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

Light\n\nGranum\n\nH\(_2\)O\n\nO\(_2\)\n\n\nNADPH\n\nNADP\(^+\)\n\nATP\n\nADP + Pi\n\nCalvin cycle\n\nChloroplast\n\nSugar\n\nCO\(_2\)
What are excited states?
Recall the Schrödinger equation

\[ H(r;R) \Psi_i(r;R) = E_i(R) \Psi_i(r;R) \]

\( i = 0 \) -- the ground electronic state with energy \( E_0 \) and wavefunction \( \Psi_0 \)

\( i = 1 \) -- the first excited electronic state with energy \( E_1 \) and wavefunction \( \Psi_1 \)

\( i = n \) -- 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**

\[ E_0 < E_1 < E_2 < \ldots < E_n < \ldots \]

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”

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

satisfies electron exchange antisymmetry

\[
\Psi(1,2, \ldots N) = -\Psi(2,1, \ldots N)
\]
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.,

Wolfgang Pauli (1900-1958)
spin and multiplicity

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

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

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

$M_s = -S, \ldots, +S$ 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

\[ S = 0, \ \text{Multiplicity} = 1 \]
**Singlet**

\[ S = 0.5, \ \text{Multiplicity} = 2 \]
**Doublet**

\[ S = 1, \ \text{Multiplicity} = 3 \]
**Triplet**
types of electronic excitations

- **ground “vacuum” state**
  - $I = 0 \quad S_0$

- **single excitations**
  - $I = 1 \quad S_1/T_1$
  - $I = 2 \quad S_2/T_2$

- **double excitations**
  - $I = 3 \quad S_3/T_3$
  - $I = 4 \quad S_4$

**frontier orbitals**

- **LU MO**

- **HO MO**

- **LU MO+1**

- **HO MO-1**

- **HO MO-2**

- **closed shell**

- **open shell**

- **closed shell**
examples of closed and open shell systems

\[ \text{H}_2: \quad 1\sigma_g^2 \quad 1\sigma_u^0 \]

\[ \text{N}_2: \quad 1\sigma_g^2 \quad 1\sigma_u^2 \quad 2\sigma_g^2 \quad 2\sigma_u^2 \quad 3\sigma_g^2 \quad \pi_{ux}^2 \quad \pi_{uy}^2 \quad \pi_g^0 \quad 3\sigma_u^0 \]

\[ \text{O}_2: \quad 1\sigma_g^2 \quad 1\sigma_u^2 \quad 2\sigma_g^2 \quad 2\sigma_u^2 \quad 3\sigma_g^2 \quad \pi_{ux}^2 \quad \pi_{uy}^2 \quad \pi_{gx}^1 \quad \pi_{gy}^1 \quad 3\sigma_u^0 \]

\[ \text{H}_2\text{O}: \quad 1a_1^2 \quad 2a_1^2 \quad 1b_2^2 \quad 3a_1^2 \quad 1b_1^2 \quad 4a_1^0 \quad 2b_2^0 \]

\[ \text{CN}: \quad 1\sigma^2 \quad 1\sigma^2 \quad 2\sigma^2 \quad 2\sigma^2 \quad 1\pi_x^2 \quad 1\pi_y^2 \quad 3\sigma^1 \quad 2\pi_x^0 \quad 2\pi_y^0 \quad 3\sigma^0 \]
H₂ dissociation by electronic excitation

First excited state (repulsive)

Single excitation with a spin flip

Ground state (bound)

1sₐₐ + 1s₉₉

EC lecture series 2020
What are other processes associated with excited states?

- Electronic transition caused by the absorption of a UV photon
- Photodissociation (PD)
- Vibrational relaxation (VR)
- Internal conversion (IC): spin conserved
- Intersystem crossing (ISC): spin not conserved
- Dissociation
- Phosphorescence

reaction coordinate R
**Configuration Interaction Singles (CIS) scheme**

<table>
<thead>
<tr>
<th>ground state</th>
<th>single excitations</th>
<th>ground state</th>
<th>excited states</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11 12 13 14</td>
<td>0</td>
<td>S1 S2 S3 S4</td>
</tr>
<tr>
<td>E$_0$</td>
<td>0 0 0 0</td>
<td>E$_0$</td>
<td>0 0 0 0 0</td>
</tr>
<tr>
<td>0 11</td>
<td>h$<em>{11}$ h$</em>{12}$</td>
<td>0 11</td>
<td>E$_1$ 0 0 0</td>
</tr>
<tr>
<td>0 12</td>
<td>h$<em>{21}$ h$</em>{22}$</td>
<td>0 12</td>
<td>0 E$_2$ 0 0</td>
</tr>
<tr>
<td>0 13</td>
<td>h$<em>{31}$ h$</em>{32}$</td>
<td>0 13</td>
<td>0 0 E$_3$ 0</td>
</tr>
<tr>
<td>0 14</td>
<td>h$<em>{41}$ h$</em>{42}$</td>
<td>0 14</td>
<td>0 0 0 E$_4$</td>
</tr>
<tr>
<td>0 0</td>
<td>h$<em>{43}$ h$</em>{44}$</td>
<td>0 0</td>
<td></td>
</tr>
</tbody>
</table>

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

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

get energies and CI vectors \( \{E_n, C_n\} \)

\( n=1, 2, \ldots \)

**E. R. Davidson**

University of Washington
<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS</td>
<td>Configuration Interaction Singles (qualitative theory, cheap)</td>
</tr>
<tr>
<td>TDDFT</td>
<td>Time-Dependent DFT family (better than qualitative, cheap and robust)</td>
</tr>
<tr>
<td>EOMCC</td>
<td>Equations Of Motion Coupled Cluster (semi-quantitative theory, expensive)</td>
</tr>
<tr>
<td>CISD</td>
<td>Configuration Interaction Singles and Doubles (quantitative theory, very expensive)</td>
</tr>
</tbody>
</table>
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:


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):

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O</td>
<td>9.287766</td>
<td>-0.724997</td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>-0.724997</td>
<td>1.306092</td>
</tr>
<tr>
<td>3</td>
<td>H</td>
<td>-0.724997</td>
<td>0.500018</td>
</tr>
</tbody>
</table>

Mulliken charges:

<p>| | |</p>
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<tbody>
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<td>1</td>
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</tr>
<tr>
<td>3</td>
<td>H</td>
</tr>
</tbody>
</table>

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 RhoCl 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