# Introduction to Computational Quantum Chemistry

Lesson 10: Electronic Transitions (UV/Vis)

Quick Review: Spectroscopy

- atoms and molecules interact with electromagnetic radiation (EMR)
- stimulates different types of motion in atoms and molecules
- the patterns of absorption and/or emission 'spectra'.
- interpretation of spectra in terms of atomic and molecular structure (and environment).
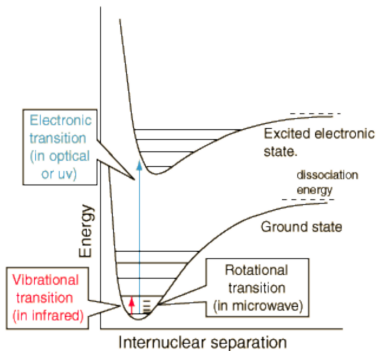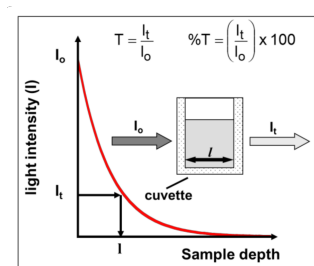
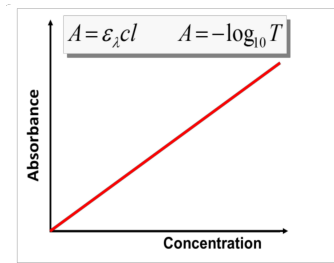# Quick Review

- absorption spectroscopy from 160 nm to 780 nm
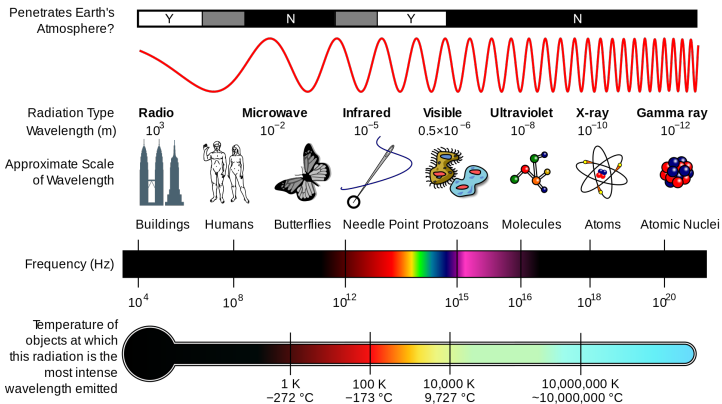
Quick Review: Beer's Law

- BEER Law, for a light absorbing medium, the light intensity falls exponentially with increasing sample conc.

$$T = \frac{I_t}{I_o} \qquad \%T = \left(\frac{I_t}{I_o}\right) \times 100$$

light intensity (I)

I_o

I_o → cuvette → I_t

l

I_t

l

Sample depth
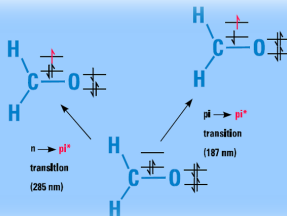
Quick Review: Beer's Law

- the negative logarithm of T is called the absorbance (A) and this is directly proportional to sample depth (called pathlength, l) and sample concentration (c).

$$A = \varepsilon_\lambda c l \qquad A = -\log_{10} T$$

Quick Review: Beer's Law
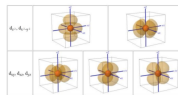
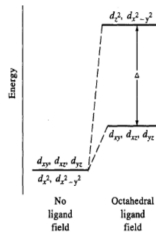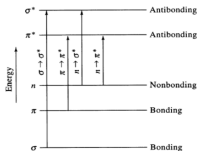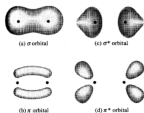- electronic transitions occur when the molecule absorbs energy.

electronic transitions:

- π, σ, and nonbonding electrons
- d and f electrons
- charge transfer

UV Spectroscopy

- electronic transitions occur when the molecule absorbs energy.

Wavefunction Based: Excited States

- the SE is written as $H\Psi = E\Psi$, however, that obscures the reality that there are infinitely many solutions to the SE, so it is better to write $H\Psi_n = E_n\Psi_n$

- Hartree-Fock theory provides us a prescription to construct an approximate ground-state wave function as a **Single** Slater determinant.

- construct an excited state wavefunction? by expanding it!

$$\Psi = a_0\Psi_{HF} + \sum_i^{occ.}\sum_r^{vir.} a_i^r \Psi_i^r + \sum_{i<j}^{occ.}\sum_{r<s}^{vir.} a_{ij}^r s \Psi_{ij}^r s + \cdots$$

- the bigger the CI matrix, the more electron correlation can be captured.

- the CI matrix can be made bigger either by increasing basis-set size (each block is then bigger) or by adding more highly excited configurations (more blocks). The ranked eigenvalues correspond to the electronic state energies.

- the higher eigenvalues are treated as the energies of the excited states.

(Prepared by Radek Marek Research Group)

Density Based: Excited States

- REVIEW on the Density Functional Theory **(DFT)**

$$E = T_e + V_{ee} - \sum \sum \frac{Ze^e}{|r - R|}$$

- the DFT properties of a many-electron system were uniquely determined by an electron density

$$\rho(r) = \sum_{i=1}^{n} n_i |\phi_i(r)|^2$$

- the energy is decomposed into kinetic and potential contributions

$$E_{DFT}(\rho) = T(\rho) + V(\rho) = \left[-1/2\nabla^2 + V_{tot}(r) \right] \phi_i(r) = \epsilon_i \phi_i(r)$$

- the potential part is broken down to classical **Vcl** and non-classical **Vxc** part: $V_{tot}(r) = V_{cl}(r) + V_{xc}(r)$

Density Based: Excited States

- Time Dependent - Density Functional Theory **(TD-DFT)**, the most used method to extract excitation energy, frequency-dependent response properites, photo-absorption spectra... particularly for its robustness and versatility.

$$E = T_e + V_{ee} - \sum \sum \frac{Ze^e}{|r - R|} + \sum r\epsilon cos\omega t$$

- the density now has time element, a physical time-dependent observable of a many-electrons system is a unique functional of time-dependent electron density $\rho(r, t)$ and of the initial state $\phi_i^0(r, t = 0)$

$$\rho(r, t) = \sum_{i=1}^{n} n_i |\phi_i(r, t)|^2$$

Density Based: Excited States

- the unknown exchange-correlation is now a 'time-dependent' potential. Vxc is also functional of the 'initial' and the 'dynamic' state as a function of time.

$$\left[-1/2\nabla^2 + V_{tot}(r,t)\right]\phi_i(r,t) = \epsilon_i\phi_i(r,t)$$

- time dependence all the way to classical **Vcl** and non-classical **Vxc** part: $V_{tot}(r,t) = V_{cl}(r) + V_{xc}(r,t)$

Time Dependent-Density Functional Theory (TD-DFT)

- TD-DFT tends to be more accurate than CIS (Configuration Interaction Singles) but is sensitive to choice of functional and certain special situations.
- eigenvectors analogous to those predicted by CIS are provided.
- charge-transfer transitions (electron-donor-acceptor complex is an association of two or more molecules) are particularly problematic.
- NOTE: there's a Semi-Empirical Method, INDO/S, that produces good excitation energy numbers relative to the experiment at least for small not complicated system.

ACTIVITY 1

- **Molecule: 2-Propenal**
- draw the molecule using Avogadro, create a Gaussian input file using **Extension Menu**
- optimized and calculate the frequency calculation using Gaussian using PBE0-31G(d)
- verify that the optimization reached a minimum, all calculated frequencies must be positive
- UV Spectra (NIST) of **2-Propenal** shown here:
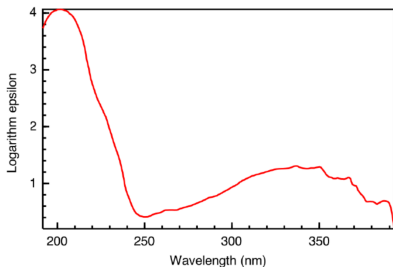
ACTIVITY 1

- **Visualizing the orbitals: 2-Propenal**
- calculate the molecular orbitals (MOs) at the optimized geometries
- use this the route section: **#n pbe1pbe/6-31G(d) pop=full formcheck**
- after the successful job, open the ***FChk** file in Avogadro
- click on **Extensions** > **Create Surface** > select **Molecular Orbital** as surface type.
- resolution: **High** ; Iso Value: **0.02** ; Color Type: **MO**
- examine the first three highest frontier (virtual and occupied) orbitals.

ACTIVITY 1

- **Visualizing the orbitals: 2-Propenal** *cont.*
- successful run look will produce orbitals like this (right Figure):
- in the Gaussian output file, look for the keyword **Orbital energies and kinetic energies** , it will report which orbitals are occupied (marked **O**) and virtual (marked **V**) as well as their corresponding energies.
- identify the characters of the frontier orbitals. Using Avogadro rotate and examine each orbitals and make a conclusion which orbitals are σ, π, n, bonding, anti-bonding??

MO# MO#
MO# MO#
MO# MO#
MO# MO#
MO# MO#

???
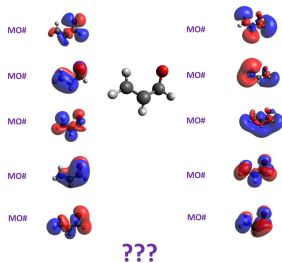
ACTIVITY 1

- **Calculation of UV Spectra: 2-Propenal**
- calculate the UV (vertical excitation) at the respective optimized geometry using Time-Dependent Density Functional Theory (TDDFT).
- use this the route section: **#n pbe1pbe/6-31G(d) TD**
- If you have done a successful calculation, look for the keyword **Excitation energies and oscillator strengths** in the output file
- It will report orbital excitations (e.g. MO14 > MO16, etc)
- It will report the wavelength where the oscillator strength is strongest; the **f** is directly related to intensity of the absorption.
- It will report the energy of the excitations as well as its coefficients; these coefficients refers to the contribution of the respected transition to the wavefunction.

ACTIVITY 1

- **calculation of UV Spectra: 2-Propenal,** *cont.*
- characterize the excitations (e.g. $\pi \rightarrow \pi^*$, ...) for the first few excited states.
  - identify which orbitals were involved in the excitations?
  - what's the nature of the excitation is it singlet or triplet?
  - compare the values with exp. excitations **E1 3.71 ev E2 6.41 ev**

ACTIVITY 1

- **Visualization of the UV Spectra Calculation: 2-Propenal**
- you can use various visualization software such as GaussView, Gabedit, Avogadro, etc for UV
- one of the simplest is to use Gabedit
  - in the Gabedit, Menu Bar : Tools > UV Spectrum > Read energies and intensities from Gaussian output file
  - it will report the integrated intensity of the absorbance with respect to the wavelength.
  - take note once have the figure, you can readjust the range and units to suit your preference.
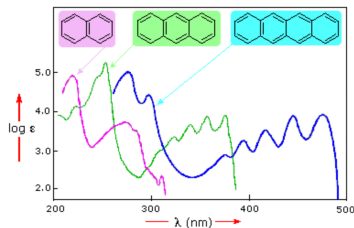
ACTIVITY 1

- **Extension**
- try to calculate 2-Propenal with CIS and INDO/S methods on the excitations
    - has the order of orbitals change?
    - are there transitions that were reported that aren't present on the PBE1 method? on the first and second, 3rd transitions, etc?
    - which method has closer fit to experimental excitations?

ACTIVITY 2 (OPTIONAL)

- try to evaluate the peaks of these **three ringed systems** and see if they can be reproduced by TDDFT.
- use the same method as stated in this lecture:
- identify which orbital transitions were responsible for these peaks?
- what significant orbital transitions that's showed in the experiment BUT were suggested **missing** in the calculation? (if there are any)

END