Charge Transfer Unveiled: An Exciting Journey Through TD-DFT

EURO Greece

it.auth

Case-study Walkthrough

CHEMISTRY SCHOOL
ARISTOTLE UNIVERSITY of THESSALONIKI

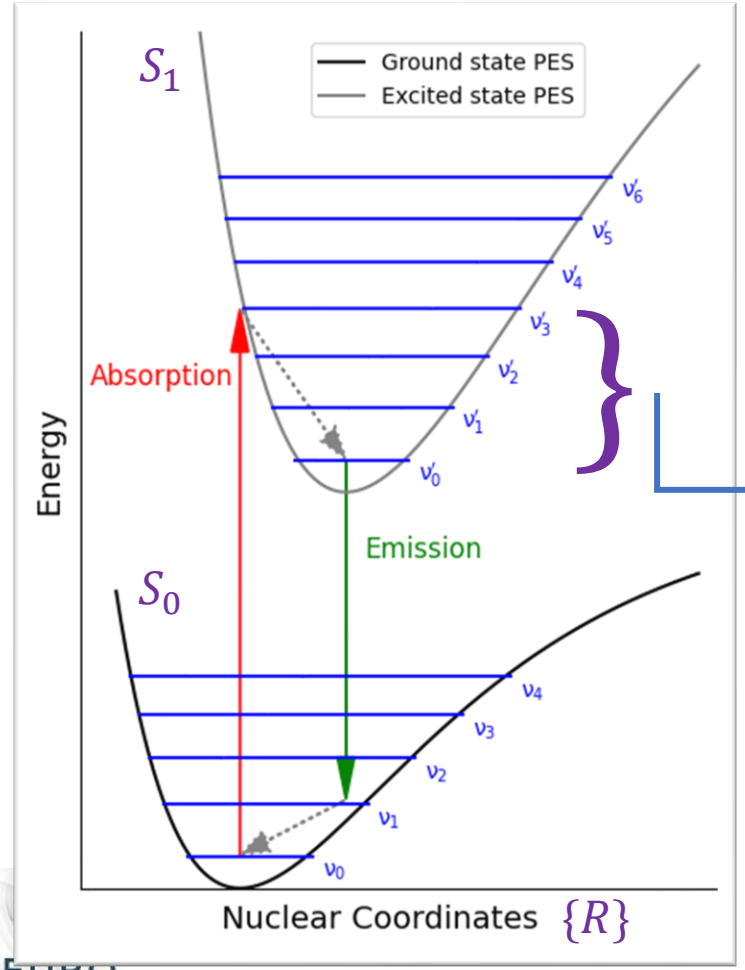
Walkthrough Tutorial by Emmanuel N. Koukaras
Assist. Prof. at Aristotle University of Thessaloniki

ARISTOTLE UNIVERSITY OF THESSALONIKI

Online Workshop – EuroCC@Greece – December 9, 2024 – Thessaloniki/Greece

Electronic Excitations

Fundamental Concepts



Electronic transitions (ultraviolet or visible/optical)
Vibronic transitions (infrared)
Rotational transitions (microwave)

Electronic transition vs
coupled electronic and vibronic transition

$\nu_0 \rightarrow \nu'_0$, no vibronic coupling
$\nu_0 \rightarrow \nu'_1$, with vibronic coupling

Vibrational Relaxation.

S_0, Ground state (singlet spin multiplicity)
S_n, n^{th} electronic excited state (singlet spin mult.)
T_1, first triplet excited state

Electronic Excitations

Excitation Processes (Types)

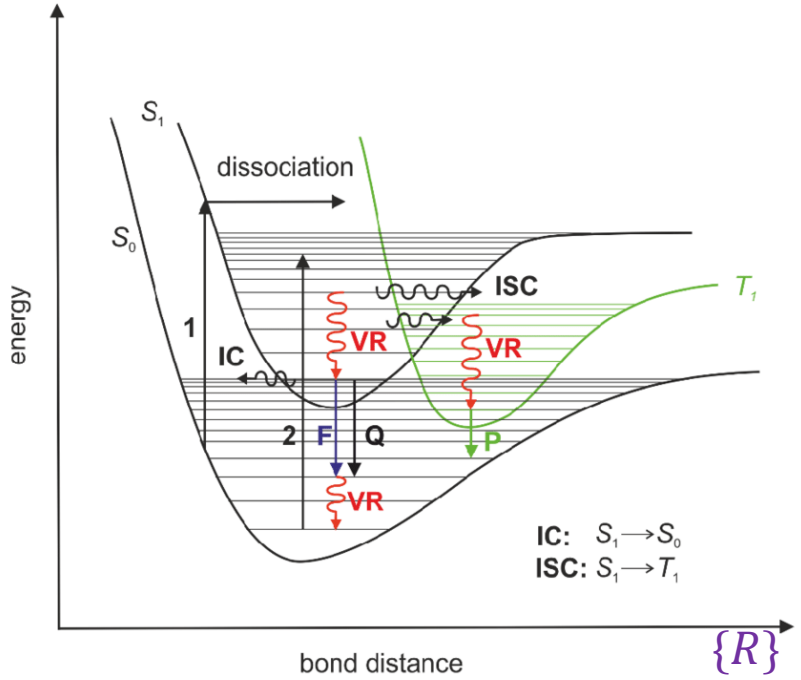


Image Source: DOI: 10.25593/opus4 – fau – 14844

Source: chem.libretexts.org

Process	Transition	Timescale (sec)
Light Absorption (Excitation)	$S_0 \rightarrow S_n$	ca. 10^{-15} (instantaneous)
Internal Conversion	$S_n \rightarrow S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	$T_1 \rightarrow S_0$	10^{-3} to 100
Non-Radiative Decay	$S_1 \rightarrow S_0$ $T_1 \rightarrow S_0$	10^{-7} to 10^{-5} 10^{-3} to 100

Radiative transitions: transitions between two molecular states where a photon is emitted or absorbed with energy equal to the energy difference of the states.
Non-radiative transitions: transitions between two molecular states without the absorption or emission of photons.

Electronic Excitations

Excitation Processes (Types)

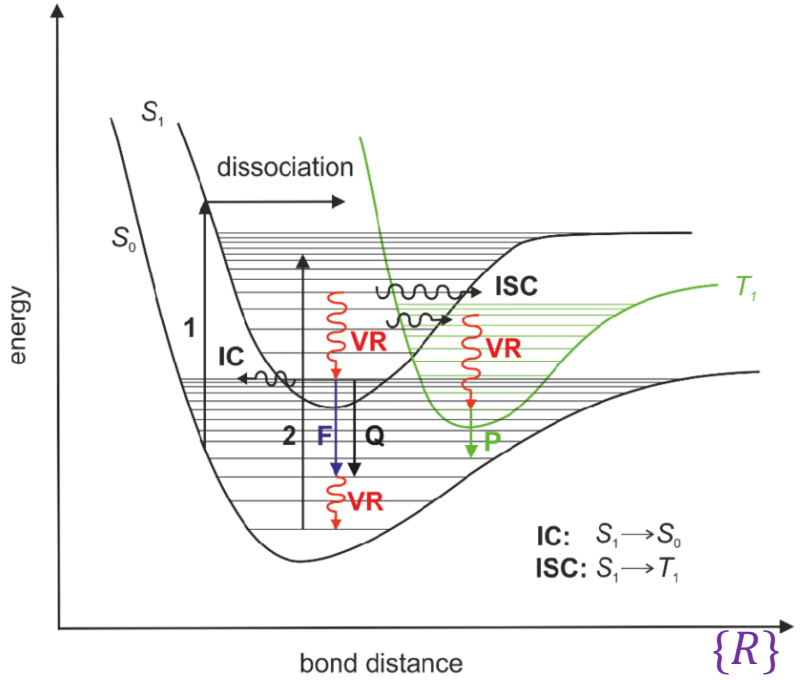


Image Source: DOI: 10.25593/opus4 – fau – 14844

Source: chem.libretexts.org

Process	Transition	Timescale (sec)
Light Absorption (Excitation)	$S_0 \rightarrow S_n$	ca. 10^{-15} (instantaneous)
Internal Conversion	$S_n \rightarrow S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	$T_1 \rightarrow S_0$	10^{-3} to 100
Non-Radiative Decay	$S_1 \rightarrow S_0$ $T_1 \rightarrow S_0$	10^{-7} to 10^{-5} 10^{-3} to 100

Absorption. Radiative transition from a lower to a higher electronic state of a molecule.
Fluorescence. Radiative transition between two electronic states of the same spin multiplicity.
Phosphorescence. Radiative transition between two electronic states of different spin multiplicity.

Electronic Excitations

Excitation Processes (Types)

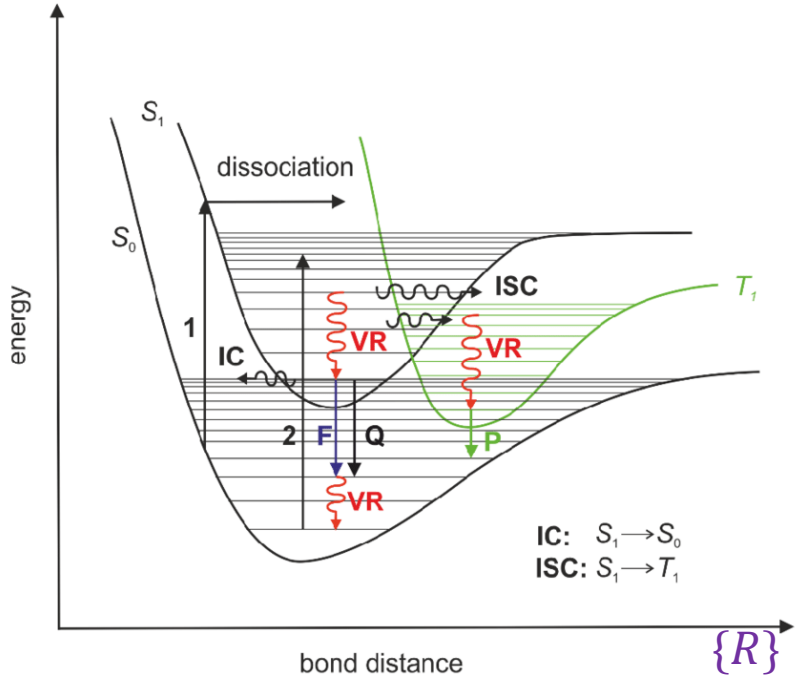


Image Source: DOI: 10.25593/opus4 – fau – 14844

Source: chem.libretexts.org

Process	Transition	Timescale (sec)
Light Absorption (Excitation)	$S_0 \rightarrow S_n$	ca. 10^{-15} (instantaneous)
Internal Conversion	$S_n \rightarrow S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	$T_1 \rightarrow S_0$	10^{-3} to 100
Non-Radiative Decay	$S_1 \rightarrow S_0$ $T_1 \rightarrow S_0$	10^{-7} to 10^{-5} 10^{-3} to 100

Intersystem Crossing. Non-radiative transition between two isoenergetic vibrational levels belonging to electronic states of different spin multiplicity.

Vibrational Relaxation. Non-radiative transition to a lower vibrational level within the *same* electronic state.

Internal Conversion. Non-radiative transition *between two* electronic states of the same spin multiplicity.

Time-Dependent Density Functional Theory (TDDFT)

Fundamental Concepts

DFT

Hohenberg–Kohn theorem 1 (one of two).

The external potential (and hence the total energy), is a unique functional of the electron density.
The ground-state expectation value of any physical observable of a many-electrons system is a unique functional of the electron density $n(r)$.

P. Hohenberg and W. Kohn, *Phys. Rev.* **136** B864 (1964)

$$\langle\psi_0|\hat{O}|\psi_0\rangle = O[n]$$

$$\hat{H}\psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N) = E\psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)$$

Boundary value problem.
Second-order differential equation

TDDFT

Runge–Gross theorem.

The time-dependent external potential is a unique functional of the time-dependent electron density.
The expectation value of any physical *time-dependent* observable of a many-electrons system is a unique functional of the *time-dependent* electron density $n(\boldsymbol{r},t)$ and of the initial state.

E. Runge and E.K.U. Gross, *Phys. Rev. Lett.* **52** 997 (1984)

$$\langle\psi_0(t)|\hat{O}|\psi_0(t)\rangle = O[n(t),\psi_0](t)$$

$$\hat{H}\psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N;t) = i\hbar\,\partial/\partial t\,\psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N;t)$$

Initial value problem.
First-order differential equation (time)

Provides response under the influence of an external scalar potential $v_{\text{ext}}(\boldsymbol{r},t)$ (ex. time-dependent electric field).

For Your Information

Noteworthy Links

1) Computational Chemistry List – CCL
http://www.ccl.net/
Running since 1991, the information stored in this mailing list/forum is unlimited.
If you're serious about Computational Chemistry, you need to sign up today. All past messages are readily available and *searchable*.

2) ORCA Input Library
https://sites.google.com/site/orcainputlibrary/
This forum can be considered as the second ORCA manual. Simple and excellent.
Does NOT replace the ORCA manual, much less technical, offers solutions to common problems.

3) Chemistry LibreTexts
https://chem.libretexts.org/Bookshelves
https://chem.libretexts.org/Courses
An **excellent** and unlimited source of information, lectures and media content.

For Your Information

People to look up

1) Dr. Joaquin Barroso's Blog
A treaty of special topics, with *many* solutions to several practical problems.
https://joaquinbarroso.com/category/td-dft/

2) Prof. Neepa Maitra
Go to person for TD-DFT formalism. Has posted several youtube video lectures from CECAM.
Find her at Rutgers:
https://sites.rutgers.edu/maitra-group/

3) Prof. Carsten A. Ullrich
Follow his very interesting work on foundations of TDDFT and applications.
https://ullrichc.mufaculty.umsystem.edu/

4) Prof. Denis Jacquemin
Follow his very interesting work on TDDFT and applications.
https://publons.com/researcher/1660859/denis-jacquemin/