

1.4 Selection rules

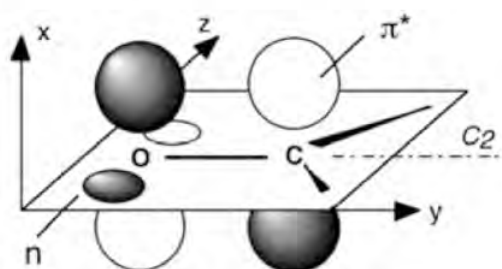
The expression of the transition dipole moment implies that each of its 3 terms has to be non-zero. These conditions are at the basis of selection rules for light absorption.

$$m_{1 \leftarrow 0} = \langle \psi_1 | \hat{R} | \psi_0 \rangle = \langle \varphi_1 | \hat{R} | \varphi_0 \rangle \cdot \langle S_1 | S_0 \rangle \cdot \langle \eta_1 | \eta_0 \rangle \neq 0$$

Symmetry-forbidden transitions

$\langle \varphi_1 | \hat{R} | \varphi_0 \rangle \neq 0$ means the symmetry of occupied orbitals must be conserved during the transition.

Example: formaldehyde



The nuclear frame of the molecule belongs to the point group C_{2v} , whose symmetry elements include identity I , a 2-fold rotation axis C_2 and two planes of symmetry $\sigma(xy)$ and $\sigma'(yz)$ crossing along the C_2 axis.

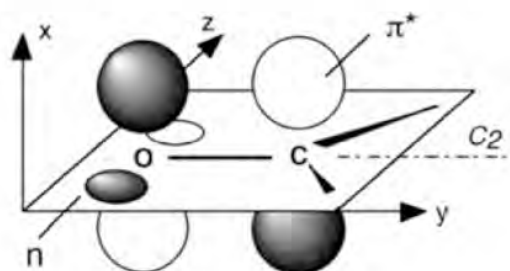
Born-Oppenheimer approximation:

Nuclei do not move during the transition. Only electrons configuration is affected. Point group, thus, remains unchanged.

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The C_{2v} character table

C_{2v}	I	C_2	$\sigma_v(xy)$	$\sigma'_v(yz)$	
A_1	1	1	1	1	T_z
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	T_x, R_y
B_2	1	-1	-1	1	T_y, R_x



The π orbital is antisymmetric with respect to rotation about C_2 axis, to reflection in the $\sigma'(yz)$ plane, but is symmetric with respect to reflection in the $\sigma(xy)$ vertical plane. It has therefore the symmetry properties of the b_1 species (small cases are used conventionally for orbitals).

Same considerations show that the π^* antibonding orbital also transforms as b_1 , while the n nonbonding orbital has the symmetry properties of b_2 species.

$$\pi \rightarrow b_1$$

$$n \rightarrow b_2$$

$$\pi^* \rightarrow b_1$$

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Electronic structure

ground state $\pi^2 n^2 \pi^{*0}$

$n\text{-}\pi^*$ excited state $\pi^2 n^1 \pi^{*1}$

$\pi\text{-}\pi^*$ excited state $\pi^1 n^2 \pi^{*1}$

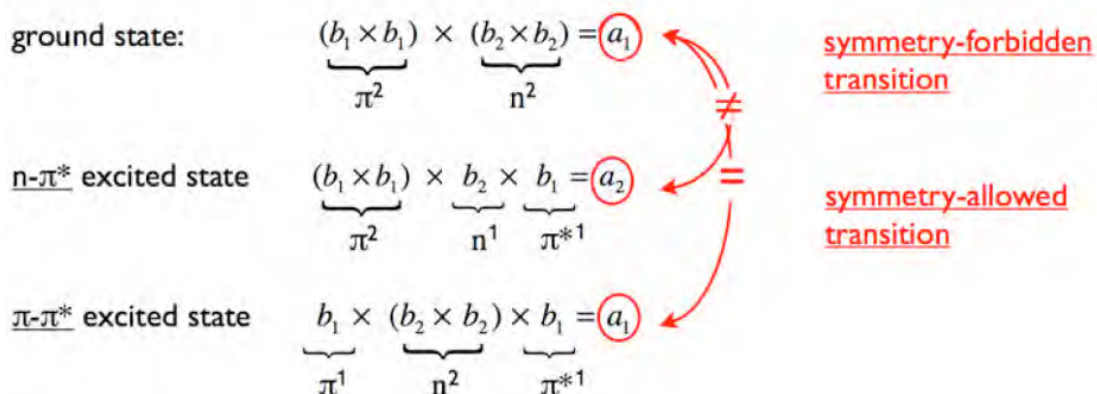
Symmetry properties

π b_1

n b_2

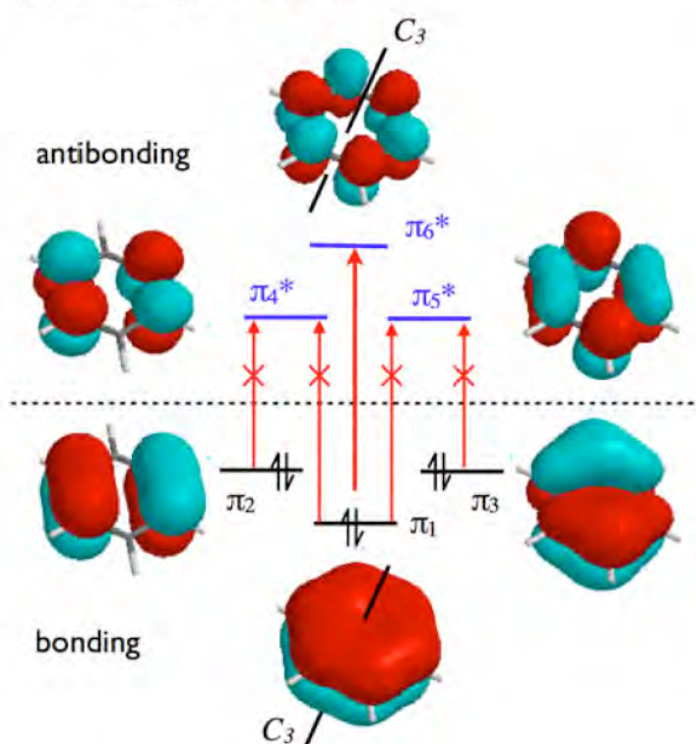
π^* b_1

Considering the irreducible representation for each electron, global symmetries of the three different states are:



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Other example: benzene



The nuclear frame of benzene belongs to the point group D_{6h} . Symmetry elements include in particular a third order rotation axis, perpendicular to the ring plane.

Among π and π^* orbitals, only π_1 and π_6^* are symmetric with respect to the C_3 rotation axis.

HOMO-LUMO transitions $\pi_2\text{-}\pi_4^*$ or $\pi_3\text{-}\pi_5^*$, for instance, are thus symmetry-forbidden and are characterized by a rather weak ϵ value ($\sim 200 \text{ mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$). The first symmetry-allowed transition of benzene is then $\pi_1\text{-}\pi_6^*$, which would take place at a much higher energy.

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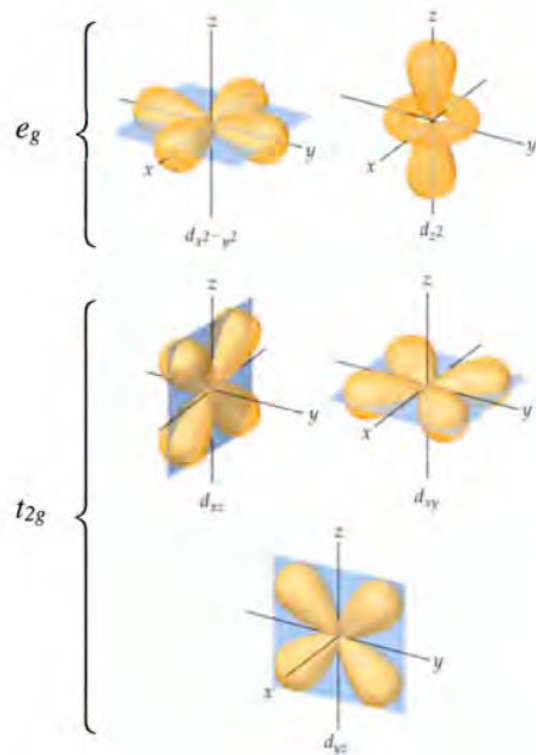
Case of transition metal complexes

The Laporte rule is a spectroscopic selection rule named after Otto Laporte (1902-1971). It is relevant in particular, to the electronic spectroscopy of transition metals. Laporte's rule states that electronic transitions conserving either symmetry or anti-symmetry with respect to an inversion center $g \rightarrow g$ (gerade) or $u \rightarrow u$ (ungerade) are forbidden.

In other words, if a molecule has a center of symmetry, transitions within a given set of p or d orbitals (i.e. those which only involve a redistribution of electrons within a given subshell) are forbidden.

$$p \not\leftrightarrow p$$

$$d \not\leftrightarrow d$$



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Vibronic coupling

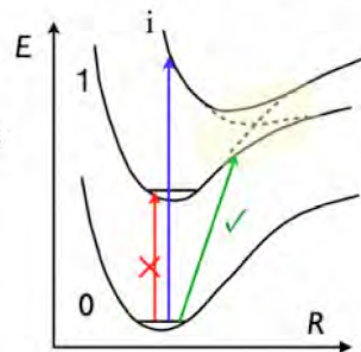
If the Born-Oppenheimer assumption is not verified, electronic and nuclear movements are coupled. This **vibronic coupling** can be treated as a perturbation of the Hamiltonian of the excited state:

$$\hat{H} = \hat{H}^0 + \hat{H}' \quad \leftarrow \text{perturbation term}$$

This yields a new expression of the transition dipole moment:

$$m_{i \leftarrow 0} = \langle \psi_i | \hat{R} | \psi_0 \rangle = \langle \psi_i^0 | \hat{R} | \psi_0^0 \rangle + \sum_k a_k \langle \psi_i^0 | \hat{R} | \psi_k^0 \rangle$$

where:
$$a_k = \frac{\langle \psi_i^0 | \hat{H}' | \psi_k^0 \rangle}{E_i^0 - E_k^0}$$

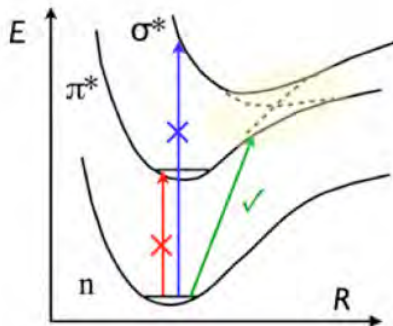
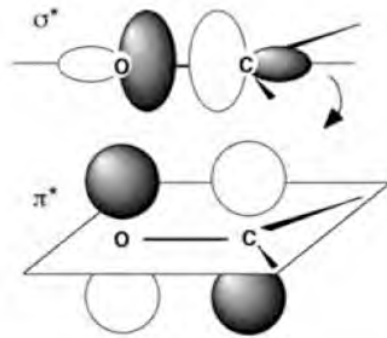


In such conditions, a formally symmetry-forbidden transition, with $\langle \psi_i^0 | \hat{R} | \psi_0^0 \rangle = 0$, can still yield a significant $m_{i \leftarrow 0}$ value, provided a coupling exists between the excited state wave function ψ_i^0 and that of another state ψ_k^0 and the energy difference $E_i^0 - E_k^0$ is small enough.

In this case, one says that the forbidden $1 \leftarrow 0$ transition "borrows" some intensity from the $i \leftarrow 0$ transition.

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Vibronic coupling in $n \rightarrow \pi^*$ transitions



In the example of formaldehyde, the $n \rightarrow \pi^*$ transition was found to be symmetry-forbidden (p. 32). Hence, $\langle \psi_1^0 | \hat{R} | \psi_0^0 \rangle = 0$.

The condition for the transition dipole moment to be non zero is therefore:

$$m_{1 \leftarrow 0} = \sum_i a_k \langle \psi_i^0 | \hat{R} | \psi_0^0 \rangle \neq 0$$

Here, the role of the ψ_i^0 state is played by the σ^* molecular orbital. Bending of the molecule out of the yz plane during a vibration causes the vibronic coupling between π^* and σ^* orbitals, whose respective b_1 and a_1 symmetries are compatible.

Although both $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions are symmetry forbidden, this π^*, σ^* coupling allows the $n \rightarrow \pi^*$ transition to "borrow" some intensity, typically yielding an oscillating strength $f_{\pi^*, n} = 2 \cdot 10^{-4}$.

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Frank-Condon principle

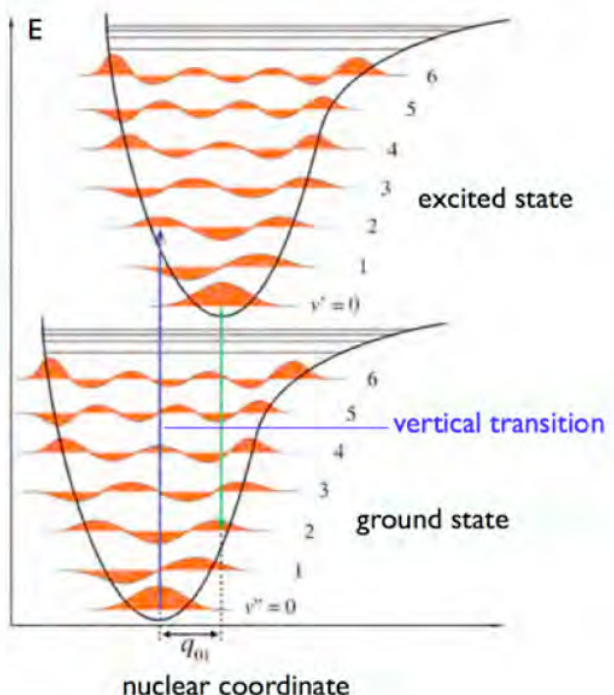
Electronic transitions take place typically on time frames of $10^{-16} - 10^{-15}$ s (0.1-1 fs). Nuclei, however, move much slower, within the 10-1000 fs timescale and can be considered as immobile during an electronic transition.

The probability of a transition depends on the nuclear wave-functions overlap integral squared.

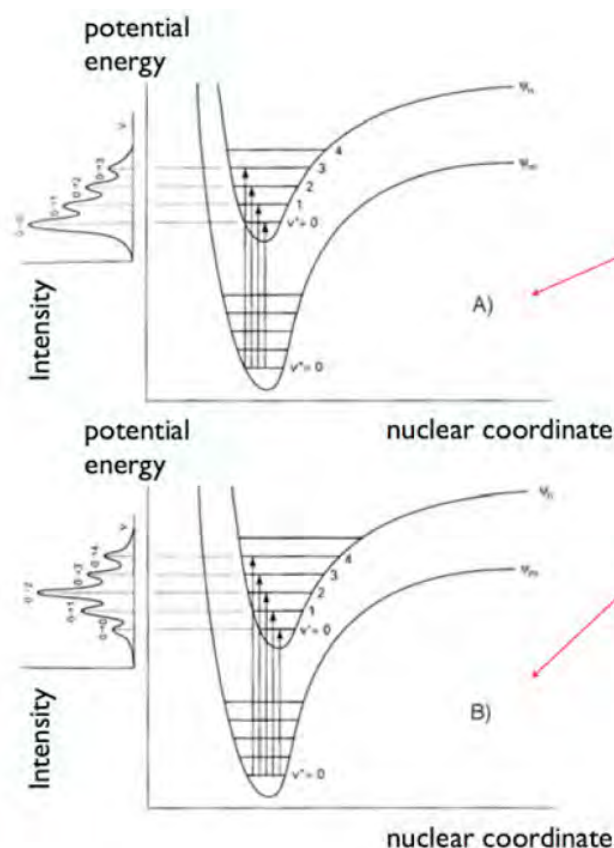
$$f_{1,0} \propto m_{1,0}^2 \propto \langle \eta_1 | \eta_0 \rangle^2$$

$$\langle \eta_1 | \eta_0 \rangle^2 \quad \text{Frank-Condon factor}$$

The intensity of a "vertical" transition thus depends upon the overlap of vibrational wave-functions.



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Vibronic absorption spectra of a molecule, constructed according to the Frank-Condon principle.

A) The excited state has an equilibrium nuclear configuration close to that of the ground state. Maximum overlap is found for the $v''=0$ to $v'=0$ transition ($0 \leftarrow 0$). This situation is rather common for rigid molecules.

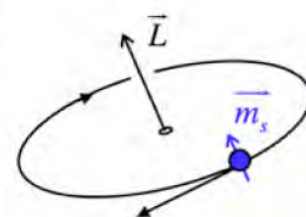
B) Nuclear equilibrium configurations of both the ground- and excited states are different. The $0 \leftarrow 0$ transition in this case is not the most intense. This situation is encountered in particular for floppy molecules and has also consequences on fluorescence spectra.

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Spin-forbidden transitions

Electron has an *intrinsic* angular momentum, independent of its *orbit* angular momentum. The intrinsic angular momentum quantum number is called the electron *spin*. Its value can be either $s = +1/2$ or $s = -1/2$. A molecule containing i electrons is then characterized by a total spin $S = \sum_i s_i$.

The spin multiplicity M is the number of possible orientations, calculated as $M=2S+1$, of the spin angular momentum corresponding to a given S value.



Spin conservation rule (Wigner rule)

$$m_{l \leftarrow 0} \propto \langle S_1 | S_0 \rangle \neq 0$$

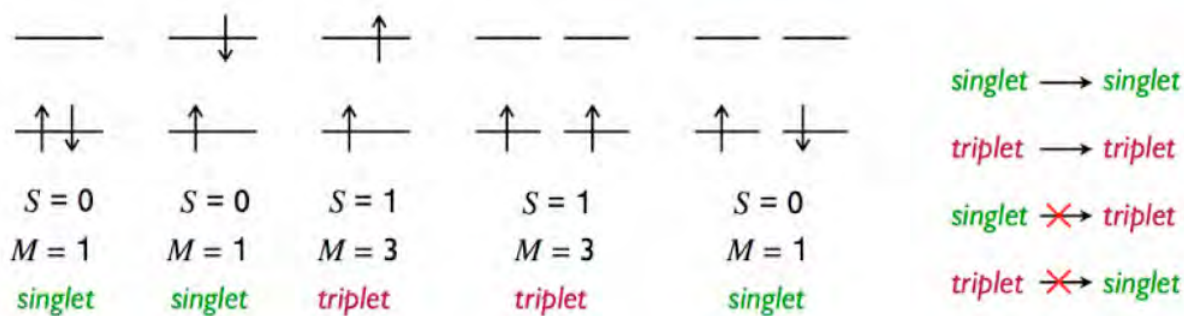
Both radiative and non-radiative transitions between terms of the same spin multiplicity M are allowed, while transitions between terms of different multiplicity are spin-forbidden.

Physically, this corresponds to a magnetic momentum conservation rule (no magnetic momentum is carried by a photon).



Eugene Wigner
(1902-1995)

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Spin-orbit coupling

Interaction of the intrinsic angular momentum of an electron with the magnetic field \vec{B} induced by the movement of other electrons on large atomic orbits (heavy atoms) as well as delocalized electrons on aromatic rings can cause spin degeneracy.

Partial allowance of a formally spin-forbidden transition can then result from this spin-orbit coupling. The oscillating strength remains, however, extremely weak, with typically $f = 2 \cdot 10^{-7}$.

