

# Program

## I. OVERVIEW

1. Modern methods of computational chemistry (MM, ab initio, DFT and Hybrid methods).
2. Introduction to the Emerson Center's facilities
3. Intro (cont.)

## II. Molecular mechanics and Molecular Dynamics

4. Molecular Mechanics and Molecular Dynamics methods
5. Applications and Practical sessions on Problem solving

## III. Transition Metal Chemistry and Catalysis

6. Computational approaches to the Transition Metal Chemistry
7. Computational Catalysis (including Organic, Inorganic and Enzymatic)
8. TS, IRC, and some Practical sessions

## IV. PhotoChemistry and Excited State Studies

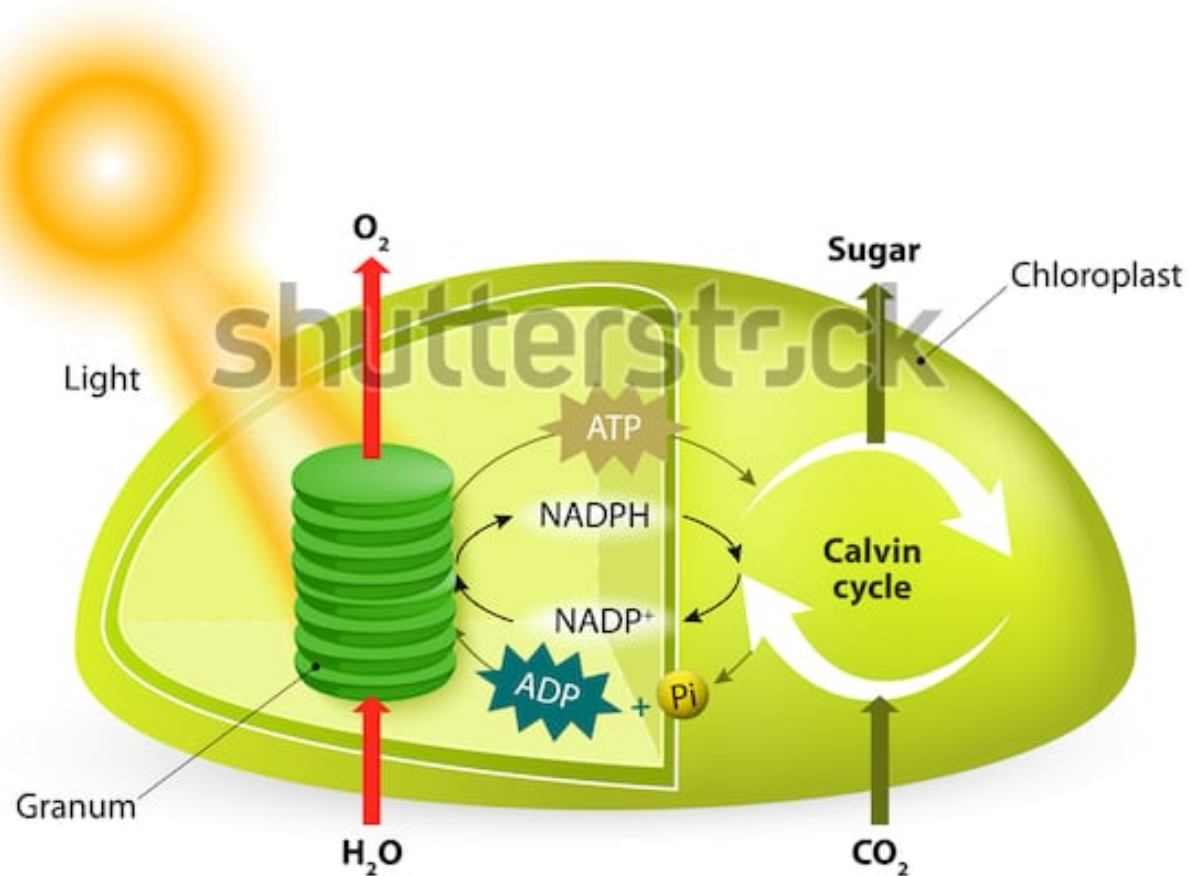
9. Introduction, Overview of Methodology, and some Simple Examples
10. A problem solving session on Spectroscopy, Radicals and PhotoChemistry

# Lecture 9

- **What are excited states?**
- **Spin & Multiplicity**
- **Electronic transitions**
- **Examples of excited state calculations**



# PROCESS OF PHOTOSYNTHESIS



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# What are excited states?

## Recall the Schrödinger equation

$$H(\mathbf{r};\mathbf{R}) \Psi_l(\mathbf{r};\mathbf{R}) = E_l(\mathbf{R}) \Psi_l(\mathbf{r};\mathbf{R})$$

$l = 0$  -- the **ground** electronic state with energy  $E_0$  and wavefunction  $\Psi_0$

$l = 1$  -- the **first excited** electronic state with energy  $E_1$  and wavefunction  $\Psi_1$

$l = n$  -- the **n-th excited** electronic state with energy  $E_n$  and wavefunction  $\Psi_n$

# Properties of ground and excited states

a) the variational condition: **ground state always the lowest**

$$E_0 < E_1 < E_2 < \dots E_n < \dots$$

b) the orthogonality condition: **the solutions are independent**

$$\langle \Psi_m | \Psi_n \rangle = 0 \quad \text{for all } n \neq m \text{ pairs}$$

and **normalized**

$$\langle \Psi_n | \Psi_n \rangle = 1 \quad \text{for all } n$$

# $N$ -electron $\Psi$ made from 1-electron “orbitals”

$$\Psi(1,2, \dots N) = \frac{1}{\sqrt{N!}} \sum_{n=1}^N \hat{A}_n \varphi_1(1) \varphi_2(2) \dots \varphi_N(N)$$

N-electron wavefunction

1-electron orbitals

$$\Psi(1,2, \dots N) = -\Psi(2,1, \dots N)$$

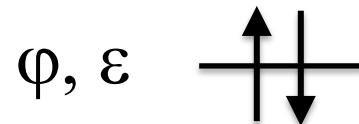
satisfies electron exchange antisymmetry

# what is electron's spin orbital?

an electron exists in a state (orbital  $\varphi$ ) and is characterized by energy ( $\varepsilon$ ) and spin of magnitude  $1/2$ : either up ( $+1/2, \alpha$ ) or down ( $-1/2, \beta$ )



Due to the Pauli exclusion principle,\* any two electrons with parallel spins cannot occupy the same orbital. But two electrons with anti-parallel spins can occupy the same orbital, e.g.,



# spin and multiplicity

spin states are called multiplets, and their characteristic is the **multiplicity**

Total spin of  $N$  electrons:  $S = |s_1 + s_2 + s_3 + \dots + s_N|$

Multiplicity =  $2S + 1$ , is the number of spin *magnetic moments*  $M_s$

$M_s = -S, \dots, +S$  with increments of 1

Ex:  $S=0$ , Multiplicity = 1,  $M_s = 0$

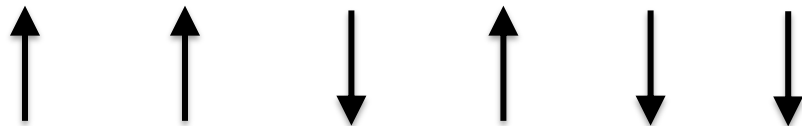
Ex:  $S=1$ , Multiplicity = 3,  $M_s = -1, 0, +1$

Ex:  $S=1/2$ , Multiplicity = 2,  $M_s = -1/2, +1/2$

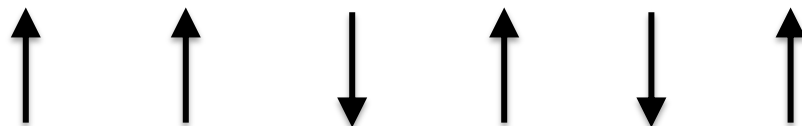
Ex:  $S=3/2$ , Multiplicity = 4,  $M_s = -3/2, -1/2, +1/2, +3/2$



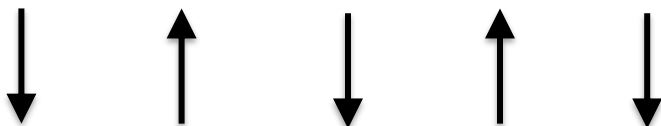
# calculating spin and multiplicity



$S = 0$ , Multiplicity = 1  
**Singlet**



$S = 1$ , Multiplicity = 3  
**Triplet**



$S = 0.5$ , Multiplicity = 2  
**Doublet**

# types of electronic excitations

ground "vacuum" state

single excitations

double excitations

$I = 0$   
 $S_0$

$I = 1$   
 $S_1/T_1$

$I = 2$   
 $S_2/T_2$

$I = 3$   
 $S_3/T_3$

$I = 4$   
 $S_4$

LU MO+1

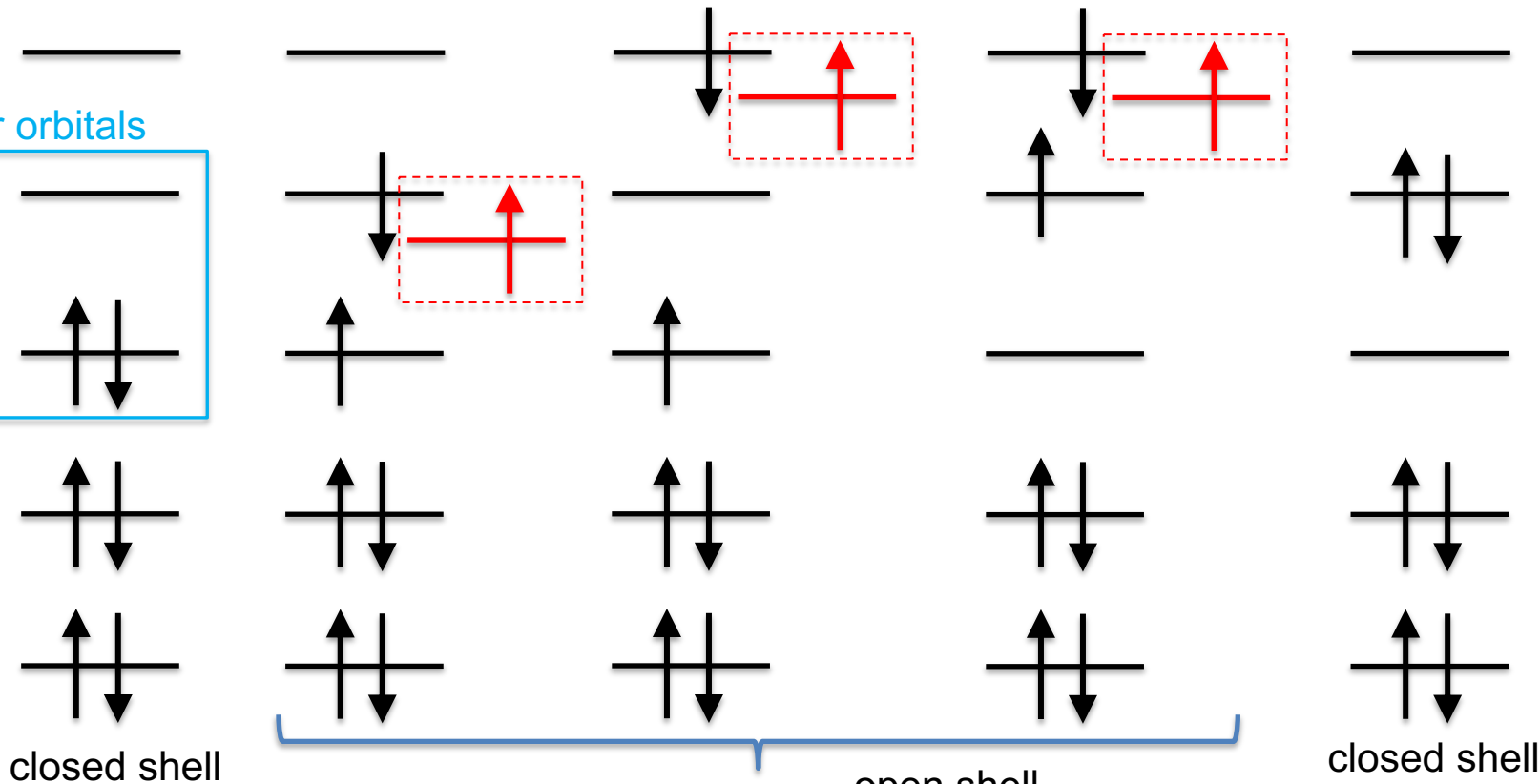
frontier orbitals

LU MO

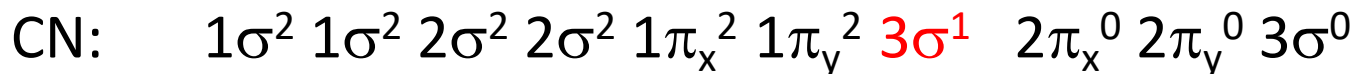
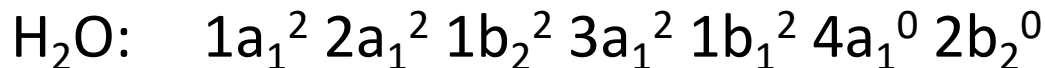
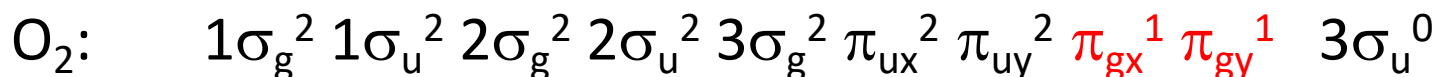
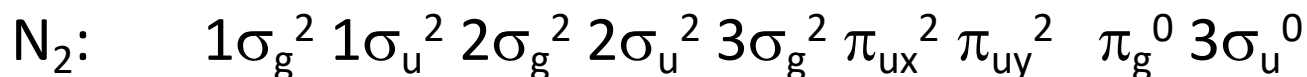
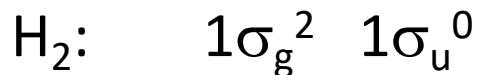
HO MO

HO MO-1

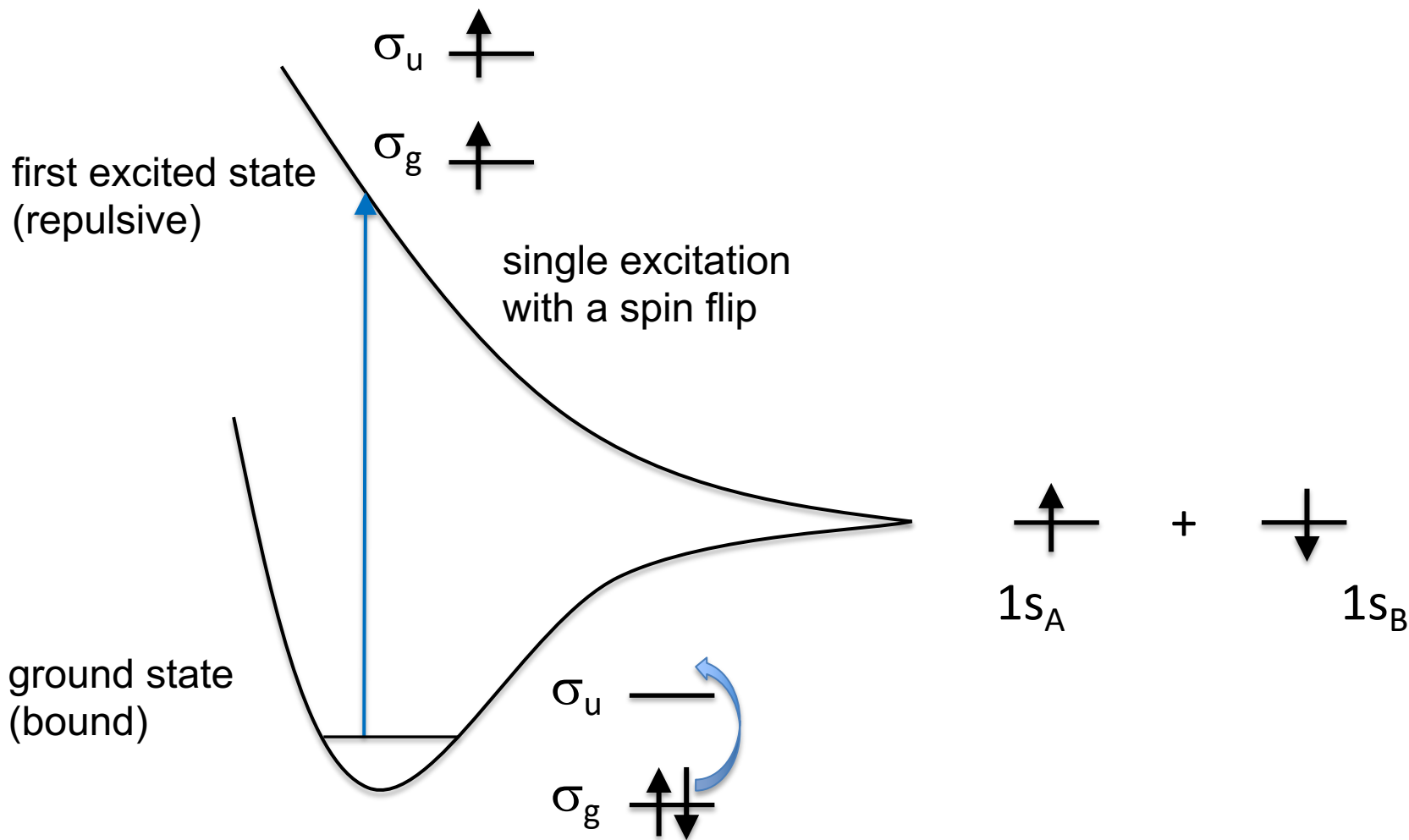
HO MO-2



## examples of closed and open shell systems

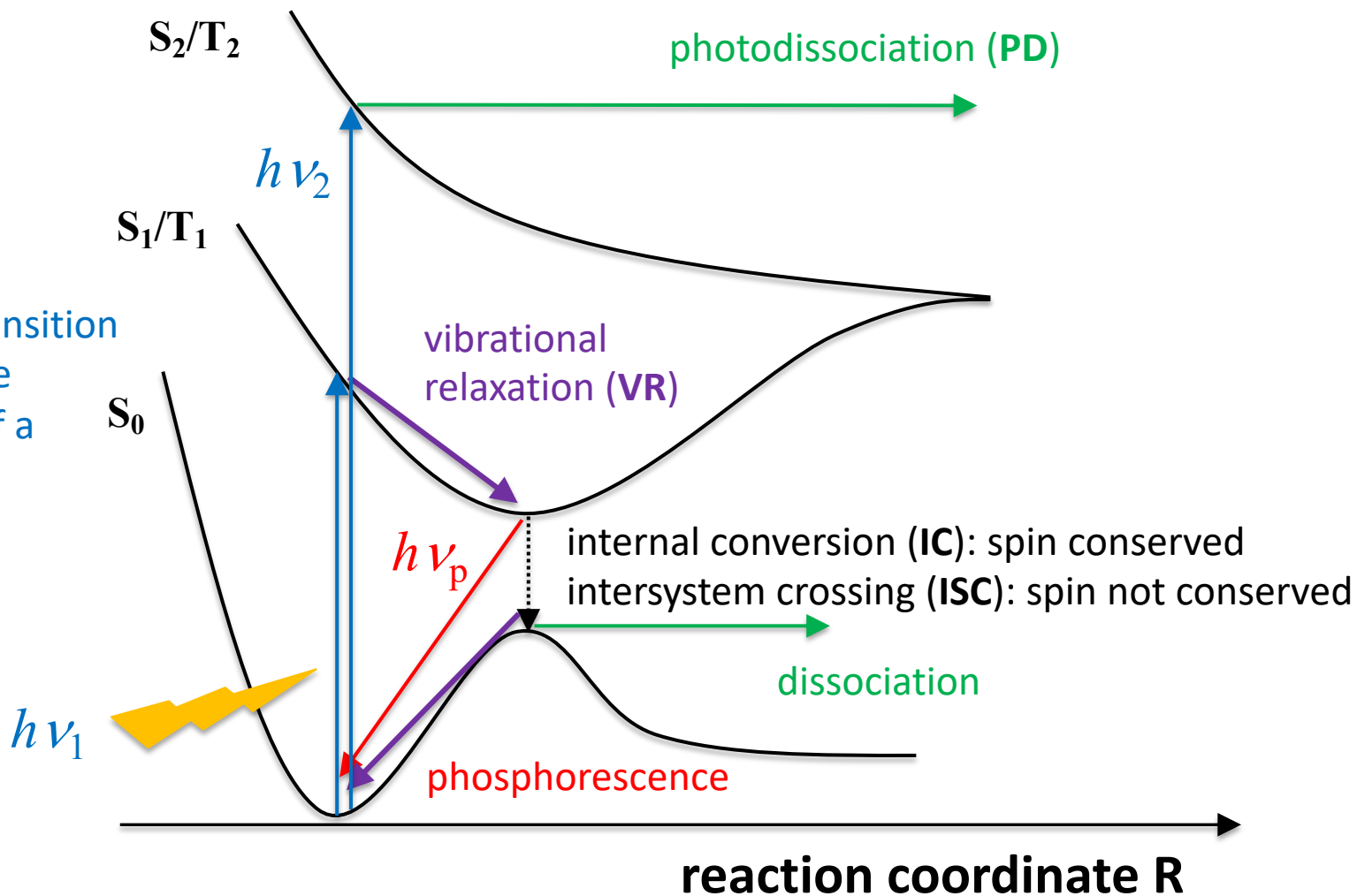


# H<sub>2</sub> dissociation by electronic excitation



# What are other processes associated with excited states?

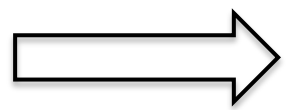
electronic transition caused by the absorption of a UV photon



# Configuration Interaction Singles (CIS) scheme

	ground state	single excitations			
	0	1 <sub>1</sub>	1 <sub>2</sub>	1 <sub>3</sub>	1 <sub>4</sub>
0	$E_0$	0	0	0	0
1 <sub>1</sub>	0	$h_{11}$	$h_{12}$	$h_{13}$	$h_{14}$
1 <sub>2</sub>	0	$h_{21}$	$h_{22}$	$h_{23}$	$h_{24}$
1 <sub>3</sub>	0	$h_{31}$	$h_{32}$	$h_{33}$	$h_{34}$
1 <sub>4</sub>	0	$h_{41}$	$h_{42}$	$h_{43}$	$h_{44}$

diagonalize\*  
matrix by  
**the Davidson\*\***  
method



get energies  
and CI vectors  
{ $E_n, \mathbf{C}_n$ }  
 $n=1, 2, \dots$

	ground state	excited states			
	0	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>4</sub>
0	$E_0$	0	0	0	0
1 <sub>1</sub>	0	$E_1$	0	0	0
1 <sub>2</sub>	0	0	$E_2$	0	0
1 <sub>3</sub>	0	0	0	$E_3$	0
1 <sub>4</sub>	0	0	0	0	$E_4$

\*re-arrange to have zeros off the diagonal, and on the diagonal will be the eigenvalues

\*\*E. R. Davidson  
University of Washington

# Practical methods for calculating excited states

**CIS** Configuration Interaction Singles  
(qualitative theory, **cheap**)

**TDDFT** Time-Dependent DFT family  
(better than qualitative, **cheap and robust**)

**EOMCC** Equations Of Motion Coupled Cluster  
(semi-quantitative theory, expensive)

**CISD** Configuration Interaction Singles and Doubles  
(quantitative theory, very expensive)

# Calculation of excited states with Gaussian: excited states of water using TD-DFT

```
%nproc=16  
#B3LYP/6-31g(d,p) td=(singlets,nstates=5,root=1) density=current  
  
excited singlet states of water at ground state optimized geometry  
  
0 1  
o 0.000000 0.000000 0.119205  
h 0.000000 0.759329 -0.476820  
h 0.000000 -0.759329 -0.476820
```



# Calculation of excited states with Gaussian: OUTPUT

Orbital symmetries:

Occupied (A1) (A1) (B2) (A1) (B1)

Virtual (A1) (B2) (B2) (A1) (B1) (A1) (B2) (A1) (A2) (A1)  
(B1) (A1) (B2) (B2) (A2) (B1) (A1) (A1) (B2) (A1)

The electronic state is 1-A1.

Alpha occ. eigenvalues -- -19.13800 -0.99732 -0.51499 -0.37102 -0.29196

Alpha virt. eigenvalues -- 0.06535 0.15123 0.75685 0.80552 0.89135

Alpha virt. eigenvalues -- 0.89353 1.01557 1.17538 1.52951 1.53766

Alpha virt. eigenvalues -- 1.64363 2.23871 2.26821 2.45009 2.64101

Alpha virt. eigenvalues -- 2.66677 3.02786 3.30721 3.53155 3.69291

Condensed to atoms (all electrons):

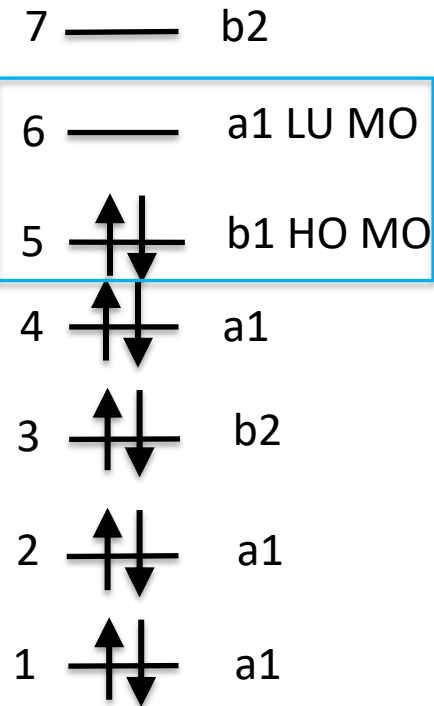
	1	2	3
1 O	9.287766	-0.724997	-0.724997
2 H	-0.724997	1.306092	0.500018
3 H	-0.724997	0.500018	1.306092

Mulliken charges:

	1
1 O	0.162227
2 H	-0.081114
3 H	-0.081114

details of the  
1st excited state  $^1B_1$

the bond order matrix  
and net atomic charges



details of the  
ground state  $^1A_1$

orbital symmetries  
and energies

# Calculation of excited states with Gaussian: OUTPUT

Excitation energies and oscillator strengths:

Excited State 1: Singlet-B1 8.0069 eV 154.85 nm f=0.0142 <S\*\*2>=0.000  
5 -> 6 0.70712 (excitation from orbital 5 to 6: HO MO to LU MO)

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -76.1254894953

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A2 10.0438 eV 123.44 nm f=0.0000 <S\*\*2>=0.000  
5 -> 7 0.70666

Excited State 3: Singlet-A1 10.5327 eV 117.71 nm f=0.0943 <S\*\*2>=0.000  
4 -> 6 0.70174

Excited State 4: Singlet-B2 12.7084 eV 97.56 nm f=0.0698 <S\*\*2>=0.000  
3 -> 6 -0.13651  
4 -> 7 0.69311

Excited State 5: Singlet-B2 14.5103 eV 85.45 nm f=0.3933 <S\*\*2>=0.000  
3 -> 6 0.69348  
4 -> 7 0.13597