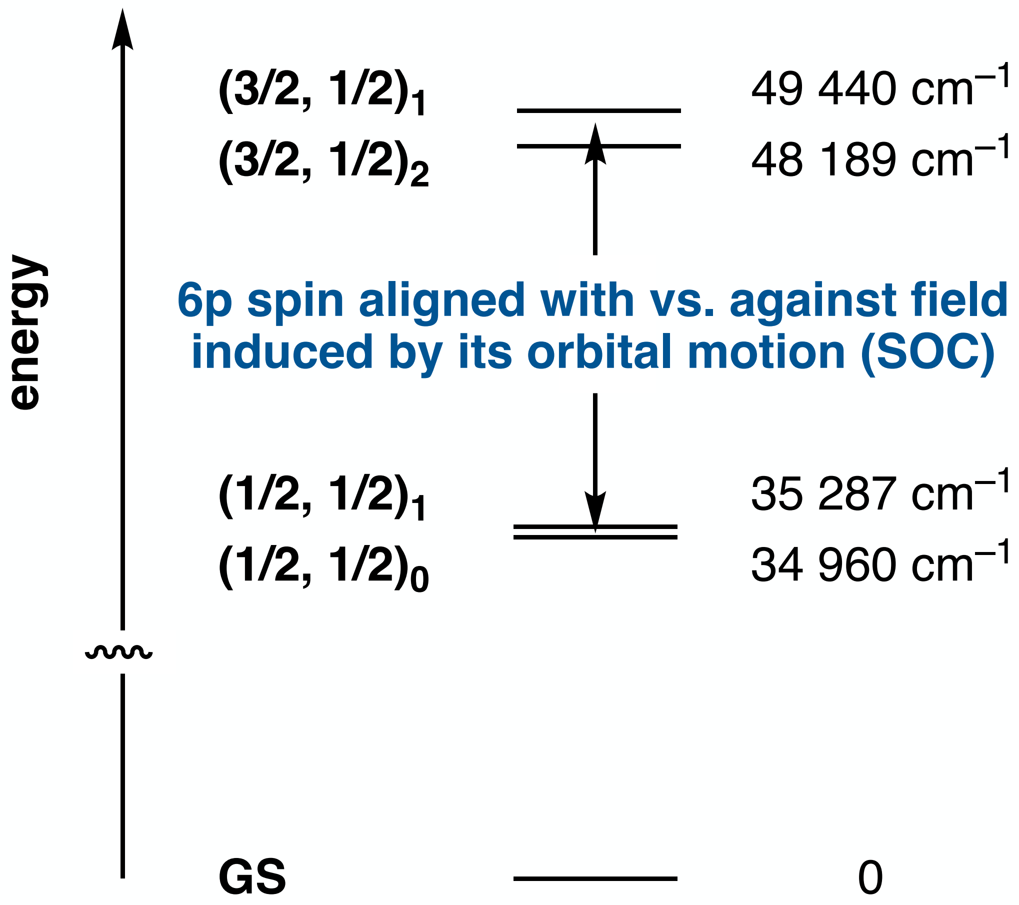
GS — 0

Pb*

[Xe]$4f^{14}5d^{10}6s^2 6p^1 7s^1$



$(3/2, 1/2)_1$ — 49 440 cm^{-1}

$(3/2, 1/2)_2$ — 48 189 cm^{-1}

6p spin aligned with vs. against field induced by its orbital motion (SOC)

$(1/2, 1/2)_1$ — 35 287 cm^{-1}

$(1/2, 1/2)_0$ — 34 960 cm^{-1}

GS — 0

Interactions between electrons dominate – SOC weak

1. Find L and S for whole atom, predicts first-order structure – ^1P and ^3P terms

2. Find whole-atom SOC from L and S, predicts fine structure – $^3P_2$, $^3P_1$, $^3P_0$

SOC dominates – Interactions between electrons weak

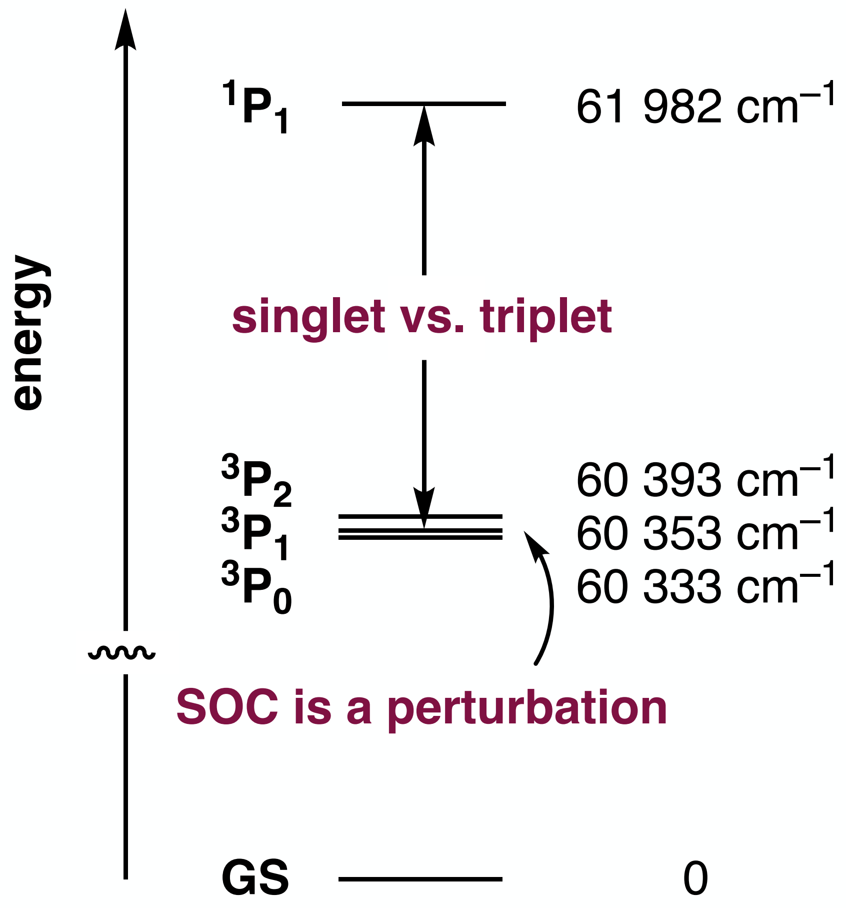
1. Find possible j for each electron, gives first-order structure – (3/2, 1/2) & (1/2, 1/2)

2. Find J for the whole atom from each e$^-$, predicts fine structure

Excited States of Carbon and Lead

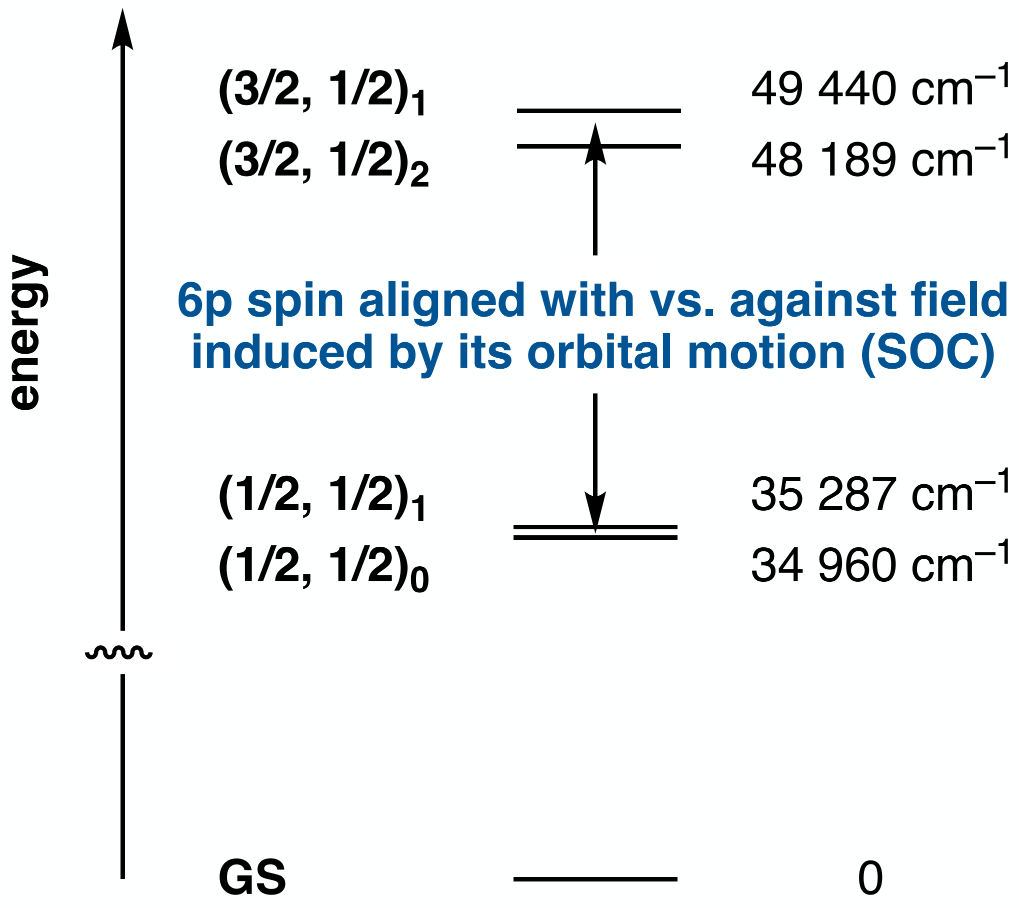
C*

[He]$2s^22p^13s^1$



Pb*

[Xe]$4f^{14}5d^{10}6s^26p^17s^1$



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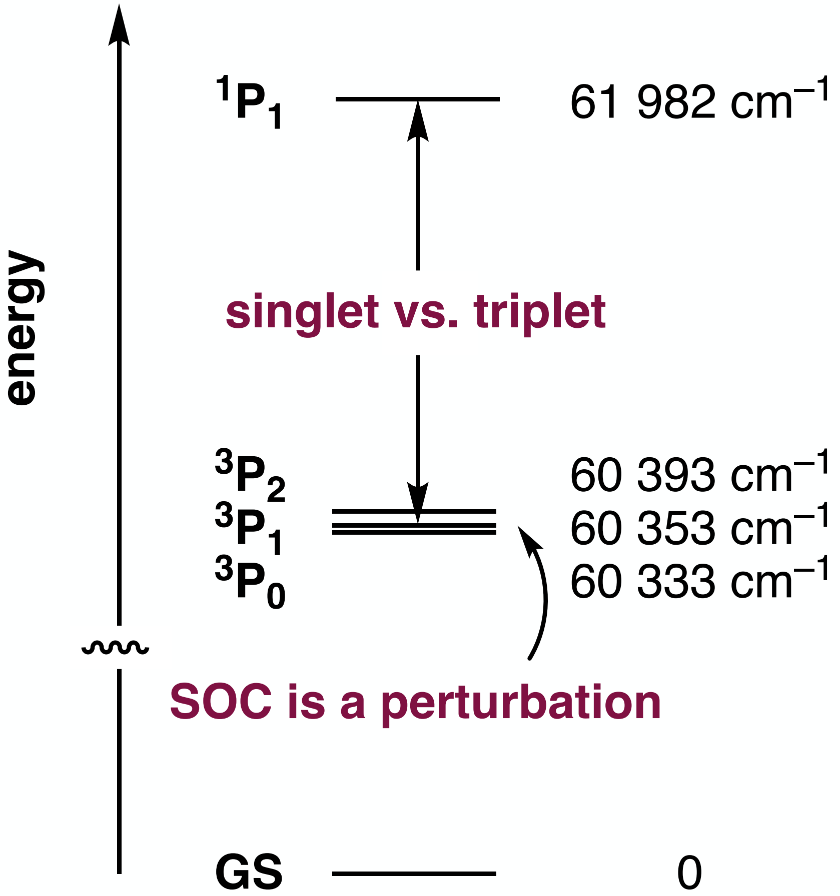
Combining l_i to find L and s_i to find S accounts for l-l and s-s interactions between electrons first

l-s interactions (SOC) are weak and only assessed for the whole atom

Excited States of Carbon and Lead

C*

[He]$2s^2 2p^1 3s^1$



energy

$^1P_1$ 61 982 cm^{-1}

singlet vs. triplet

$^3P_2$ 60 393 cm^{-1}

$^3P_1$ 60 353 cm^{-1}

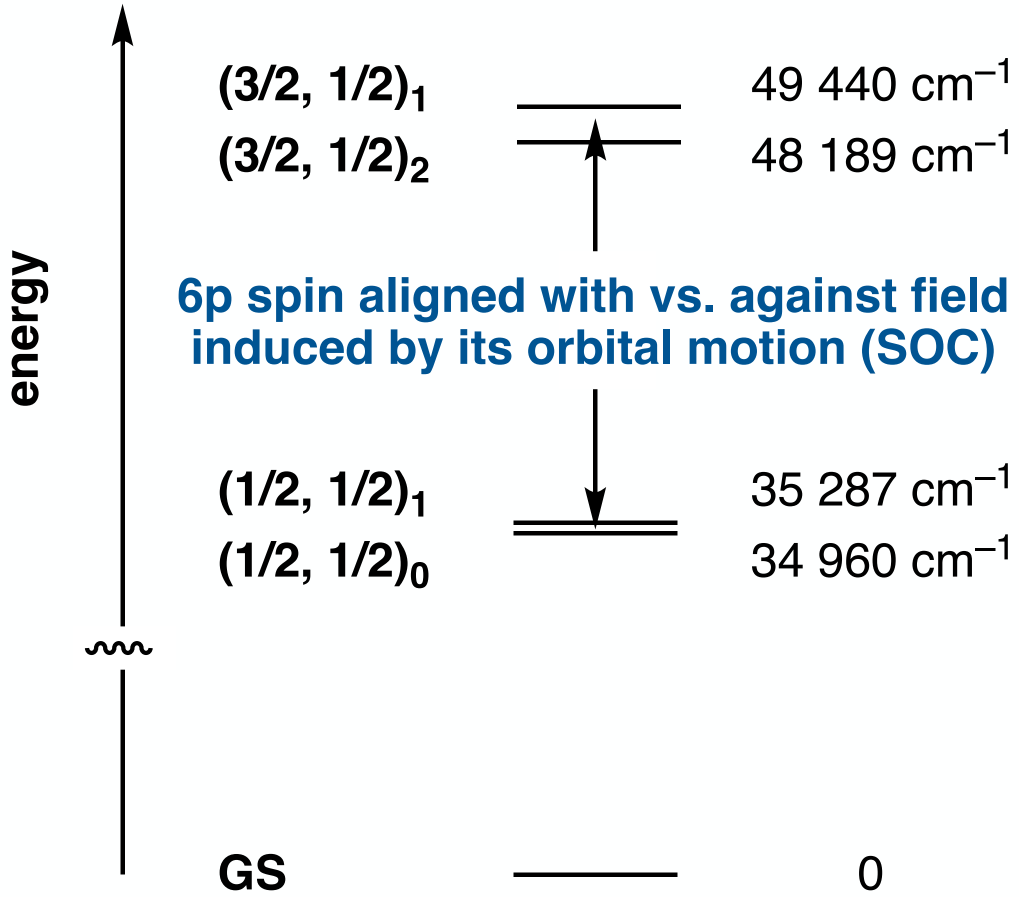
$^3P_0$ 60 333 cm^{-1}

SOC is a perturbation

GS 0

Pb*

[Xe]$4f^{14} 5d^{10} 6s^2 6p^1 7s^1$



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6p spin aligned with vs. against field induced by its orbital motion (SOC)

$(1/2, 1/2)_1$ 35 287 cm^{-1}

$(1/2, 1/2)_0$ 34 960 cm^{-1}

GS 0

l-s interactions (SOC) are strong and assessed first by combining them in $j_i = l_i + s_i$ for each electron

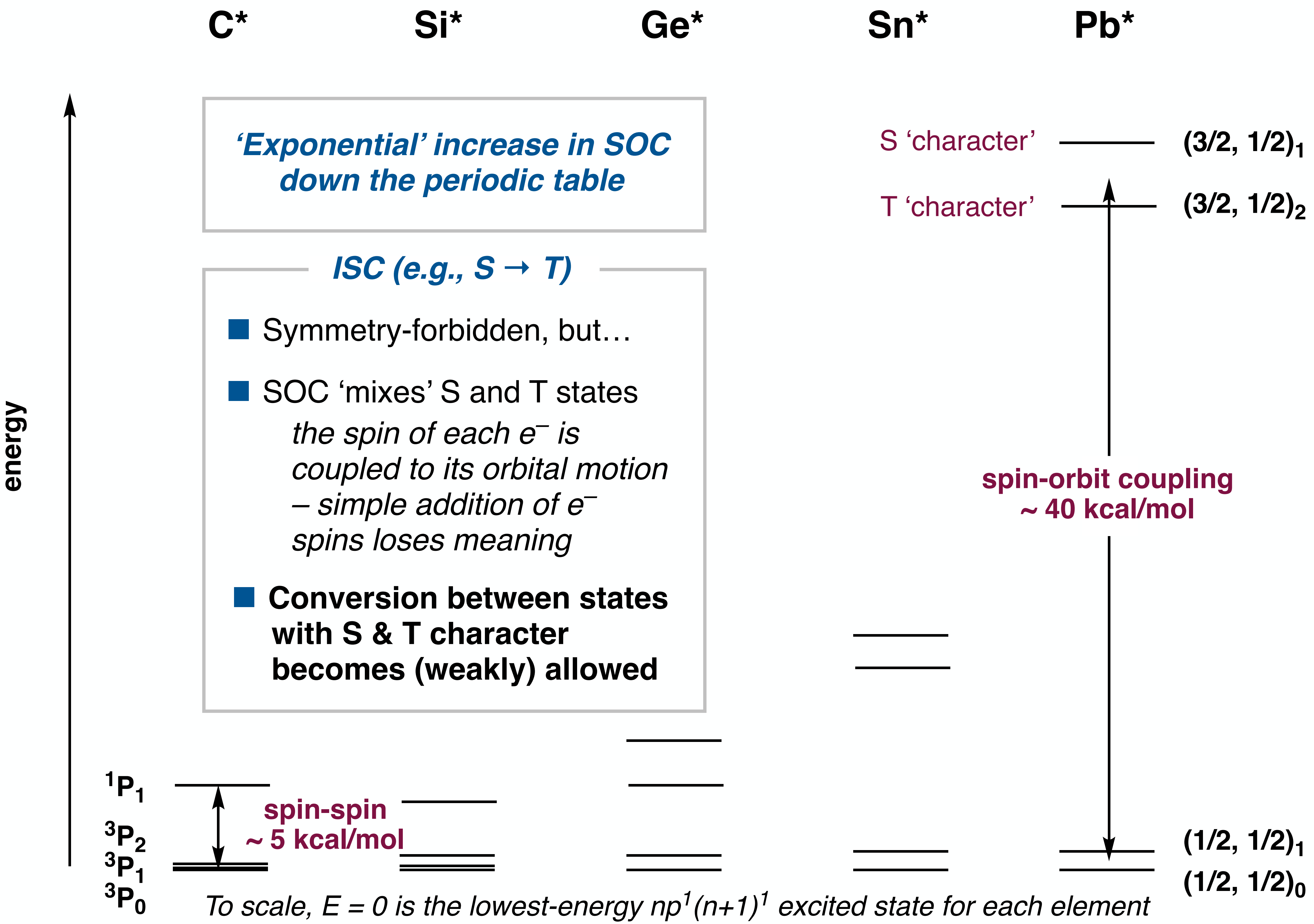
interactions between electrons are weak and only assessed by combining their TOTAL angular momenta

SOC dominates –
Interactions between electrons weak

1. Find possible j for each electron, gives first-order structure – (3/2, 1/2) & (1/2, 1/2)

2. Find J for the whole atom from each e⁻, predicts fine structure

'First' Excited States of Group 14 Elements



C* **Si*** **Ge*** **Sn*** **Pb***

'Exponential' increase in SOC down the periodic table

ISC (e.g., S → T)

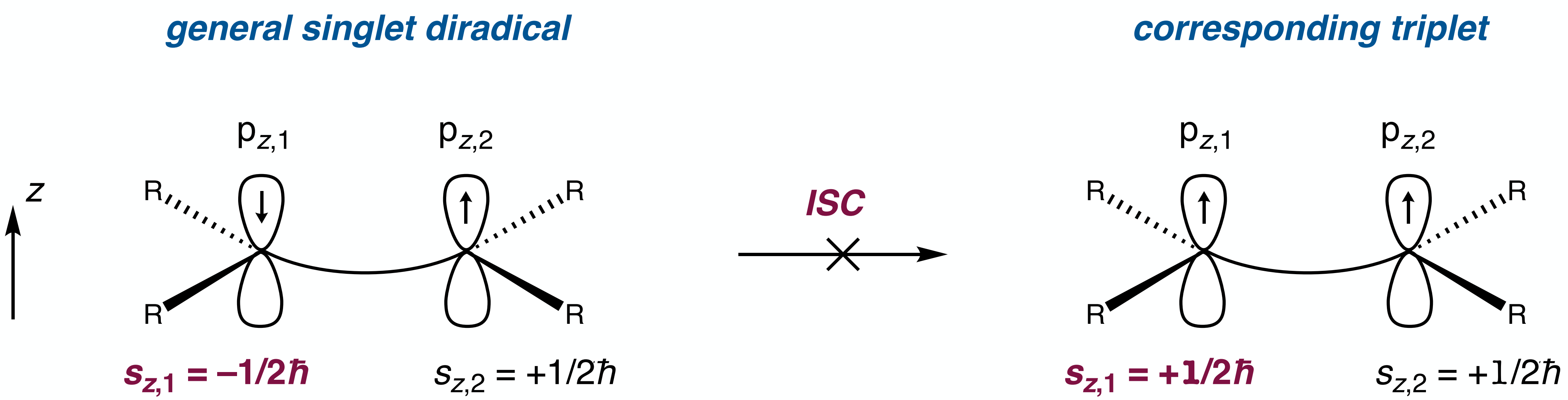
- Symmetry-forbidden, but…
- SOC 'mixes' S and T states
  the spin of each e⁻ is coupled to its orbital motion – simple addition of e⁻ spins loses meaning
- **Conversion between states with S & T character becomes (weakly) allowed**

To scale, E = 0 is the lowest-energy $np^1(n+1)^1$ excited state for each element

Adapted from physics.nist.gov

A Physical Model for Intersystem Crossing

- A change resulting in ISC must adhere to conservation laws



general singlet diradical

corresponding triplet

- Spin flip involves a change in the *z*-component of spin angular momentum
- Angular momentum must be conserved in every axis – no ISC ‘in isolation’ … but

Change in spin angular momentum can be offset by a change in orbital angular momentum

Turro, N. J.; Ramamurthy, V.; Scaiano, S. C. *Modern Molecular Photochemistry of Organic Molecules*, University Science Books, 2010.

A Physical Model for Intersystem Crossing

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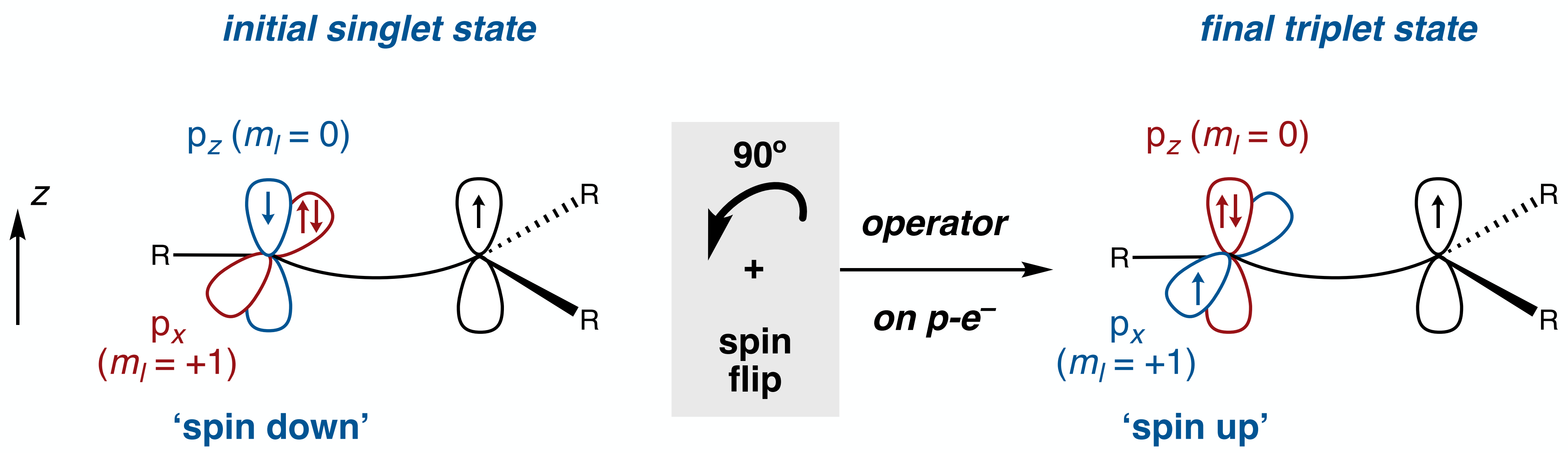
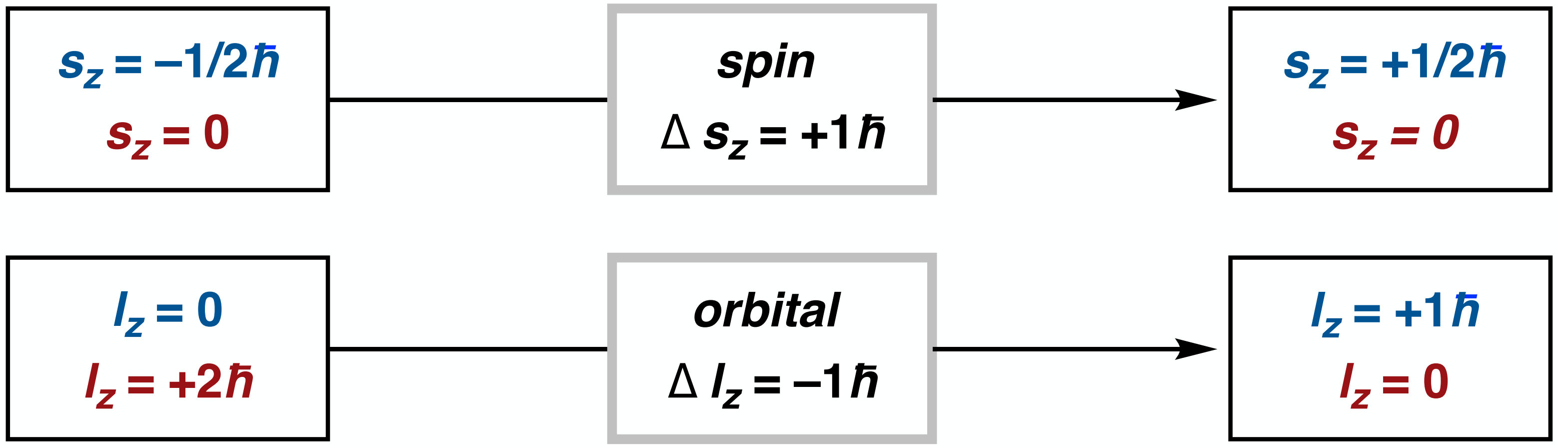


initial singlet state

final triplet state

Angular momentum balance sheet



$s_z = -1/2\hbar$
$s_z = 0$

spin
$\Delta s_z = +1\hbar$

$s_z = +1/2\hbar$
$s_z = 0$

$l_z = 0$
$l_z = +2\hbar$

orbital
$\Delta l_z = -1\hbar$

$l_z = +1\hbar$
$l_z = 0$

No change in total angular momentum

A Physical Model for Intersystem Crossing

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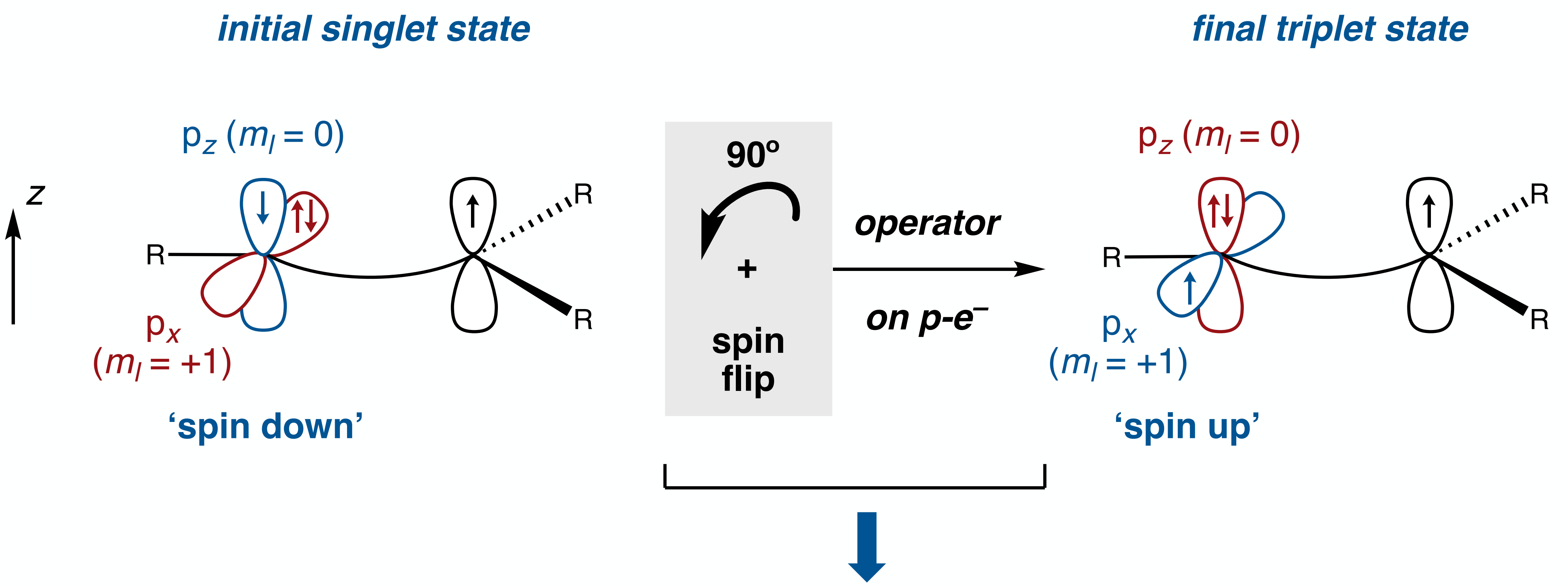

initial singlet state

‘spin down’

90°

+

spin flip

operator on p-e⁻

final triplet state

‘spin up’

This is the spin-orbit operator $\hat{H}_{SO}$

- $\hat{H}_{SO}$ enables ISC via the torque of electrons’ spin and orbital magnetic moments on each other
- Involves exchanging the orbital of the electron undergoing the spin flip with another orbital
  - Necessarily changes the (sub)-orbital of the electron undergoing the spin flip
- A few molecular features lead to faster ISC

A Physical Model for Intersystem Crossing

Probability of ISC increases as the term

$$\frac{<\psi_{init}\ |\ \hat{H}_{SO}\ |\ \psi_{final}>}{|\ E_{init} - E_{final}\ |}$$

becomes large for any possible H_{so}

DOES NOT NEED TO BE A 90^{o} ROTATION

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$$\frac{<\psi_{init}\,|\,\hat{H}_{SO}\,|\,\psi_{final}>}{|\,E_{init}-E_{final}\,|}$$

becomes large for any possible H_{so}

Factors that promote faster ISC via $\hat{H}_{SO}$

- Initial and final states should look as similar as possible
  - Orbitals being exchanged need similar shapes (ignoring orientation)
  - Orbitals being exchanged need similar energies
- Electron velocity should be as high as possible (maximizes μ_l to torque μ_s)
  - MO containing the e^- of interest should contain a heavy atom (Z^4 term)
  - MO can also be highly localized (e^- always near a nucleus, even if light)

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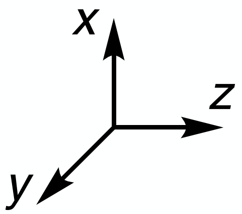
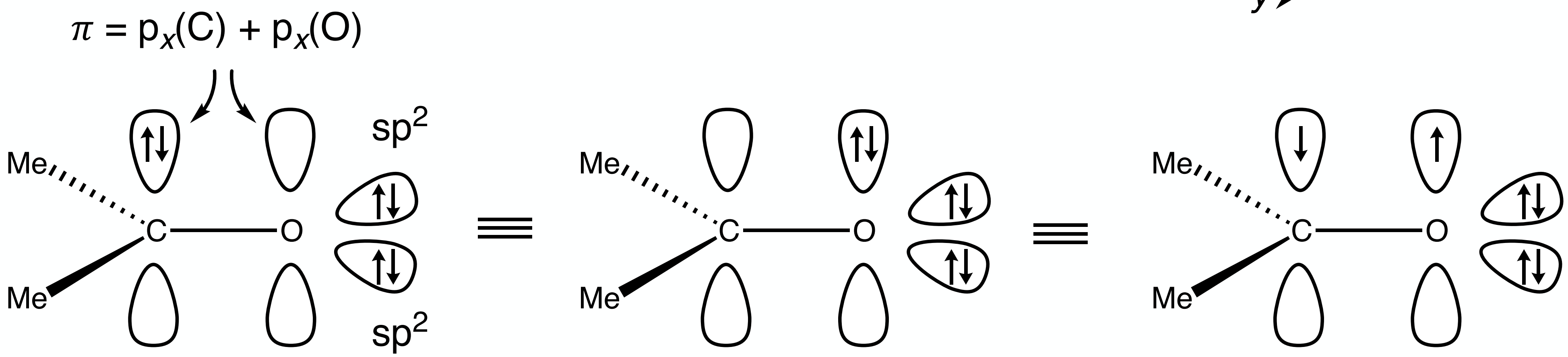
An Example of ISC via $\hat{H}_{SO}$

- MO representations of ground and excited states of acetone

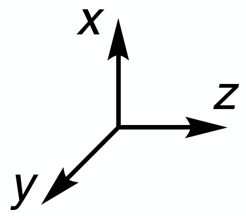


Ground state



- π MO depicted as constituent p orbitals to clarify symmetry
- Depictions showing electron(s) in either constituent p orbital are equivalent

An Example of ISC via $\hat{H}_{SO}$



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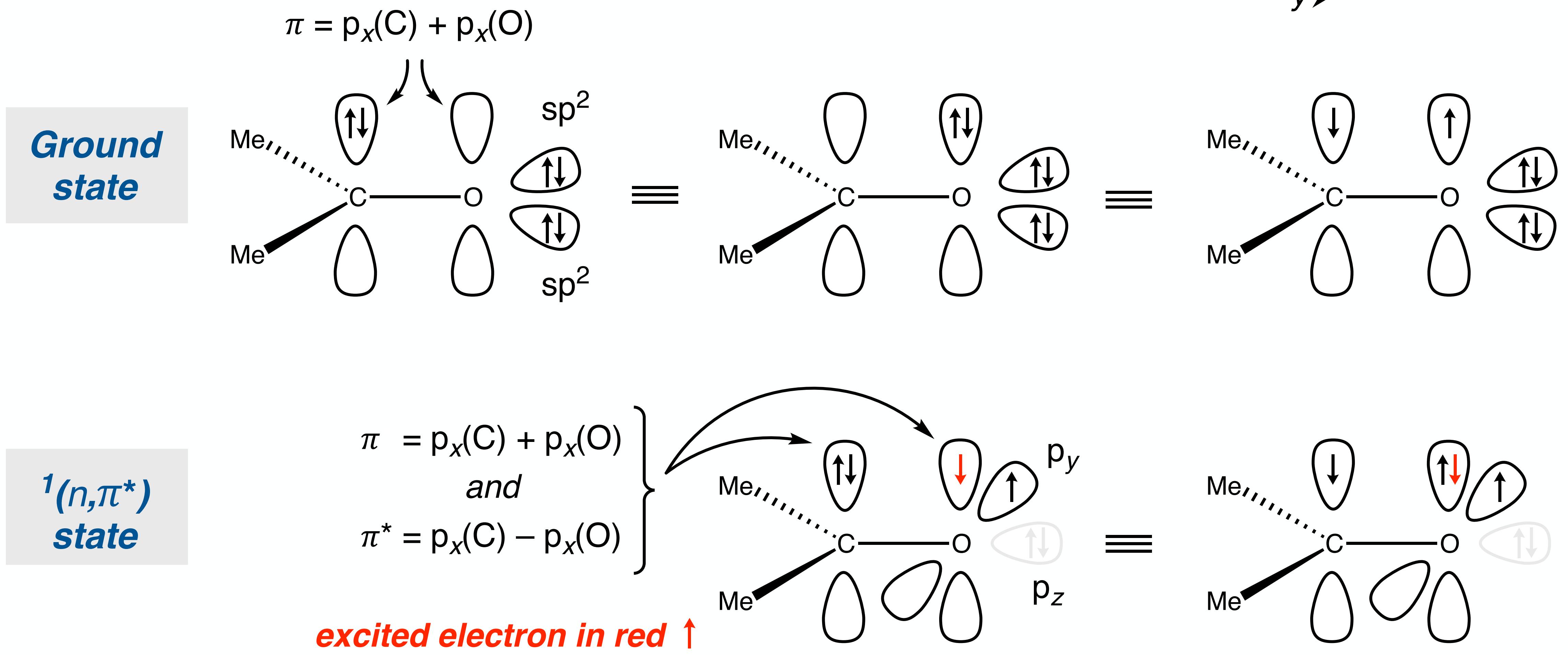


$\pi = p_x(C) + p_x(O)$

Ground state

^{1}(n,π*) state

$\pi \; = p_x(C) + p_x(O)$

and

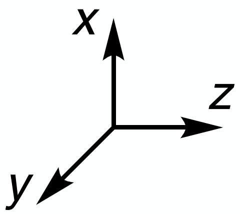
$\pi^* = p_x(C) - p_x(O)$

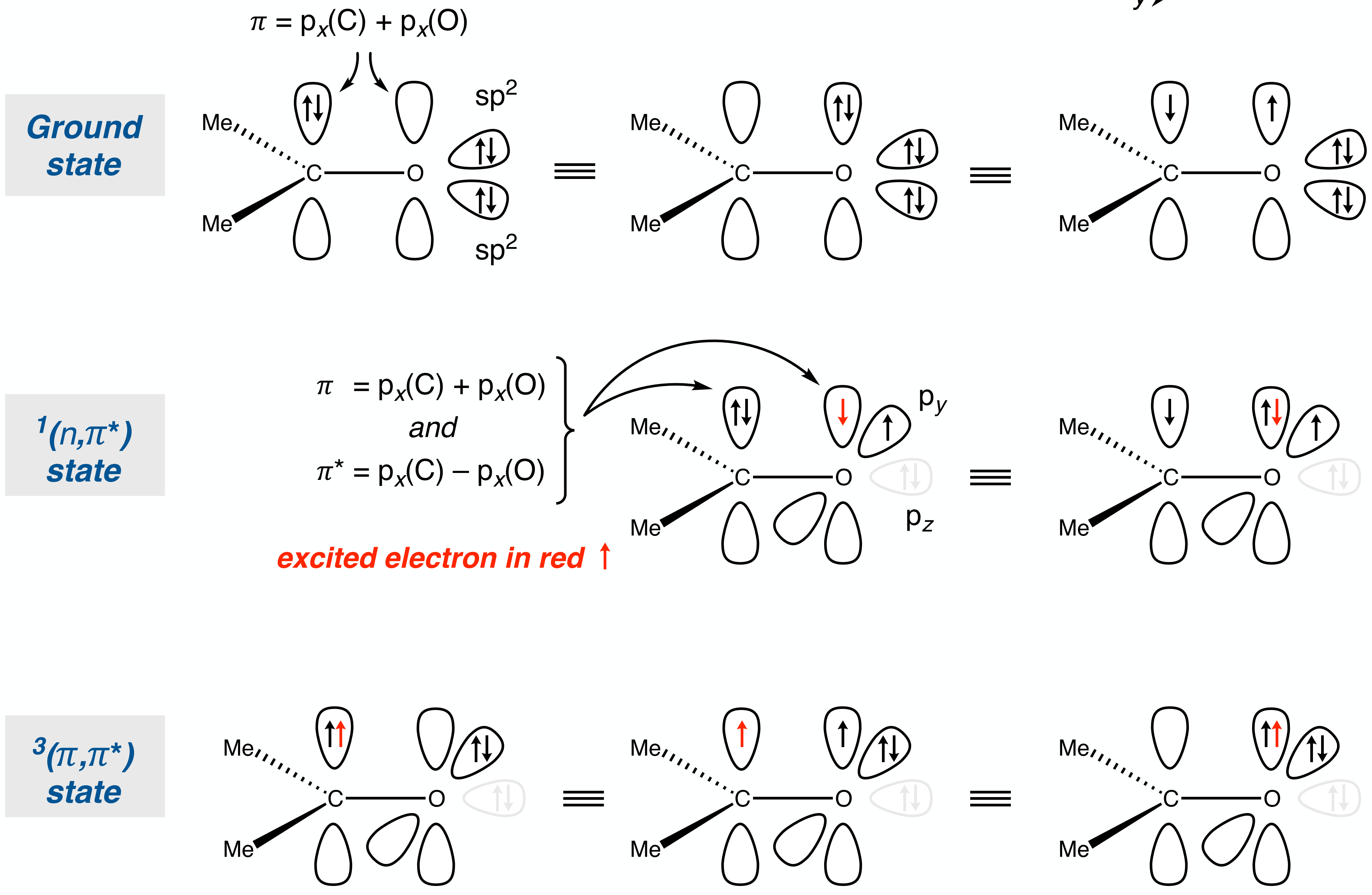
excited electron in red ↑

- π and π^* MOs lumped together to simplify symmetry
- Consider electrons in π and π^* MOs independently

An Example of ISC via $\hat{H}_{SO}$

- MO representations of ground and excited states of acetone





$\pi = p_x(C) + p_x(O)$

Ground state

$^1(n,\pi^*)$ state

$\pi \ = p_x(C) + p_x(O)$

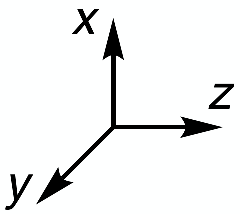
and

$\pi^* = p_x(C) - p_x(O)$

excited electron in red ↑

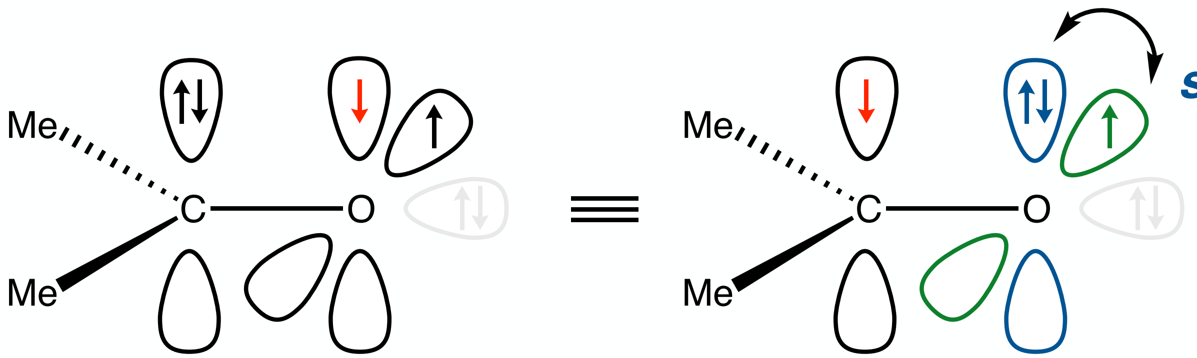
$^3(\pi,\pi^*)$ state

An Example of ISC via $\hat{H}_{SO}$



- Illustration of the symmetry considerations needed for ISC:
- If acetone is initially excited to a $^1(n,\pi^*)$ state, what triplet state may it relax to?

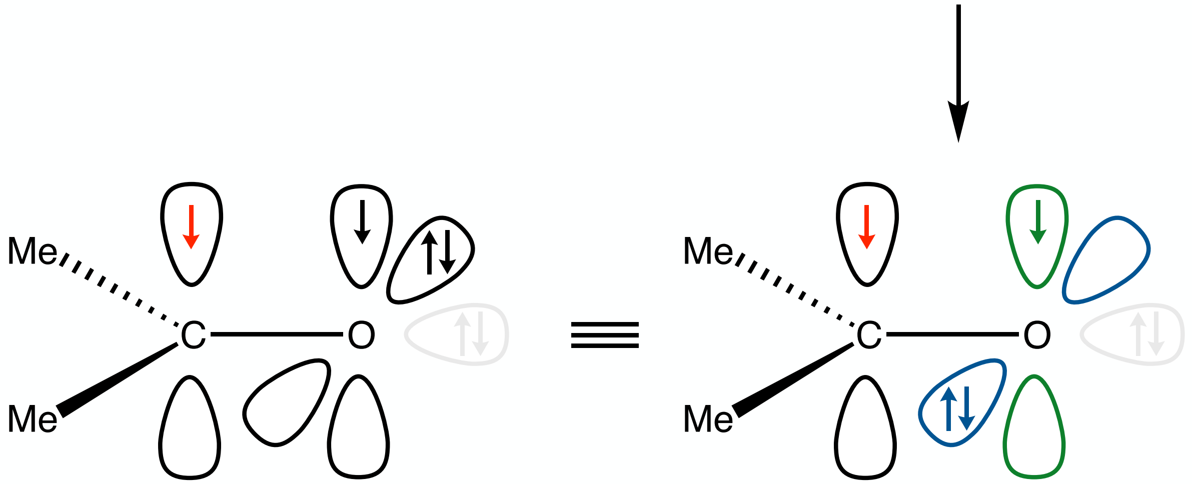
$^1(n,\pi^*)$ state



Exchange these orbitals & spin flip using this depiction

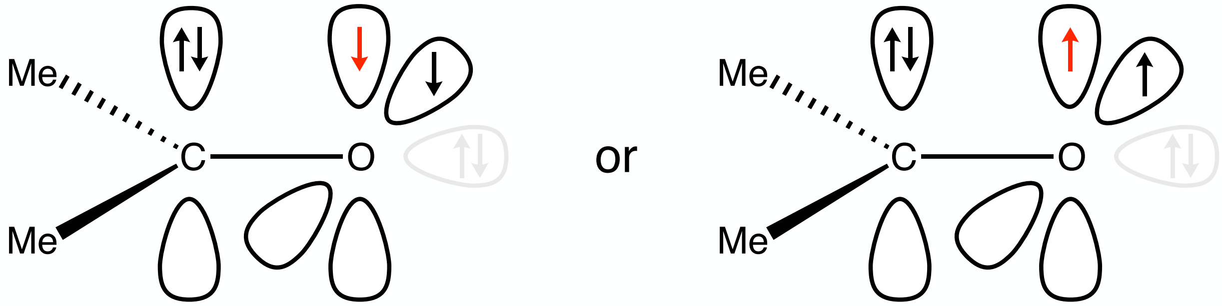
- Net transfer of e^- between m_l levels
- Unpaired e^- can undergo spin flip
- Simplifies the picture to 1 atom

$^3(\pi,\pi^*)$ state



Possible without a heavy atom since the MO is highly localized

$^3(n,\pi^*)$ state

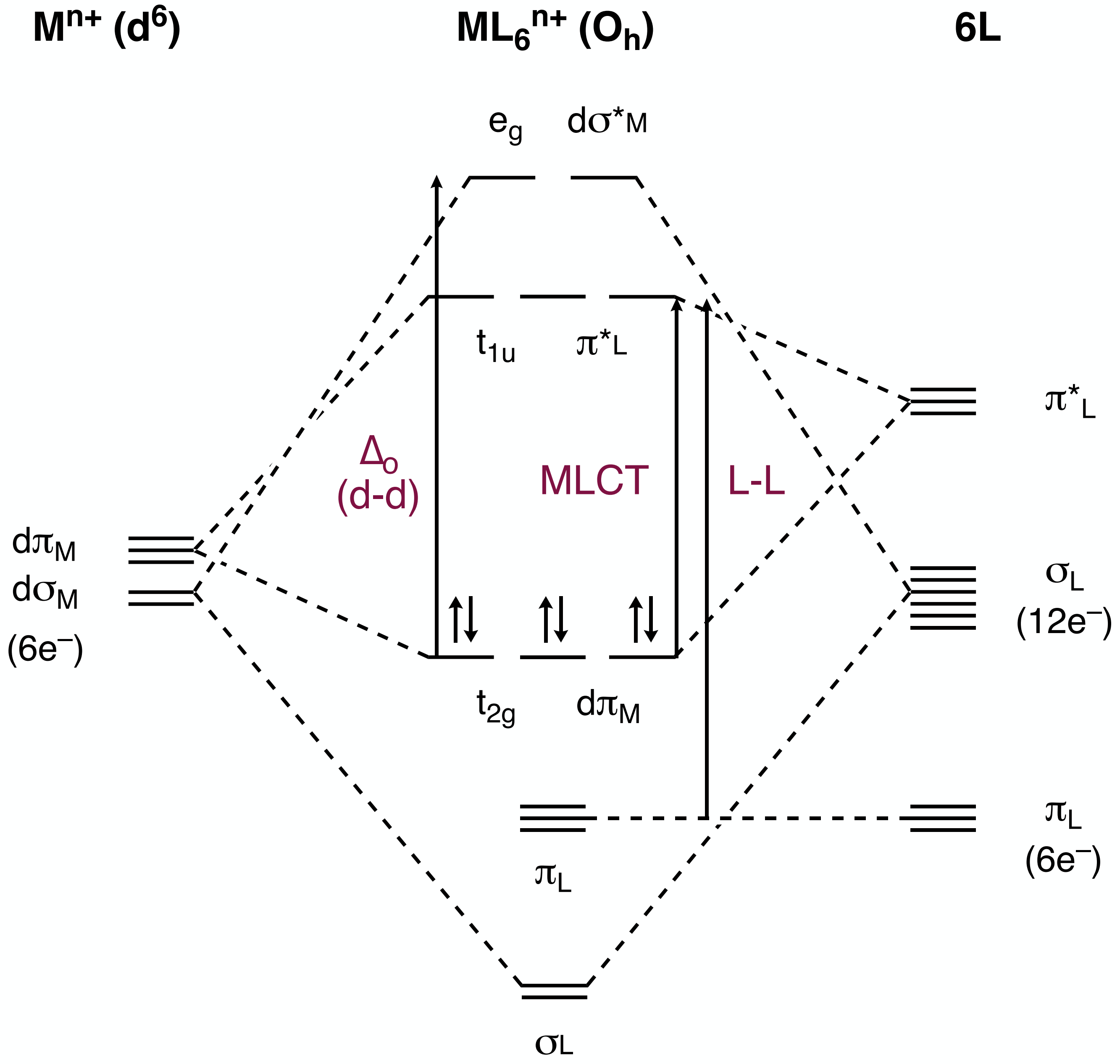


Not directly accessible via ISC

- Requires spin flip *without* changing the orbital angular momentum

Energies of Inorganic Complexes

- Simplified MO diagram and SOC analysis explains much of why Ir complexes are priveleged
- As a starting point (and for clarity), consider a d^6 octahedral complex, e.g., $M(py)_6^{n+}$



Key points on energies

- Ideal hierarchy is depicted
- **MLCT** excited with visible/near-UV light
  Involvement of heavy M enables SOC, ISC
  d-d states may have issues with e^- transfer
  L-L states do not involve M, have low SOC
- MLCT is not useful if its energy is too low
  A problem for many Rh, Os catalysts
- L-L states interfere if $d\pi_M$ too low/π_L too high
- Small Δ_o leads to low-energy d-d states
  A problem for many 3rd-row catalysts
- Low-*E* L-L or d-d states deactivate MLCT states and have too little energy to be useful themselves

"Photochemistry and Photophysics of Coordination Compounds II." Balzani, V.; Campagna, S.; eds. *Top. Curr. Chem.* **2007**, *281*.

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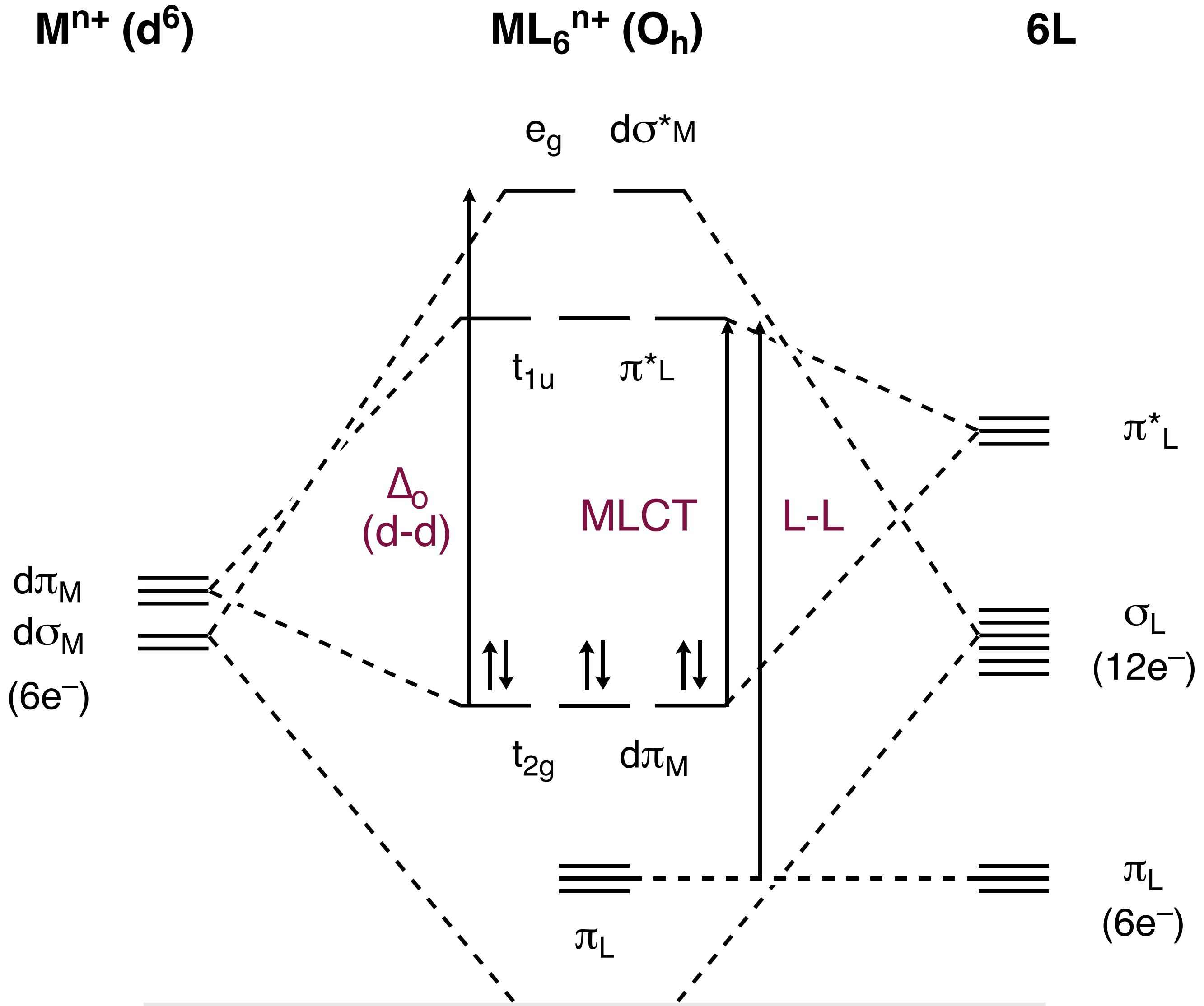

Ir catalysts generally have this ordering (as do other classes of photocatalysts)

Key points on energies

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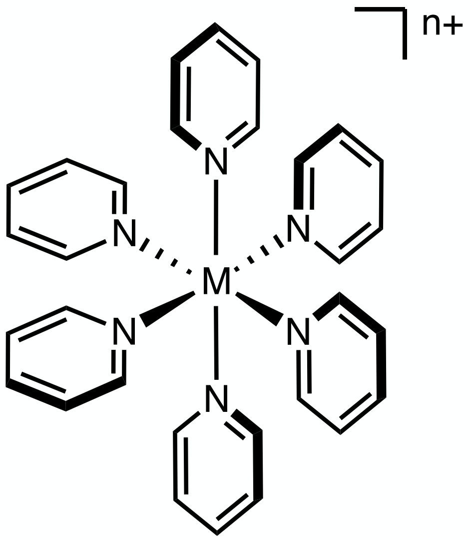
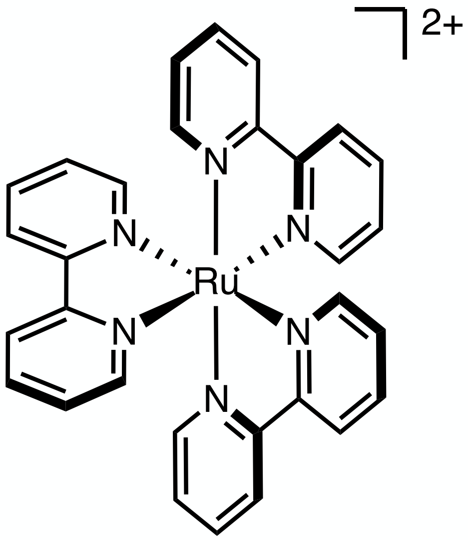
Energies of Inorganic Complexes

- Simplified MO diagram and SOC analysis explains much of why Ir complexes are priveleged
- Real 6-coordinate complexes have lower symmetry, but O_h is a reasonable approximation

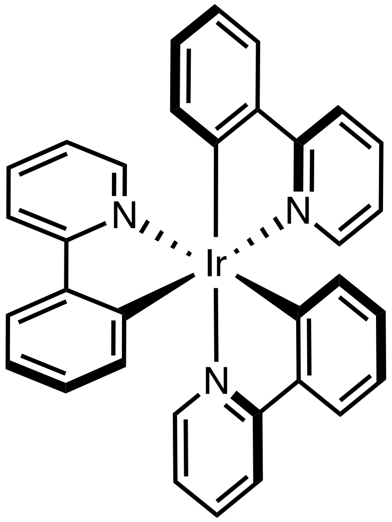
ML_6^{n+} (O_h)



$Ru(bpy)_3^{2+}$ (D_3)



$Ir(ppy)_3$ (C_3)



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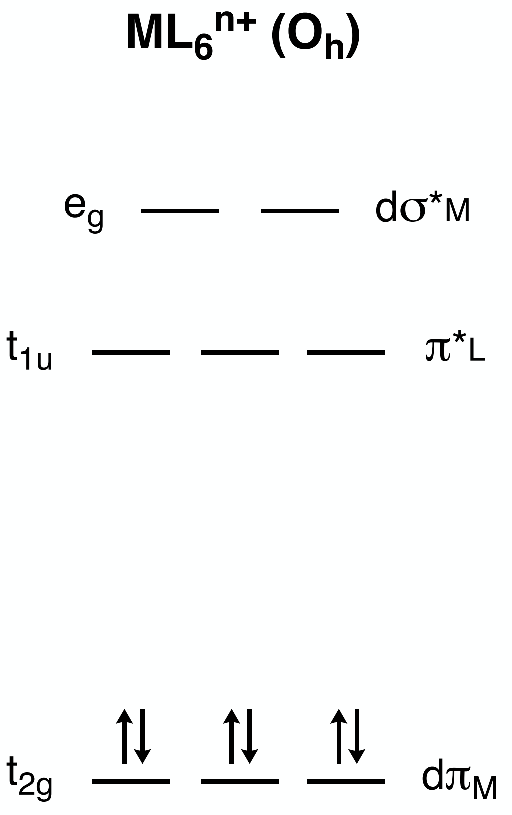
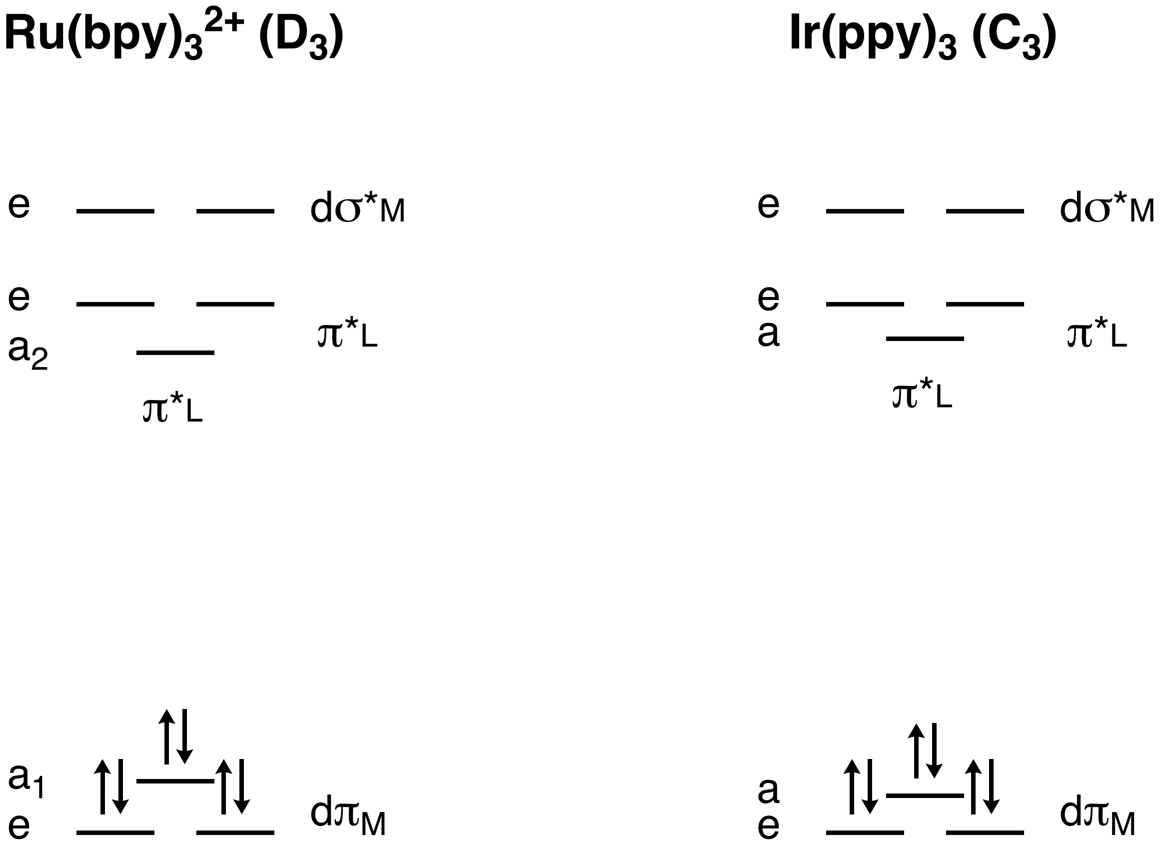


ML_6^{n+} (O_h)



$Ru(bpy)_3^{2+}$ (D_3)

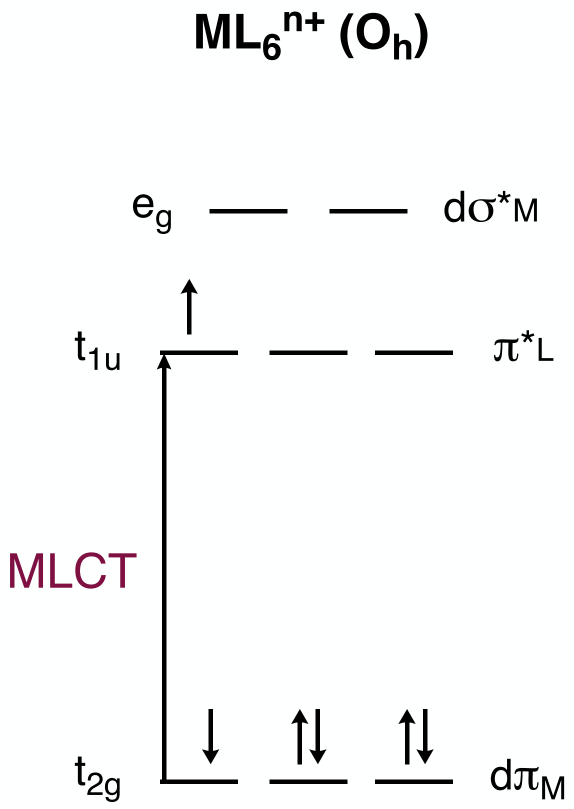
$Ir(ppy)_3$ (C_3)

pseudo-octahedral complexes

Descent in symmetry can be treated as a perturbation

Intersystem Crossing in Octahedral Inorganic Complexes

- Simplified MO diagram and SOC analysis explains much of why Ir complexes are priveleged
- Following MLCT, consider the SOC interaction needed to facilitate ISC from S_1 to T_1



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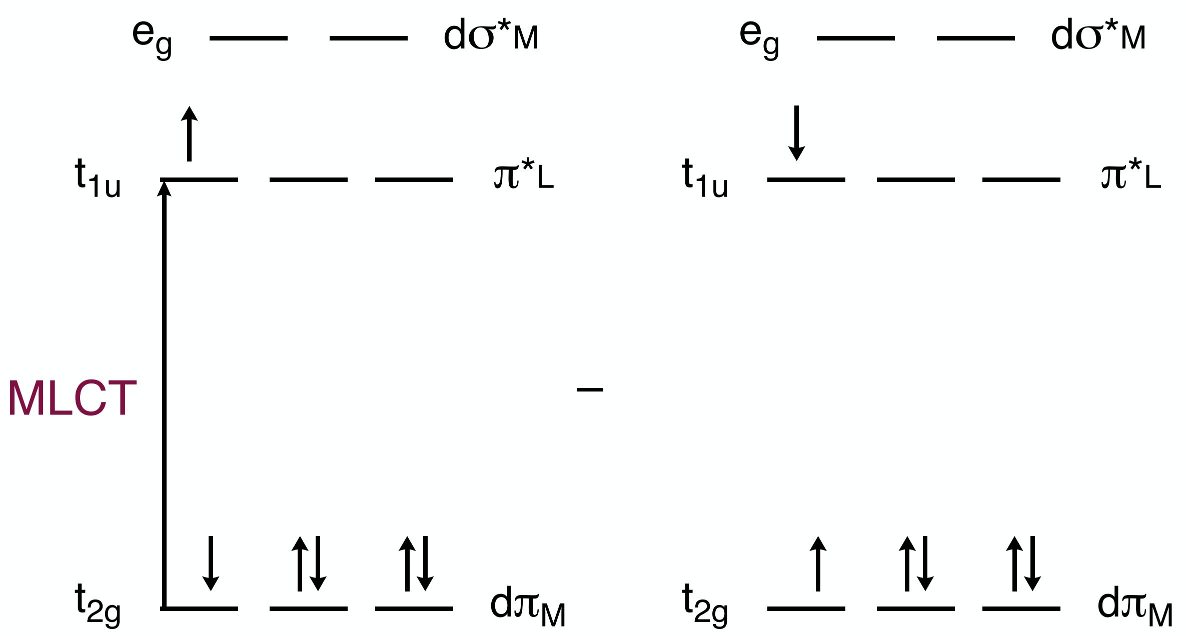

This is a better representation of S_1

- The corresponding sum is a substate of T_1, along with the 'two up' and 'two down' states
- We will neglect this detail for clarity

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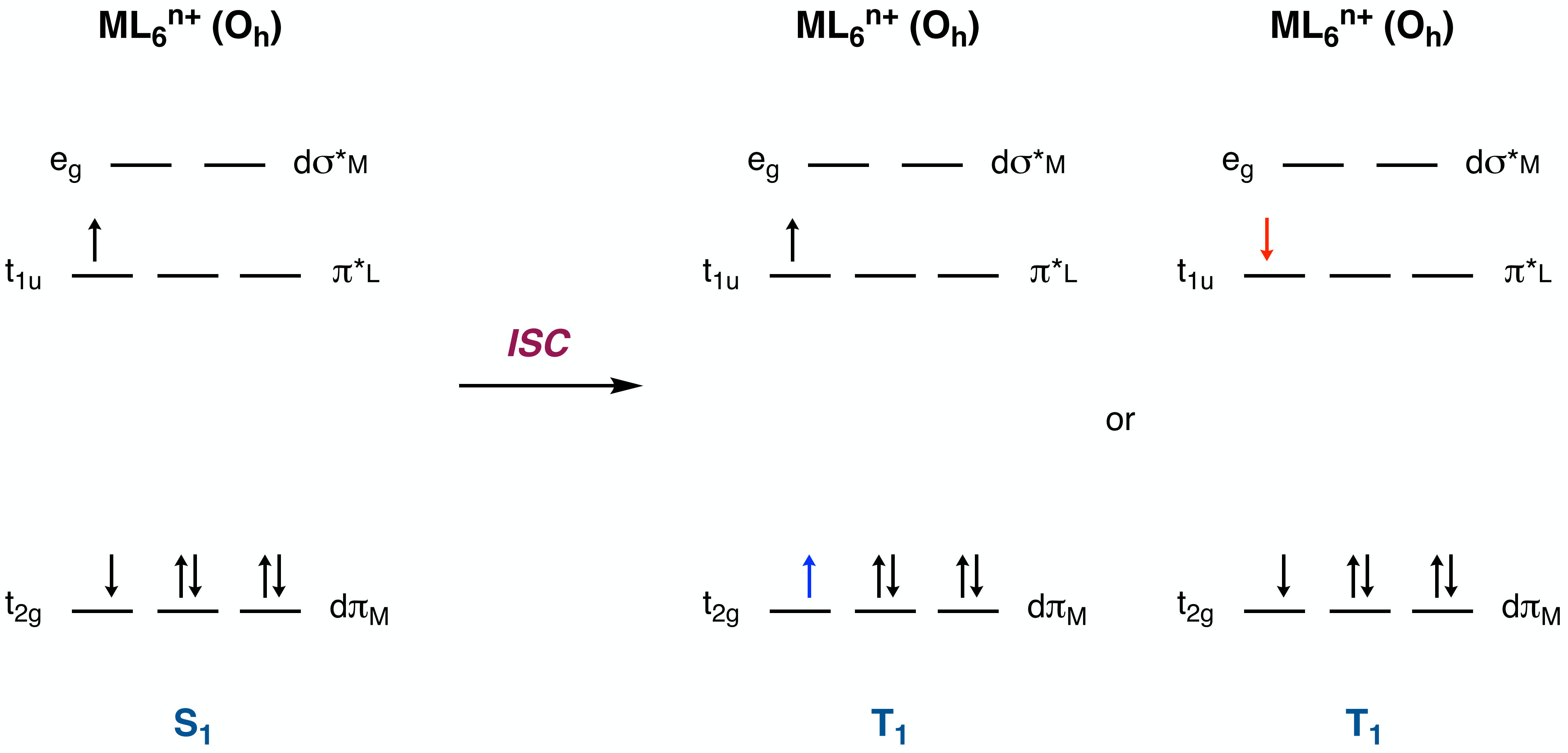
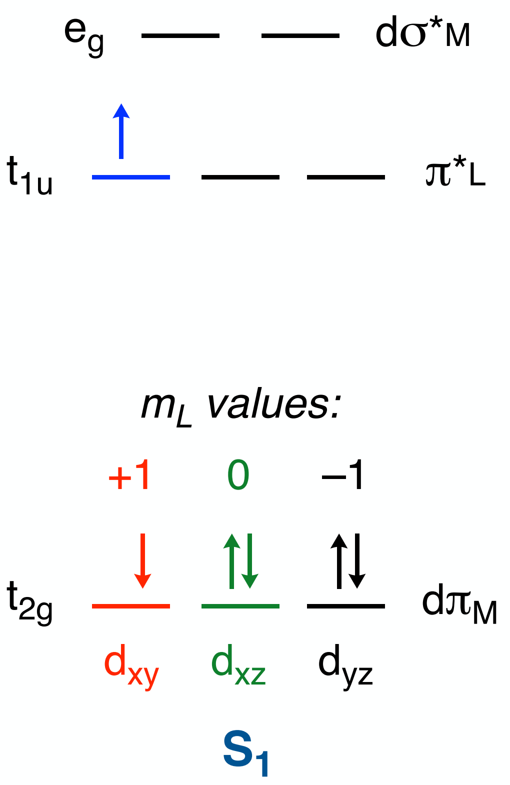


What is the mechanism of the spin flip?

Intersystem Crossing in Octahedral Inorganic Complexes

- Simplified MO diagram and SOC analysis explains much of why Ir complexes are priveleged
- Following MLCT, consider the SOC interaction needed to facilitate ISC from S_1 to T_1
  - Need a spin flip AND a change in orbital angular momentum by net e^- transfer between orbitals
  - The orbitals should be metal-centered, have similar shapes and energies, but different m_L values



e_g $d\sigma^*_M$

t_{1u} π^*_L

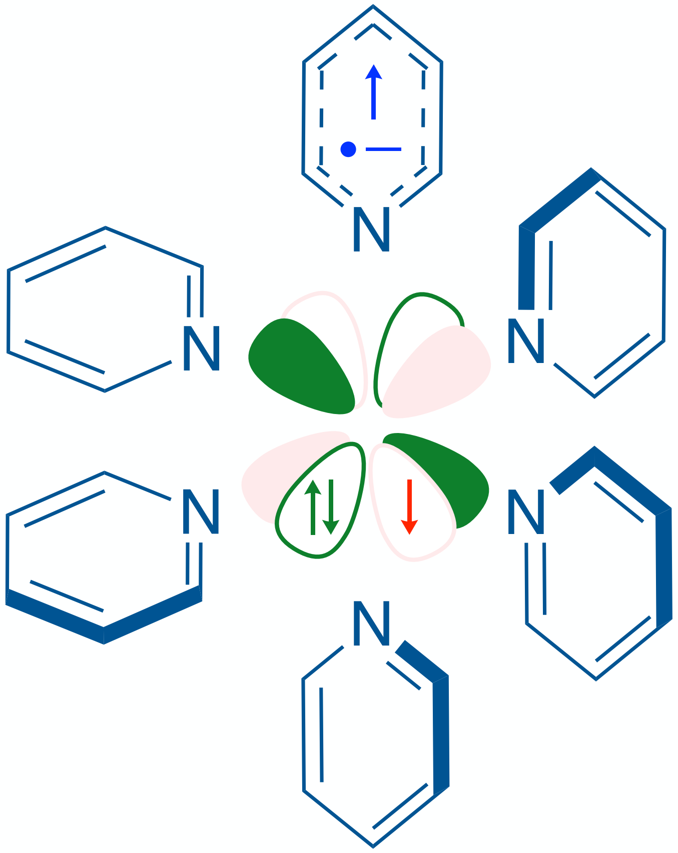
m_L values:

+1 0 −1

t_{2g} $d\pi_M$

d_{xy} d_{xz} d_{yz}

S_1



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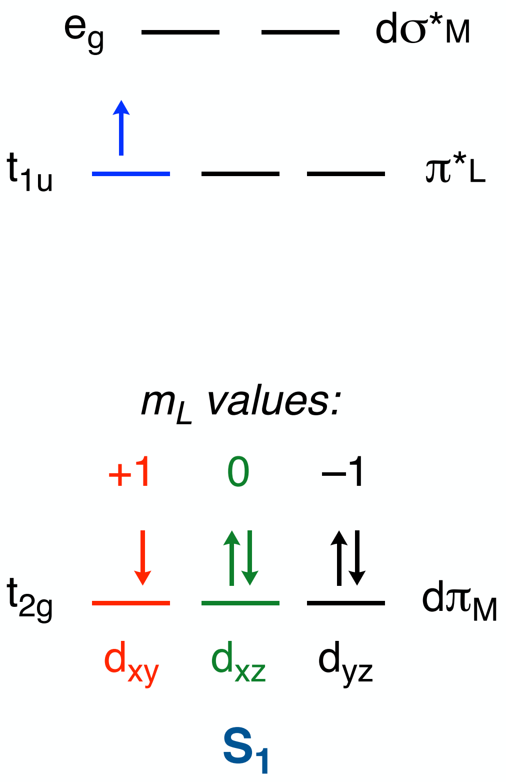

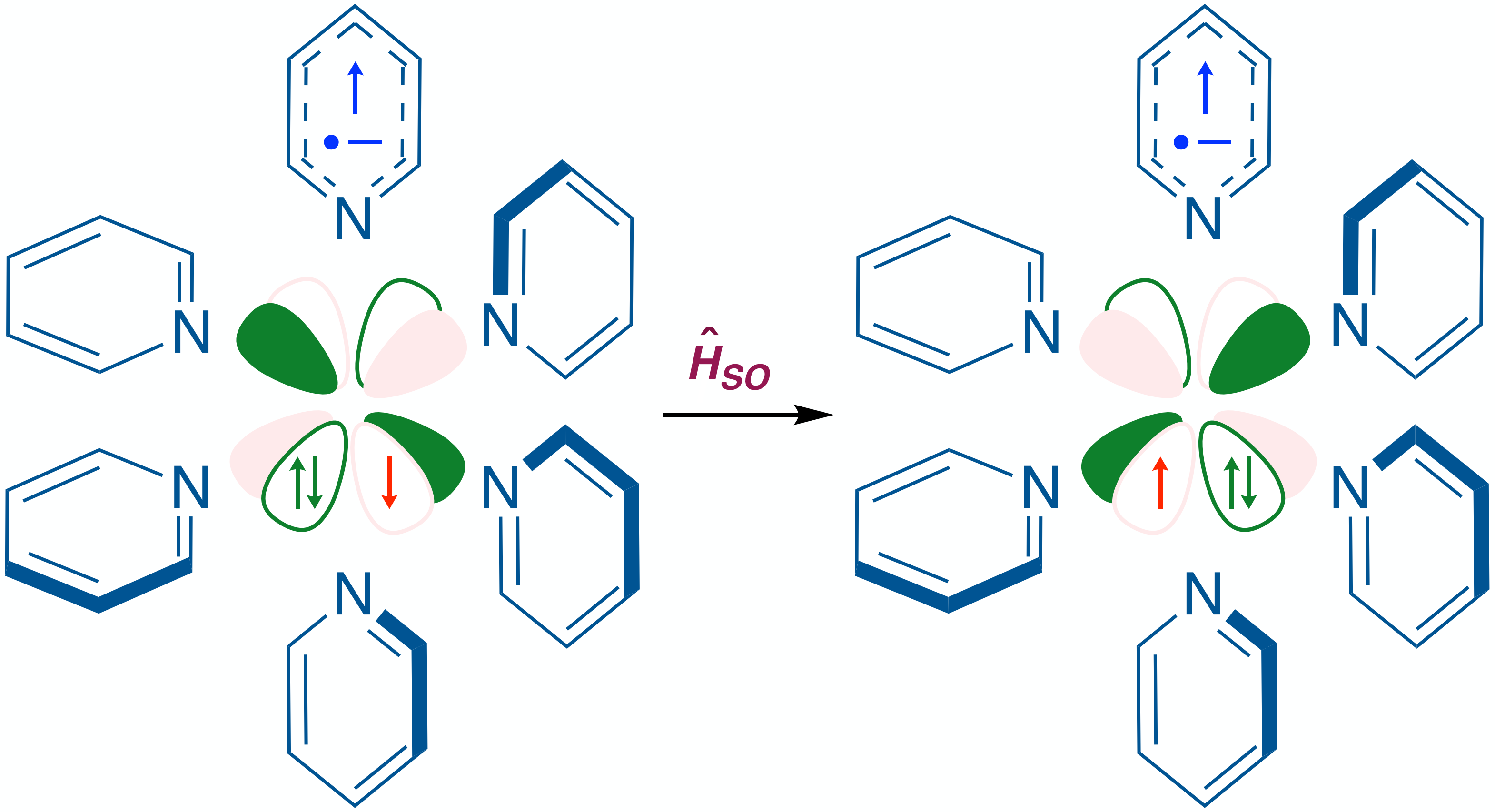

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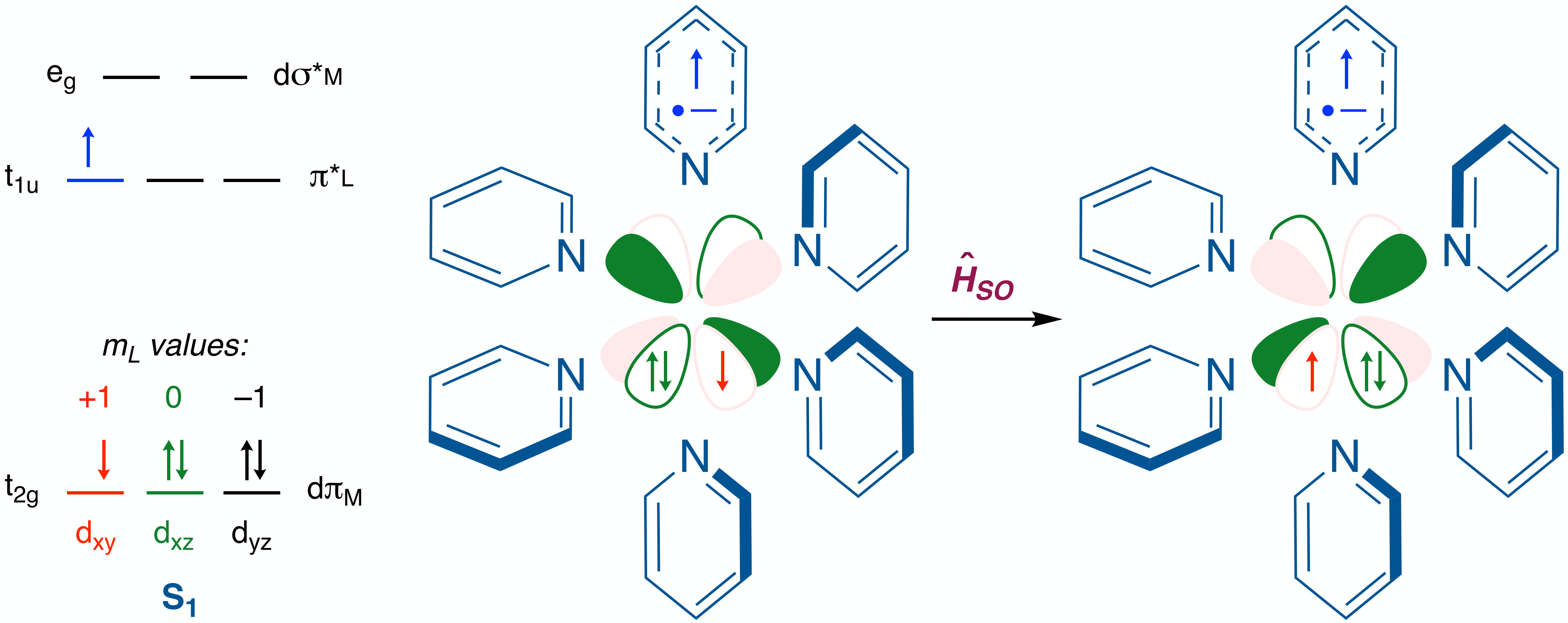

Disclaimer for the rest of this presentation: in molecules, metal-centered MOs are not individual d_{xy}, d_{xz}, and d_{yz} orbitals but appropriate linear combinations of these (in addition to ligand contributions) with m_L values that increment by 1, but we are simplifying these MOs to pure d orbitals for clarity

Intersystem Crossing in Octahedral Inorganic Complexes

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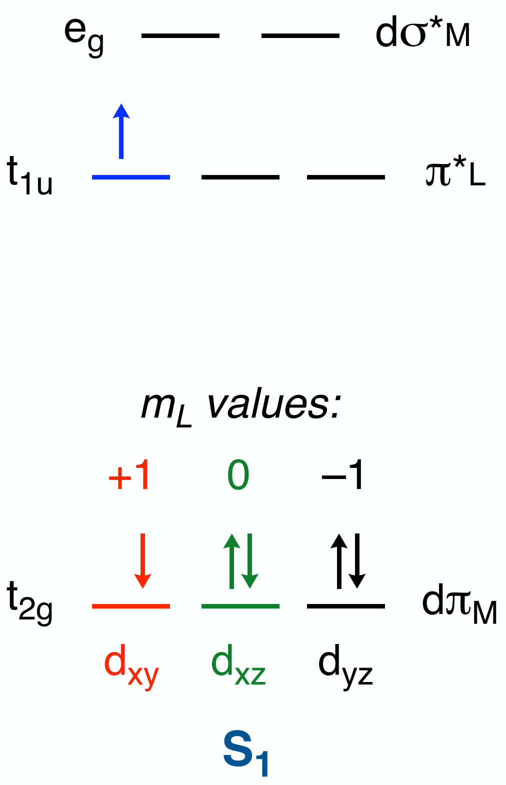

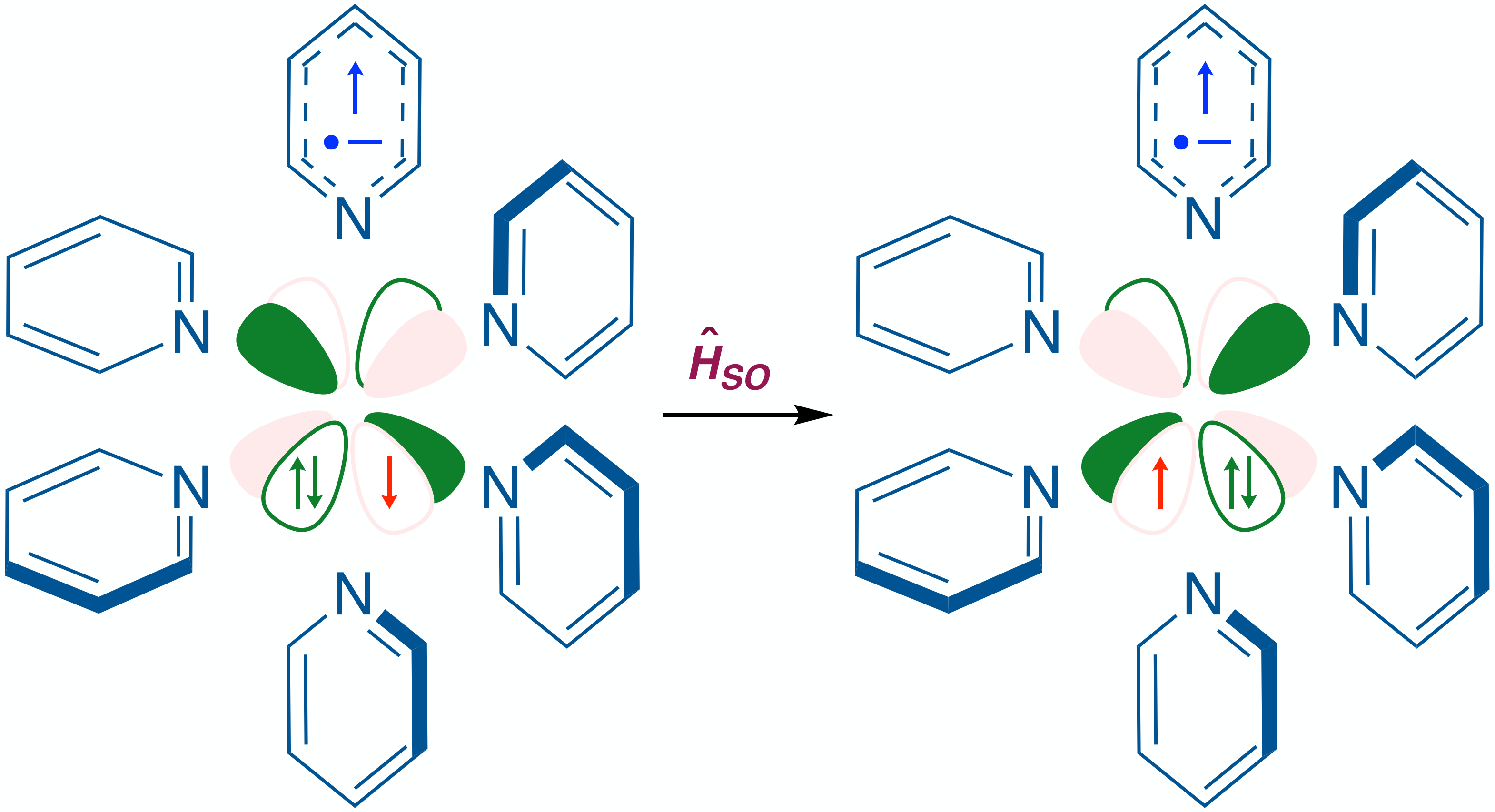

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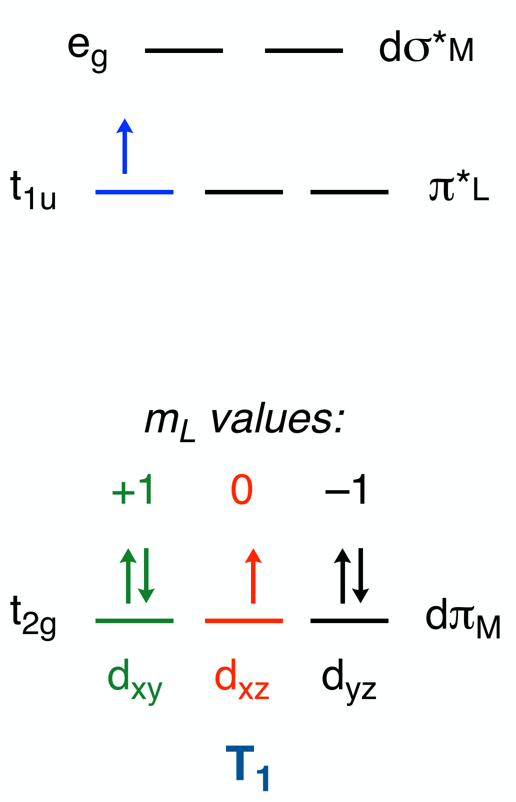
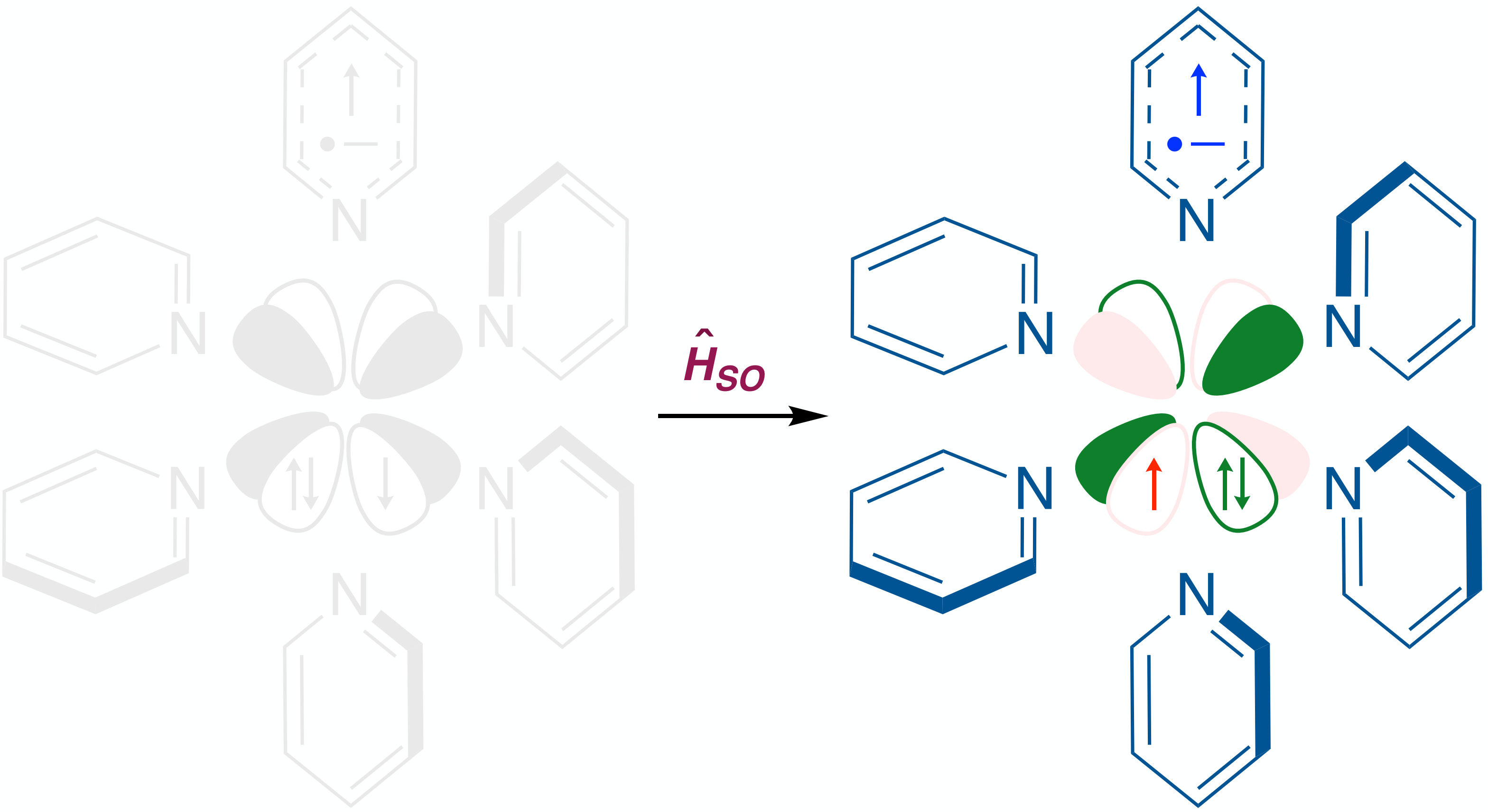
  - The orbitals should be metal-centered, have similar shapes and energies, but different m_L values





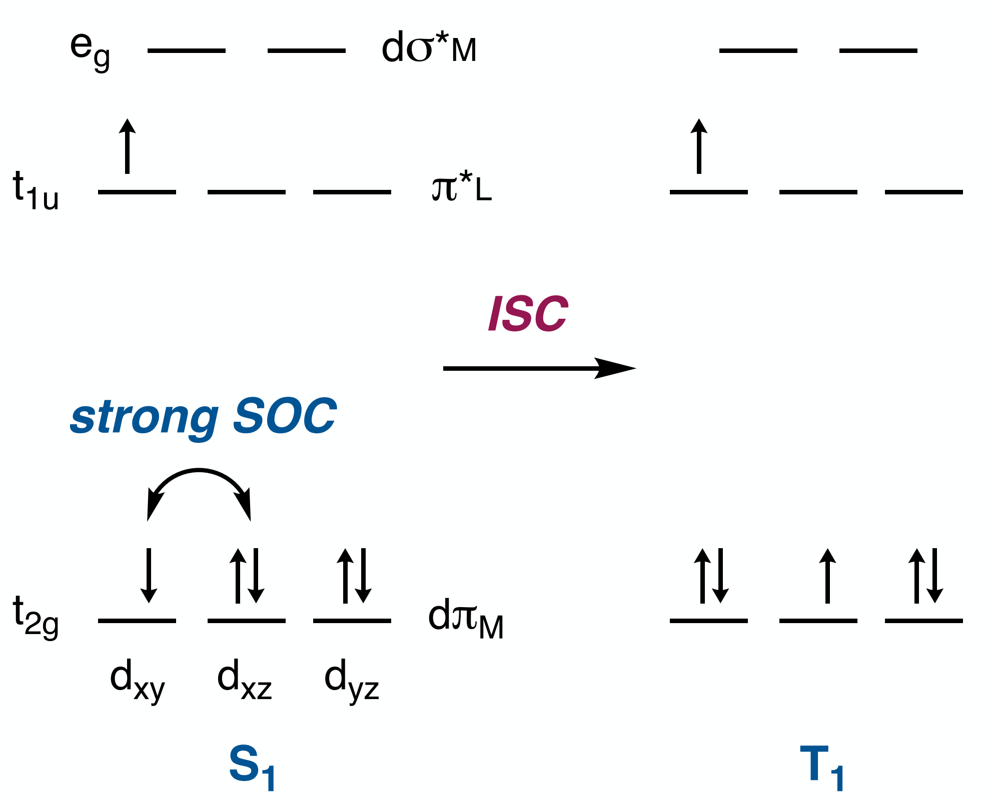
SOC enables ISC in pseudo-octahedral complexes

- Spin flip changes spin angular momentum by 1 unit
- Swapping of t_{2g} orbitals differing by 1 level of orbital angular momentum (*L*) and by 1 e$^-$ causes an offsetting change in *L*
- **Strong SOC – at metal, orbitals have same shape and energy**

Intersystem Crossing in Square Planar Inorganic Complexes

- Simplified MO diagram and SOC analysis explains much of why Ir complexes are priveleged
- **Compare octahedral geometry to square planar**

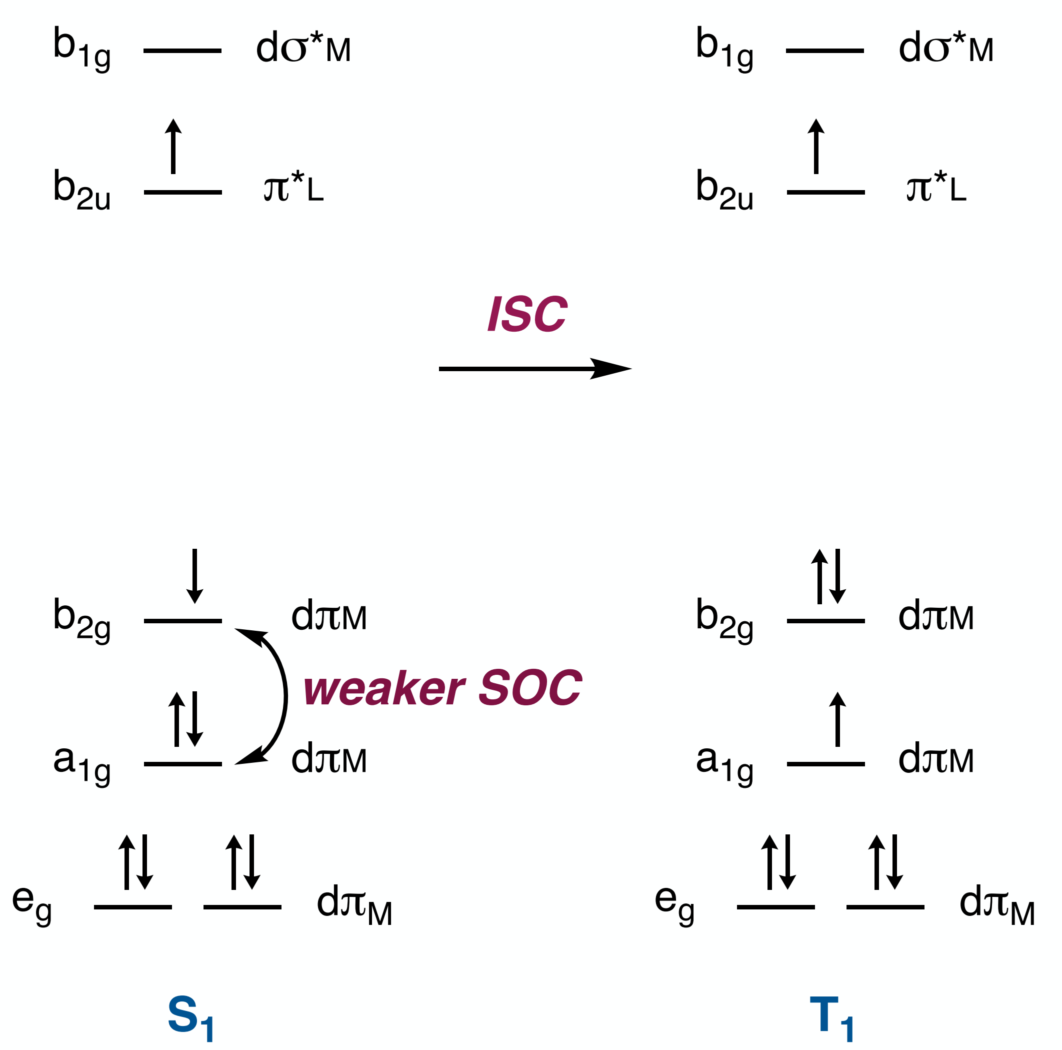
ML_6^{n+} (O_h)



At metal, orbitals have same shape & energy

SOC is weaker in square planar complexes

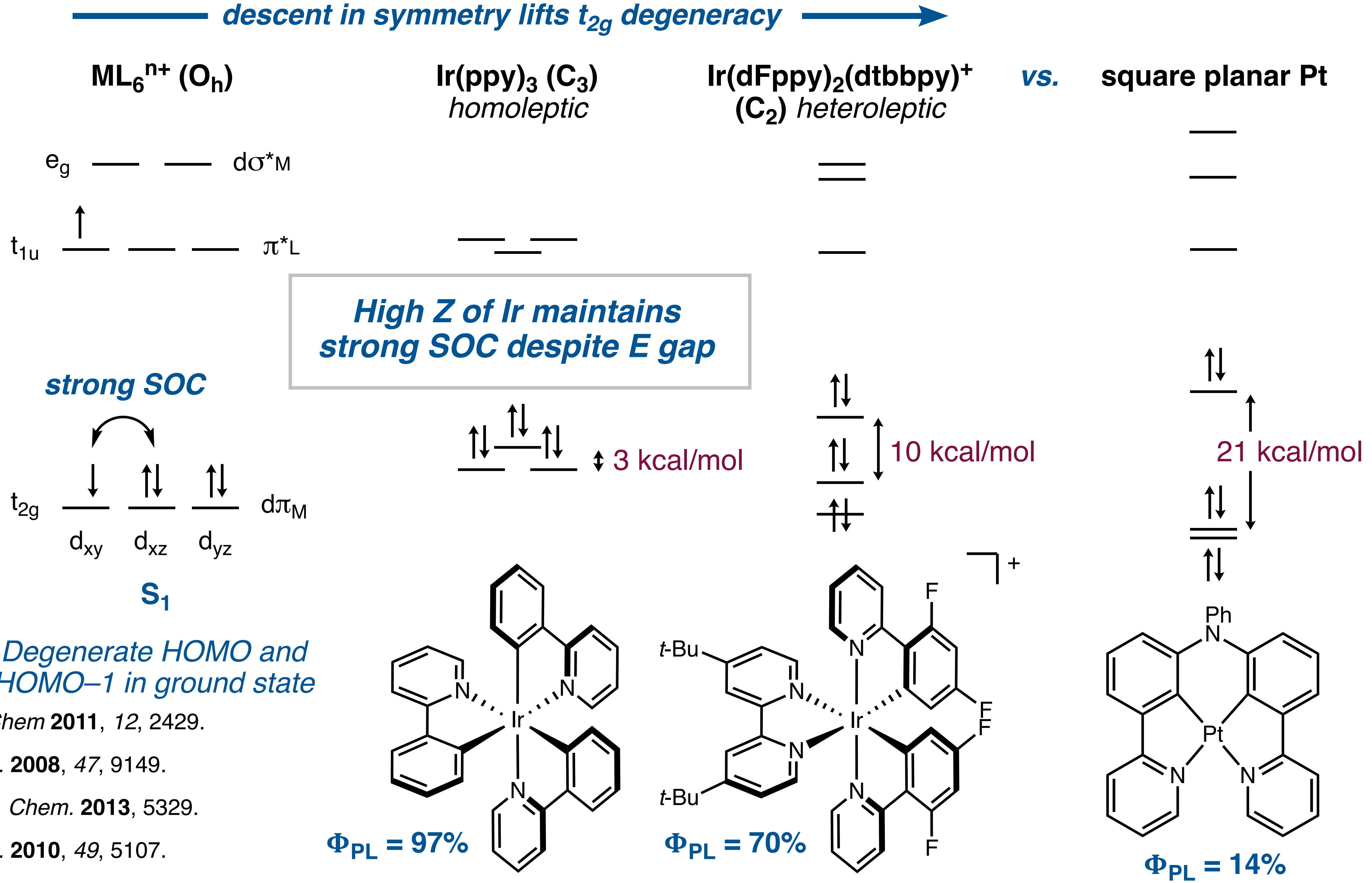
ML_4^{n+} (D_{4h})



Relevant orbitals have a significant energy gap

Intersystem Crossing in Square Planar Inorganic Complexes

- Simplified MO diagram and SOC analysis explains much of why Ir complexes are priveleged
- Some examples of the HOMO and HOMO–1 energy gaps in photocatalysts



descent in symmetry lifts t_{2g} degeneracy

ML_6^{n+} (O_h)

$Ir(ppy)_3$ (C_3) *homoleptic*

$Ir(dFppy)_2(dtbbpy)^+$ (C_2) *heteroleptic*

vs.

square planar Pt

High Z of Ir maintains strong SOC despite E gap

strong SOC

S_1

Degenerate HOMO and HOMO–1 in ground state

Φ_{PL} = 97%

Φ_{PL} = 70%

Φ_{PL} = 14%

ChemPhysChem **2011**, *12*, 2429.

Inorg. Chem. **2008**, *47*, 9149.

Eur. J. Inorg. Chem. **2013**, 5329.

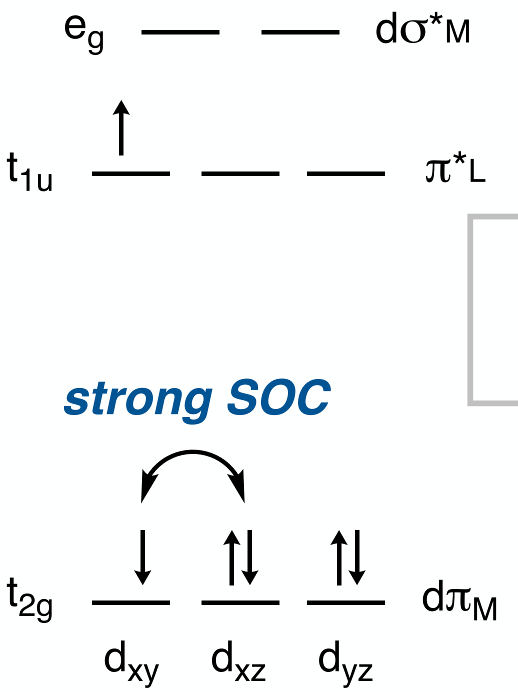
Inorg. Chem. **2010**, *49*, 5107.

Intersystem Crossing in Square Planar Inorganic Complexes

- Simplified MO diagram and SOC analysis explains much of why Ir complexes are priveleged
- Some examples of the HOMO and HOMO–1 energy gaps in photocatalysts

descent in symmetry lifts t_{2g} degeneracy →

ML_6^{n+} (O_h)



S_1

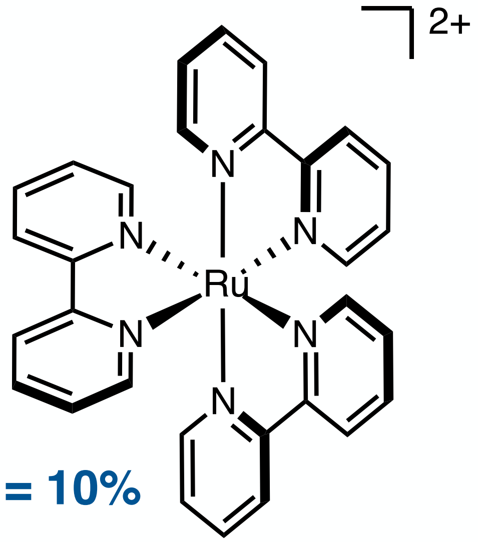
Degenerate HOMO and HOMO–1 in ground state

$Ru(bpy)_3^{2+}$ (D_3)
homoleptic

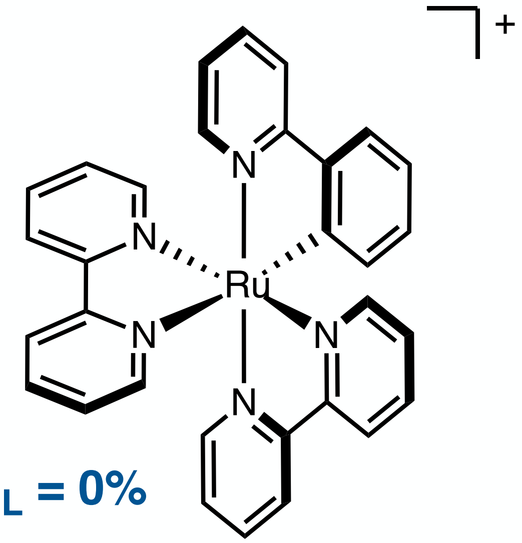
$Ru(ppy)(bpy)_2^+$
(C_1) *heteroleptic*

Heteroleptic Ru (lower Z than Ir) is not emissive

NOTE: luminescence yield is a very imperfect metric for ISC yield due to radiationless deactivation pathways (ISC efficiency for $Ru(bpy)_3^{2+}$ is near unity, for example), but the trends within groups can be taken as suggestive



Φ_{PL} = 10%



Φ_{PL} = 0%

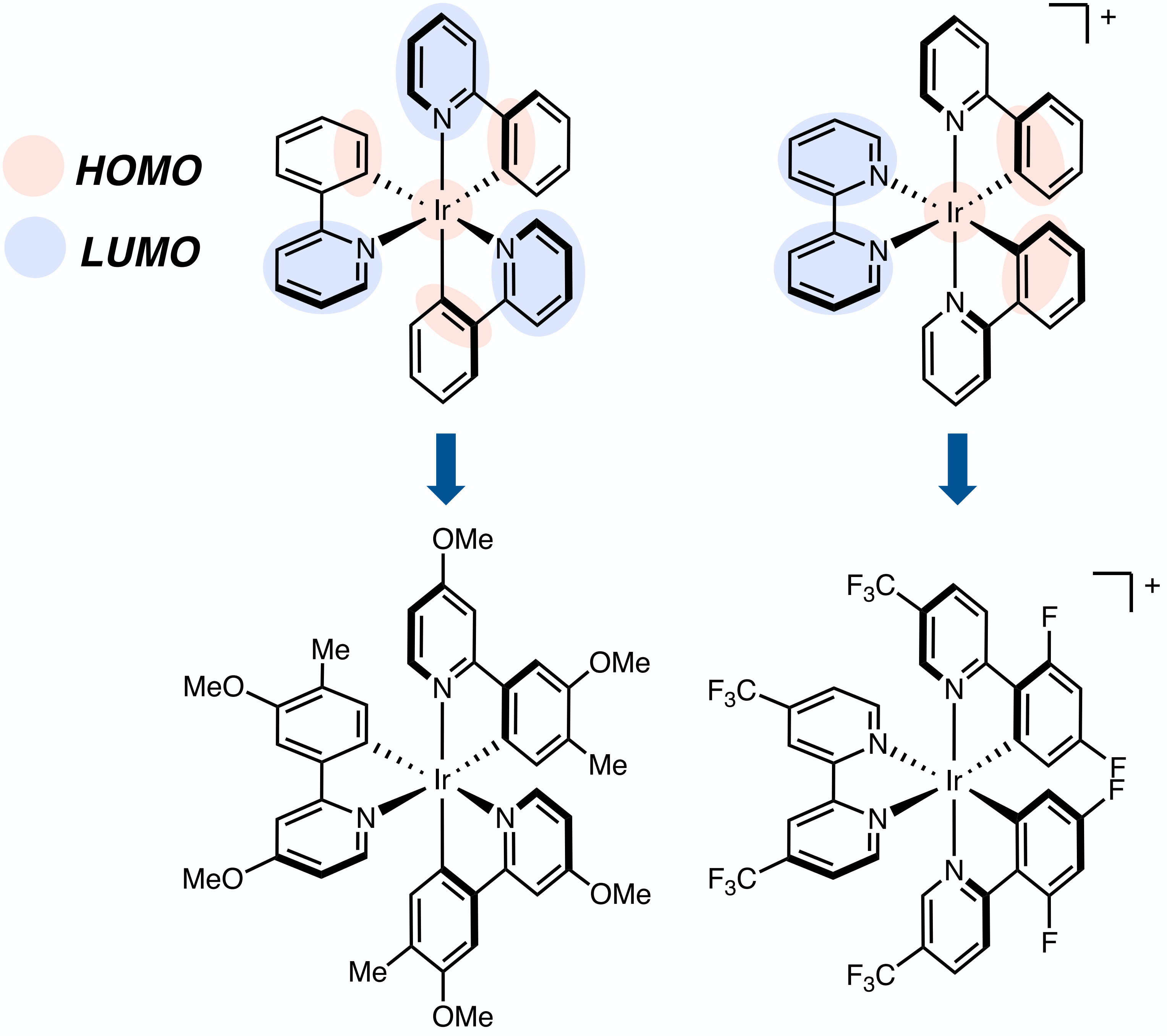
Polyhedron **1990**, *9*, 1939.

Inorg. Chem. **2009**, *48*, 9631.

What Makes Ir the Basis for an Effective Photo(redox) Catalyst Class?

Homoleptic

Heteroleptic



- ‘Super reductant’
- ‘Super oxidant’

Dramatic modifications do not compromise access to the triplet excited state

- Appropriate MO energy ordering
- Orbitals engaged in SOC have similar shape and energy – ***pseudo-octagedral geometry***
- Ir low on the periodic table

$$\text{SOC} \propto Z^4$$

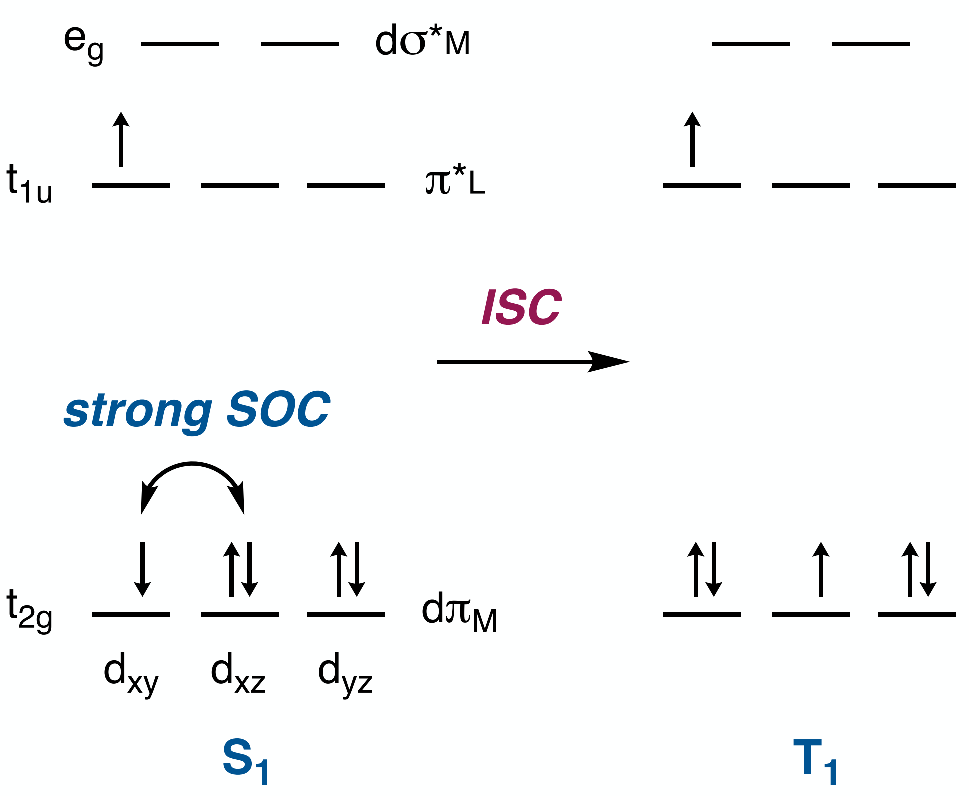
Overcomes descent in symmetry from O_h to C_3 and even C_1 (heteroleptic)

Does not hold for Ru

The Triplet Excited State of Iridium Photocatalysts

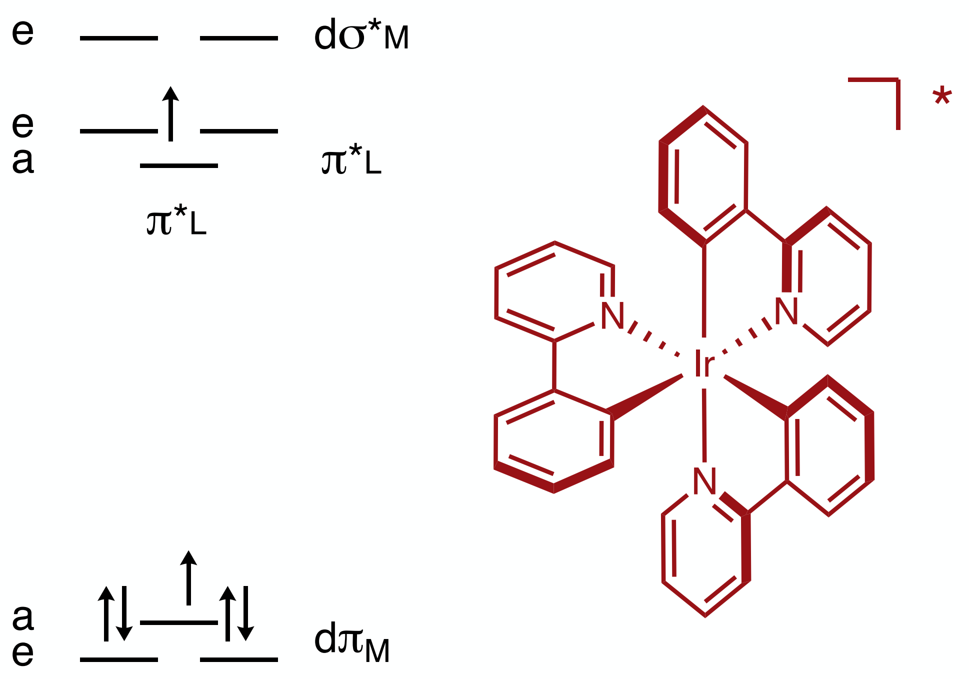
- We now have a model for ISC in pseudo-octahedral complexes (includes all of our Ir photocatalysts)
- The fine structure and properties of the T_1 substates can tell us more about how our photocatalysts work
- A simple model for these substates also suggests why Ir is such a versatile photo(redox) catalytic platform

ML_6^{n+} (O_h)



Model for ISC in pseudo-octahedral complexes

$Ir(ppy)_3$ (C_3)



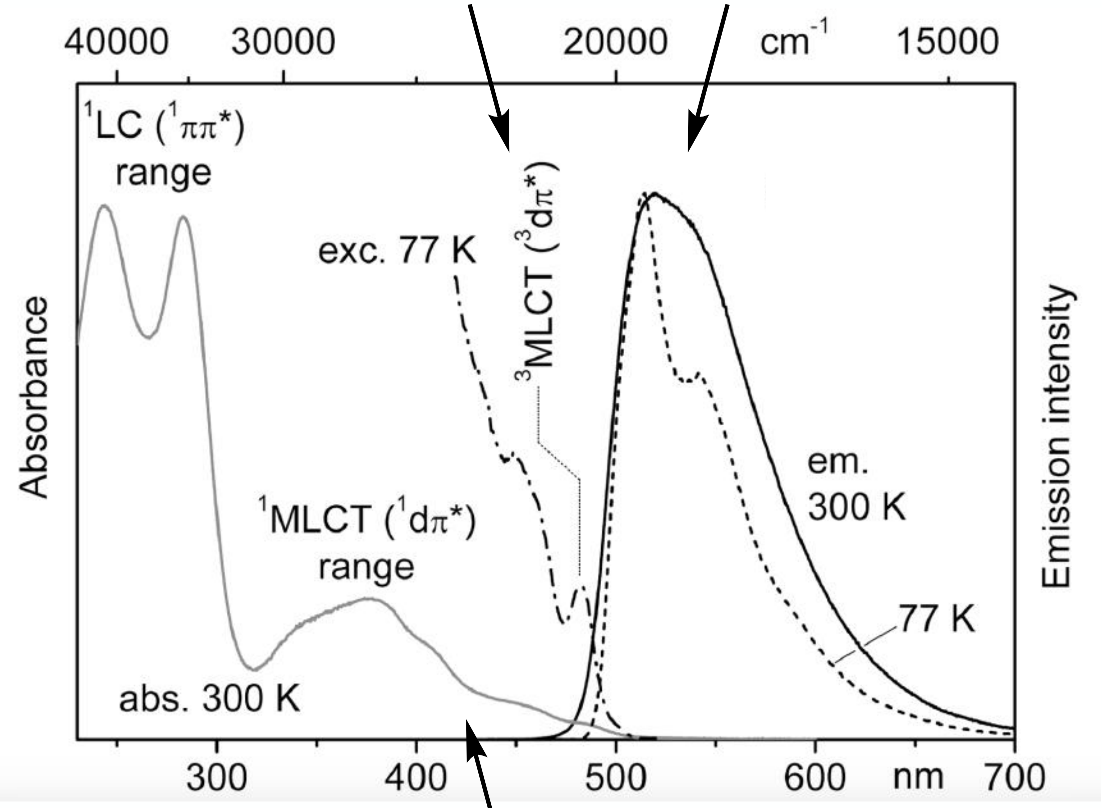
This is our 'active' photocatalyst… What exactly does it look like?

The Triplet Excited State of Ir(ppy)$_3$

- T$_1$ state studied at low temperature to avoid thermal population of higher-energy vibrational modes
- Some features to note about UV-Vis spectra:

direct excitation to triplet state

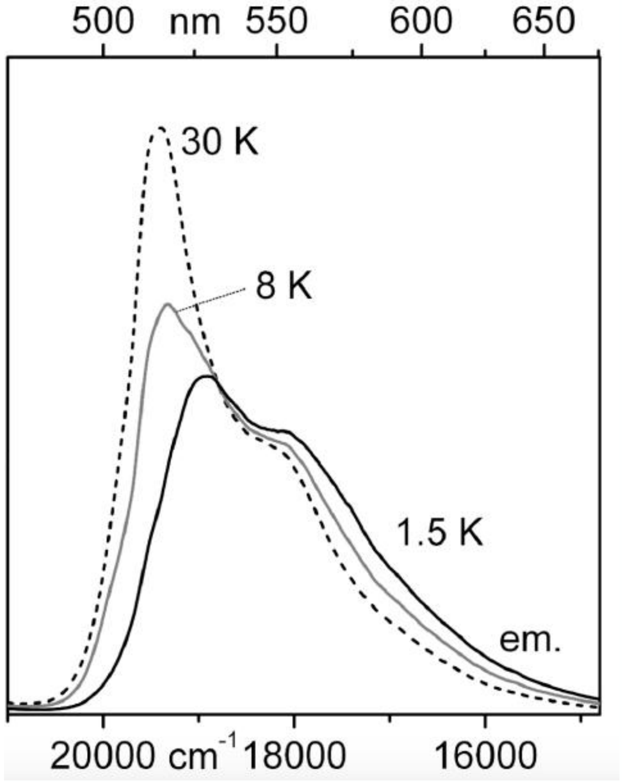
sharpening at low temperature

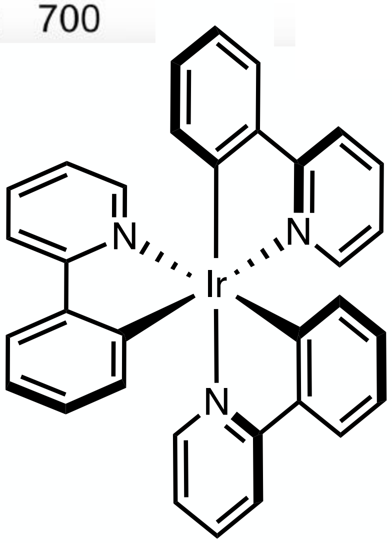


blue light absorption

still broad…

even lower temperature





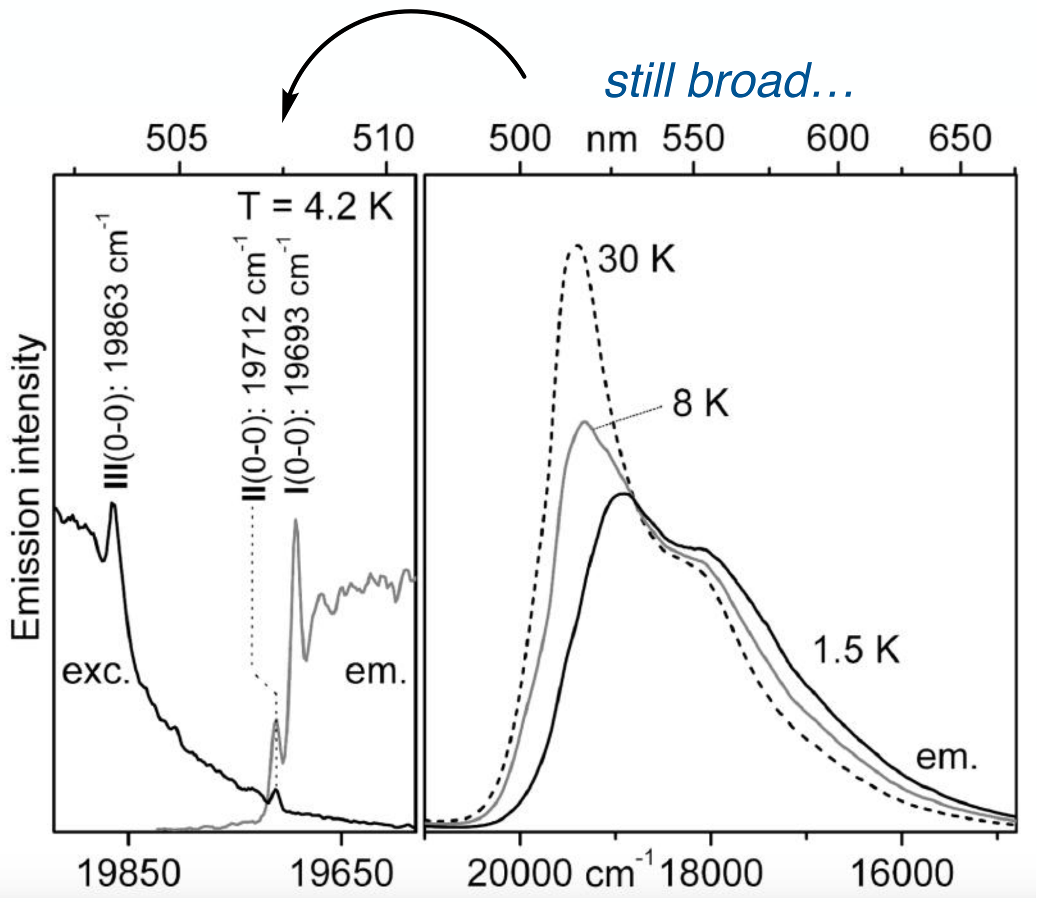
Hofbeck, T.; Yersin, H. *Inorg. Chem.* **2010**, *49*, 9290.

The Triplet Excited State of Ir(ppy)$_3$

- T_1 state studied at low temperature to avoid thermal population of higher-energy vibrational modes
- Even higher resolution obtained by aiming at a single site and irradiating at a resonant wavelength

'site-selective exitation'

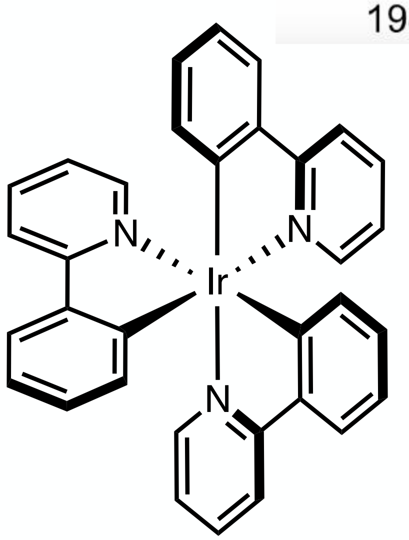
still broad…



- This experiment resolves the fine structure of T_1
- 3 substates are detected (makes sense for a triplet)
- The highest-energy substate (III) is not observed in the emission spectrum
    - Only 0.1% thermally populated around 35 K, at which point resolution is already lost
- Substate I lies at 19 693 cm^{-1} = 56.3 kcal/mol above S_0

II is 19 cm^{-1} = 0.054 kcal/mol higher

III is 170 cm^{-1} = 0.49 kcal/mol higher

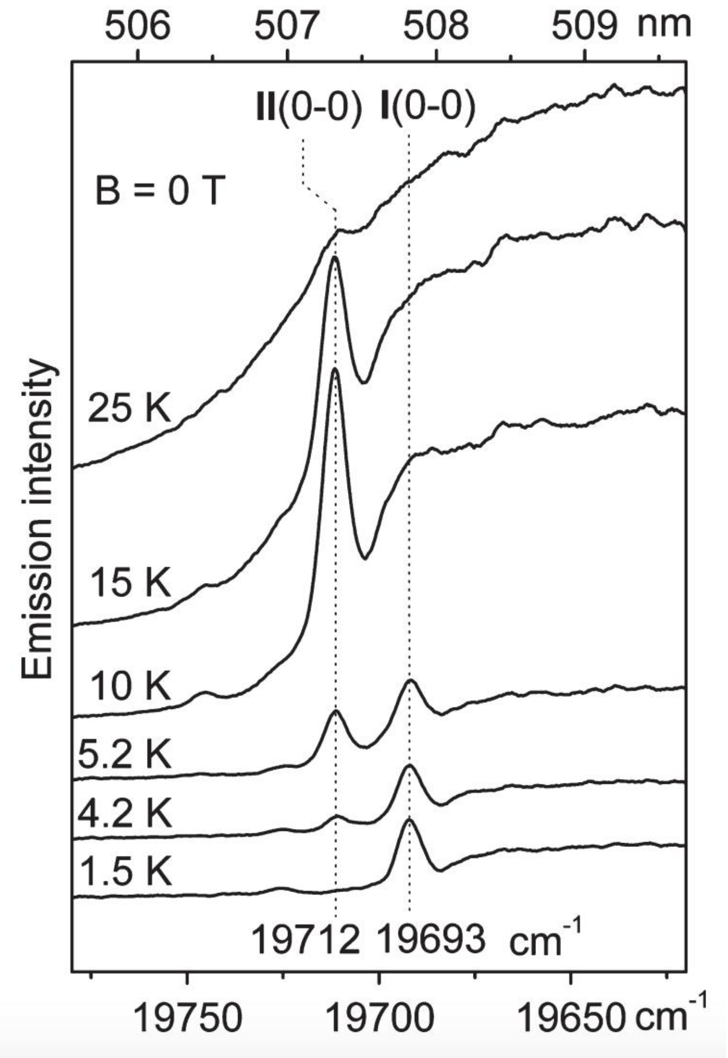


19 863 cm^{-1}
(503.45 nm)

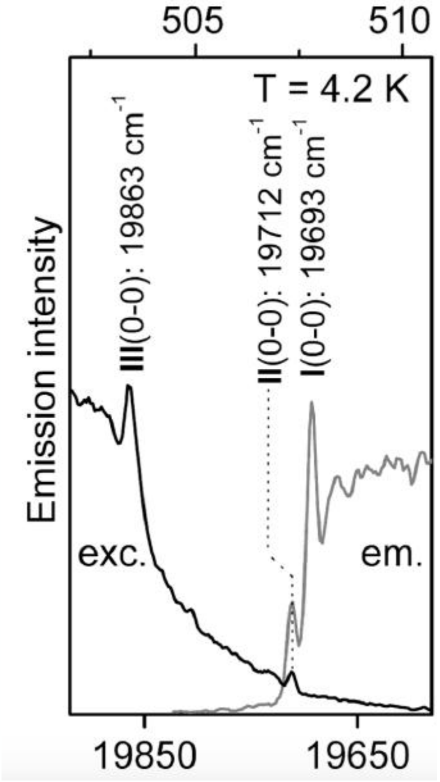
The Triplet Excited State of Ir(ppy)$_3$

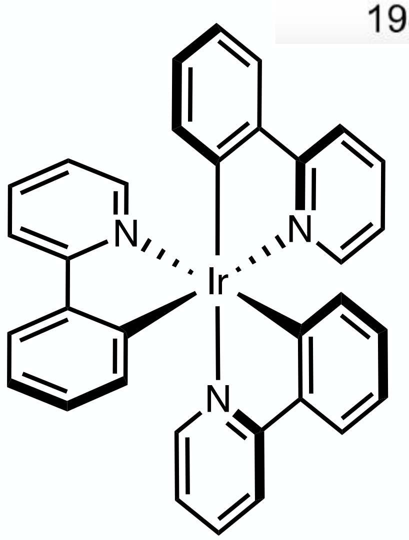
- T_1 state studied at low temperature to avoid thermal population of higher-energy vibrational modes
- Even higher resolution obtained by aiming at a single site and irradiating at a resonant wavelength

Ir(ppy)$_3$ Emission spectrum



emission at many low temperatures



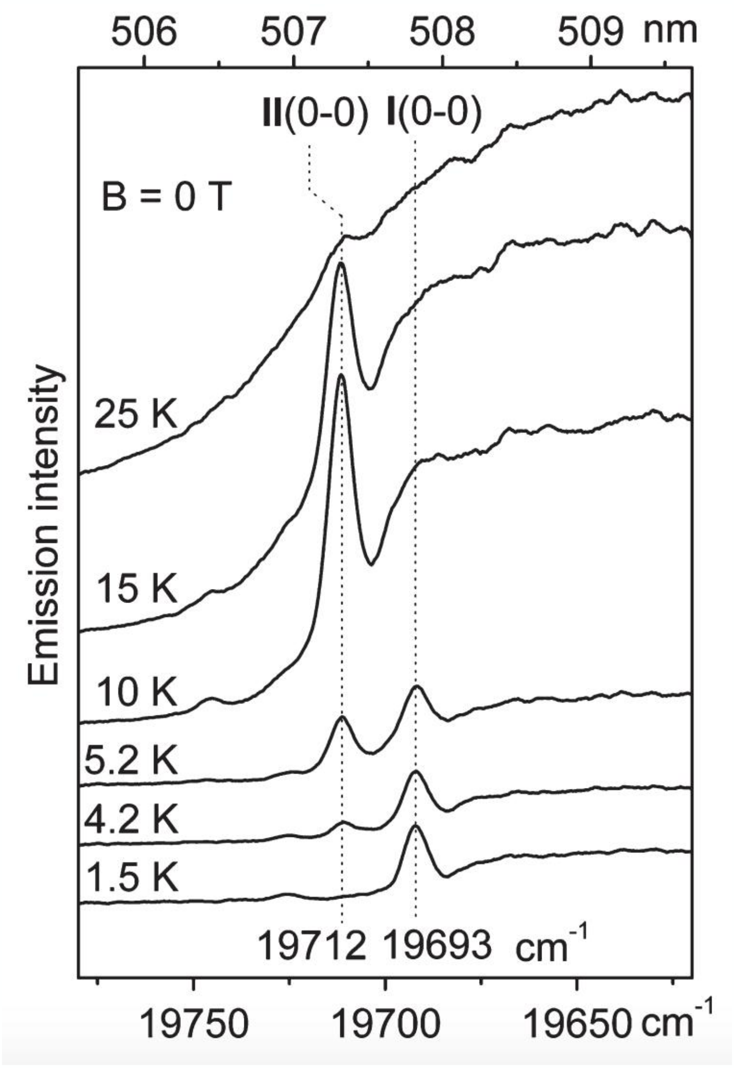


19 863 cm^{-1}
(503.45 nm)

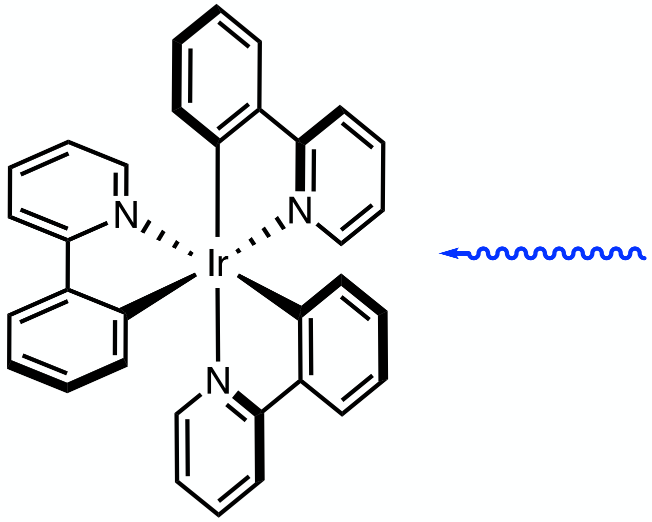
The Triplet Excited State of Ir(ppy)$_3$

- T_1 state studied at low temperature to avoid thermal population of higher-energy vibrational modes
- Even higher resolution obtained by aiming at a single site and irradiating with the wavelength of substate III

Ir(ppy)$_3$ Emission spectrum



- Only substate I emits below 3–4 K (substate II is 19 cm^{-1} higher)
- Substate I is weakly emitting – intensity quickly surpassed by II
- Substate II should be 0.5% of the Boltzmann population at 5.2 K
- Coupling to higher vibrational modes smears out fine structure around 25 K



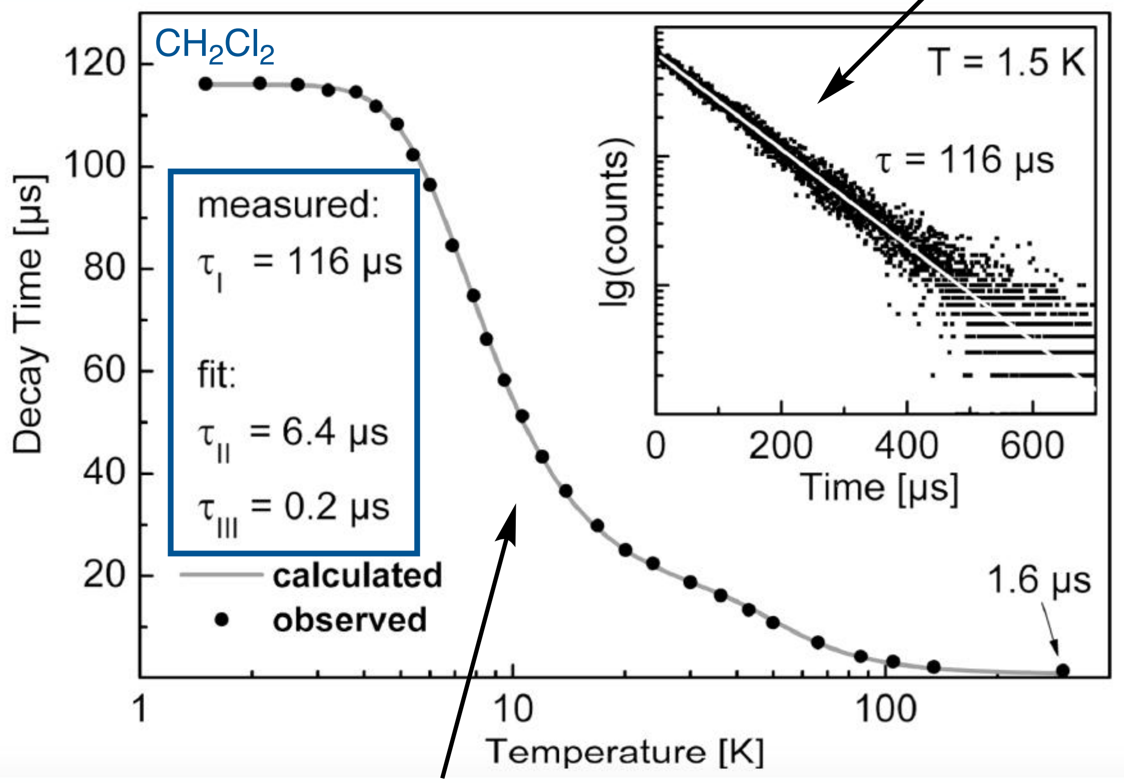
19 863 cm^{-1}
(503.45 nm)

The Triplet Excited State of Ir(ppy)$_3$

- The lifetimes and decay rates of each substate can also be measured
- The 3 substates behave very differently

direct measurement of τ_I –
nothing else emits at 1.5 K

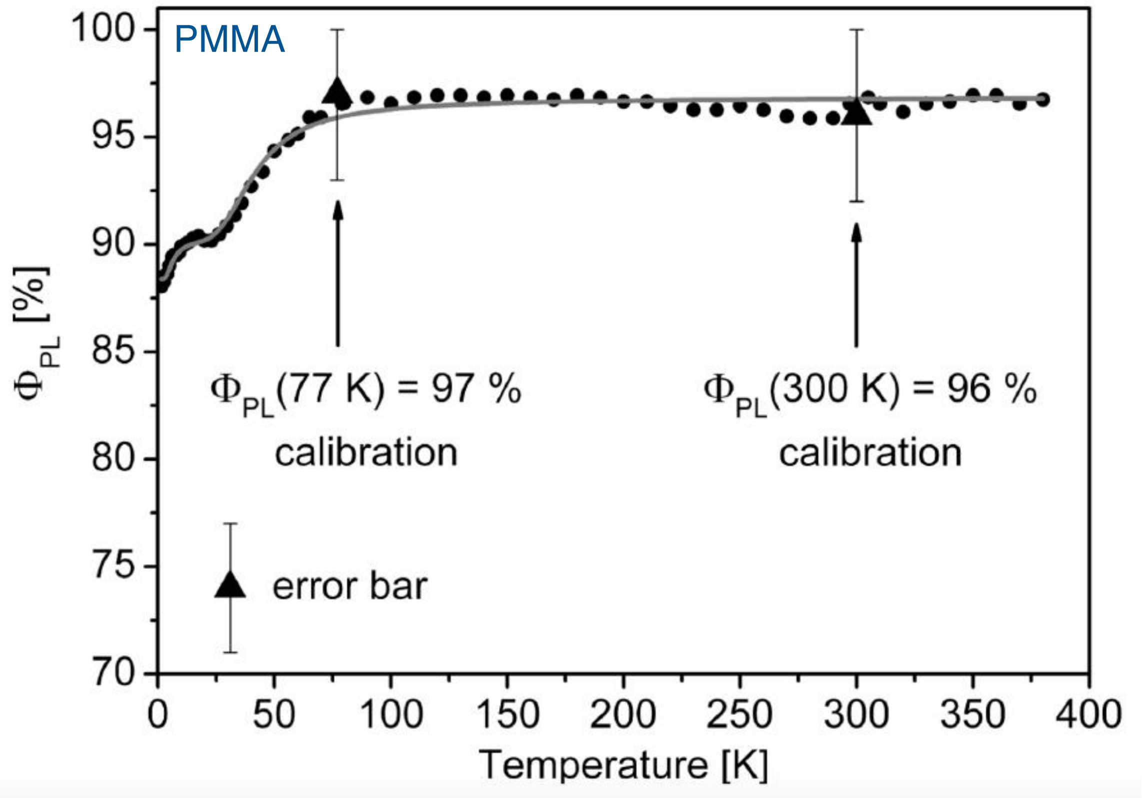
Ir(ppy)$_3$ Lifetime vs. T



τ_{II} and τ_{III} are fit from the observed
average lifetimes at higher temperatures

Lifetimes vary by over an order of magnitude within T$_1$

Ir(ppy)$_3$ Photoluminescence yield vs. T

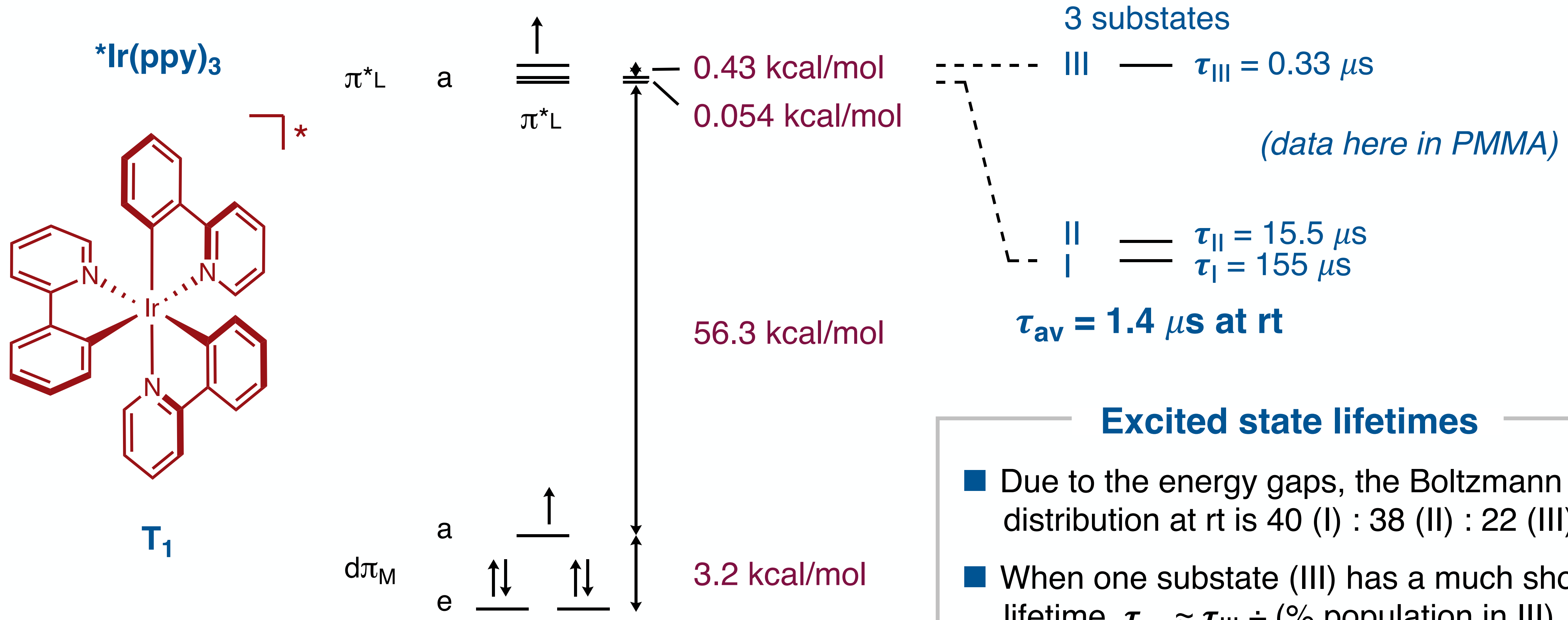


enables determination of radiative and non-radiative decay rates

substate	I	II	III
k_r (s^{-1})	5 700	58 000	2 900 000
k_{nr} (s^{-1})	800	7 000	10 000

The Triplet Excited State of Ir(ppy)$_3$

- What can be learned from this information?
- The overall picture of the T_1 state is:



0.43 kcal/mol

0.054 kcal/mol

56.3 kcal/mol

3.2 kcal/mol

3 substates

III — τ_{III} = 0.33 μs

(data here in PMMA)

II — τ_{II} = 15.5 μs

I — τ_{I} = 155 μs

τ_{av} = 1.4 μs at rt

This general excited state structure holds across many photocatalysts

- 3 substates including a ‘dark’ low-E and ‘bright’ high-E
- Exact lifetimes and energies vary substantially
- ΔE(I,III) is a proxy for strength of SOC & is >>ΔE(I,II)

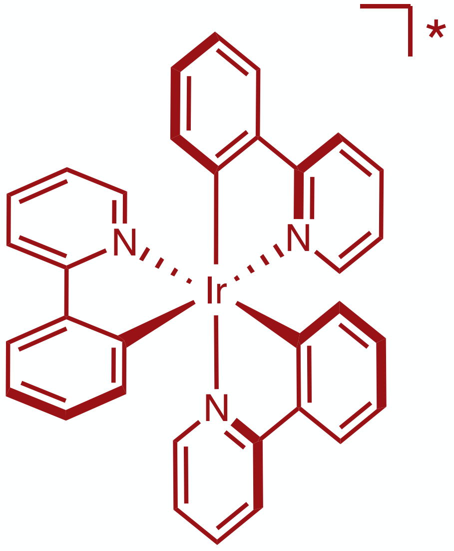
Excited state lifetimes

- Due to the energy gaps, the Boltzmann distribution at rt is 40 (I) : 38 (II) : 22 (III)
- When one substate (III) has a much shorter lifetime, $\tau_{av} \approx \tau_{III} \div$ (% population in III)
    - Effectively $\tau_{av} \approx 5 \times \tau_{III}$ for Ir(ppy)$_3$
- The existence of darker substates rescues these complexes from having very short T_1
- Especially notable when τ_{III} is even shorter
- This feature is an impediment in LED design (want emission to be fast)

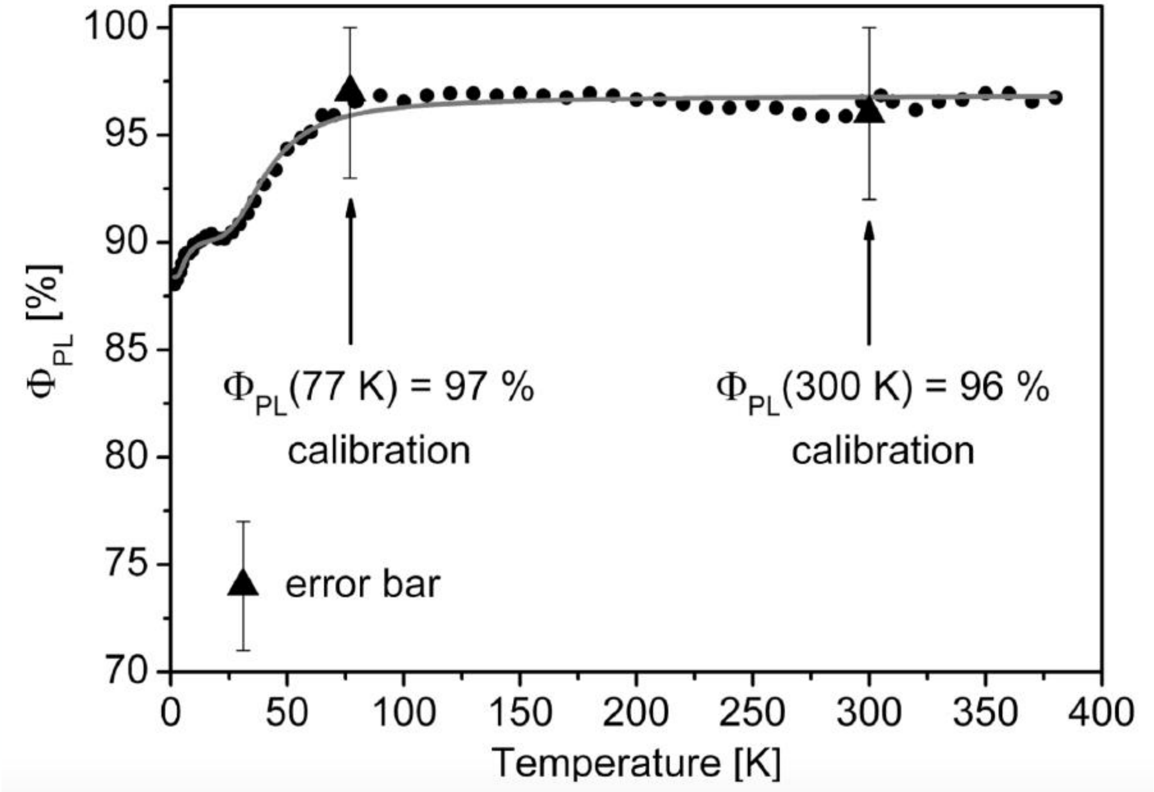
The Triplet Excited State of Ir(ppy)$_3$

- What can be learned from this information?
- The overall picture of the T_1 state is:

***Ir(ppy)$_3$**



T_1



Photoluminescence

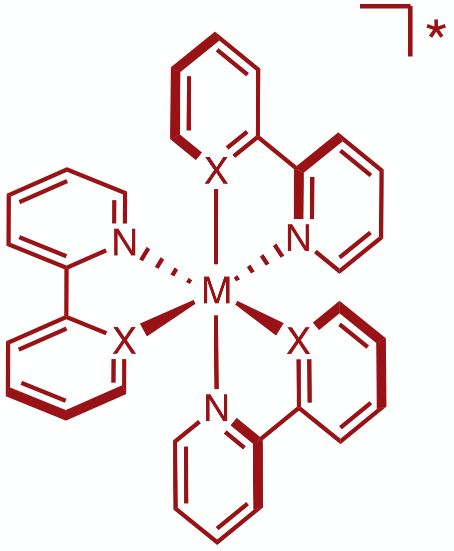
- The high and nearly temperature-invariant Φ_{PL} is also remarkable
- Core features of Ir polypyridyls (pseudo-O_h and high Z) ensure broadly high SOC and Φ_{ISC}
  - Unlike other metals, almost all such Ir complexes have modest to excellent emission
  - Good rt emission is usually the exception and requires very specific ligand types (which may also be much more tedious to prepare than a ppy derivative)
  - Other factors matter (non-radiative decay), but this feature reflects the consistently excellent access to the triplet excited state needed in photocatalysis when using Ir

The Triplet Excited State of Pseudo-octahedral Complexes

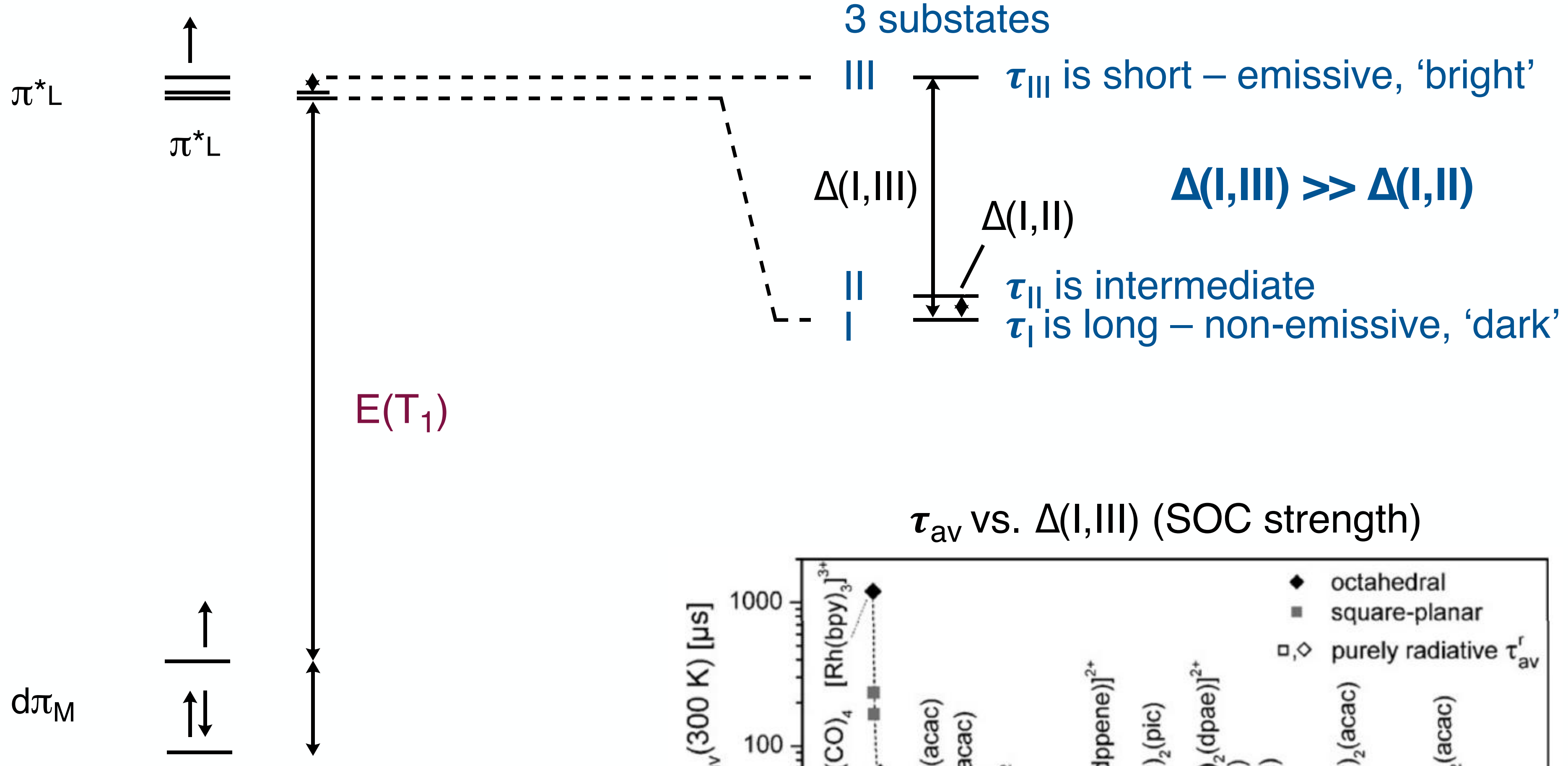
- The qualitative description of the T_1 state of $Ir(ppy)_3$ also describes almost all pseudo-O_h polypyridyls

Why is this T_1 structure so general?

Metal polypyridyl



T_1



3 substates

τ_{III} is short – emissive, 'bright'

$\Delta(I,III) >> \Delta(I,II)$

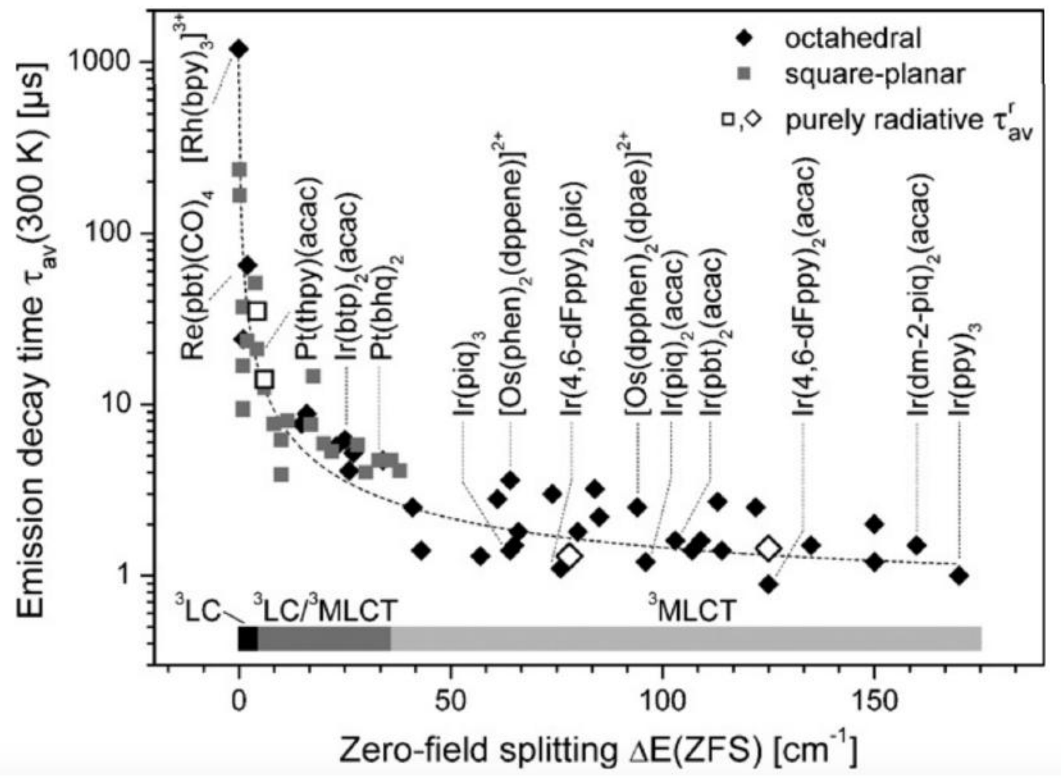
τ_{II} is intermediate

τ_{I} is long – non-emissive, 'dark'

This general excited state structure holds across many photocatalysts

- 3 substates including a 'dark' low-E and 'bright' high-E
- Exact lifetimes and energies vary substantially
- $\Delta E(I,III)$ is a proxy for strength of SOC & is $>>\Delta E(I,II)$

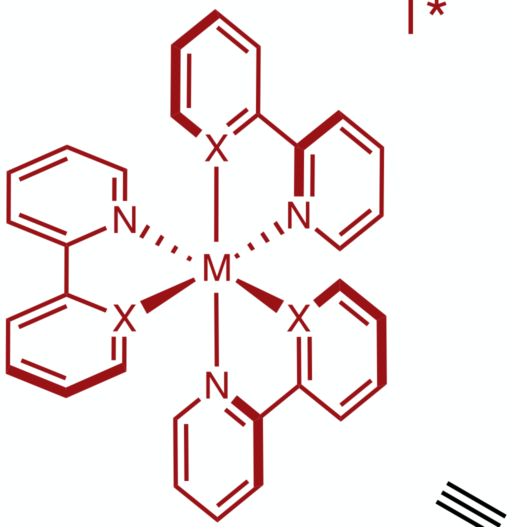
τ_{av} vs. $\Delta(I,III)$ (SOC strength)



The First Excited State of Pseudo-octahedral Complexes

- A very simple semi-empirical model predicts this structure with few *a priori* assumptions
- This ‘pseudo angular momentum’ model is constructred in the following manner:
  - Treat the ES* of such a complex as a ligand-centered electron and a mixed metal-ligand hole (MLCT), each with *L* = 1, in O_h geometry
  - Account for the interaction between the spins of the electron & hole and the SOC of the hole (due to its metal character)
  - Descend to trigonal symmetry (D_3 or C_3) by adding a perturbation to the Hamiltonian that depends on the *z*-orbital angular momentum
  - Add an *x*,*y*-orbital angular momentum perturbation (Jahn-Teller distortion) to model a localized excitation of a heteroleptic complex (C_2 or C_1)

Metal polypyridyl



ES*

≡

hole ↑

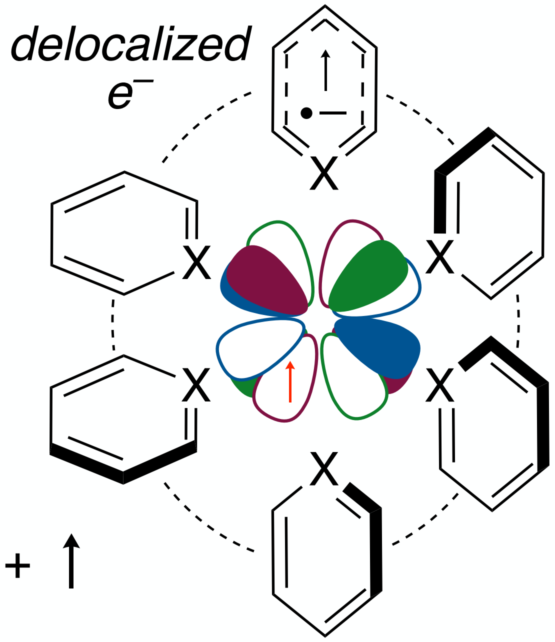
L = 1

electron ↑

spin-spin interaction ↑ + ↑

spin-orbit interaction ↑ only

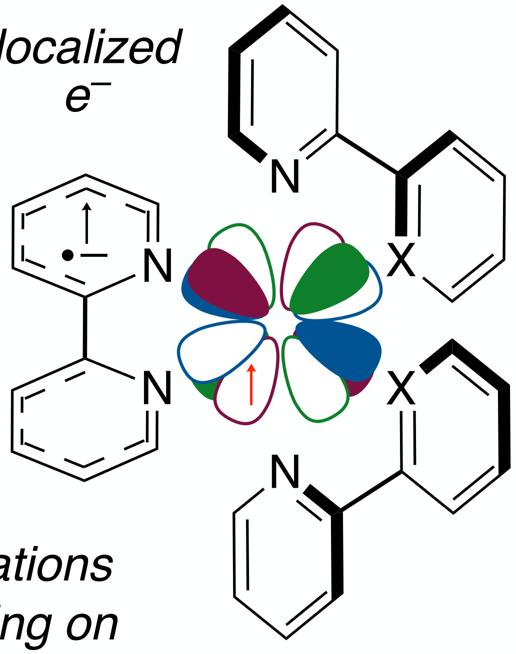
delocalized e⁻



O_h

descent in symmetry →

localized e⁻



perturbations depending on L_z & $L_{x,y}$

C_2 or C_1

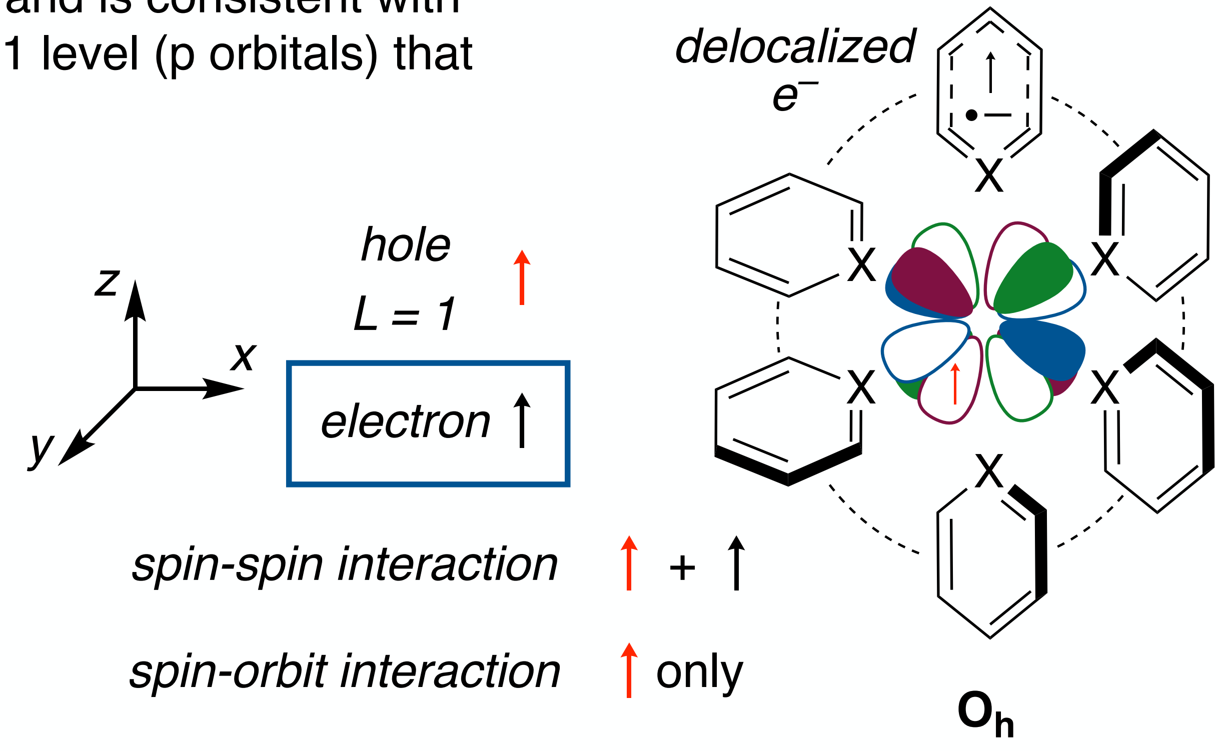
A Model for the First Excited State of Octahedral Complexes

- First, list the orbitals and quantum numbers available to the electron and hole
- As seen earlier in MO diagrams for O_h, the ground state LUMO (excited state HOMO) is a T_{1u} representation of ligand-centered π^* orbitals, call them $\pi_{Lx}{}^*$, $\pi_{Ly}{}^*$, and $\pi_{Lz}{}^*$
  - As for p orbitals in O_h, the 3 T_{1u} wavefunctions may be given by the linear combination of these orbitals

$$\text{LUMO } (L_z = 0) = \frac{\pi_{Lx}{}^* + \pi_{Ly}{}^* + \pi_{Lz}{}^*}{\sqrt{3}} \qquad \text{LUMO } (L_z = \pm 1) = \frac{\pi_{Lz}{}^* + e^{\pm 2\pi i/3}\pi_{Lx}{}^* + e^{\mp 2\pi i/3}\pi_{Ly}{}^*}{\sqrt{3}}$$

where L_z denotes the z-component orbital angular momentum of each wavefunction

- NOTE: this model is termed 'pseudo angular momentum' because it treats the threefold-degenerate T_{2g} and T_{1u} levels in isolation from the rest of the molecule, assigning them an orbital angular momentum of L = 1
  - This strategy drastically simplifies the theory and is consistent with the familiar atomic orbital analogy of the L = 1 level (p orbitals) that are threefold degenerate in O_h



Powell, B. J. *Sci. Rep.* **2015**, *5*, 10815.

Powell, B. J. arXiv:1501.06333.

A Model for the First Excited State of Octahedral Complexes

- First, list the orbitals and quantum numbers available to the electron and hole

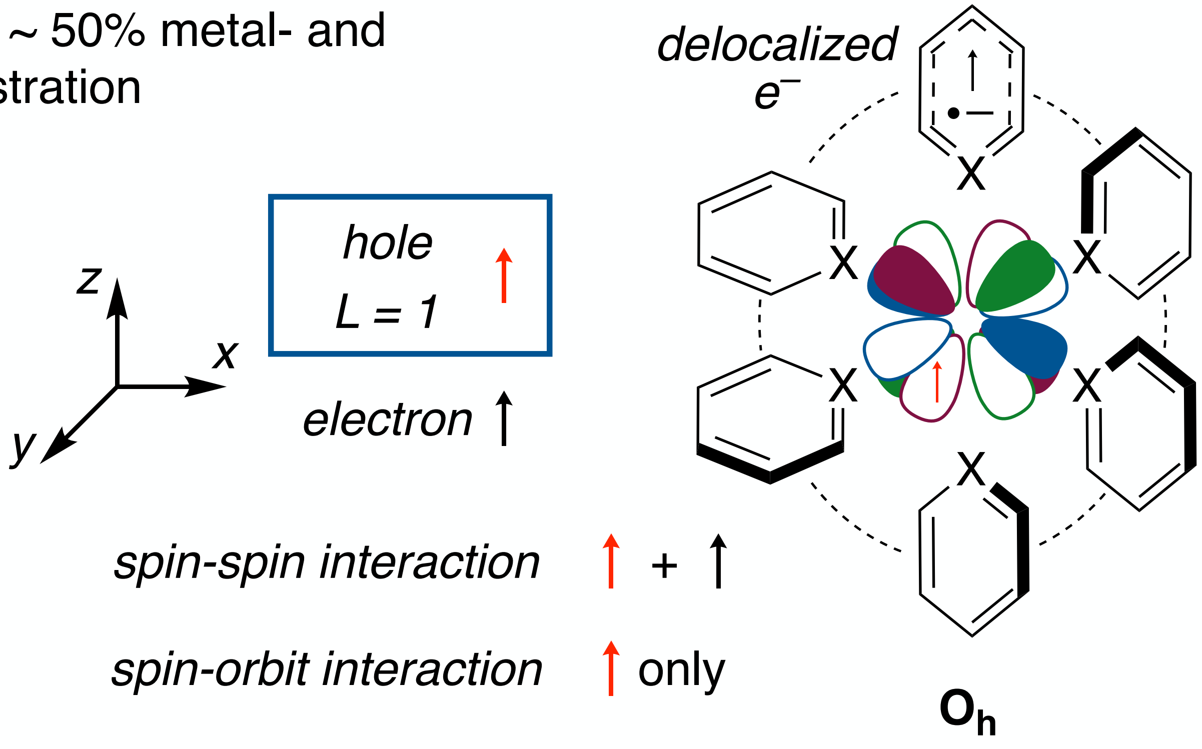
- The ground state HOMO (excited state LUMO) is a T_{2g} representation of metal-centered d orbitals (d_{xy}, d_{xz}, d_{yz}) and ligand-centered π orbitals (π_{Lx}, π_{Ly}, and π_{Lz}) which may be expressed as

$$\text{HOMO } (L_z = 0) = \frac{d_{xy} + d_{xz} + d_{yz}}{\sqrt{3}} \cos\theta + \frac{\pi_{Lx}^* + \pi_{Ly}^* + \pi_{Lz}^*}{\sqrt{3}} \sin\theta$$

$$\text{HOMO } (L_z = \pm 1) = \frac{d_{xy} + e^{\pm 2\pi i/3} d_{xz} + e^{\mp 2\pi i/3} d_{yz}}{\sqrt{3}} \cos\theta + \frac{\pi_{Lz}^* + e^{\pm 2\pi i/3} \pi_{Ly}^* + e^{\mp 2\pi i/3} \pi_{Lx}^*}{\sqrt{3}} \sin\theta$$

- The $\cos\theta$ and $\sin\theta$ terms represent the extent of mixing in the HOMO

- Calculations for $Ir(ppy)_3$ suggest that the HOMO is ~ 50% metal- and ligand-centered, so we will use $\theta = \pi/4$ for this illustration



hole
L = 1 ↑

electron ↑

spin-spin interaction ↑ + ↑

spin-orbit interaction ↑ only

A Model for the First Excited State of Octahedral Complexes

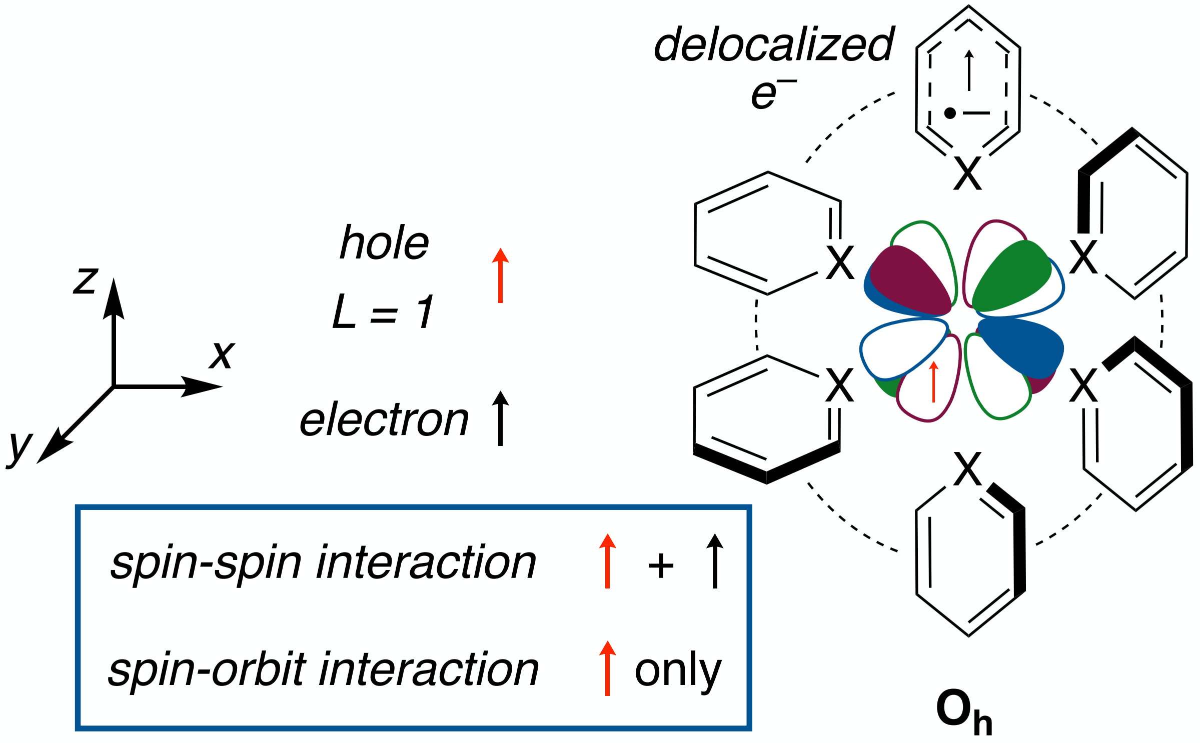
- We can now begin building the energetic model for the excited state
- As suggested in the diagram below, the Hamiltonian will be very simple, capturing only 2 interactions

$$\boxed{\hat{H}\,(\mathrm{O_h}) = J\,\vec{\boldsymbol{S}}_{\mathrm{HOMO}}\cdot\vec{\boldsymbol{S}}_{\mathrm{LUMO}} + \lambda\,\vec{\boldsymbol{L}}_{\mathrm{HOMO}}\cdot\vec{\boldsymbol{S}}_{\mathrm{HOMO}}}$$

- Constants J and λ can be adjusted to capture the strength of the spin-spin and spin-orbit interactions
  - From empirical data, we can extract these values for compounds we intend to model from the expressions $J = J_\pi \sin^2\theta$ (from the ligand) and $\lambda = \lambda_d \sin^2\theta$ (from the metal)
  - Again using $\mathrm{Ir(ppy)_3}$ as a example, we can use the values $J_\pi = 2$ eV (for ppy), $\lambda_d = 0.43$ eV (for Ir), and $\theta \approx \pi/4$ to represent equal metal and ligand contributions to the HOMO to obtain example constants

$J \approx 1$ eV for $\mathrm{Ir(ppy)_3}$

$\lambda \approx 0.215$ eV for $\mathrm{Ir(ppy)_3}$



spin-spin interaction ↑ + ↑

spin-orbit interaction ↑ only

A Model for the First Excited State of Octahedral Complexes

- We can now begin building the energetic model for the excited state
- As suggested in the diagram below, the Hamiltonian will be very simple, capturing only 2 interactions

$$\boxed{\hat{H}\,(O_h) = J\,\vec{\boldsymbol{S}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{LUMO}} + \lambda\,\vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}}}$$

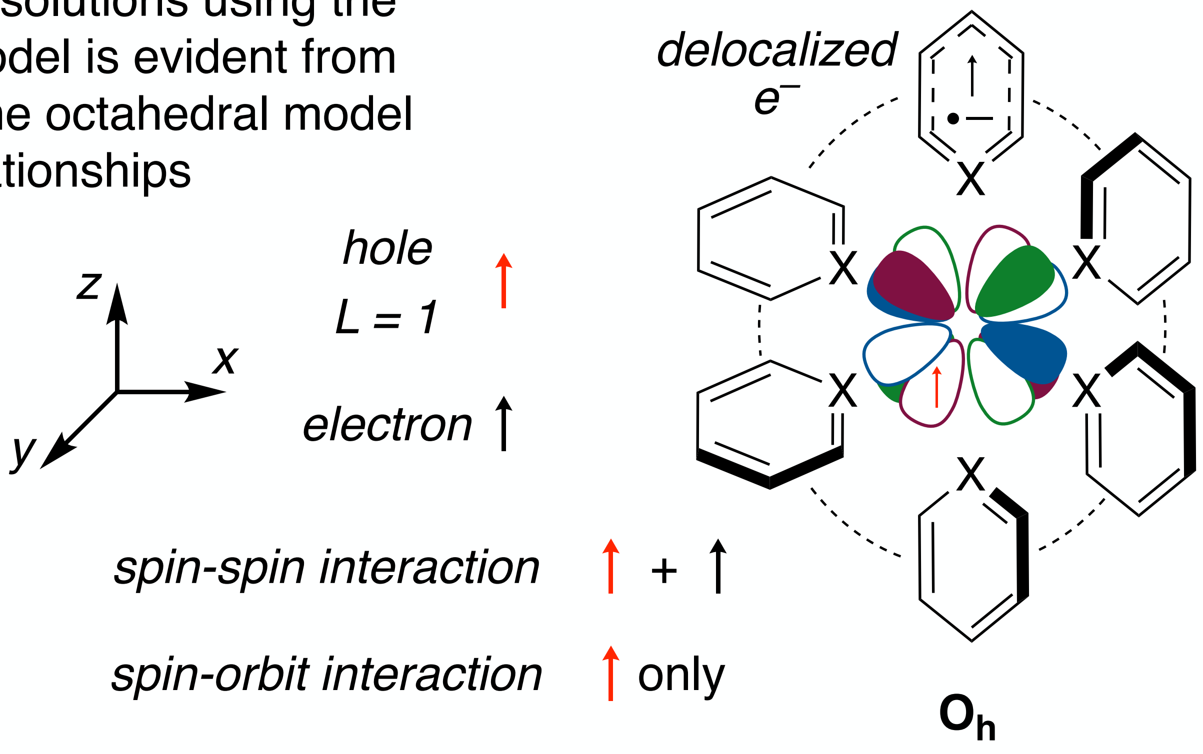
- $\vec{\boldsymbol{L}}_{\mathrm{LUMO}}$ is not part of this model, so we may disregard it (a further simplification)
- As presented earlier, the total angular momentum is a conserved quantity, and here is expressed as

$$\boxed{\vec{\boldsymbol{I}} = \vec{\boldsymbol{L}} + \vec{\boldsymbol{S}} \qquad \textit{total angular momentum}}$$

I is therefore a quantum number with the range

$$I = |\,L - S\,|,\ |\,L - S\,| + 1,\ \ldots\ L + S - 1,\ L + S$$

- The results of this work are obtained by numerical solutions using the specified Hamiltonians, but the simplicity of the model is evident from the ability to capture nearly the entire solution to the octahedral model from a few quantum mechanical identities and relationships



hole ↑

L = 1

electron ↑

spin-spin interaction ↑ + ↑

spin-orbit interaction ↑ only

A Model for the First Excited State of Octahedral Complexes

- We can now begin building the energetic model for the excited state
- As suggested in the diagram below, the Hamiltonian will be very simple, capturing only 2 interactions

$$\boxed{\hat{H}\,(\mathrm{O_h}) = J\,\vec{\boldsymbol{S}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{LUMO}} + \lambda\,\vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}}}$$

- The following identities and relations help simplify this Hamiltonian:

simple addition of two spins

$$(\vec{\boldsymbol{S}}_{\mathrm{HOMO}} + \vec{\boldsymbol{S}}_{\mathrm{LUMO}})^2 = 1 \qquad \text{(for any triplet)} \qquad (\vec{\boldsymbol{S}}_{\mathrm{HOMO}} + \vec{\boldsymbol{S}}_{\mathrm{LUMO}})^2 = 0 \qquad \text{(for any singlet)}$$

expansion of the above 'quadratic' expression

$$(\vec{\boldsymbol{S}}_{\mathrm{HOMO}} + \vec{\boldsymbol{S}}_{\mathrm{LUMO}})^2 = \vec{\boldsymbol{S}}_{\mathrm{HOMO}}{}^2 + \vec{\boldsymbol{S}}_{\mathrm{LUMO}}{}^2 \pm 2\,\vec{\boldsymbol{S}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{LUMO}} \qquad \text{(for triplets and singlets, respectively)}$$

the quantized magnitude of spin angular momentum

$$\vec{\boldsymbol{S}}_{\mathrm{HOMO}}{}^2 = \vec{\boldsymbol{S}}_{\mathrm{LUMO}}{}^2 = 3/4 \qquad \text{(for any single spin)}$$

substitution of the identities into the expanded expression then gives

$$\begin{array}{lcl} 1 = 3/4 + 3/4 + 2\,\vec{\boldsymbol{S}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{LUMO}} & \Rightarrow & \vec{\boldsymbol{S}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{LUMO}} = -1/4 \qquad \text{(for triplets)} \\ 0 = 3/4 + 3/4 - 2\,\vec{\boldsymbol{S}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{LUMO}} & \Rightarrow & \vec{\boldsymbol{S}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{LUMO}} = +3/4 \qquad \text{(for singlets)} \end{array}$$

These values are the first part of the expression for H (O_h)

A Model for the First Excited State of Octahedral Complexes

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- The following identities and relations help simplify this Hamiltonian:

partial expansion of the total angular momentum of the system (recall that we can neglect L_{LUMO})

$$\vec{\boldsymbol{I}}^{\,2} = (\vec{\boldsymbol{L}}_{\mathrm{HOMO}} + \vec{\boldsymbol{S}}_{\mathrm{HOMO}} + \vec{\boldsymbol{S}}_{\mathrm{LUMO}})^2 = \vec{\boldsymbol{L}}_{\mathrm{HOMO}}{}^2 + 2\,\vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} + 2\,\vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{LUMO}} + (\vec{\boldsymbol{S}}_{\mathrm{HOMO}} + \vec{\boldsymbol{S}}_{\mathrm{LUMO}})^2$$

and substituting in the following values

$\vec{\boldsymbol{I}}^{\,2} = I(I + 1)$ (the expression for the magnitude of any quantum number)

$\vec{\boldsymbol{L}}_{\mathrm{HOMO}}{}^2 = L_{\mathrm{HOMO}}(L_{\mathrm{HOMO}} + 1) = 1(1 + 1) = 2$ (as above and since $L_{\mathrm{HOMO}} = 1$ for this model)

$\vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{LUMO}} = 0$ (since the LUMO is metal-free and thus does not involve a strong SOC term)

$(\vec{\boldsymbol{S}}_{\mathrm{HOMO}} + \vec{\boldsymbol{S}}_{\mathrm{LUMO}})^2 = 1, 0$ (for triplets and singlets, respectively)

leads to the simplified relationship

$$I(I + 1) = 2 + 2\,\vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} + 1 \Rightarrow \vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} = \frac{3 - I(I + 1)}{2} \qquad \text{(for triplets)}$$

$$I(I + 1) = 2 + 2\,\vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} + 0 \Rightarrow \vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} = \frac{2 - I(I + 1)}{2} \qquad \text{(for singlets)}$$

A Model for the First Excited State of Octahedral Complexes

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- Lastly, using the range of possible values for total angular momentum *I*

$$I = |L - S|,\ |L - S| + 1,\ \ldots\ L + S - 1,\ L + S$$

$$\Rightarrow\ I = 0, 1, 2 \qquad \text{(for triplets, as } L = 1 \text{ and } S = 1\text{) and} \qquad I = 0 \qquad \text{(for singlets, as } L = 1 \text{ and } S = 0\text{)}$$

enables substate-dependent solutions for the spin-orbit term

$$\boxed{\begin{aligned} \vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} &= +3/2 \\ \vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} &= +1/2 \\ \vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} &= -3/2 \\ \vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} &= 0 \end{aligned}} \qquad \begin{aligned} &\text{(for triplets with } I = 0) \\ &\text{(for triplets with } I = 1) \\ &\text{(for triplets with } I = 2) \\ &\text{(for singlets, } I = 1) \end{aligned}$$

leads to the simplified relationship

$$I(I + 1) = 2 + 2\,\vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} + 1 \Rightarrow \vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} = \frac{3 - I(I + 1)}{2} \qquad \text{(for triplets)}$$

$$I(I + 1) = 2 + 2\,\vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} + 0 \Rightarrow \vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} = \frac{2 - I(I + 1)}{2} \qquad \text{(for singlets)}$$

A Model for the First Excited State of Octahedral Complexes

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- Lastly, using the range of possible values for total angular momentum I

$$I = |L - S|,\ |L - S| + 1,\ \ldots\ L + S - 1,\ L + S$$

$\Rightarrow\ I = 0, 1, 2$ (for triplets, as $L = 1$ and $S = 1$) and $I = 0$ (for singlets, as $L = 1$ and $S = 0$)

enables substate-dependent solutions for the spin-orbit term

$\vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} = +3/2$ (for triplets with $I = 0$)

$\vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} = +1/2$ (for triplets with $I = 1$)

$\vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} = -3/2$ (for triplets with $I = 2$)

$\vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} = 0$ (for singlets, $I = 1$)

lastly, recalling that the spin-spin term is evaluated as

$\vec{\boldsymbol{S}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{LUMO}} = -1/4$ (for triplets)

$\vec{\boldsymbol{S}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{LUMO}} = +3/4$ (for singlets)

and since the Hamiltonian operator corresponds to the energies of the wavefunctions ψ that are solutions to the Schrödinger equation

$$\hat{H}\,\psi = E\,\psi$$

A Model for the First Excited State of Octahedral Complexes

- We can now begin building the energetic model for the excited state
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$$\boxed{\hat{H}\,(\mathrm{O_h}) = J\,\vec{\boldsymbol{S}}_{\mathrm{HOMO}}\cdot\vec{\boldsymbol{S}}_{\mathrm{LUMO}} + \lambda\,\vec{\boldsymbol{L}}_{\mathrm{HOMO}}\cdot\vec{\boldsymbol{S}}_{\mathrm{HOMO}}}$$

- Application of the previous relationships then lead to the following expressions for the energy levels

$E/J = -3/2\,\lambda/J - 1/4$ (for triplets with $l = 0$)

$E/J = +1/2\,\lambda/J - 1/4$ (for triplets with $l = 1$) **$E/J = +3/4$ (for singlets, $l = 1$)**

$E/J = +3/2\,\lambda/J - 1/4$ (for triplets with $l = 2$)

A Model for the First Excited State of Octahedral Complexes

- The pseudo orbital angular momentum model for the excited state energies of octahedral complexes is thus

$$\boxed{\hat{H}(O_h) = J\,\vec{S}_{\mathrm{HOMO}} \cdot \vec{S}_{\mathrm{LUMO}} + \lambda\,\vec{L}_{\mathrm{HOMO}} \cdot \vec{S}_{\mathrm{HOMO}}}$$

$E/J = -3/2\,\lambda/J - 1/4$ **(for triplets with $l = 0$)**

$E/J = +1/2\,\lambda/J - 1/4$ **(for triplets with $l = 1$)**

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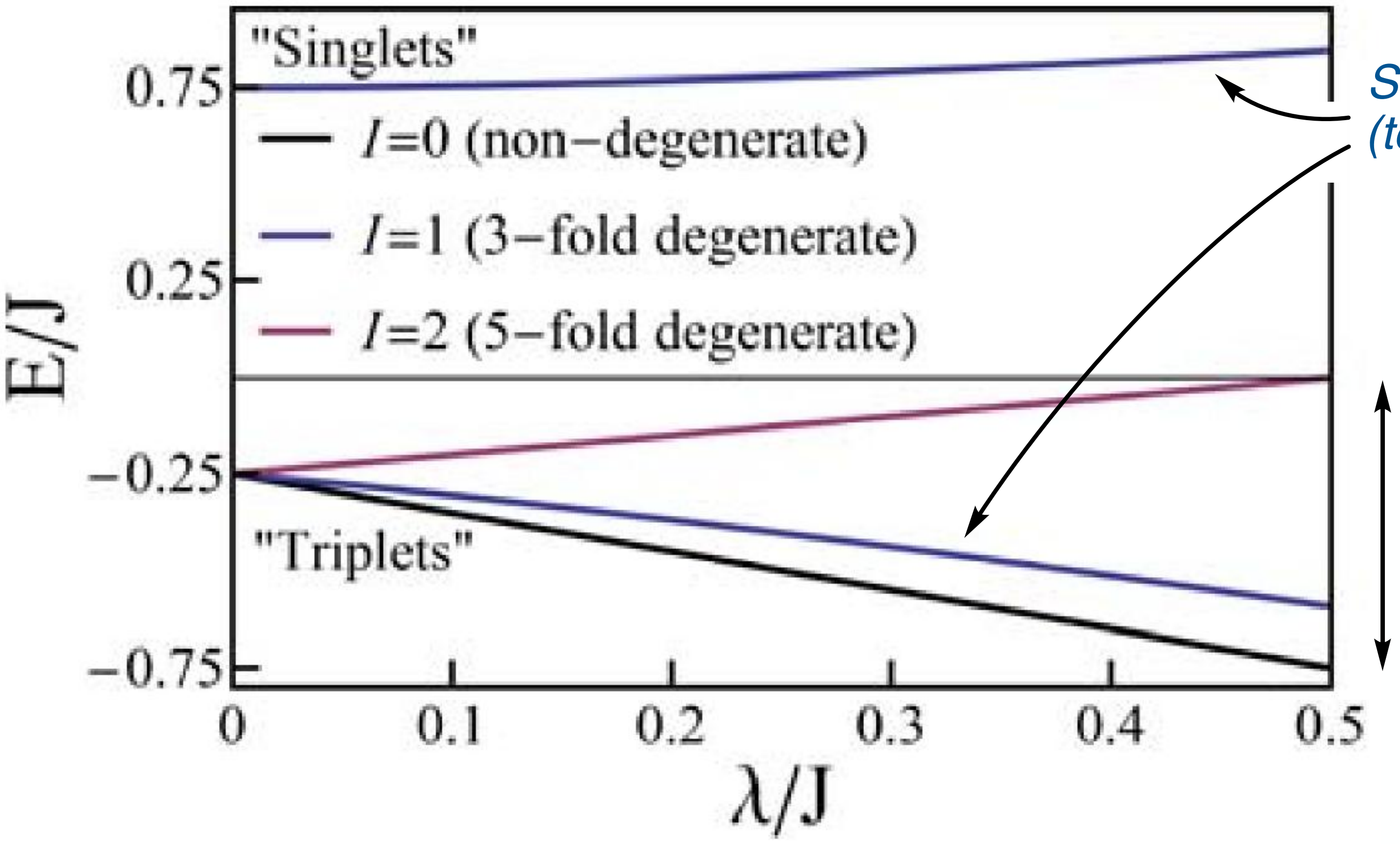
$E/J = +3/2\,\lambda/J - 1/4$ **(for triplets with $l = 2$)**

- Results of this study are presented as plots of *E* as the constant terms in its expressions are varied
  - Since this model makes only relative predictions for *E*, results are scaled by spin-spin term *J*



SOC mixes singlet and triplet l = 1 states (total angular momentum is conserved) – note the deviation from linearity

(this is captured in full numerical solutions and not in the simplified linear relations above)

spltting between triplet substates increases with stronger SOC

stronger SOC →

A Model for the First Excited State of Octahedral Complexes

- The pseudo orbital angular momentum model for the excited state energies of octahedral complexes is thus

$$\boxed{\hat{H}\,(O_h) = J\,\vec{\boldsymbol{S}}_{\mathrm{HOMO}}\cdot\vec{\boldsymbol{S}}_{\mathrm{LUMO}} + \lambda\,\vec{\boldsymbol{L}}_{\mathrm{HOMO}}\cdot\vec{\boldsymbol{S}}_{\mathrm{HOMO}}}$$

$E / J = -3/2\ \lambda / J - 1/4$ **(for triplets with $l = 0$)**

$E / J = +1/2\ \lambda / J - 1/4$ **(for triplets with $l = 1$)**

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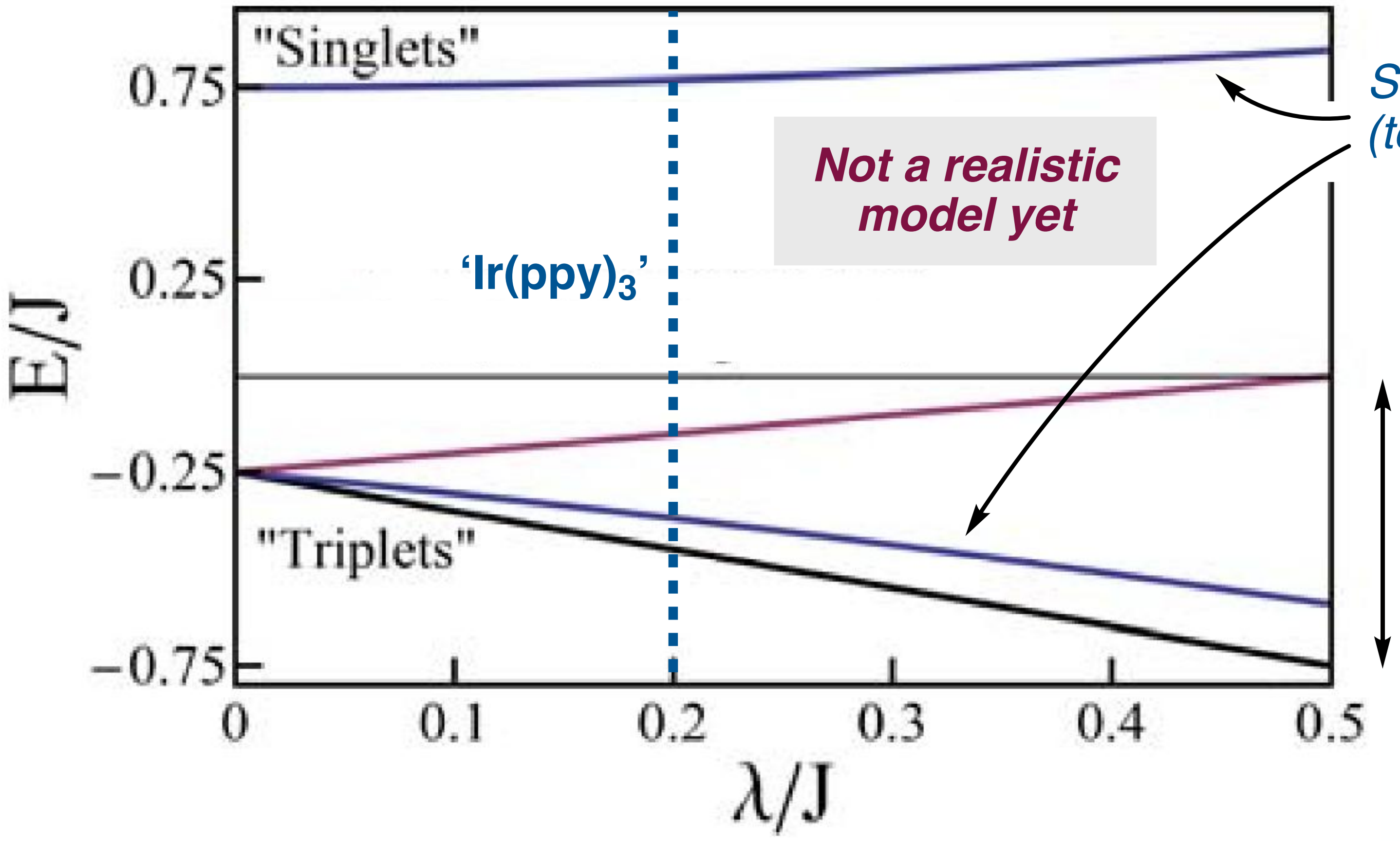


Not a realistic model yet

SOC mixes singlet and triplet l = 1 states (total angular momentum is conserved) – note the deviation from linearity

(this is captured in full numerical solutions and not in the simplified linear relations above)

spltting between triplet substates increases with stronger SOC

- Recall for Ir(ppy)$_3$ that $J \approx 1$ eV and $\lambda \approx 0.2$ eV, so $J / \lambda \approx 0.2$ (though we are in still in O_h…)

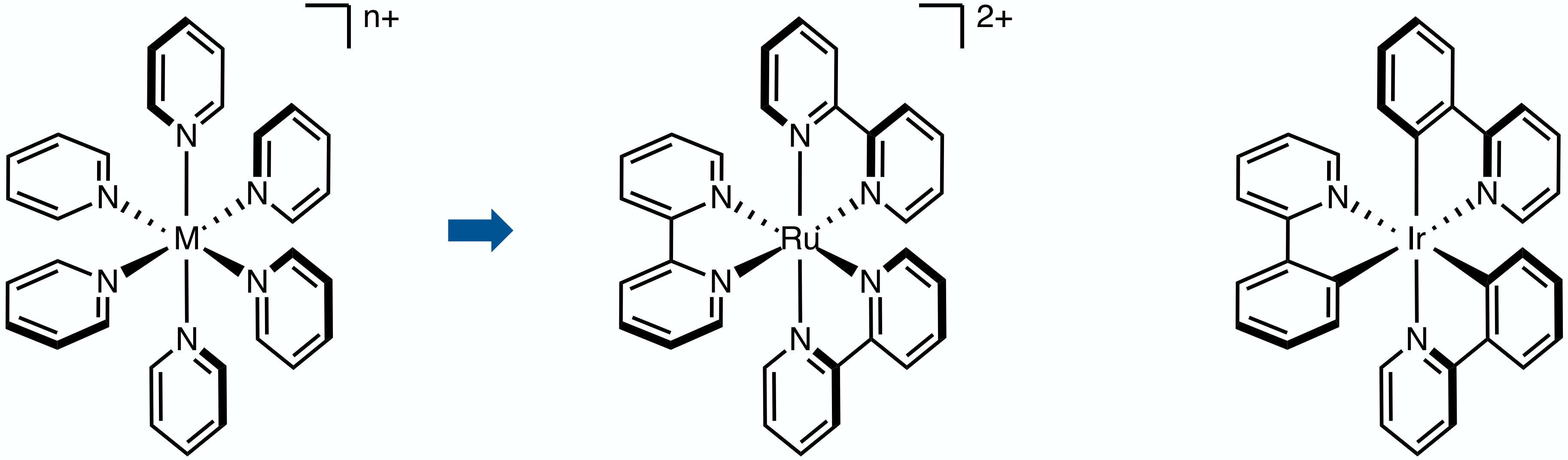
stronger SOC →

A Model for the First Excited State of Trigonal, Pseudo-octahedral Complexes

- The next step in this model is to descend in symmetry to D_3 (or C_3) by adding a perturbation term to O_h
  - As seen earlier, this is a reasonable assumption for relevant pseudo-octahedral complexes since the splitting among $d\pi_M$ orbitals is much less than the T_1–S_0 gap

$$\hat{H}\,(\mathrm{trig}) = \hat{H}\,(O_h) + \text{perturbation} = J\,\vec{\boldsymbol{S}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{LUMO}} + \lambda\,\vec{\boldsymbol{L}}_{\mathrm{HOMO}} \cdot \vec{\boldsymbol{S}}_{\mathrm{HOMO}} + \text{perturbation}$$

ML_6^{n+} (O_h) **$Ru(bpy)_3^{2+}$ (D_3)** **$Ir(ppy)_3$ (C_3)**



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$$\boxed{\hat{H}\,(\text{trig}) = \hat{H}\,(O_h) + \text{perturbation} = J\,\vec{\boldsymbol{S}}_{\text{HOMO}} \cdot \vec{\boldsymbol{S}}_{\text{LUMO}} + \lambda\,\vec{\boldsymbol{L}}_{\text{HOMO}} \cdot \vec{\boldsymbol{S}}_{\text{HOMO}} + \text{perturbation}}$$

- What should this perturbation term be, however? What will its effect be?
- Consider a general 3-component system with trigonal (D_3, C_3, etc.) symmetry
    - Chosen since the 3-component HOMO and LUMO of the excited state are descending to these symmetries
    - The Hückel model for the energy of such a system is

$$\hat{H}\psi = E\psi \qquad \text{with} \qquad \hat{H}\psi = \begin{bmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{bmatrix}$$

α = energy of each component
β = exchange energy between components

we want to find E and ψ, which will be some linear combination of the orbitals of the 3 components

$$\psi = \begin{bmatrix} c_1\,\phi_1 \\ c_2\,\phi_2 \\ c_3\,\phi_3 \end{bmatrix}$$

ϕ_1, ϕ_2, ϕ_3 = the orbitals of each component of the system

finding the solution to this system thus amounts to solving

$$(\hat{H} - E)\,\psi = 0 \quad \Rightarrow \quad \begin{bmatrix} \alpha-E & \beta & \beta \\ \beta & \alpha-E & \beta \\ \beta & \beta & \alpha-E \end{bmatrix} \begin{bmatrix} c_1\,\phi_1 \\ c_2\,\phi_2 \\ c_3\,\phi_3 \end{bmatrix} = \begin{bmatrix} \alpha-E & \beta & \beta \\ \beta & \alpha-E & \beta \\ \beta & \beta & \alpha-E \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} \begin{bmatrix} \phi_1, \phi_2, \phi_3 \end{bmatrix} = 0$$

A Model for the First Excited State of Trigonal, Pseudo-octahedral Complexes

- Since the orbitals of the 3 components are non-zero, we must solve the system of equations

$$\begin{bmatrix} c_1(\alpha-E)/\beta & c_2 & c_3 \\ c_1 & c_2(\alpha-E)/\beta & c_3 \\ c_1 & c_2 & c_3(\alpha-E)/\beta \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \quad \text{or} \quad \begin{bmatrix} c_1x & c_2 & c_3 \\ c_1 & c_2x & c_3 \\ c_1 & c_2 & c_3x \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \quad \text{using } x = (\alpha-E)/\beta$$

we can arrive at reduced row echelon form by the sequence

$$\begin{tikzcd}
\begin{bmatrix} c_1x & c_2 & c_3 \\ c_1 & c_2x & c_3 \\ c_1 & c_2 & c_3x \end{bmatrix} \arrow[r, "{-\ \text{row } 2\times x}", "{\text{row } 3\times x}"'] & \begin{bmatrix} c_1x & c_2 & c_3 \\ c_1x & c_2x^2 & c_3x \\ c_1x & c_2x & c_3x^2 \end{bmatrix} \arrow[r, "(2)-(1)", "(3)-(1)"'] & \begin{bmatrix} c_1x & c_2 & c_3 \\ 0 & c_2x^2-c_2 & c_3x-c_3 \\ 0 & c_2x-c_2 & c_3x^2-c_3 \end{bmatrix} \arrow[d, equal] \\
 & \begin{bmatrix} c_1x & c_2 & c_3 \\ 0 & c_2(x-1)(x+1) & c_3(x-1) \\ 0 & c_2(x-1)(x+1) & c_3(x-1)(x+1)^2 \end{bmatrix} \arrow[dl, "(3)-(2)"] & \begin{bmatrix} c_1x & c_2 & c_3 \\ 0 & c_2(x-1)(x+1) & c_3(x-1) \\ 0 & c_2(x-1) & c_3(x-1)(x+1) \end{bmatrix} \arrow[l, "(3)\times(x+1)"] \\
\begin{bmatrix} c_1x & c_2 & c_3 \\ 0 & c_2(x-1)(x+1) & c_3(x-1) \\ 0 & 0 & c_3[(x-1)(x+1)^2-(x-1)] \end{bmatrix} \arrow[rr, "{\substack{(1)\times x(x-1)(x+2) \\ (2)\times x(x+2) \\ \text{simplify } (3)}}"] & & \begin{bmatrix} c_1x^2(x-1)(x+2) & c_2x(x-1)(x+2) & c_3x(x-1)(x+2) \\ 0 & c_2x(x-1)(x+1)(x+2) & c_3x(x-1)(x+2) \\ 0 & 0 & c_3x(x-1)(x+2) \end{bmatrix} \arrow[d, "(2)-(3)", "(1)-(3)"'] \\
\begin{bmatrix} c_1x^2(x-1)(x+1)(x+2) & 0 & 0 \\ 0 & c_2x(x-1)(x+1)(x+2) & 0 \\ 0 & 0 & c_3x(x-1)(x+2) \end{bmatrix} & & \begin{bmatrix} c_1x^2(x-1)(x+2) & c_2x(x-1)(x+2) & 0 \\ 0 & c_2x(x-1)(x+1)(x+2) & 0 \\ 0 & 0 & c_3x(x-1)(x+2) \end{bmatrix} \arrow[ll, "(1)\times(x+1)-(2)"']
\end{tikzcd}$$

A Model for the First Excited State of Trigonal, Pseudo-octahedral Complexes

- With the system simplified to

$$\begin{bmatrix} c_1 x^2(x-1)(x+1)(x+2) & 0 & 0 \\ 0 & c_2 x(x-1)(x+1)(x+2) & 0 \\ 0 & 0 & c_3 x(x-1)(x+2) \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \quad \text{and } x = (\alpha - E)/\beta$$

- We have solutions for x of $x = -2, -1, 0, +1$, but substitution of $x = -1$ or $x = 0$ into

$$\begin{bmatrix} c_1 x & c_2 & c_3 \\ c_1 & c_2 x & c_3 \\ c_1 & c_2 & c_3 x \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \text{ both quickly lead to rref } \begin{bmatrix} c_1 & 0 & 0 \\ 0 & c_2 & 0 \\ 0 & 0 & c_3 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \text{ (a meaningless solution)}$$

- $x = -2$ corresponds to E = $\alpha + 2\beta$ and substitution into the original matrix leads to

$$\begin{bmatrix} -2c_1 & c_2 & c_3 \\ c_1 & -2c_2 & c_3 \\ c_1 & c_2 & -2c_3 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \text{ and rref } \begin{bmatrix} c_1 & -c_2 & 0 \\ 0 & c_2 & -c_3 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \Rightarrow$$

$c_1 = c_2 = c_3$
(we are free to choose the value)

- $x = +1$ corresponds to $E = \alpha - \beta$ and substitution into the original matrix leads to

$$\begin{bmatrix} c_1 & c_2 & c_3 \\ c_1 & c_2 & c_3 \\ c_1 & c_2 & c_3 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \text{ and rref } \begin{bmatrix} c_1 & c_2 & c_3 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \Rightarrow$$

$c_1 = -(c_2 + c_3)$ (degenerate)
(choose any 2 pairs of c_2 and c_3)

- We may select any values, and it is tempting to use 1 or other simple real numbers, but if we select

for $x = -2$ ($E = \alpha + 2\beta$), **$c_1 = c_2 = c_3 = 1/\sqrt{3}$**

and for $x = +1$ ($E = \alpha - \beta$),
(has 2 solutions)

$$\begin{aligned} c_2 &= e^{\pm 2\pi i/3}/\sqrt{3} = -1/(2\sqrt{3}) \pm 1/2\, i \\ c_3 &= e^{\mp 2\pi i/3}/\sqrt{3} = -1/(2\sqrt{3}) \mp 1/2\, i \end{aligned}, \quad c_1 = 1/\sqrt{3}$$

(same c_1 in both cases)

A Model for the First Excited State of Trigonal, Pseudo-octahedral Complexes

- Then the solutions to our 3-component system are

$$\boxed{E_1 = \alpha + 2\beta \qquad \psi_1 = \frac{\phi_1 + \phi_2 + \phi_3}{\sqrt{3}} \qquad E_{2,3} = \alpha - \beta \qquad \psi_{2,3} = \frac{\phi_1 + e^{\pm 2\pi i/3}\phi_2 + e^{\mp 2\pi i/3}\phi_3}{\sqrt{3}}}$$

this is the a general model for any system of 3 equivalent components, symmetrically positioned in a trigonal point group, that have an exchange interaction

- Critically, if we compare this solution to our model for the HOMO and LUMO of metal polypyridyls…

$$\text{HOMO } (L_z = 0) = \frac{\mathrm{d}_{xy} + \mathrm{d}_{xz} + \mathrm{d}_{yz}}{\sqrt{3}} \cos\theta + \frac{\pi_{\mathrm{L}x}{}^* + \pi_{\mathrm{L}y}{}^* + \pi_{\mathrm{L}z}{}^*}{\sqrt{3}} \sin\theta$$

$$\text{HOMO } (L_z = \pm 1) = \frac{\mathrm{d}_{xy} + e^{\pm 2\pi i/3}\mathrm{d}_{xz} + e^{\mp 2\pi i/3}\mathrm{d}_{yz}}{\sqrt{3}} \cos\theta + \frac{\pi_{\mathrm{L}z}{}^* + e^{\pm 2\pi i/3}\pi_{\mathrm{L}y}{}^* + e^{\mp 2\pi i/3}\pi_{\mathrm{L}x}{}^*}{\sqrt{3}} \sin\theta$$

$$\text{LUMO } (L_z = 0) = \frac{\pi_{\mathrm{L}x}{}^* + \pi_{\mathrm{L}y}{}^* + \pi_{\mathrm{L}z}{}^*}{\sqrt{3}} \qquad \text{LUMO } (L_z = \pm 1) = \frac{\pi_{\mathrm{L}z}{}^* + e^{\pm 2\pi i/3}\pi_{\mathrm{L}y}{}^* + e^{\mp 2\pi i/3}\pi_{\mathrm{L}x}{}^*}{\sqrt{3}}$$

The solutions are constructed in the exact same manner from their constituent orbitals

⬇

This is an appropriate model for the descent in symmetry from O_h to D_3 or C_3

A Model for the First Excited State of Trigonal, Pseudo-octahedral Complexes

- Descending from O_h to D_3 or C_3, the previously 3-fold degenerate HOMO and LUMO are split
  - Comparing the form of the trigonal symmetry model

$$E_1 = \alpha + 2\beta \qquad \psi_1 = \frac{\phi_1 + \phi_2 + \phi_3}{\sqrt{3}} \qquad E_{2,3} = \alpha - \beta \qquad \psi_{2,3} = \frac{\phi_1 + e^{\pm 2\pi i/3}\phi_2 + e^{\mp 2\pi i/3}\phi_3}{\sqrt{3}}$$

to the wavefunctions used to model the excited state of photocatalysts,

$$\text{LUMO } (L_z = 0) = \frac{\pi_{\text{L}x}^* + \pi_{\text{L}y}^* + \pi_{\text{L}z}^*}{\sqrt{3}} \qquad \text{LUMO } (L_z = \pm 1) = \frac{\pi_{\text{L}z}^* + e^{\pm 2\pi i/3}\pi_{\text{L}y}^* + e^{\mp 2\pi i/3}\pi_{\text{L}x}^*}{\sqrt{3}}$$

the $L_z = \pm 1$ LUMO remains 2-fold degenerate, but separates from the $L_z = 0$ level by $E = 3\beta$

(the result is also true for the HOMO, though β need not have the same value in both cases)

- If we define these splittings as Δ for the HOMO and Γ for the LUMO, but first
  - We have generally ignored L_z (LUMO) and will do so here, it adds 2 degenerate solutions higher by Γ
  - Recognize that we need a term that separates the $L_z = \pm 1$ levels from the $L_z = 0$ level

we may write the following model for the excited state of a trigonal pseudo-octahedral complex

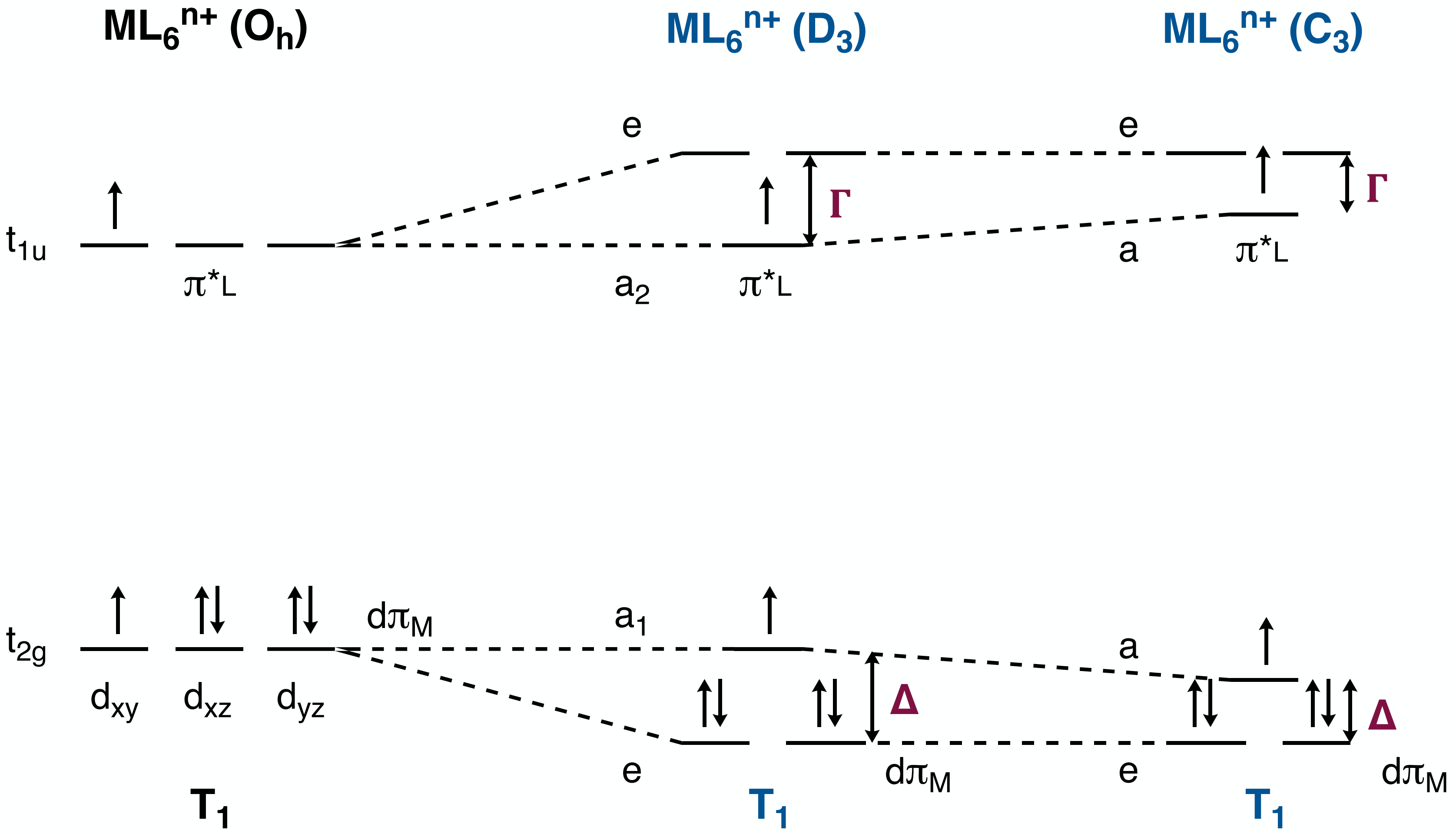
$$\boxed{\hat{H}\,(\text{trig}) = J\, \vec{\boldsymbol{S}}_{\text{HOMO}} \cdot \vec{\boldsymbol{S}}_{\text{LUMO}} + \lambda\, \vec{\boldsymbol{L}}_{\text{HOMO}} \cdot \vec{\boldsymbol{S}}_{\text{HOMO}} + \Delta(L_z)^2}$$

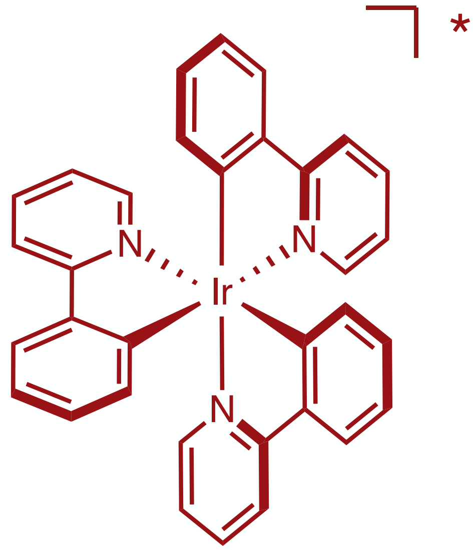
A Model for the First Excited State of Trigonal, Pseudo-octahedral Complexes

- In terms of a molecular orbital level diagram, we get the a result that makes sense:

$$\boxed{\hat{H}\,(\text{trig}) = J\,\vec{S}_{\text{HOMO}}\cdot\vec{S}_{\text{LUMO}} + \lambda\,\vec{L}_{\text{HOMO}}\cdot\vec{S}_{\text{HOMO}} + \Delta(L_z)^2}$$

- Effect of the perturbation to O_h – $\Delta(L_z)^2$



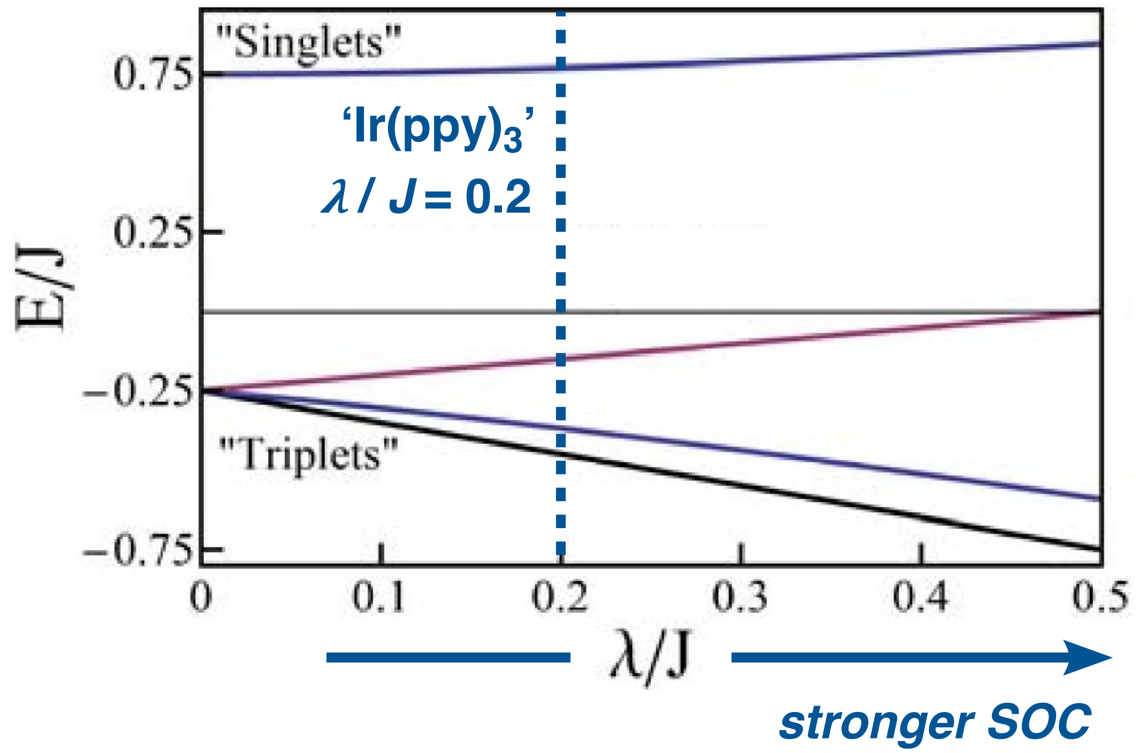


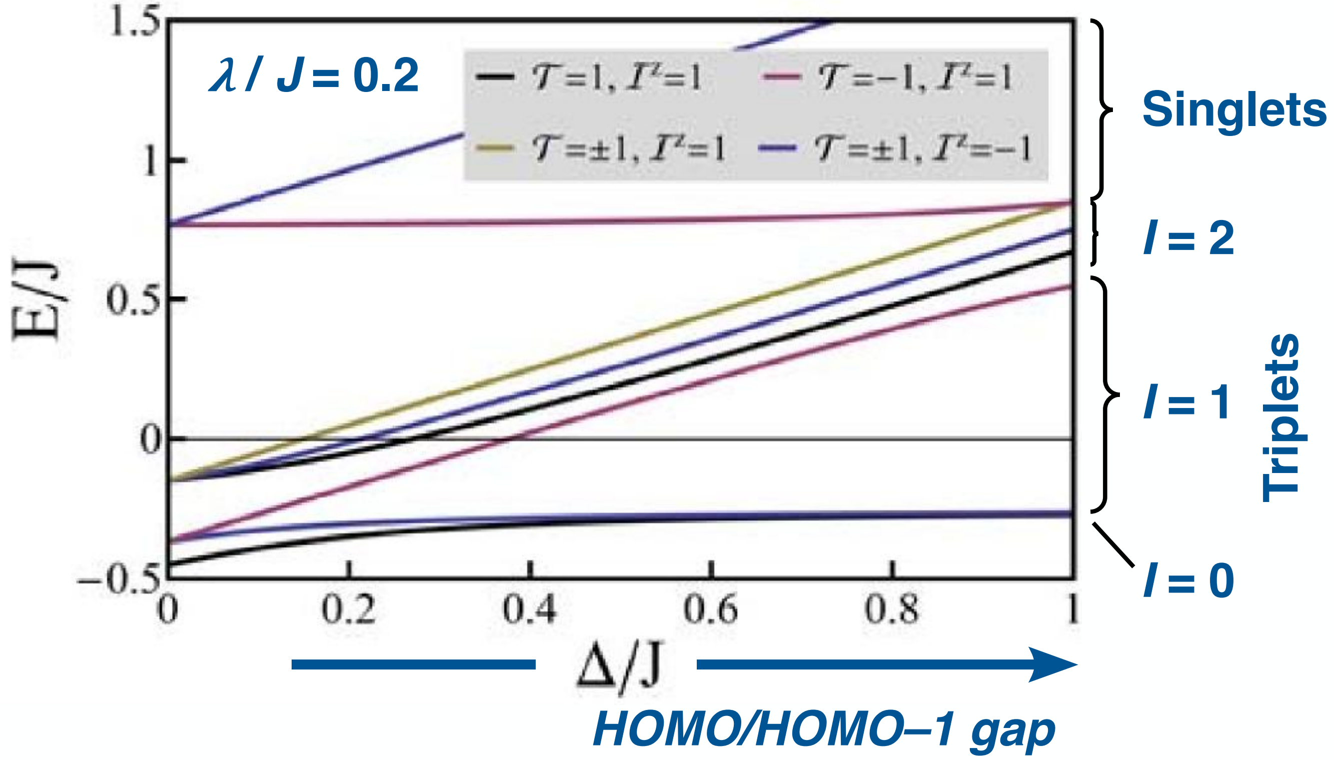
$\Delta \approx 0.14$ eV for $Ir(ppy)_3$

- The perturbation stabilizes the HOMO and destabilizes the LUMO as shown since the e solutions interact but the a_1 and a_2 solutions may not due to symmetry
- The magnitude of the splitting is lower in C_3 since the distinct a_1 and a_2 orbitals inheret the same symmetry (a)

A Model for the First Excited State of Trigonal, Pseudo-octahedral Complexes

- The descent from O_h to trigonal symmetry lifts many substate degeneracies, leaves 3 low-*E* triplets





Octahedral model

$$\hat{H}(O_h) = J\,\vec{\boldsymbol{S}}_{\mathrm{HOMO}}\cdot\vec{\boldsymbol{S}}_{\mathrm{LUMO}} + \lambda\,\vec{\boldsymbol{L}}_{\mathrm{HOMO}}\cdot\vec{\boldsymbol{S}}_{\mathrm{HOMO}}$$

Trigonal model

$$\hat{H}(\mathrm{trig}) = J\,\vec{\boldsymbol{S}}_{\mathrm{HOMO}}\cdot\vec{\boldsymbol{S}}_{\mathrm{LUMO}} + \lambda\,\vec{\boldsymbol{L}}_{\mathrm{HOMO}}\cdot\vec{\boldsymbol{S}}_{\mathrm{HOMO}} + \Delta(L_z)^2$$

For Ir(ppy)$_3$:
$J \approx 1$ eV, $\lambda \approx 0.22$ eV, $\Delta \approx 0.14$ eV,
so **$\lambda / J \approx 0.22$, $\Delta / J \approx 0.14$**

A Model for the First Excited State of Trigonal, Pseudo-octahedral Complexes

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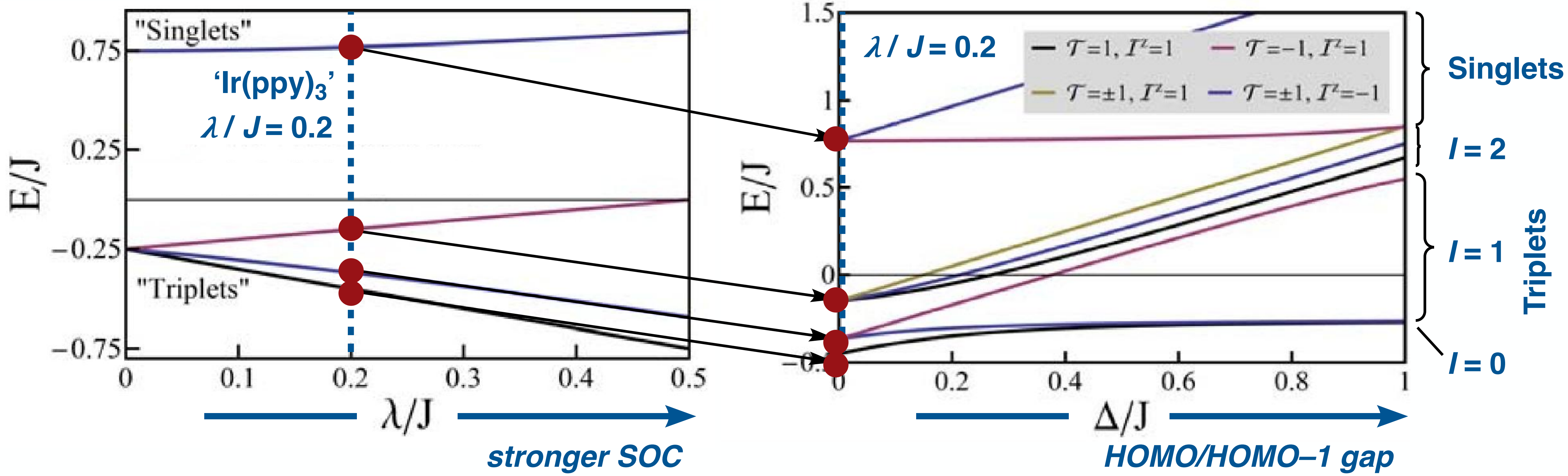

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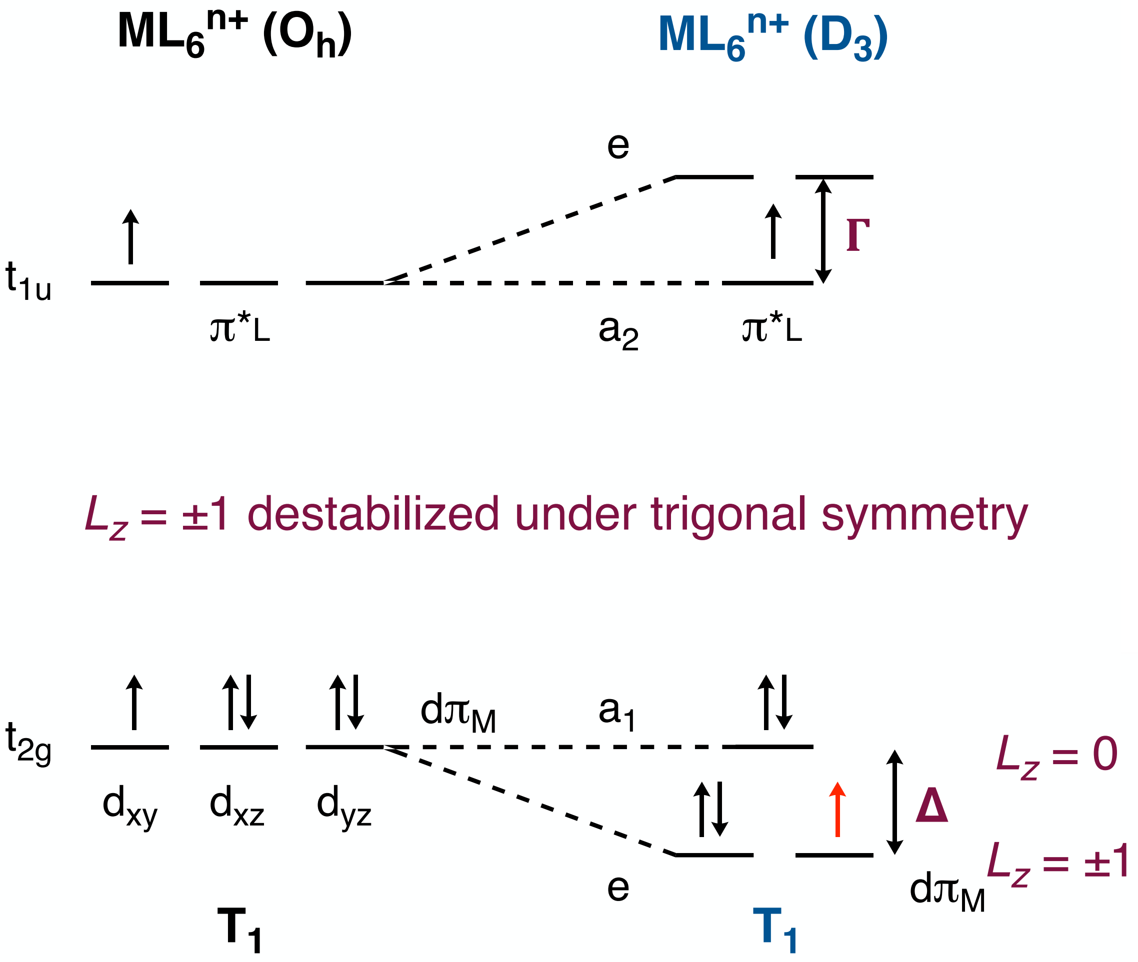
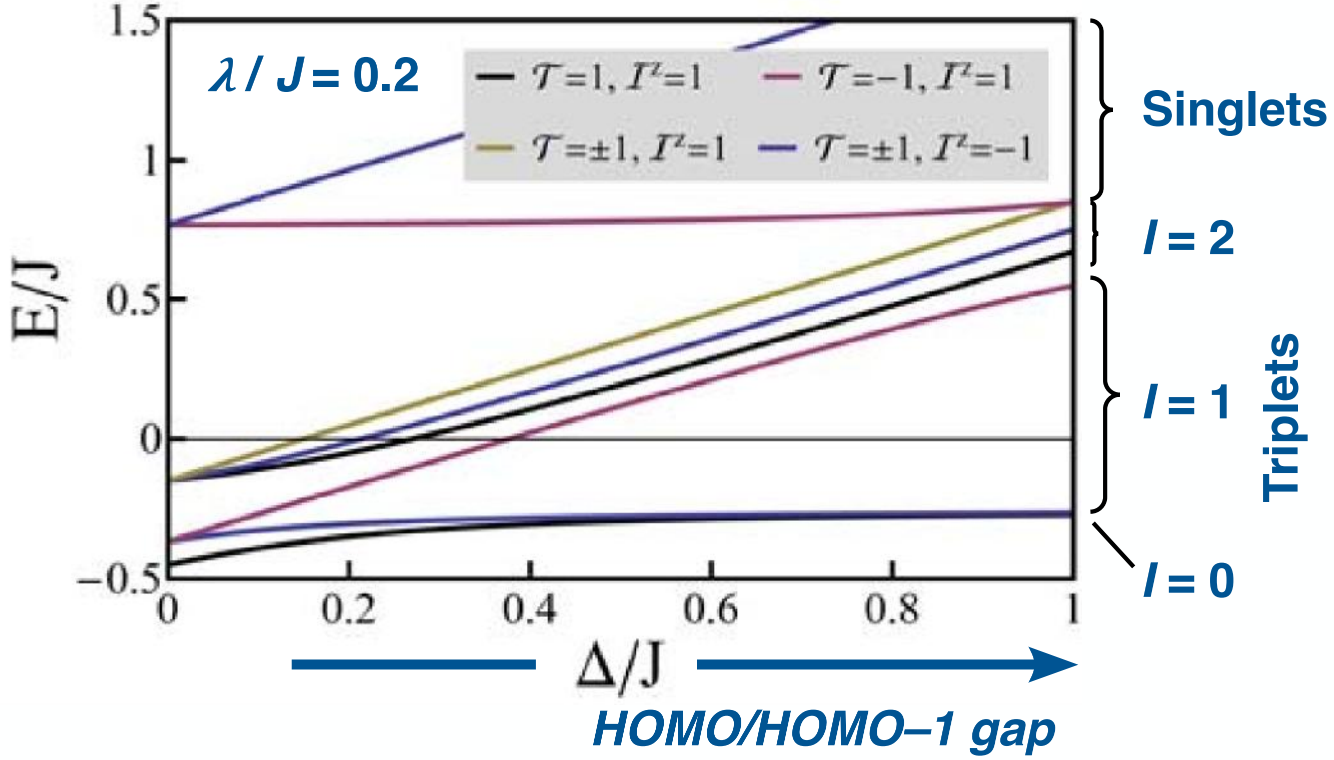


$L_z = \pm1$ destabilized under trigonal symmetry



HOMO/HOMO–1 gap

Trigonal model

$$\hat{H}\,(\text{trig}) = J\,\vec{S}_{\text{HOMO}} \cdot \vec{S}_{\text{LUMO}} + \lambda\,\vec{L}_{\text{HOMO}} \cdot \vec{S}_{\text{HOMO}} + \Delta(L_z)^2$$

Effect of Δ –
raises *E* unless $L_z = 0$ ➡ **Leaves 3 low-*E* triplets**
(one *l* = 0 and two *l* = 1)

A Model for the First Excited State of Trigonal, Pseudo-octahedral Complexes

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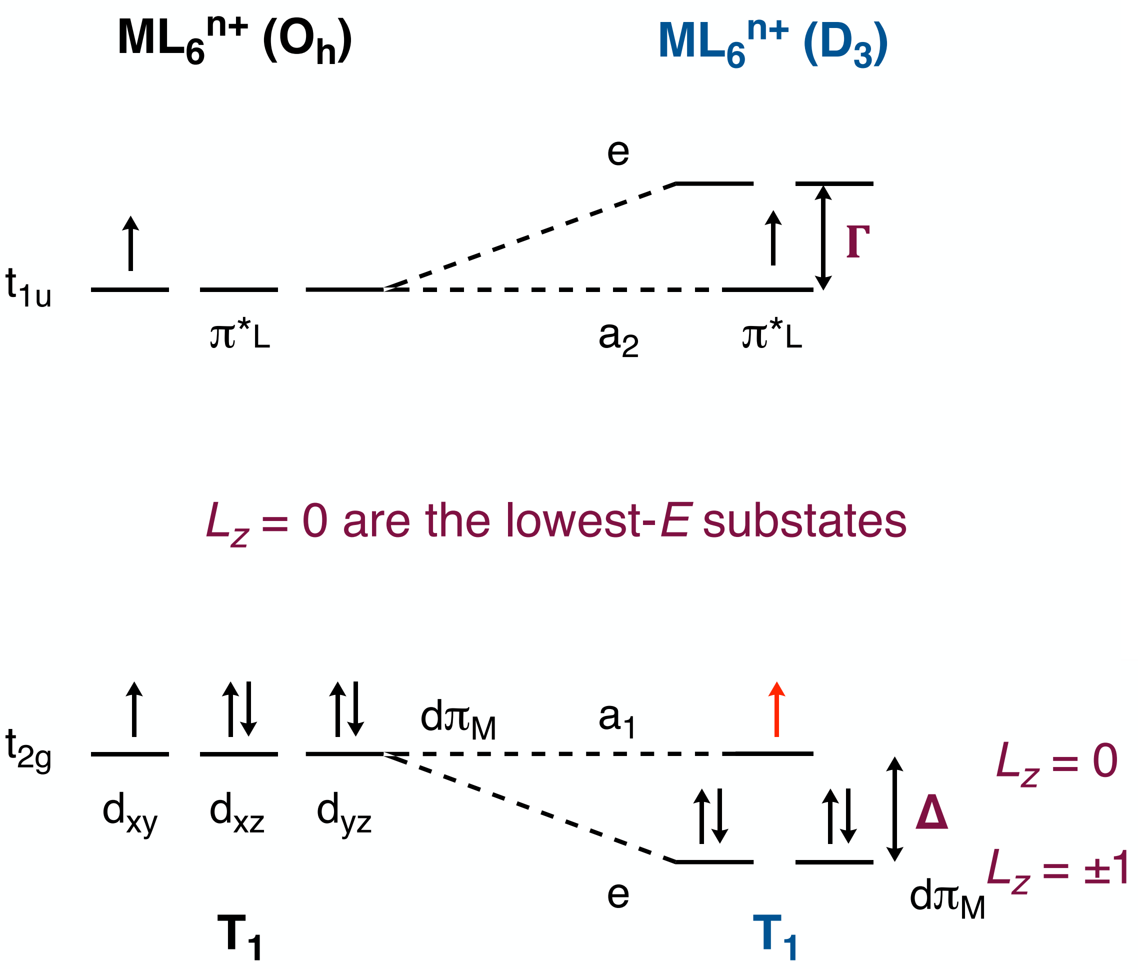
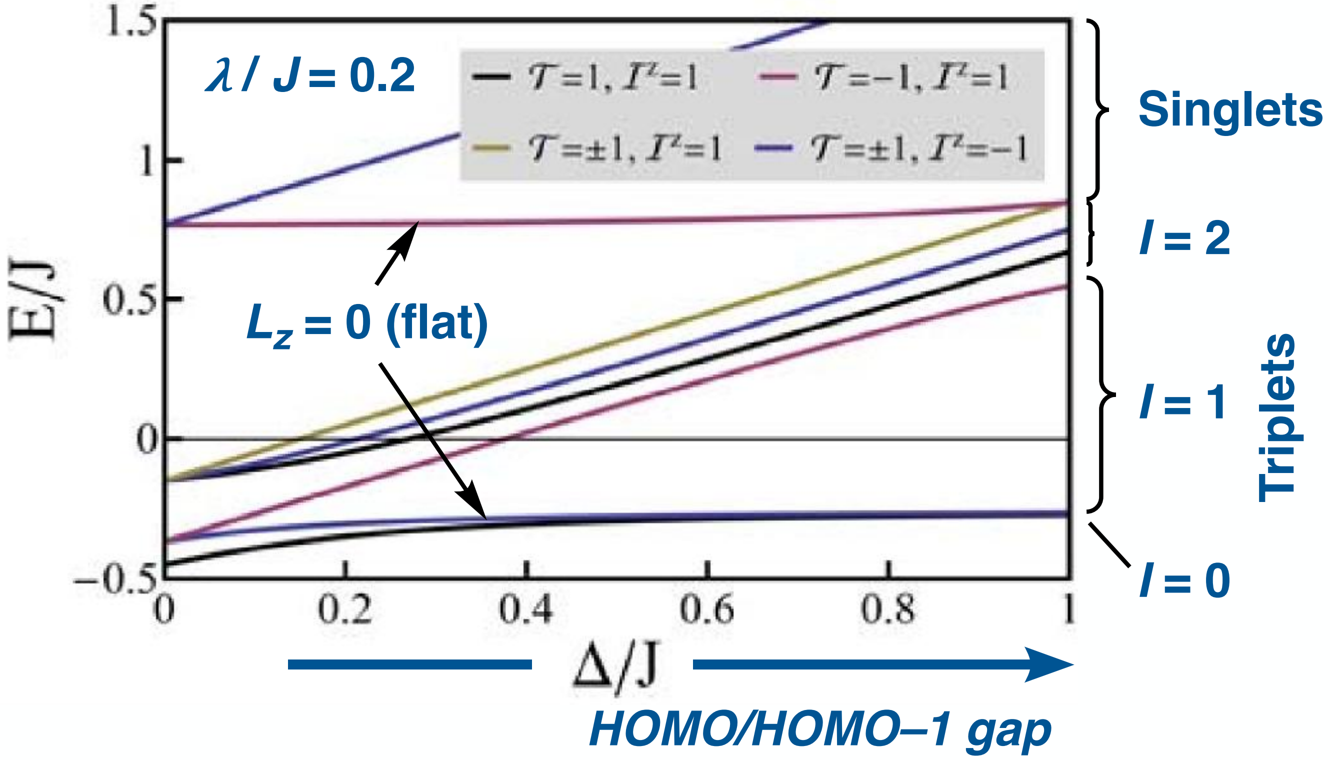


$L_z = 0$ are the lowest-*E* substates



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Effect of Δ – raises *E* unless $L_z = 0$ ➡ **Leaves 3 low-*E* triplets (one $I = 0$ and two $I = 1$)**

- More realistic than O_h, but 2 of the 3 substates of T_1 remain degenerate

A Model for the First Excited State of Trigonal, Pseudo-octahedral Complexes

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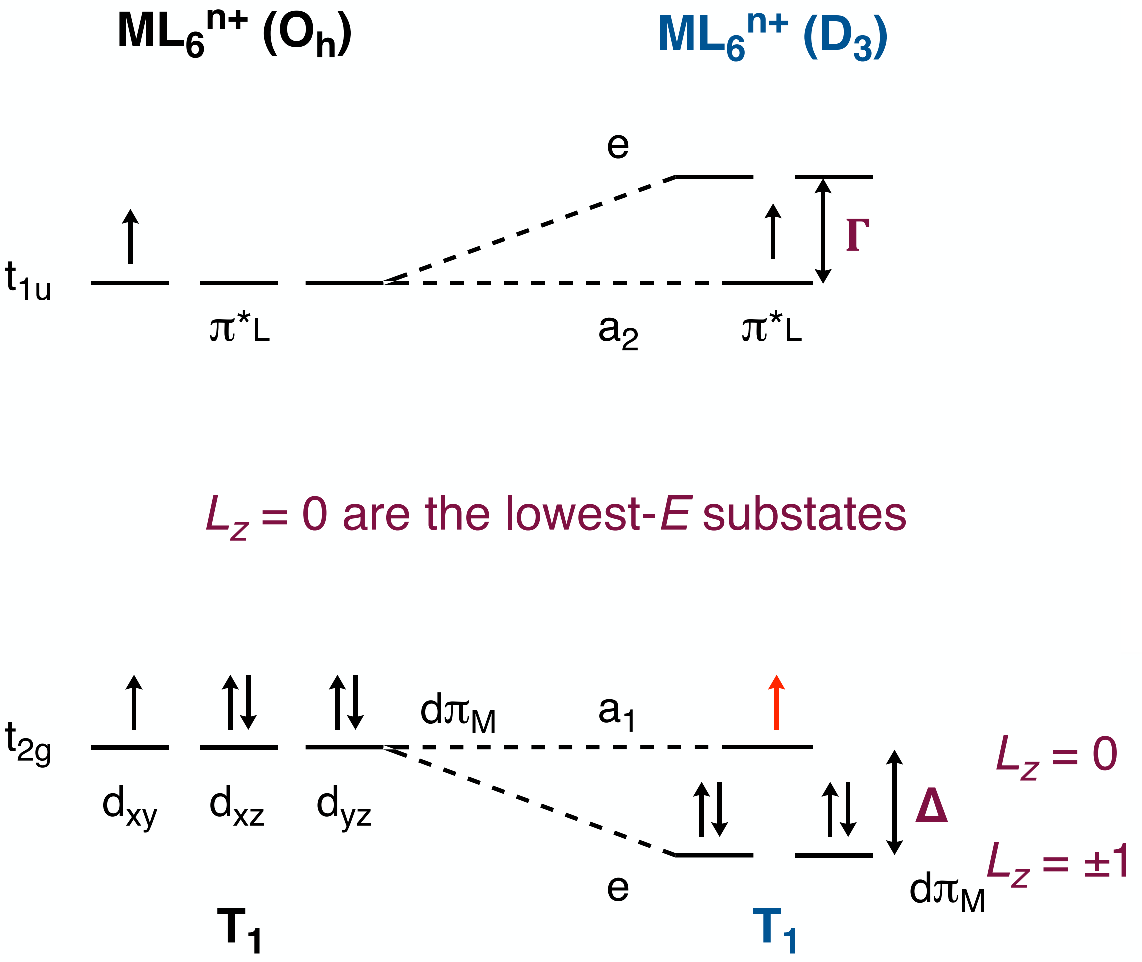
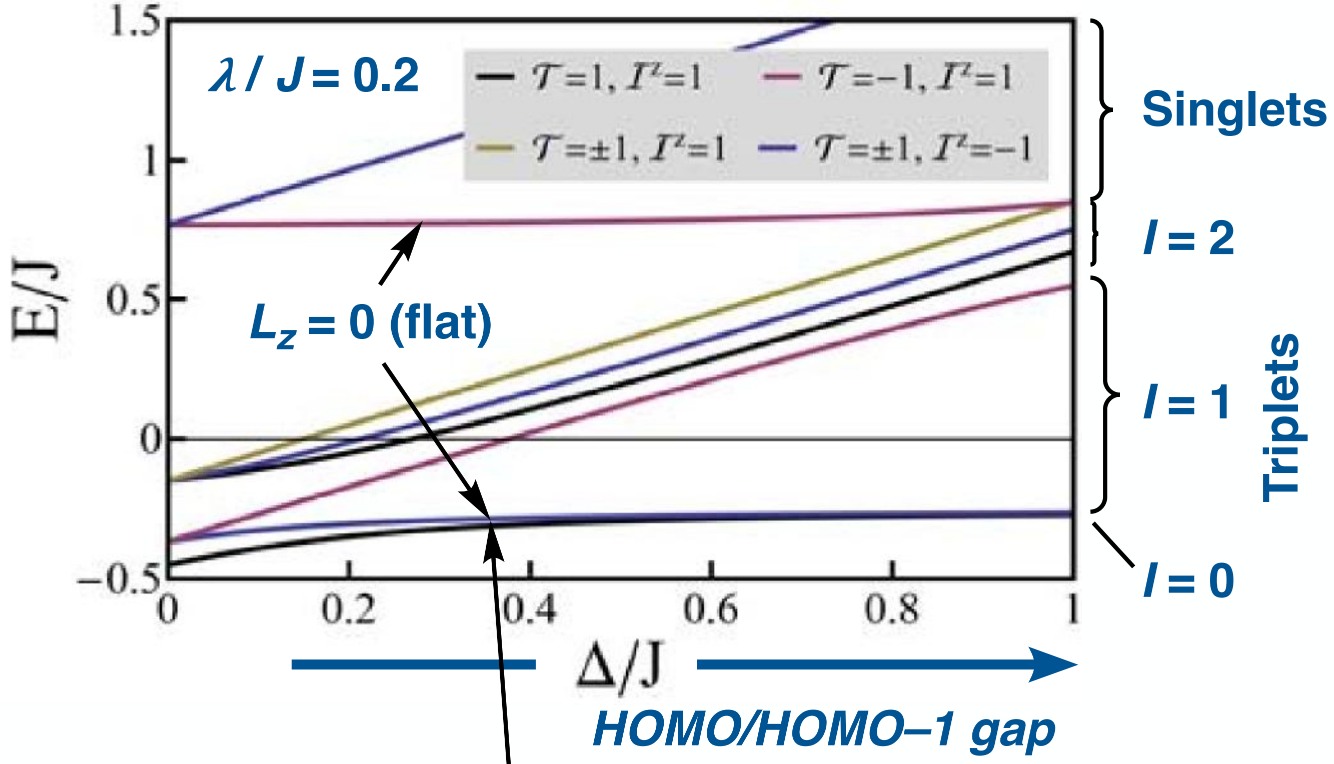


$L_z = 0$ are the lowest-*E* substates



HOMO/HOMO–1 gap

these are the lowest blue and black lines
what do these substates look like?

Effect of Δ –
raises *E* unless $L_z = 0$

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(one $l = 0$ and two $l = 1$)

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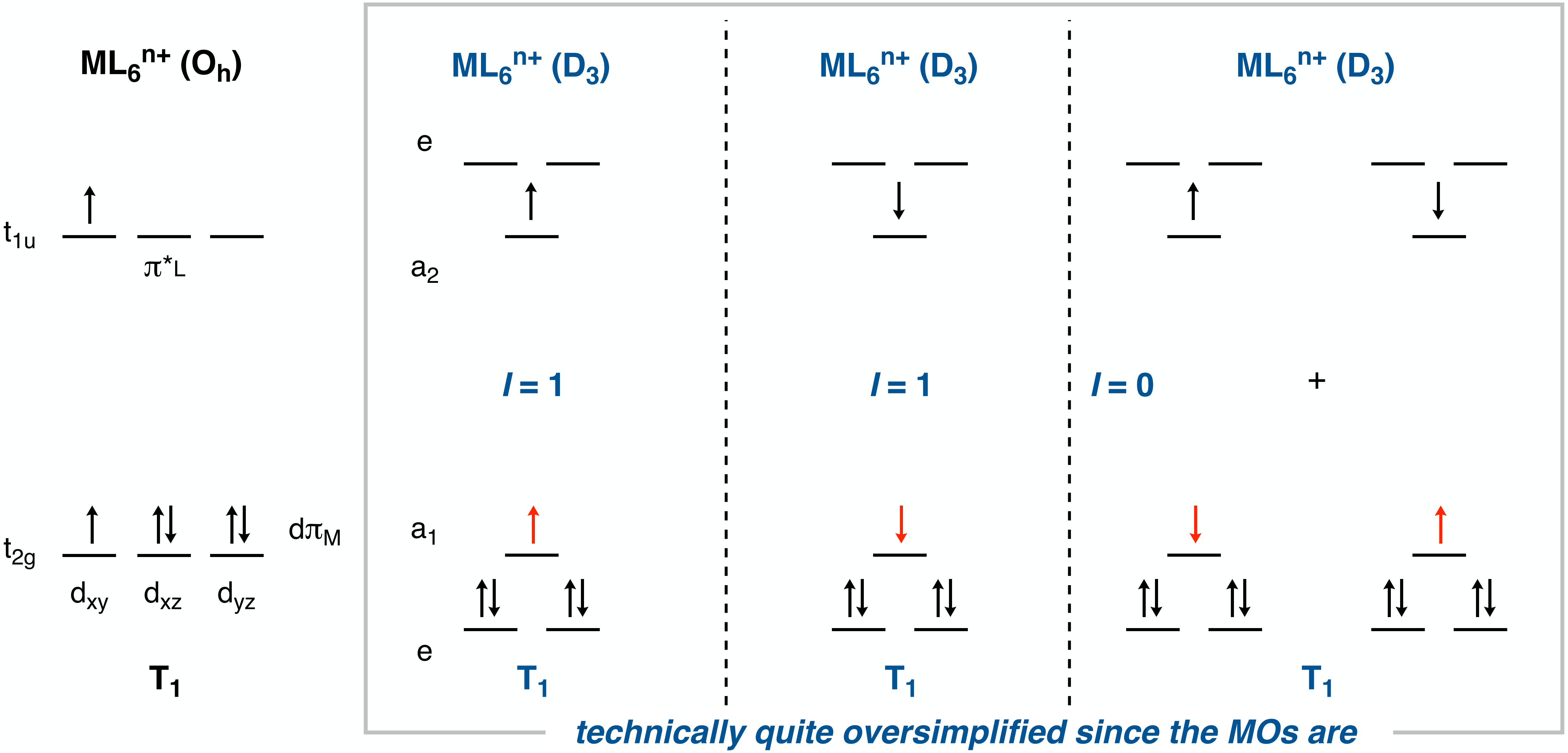


technically quite oversimplified since the MOs are much nastier combinations of metal/ligand-centered orbitals and spin states, but not an unreasonable way to picture the key interactions

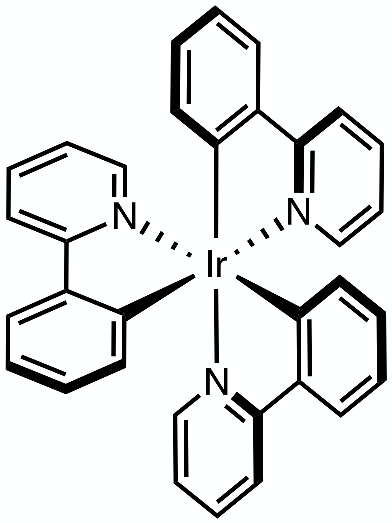
Effect of Δ – raises *E* unless $L_z = 0$ ➡ **Leaves 3 low-*E* triplets (one *l* = 0 and two *l* = 1)**

- More realistic than O_h, but 2 of the 3 substates of T_1 remain degenerate

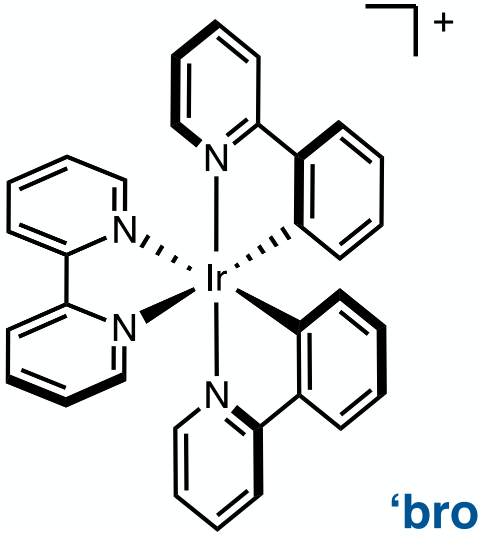
A Model for the First Excited State of Broken Trigonal, Pseudo-octahedral Complexes

- The final step is to descend from trigonal symmetry (D_3 or C_3) to ‘broken’ trigonal symmetry
  - This symmetry change may come from treating an excited state as localized or by considering a heteroleptic photocatalyst instead of a homoletpic one

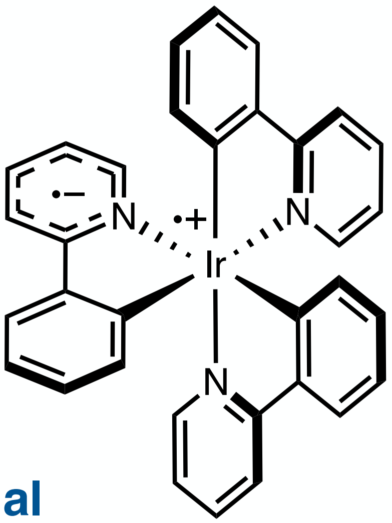
Ir(ppy)$_3$ (C_3)



Ir(ppy)$_2$(bpy)$^+$ (C_2)



localized excited state of Ir(ppy)$_3$ (C_1)



‘broken’ trigonal symmetry

- This is a perturbation to trigonal symmetry, in analogy to trigonal symmetry as a perturbation of O_h
  - We introduce a term δ which alters the energy of states with net orbital angular momentum in *x*, *y*

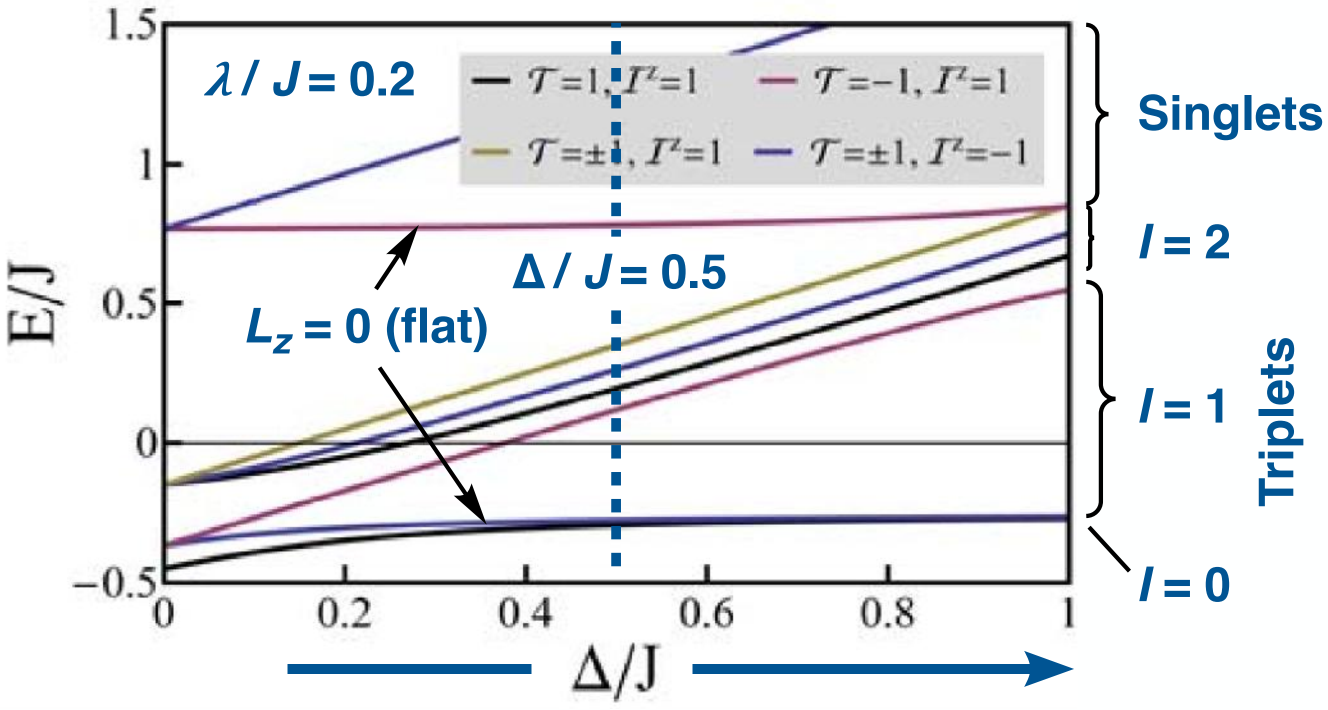
$$\boxed{\hat{H}(\text{trig}') = J\,\vec{\boldsymbol{S}}_{\text{HOMO}} \cdot \vec{\boldsymbol{S}}_{\text{LUMO}} + \lambda\,\vec{\boldsymbol{L}}_{\text{HOMO}} \cdot \vec{\boldsymbol{S}}_{\text{HOMO}} + \Delta(L_z)^2 + \delta[(L_x)^2 - (L_y)^2]}$$

A Model for the First Excited State of Broken Trigonal, Pseudo-octahedral Complexes

- The descent from trigonal to borken trigonal symmetry lifts all degeneracies
  - Focus on the T_1 substates – the entire picture is very complex and adds little information

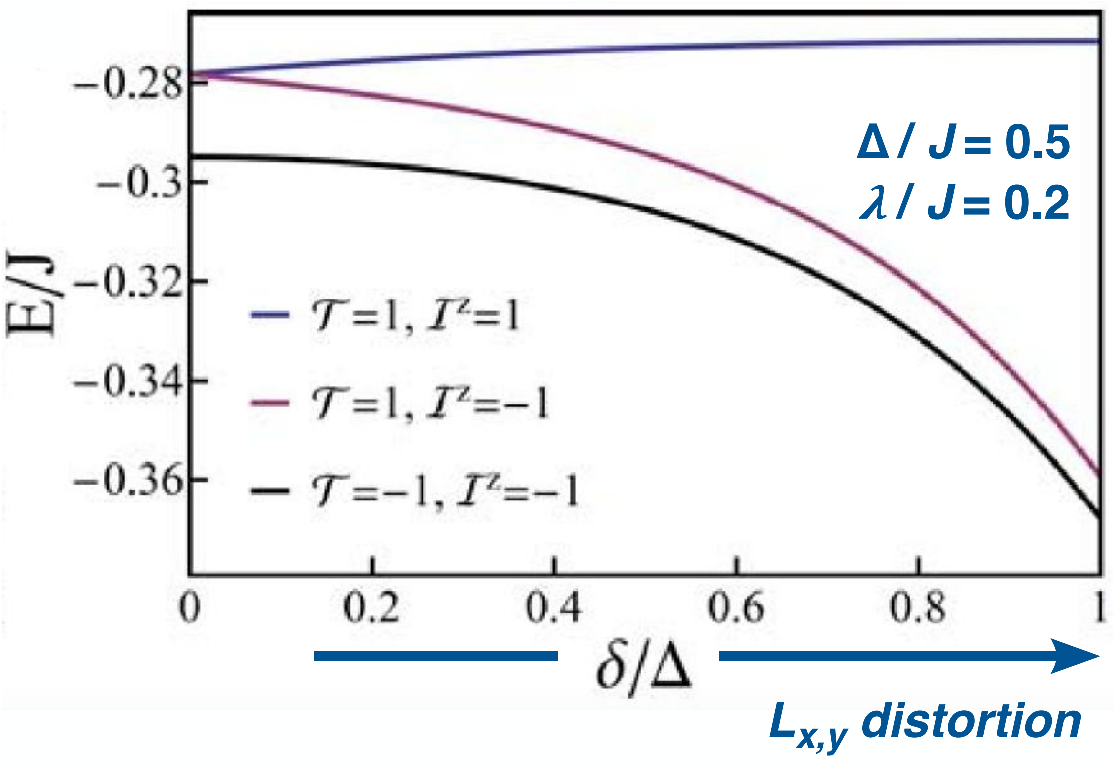
Trigonal model

$$\hat{H}(\text{trig}) = J\,\vec{S}_{\text{HOMO}} \cdot \vec{S}_{\text{LUMO}} + \lambda\,\vec{L}_{\text{HOMO}} \cdot \vec{S}_{\text{HOMO}} + \Delta(L_z)^2$$



Broken trigonal model

$$\hat{H}(\text{trig}') = \hat{H}(\text{trig}) + \delta[(L_x)^2 - (L_y)^2]$$



- Describes the T_1 state as 3 substates
  - 1 non-degenerate with $I = 0$, lowest-E
  - 2 degenerate with $I = 1$, next-to-lowest-E
- Descent from O_h to trigonal leaves these substates as low-E due to a lack of *z*-orbital angular momentum

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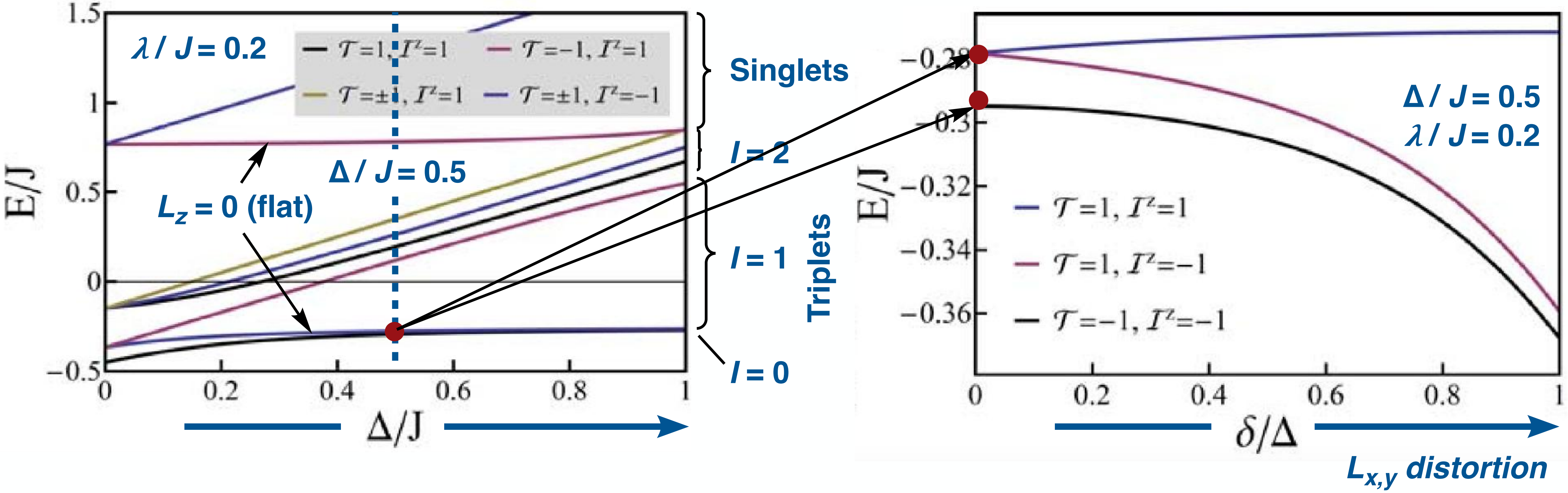

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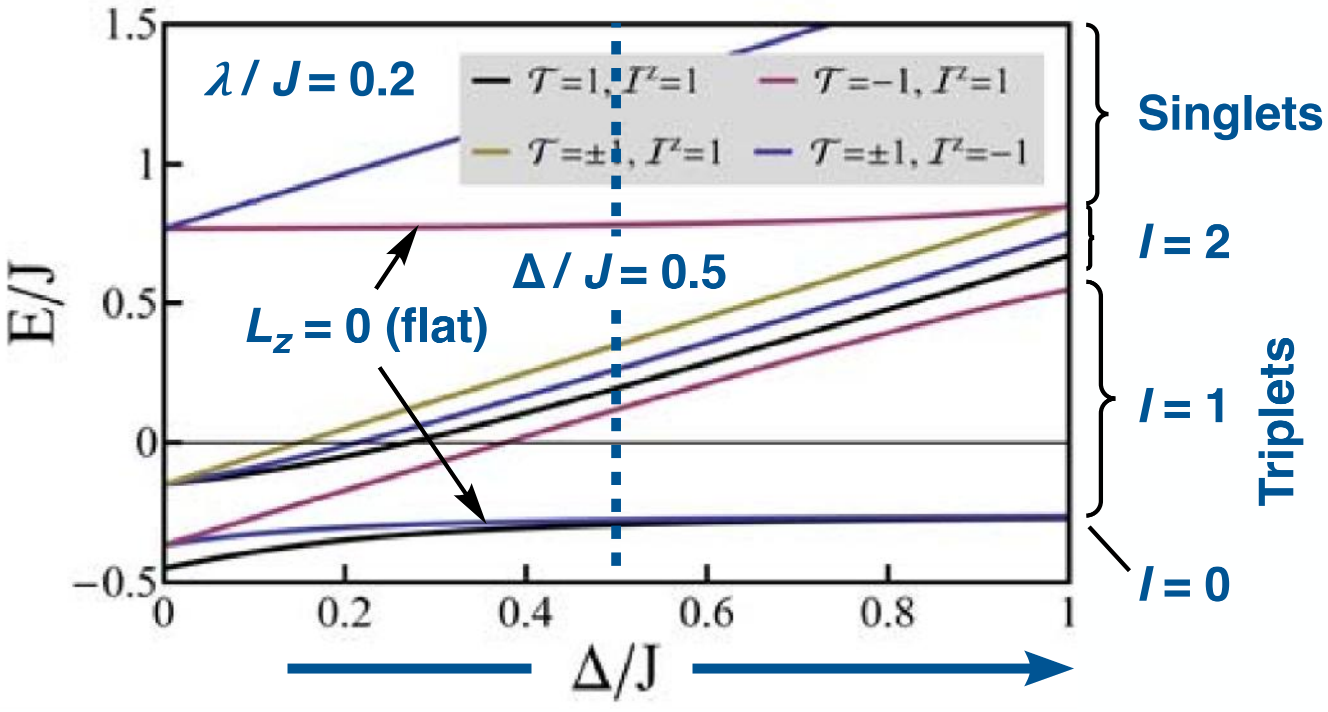

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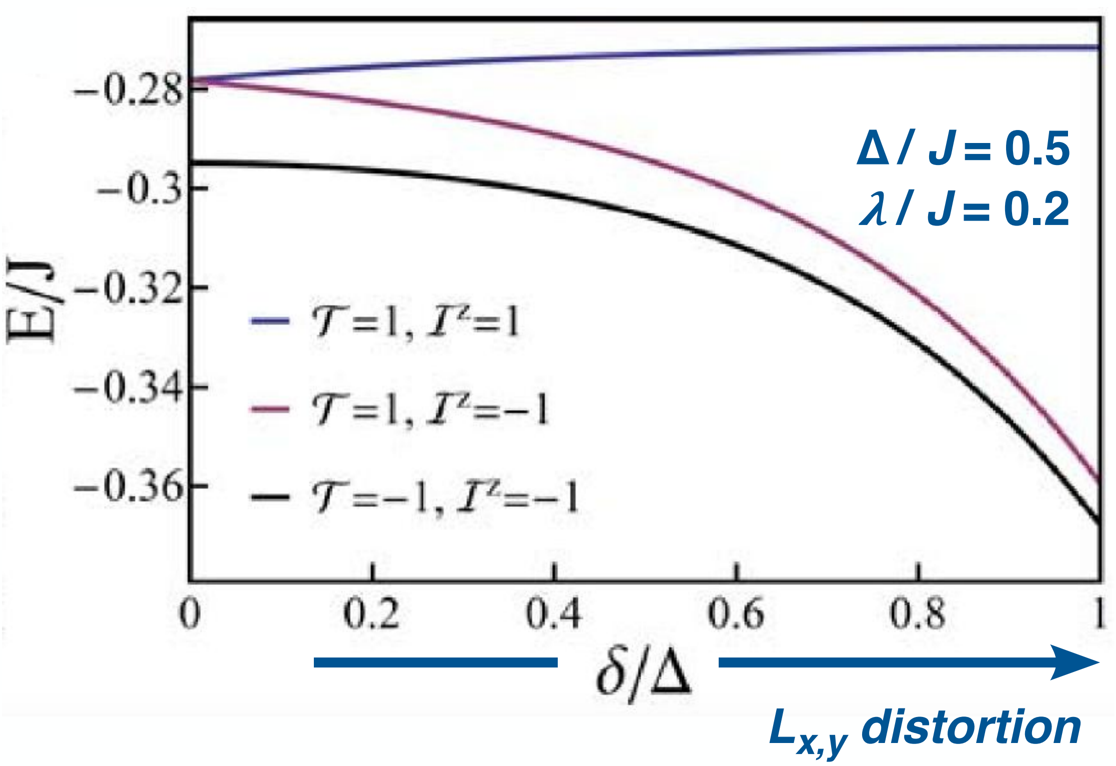

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- Splits the low-lying $I = 1$ substate
  - Due to their disparate $L_{x,y}$ values
- Allows assignment of substates I, II, III
- As in real systems, ΔE(II,III) >> ΔE(I,II)

A Model for the First Excited State of Broken Trigonal, Pseudo-octahedral Complexes

- A summary of the pseudo angular momentum model

Octahedral model

$$\hat{H}(O_h) = J\,\vec{\boldsymbol{S}}_{HOMO} \cdot \vec{\boldsymbol{S}}_{LUMO} + \lambda\,\vec{\boldsymbol{L}}_{HOMO} \cdot \vec{\boldsymbol{S}}_{HOMO}$$

Trigonal model

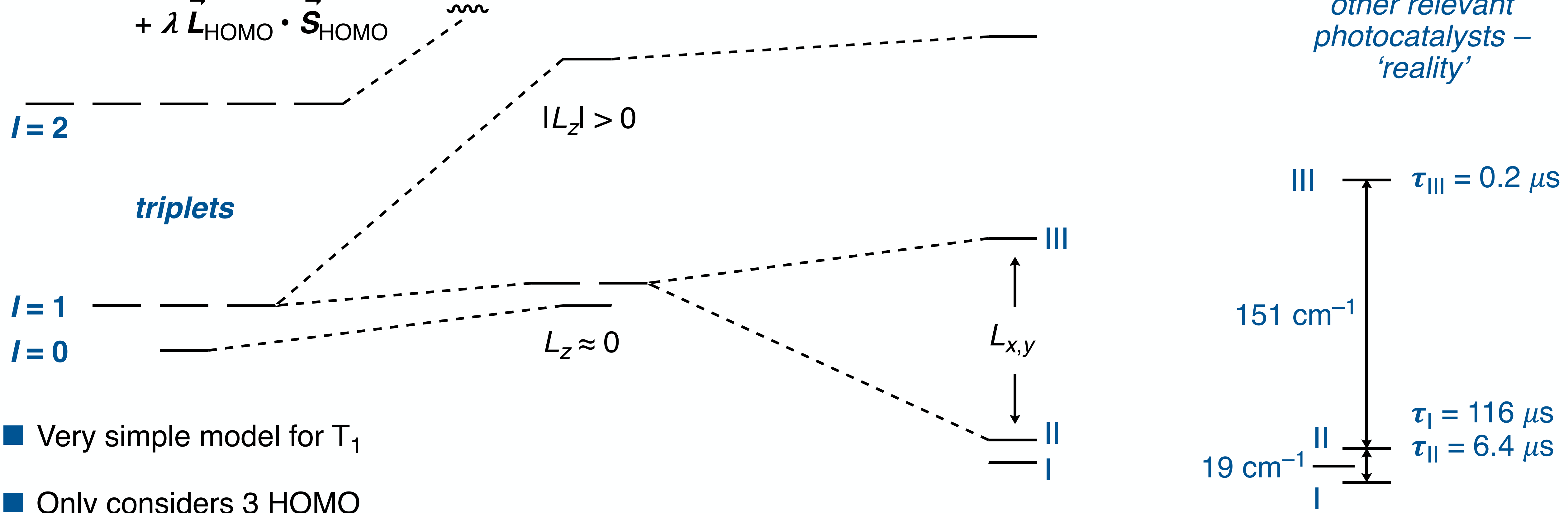
$$\hat{H}(\text{trig}) = \hat{H}(O_h) + \Delta(L_z)^2$$

Broken trigonal model

$$\hat{H}(\text{trig}') = \hat{H}(\text{trig}) + \delta[(L_x)^2 - (L_y)^2]$$

Ir(ppy)$_3$ T$_1$ substates

similar to many other relevant photocatalysts – 'reality'



- Very simple model for T$_1$
- Only considers 3 HOMO and 3 LUMO orbitals
- Only considers e$^-$/hole spin-spin, and hole spin-orbit interactions
- Almost fully solvable from simple quantum mechanical identities

- Treats descent in symmetry as a simple perturbation to O$_h$
- Predicts 3 substates of T$_1$ much lower in energy than other excited states due to $L_z \approx 0$ (2 degenerate)

- Treats further descent in symmetry as an additional, analogous perturbation
- Predicts a realistic splitting of the T$_1$ substates

Excellent qualitative approximation

A Model for the First Excited State of Broken Trigonal, Pseudo-octahedral Complexes

- Some key conclusions from the pseudo angular momentum model
  - The energetic structure underlying our photocatalysts derive from a few simple general molecular features
  - Earlier consideration of intersystem crossing showed that the global structure of excited state energies resulting from octahedral or near-octahedral geometry was essential to photocatalyst generality
  - Given appropriate ligand/metal energies and strong spin-orbit coupling, this model suggests that *the fine structure of the excited state energies can also be seen as a consequence of pseudo-octahedral geometry*

Appreciable changes to the ligand framework to adjust specific properties do not compromise the generally desired reactivity