Calculating Excited States

Developed by: Andrew T.B. Gilbert
Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia
Edited by: Anna I. Krylov
Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482

Description: In this lab we will compute the excited states of several poly-aromatic molecules and try to predict the frequency at which they phosphoresce.

Suggested level: graduate/advanced undergraduate.

Learning objectives: Learn how compute electronically excited states and their structures; review concepts of Stokes shift, spin-symmetry, optically dark and bright states.

I. BACKGROUND

The electronic Schrödinger equation (SE)

$$\hat{\mathrm{H}}\Psi_n = E_n\Psi_n \tag{1}$$

is an eigenvalue equation where the eigenvalues, E_n, correspond to energies of different electronic states of the system. Up until now we have been focused on the lowest energy solution of the SE, E_0 (*i.e.* the ground state), however, if we want to consider photochemistry or predict UV spectra we must also consider the higher-energy states as well.

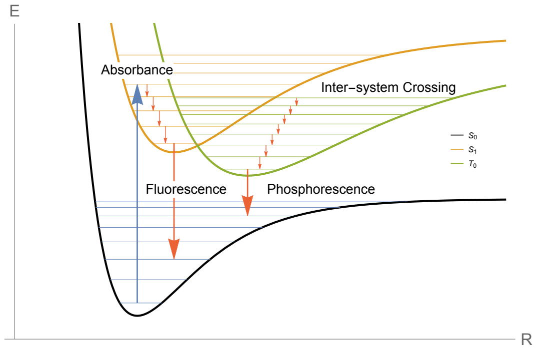
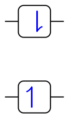


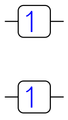
FIG. 1: Diagram showing the difference between fluorescence and phosphorescence. The small red arrows indicate thermal (structural) relaxation. The difference between absorbed and emitted energy is called Stokes shift.

In a UV experiment, a molecule absorbs a photon and gets excited into a higher energy state. The molecule can then emit a photon and relax back to the ground state in a process called fluorescence. If structural relaxation occurs, there will be an energy difference (red-shift) between the absorbed and emitted photons; this difference is called Stokes shift.

Usually excited states are short-lived, but in some cases inter-system crossing can occur whereby the molecule passes non-radiatively between states of different spin, *e.g.* the first excited singlet to the lowest energy triplet ($S_1 \rightarrow T_0$).



Singlet



Triplet

These transitions are spin-forbidden and so the resultant T_0 state can have a significant lifetime before it emits a photon and relaxes back to the (singlet) ground state, a process called phosphorescence.

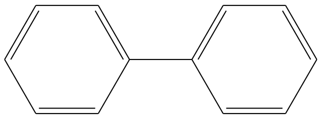
In this lab we will use configuration interaction with singles (CIS) to calculate excitation energies between electronic states. CIS is an uncorrelated method for excited states and, therefore, can be thought of a as a extension of Hartree-Fock theory to excited states. The CIS wave function is built up from a linear combination of singly-substituted determinants obtained from the ground-state determinant:

$$|\Psi\rangle = c_0|\Phi_0\rangle + \sum_{i}^{\text{occ}}\sum_{a}^{\text{vir}} c_i^a|\Phi_i^a\rangle \tag{2}$$

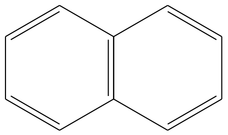
where $|\Phi_0^{\text{CIS}}\rangle$ is the Hartree-Fock determinant, and $|\Phi_i^a\rangle$ is the determinant formed by moving an electron from orbital i to orbital a. The unknown mixing coefficients, c_i^a, are called amplitudes and are found variationally. The amplitudes tell us how much of a given determinant contributes to a particular state.

II. METHOD

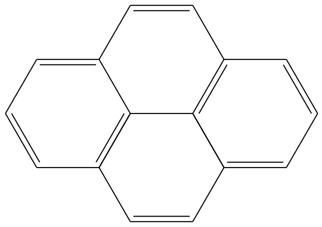
All calculations will use the 6-31G basis and either HF or CIS as the method. We will consider the following three molecules:



Biphenyl



Naphthelene



Pyrene

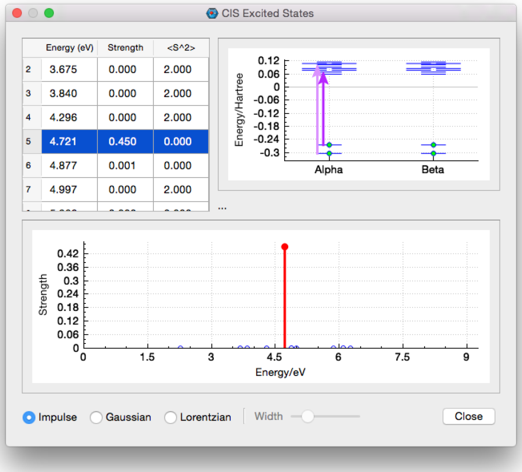
For each molecule:

1. Draw the structure in IQmol and clean it up by minimizing and symmetrizing. Note that the ground state of biphenyl is non-planer and the MMFF94 force field gives a better initial geometry.

2. Optimize the geometry of the ground state using HF/6-31G.

3. Run a Q-Chem CIS energy calculation by setting the Method to CIS, (note that it is quite far down the list of methods). Set the Number Of Roots to 5; this determines how many excited states will be computed. Make sure both the Singlets and Triplets options are checked.

4. When the calculation has completed, open the Excited States dialog by double-clicking the item in the Model View. The following dialog will appear:



CIS Excited States

	Energy (eV)	Strength	<S^2>
2	3.675	0.000	2.000
3	3.840	0.000	2.000
4	4.296	0.000	2.000
5	4.721	0.450	0.000
6	4.877	0.001	0.000
7	4.997	0.000	2.000

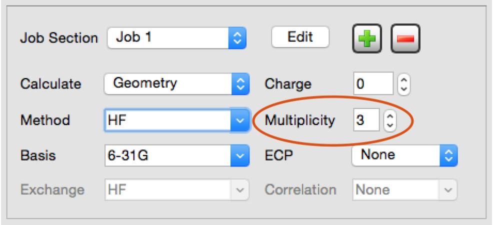
● Impulse ○ Gaussian ○ Lorentzian

The dialog contains a table of excitation energies (in eV) along with their intensities. Clicking on one of the transitions displays the significant configurations that describe the state in the MO diagram.

5. Record the energies of any transitions with significant strength (> 0.1), along with which orbitals are involved in the transition. These are indicated by the start and end points of the purple arrows. The darkness of the arrows is proportional to the amplitudes, c_i^a, so it is easy to spot which configurations are most important.

6. Identify the main orbitals (occupied and virtual) involved in the lowest-energy triplet excitation. Plot these orbitals and use these to predict the changes in bond lengths going from the singlet to the triplet state.

7. Perform a geometry optimization to obtain the equilibrium geometry of the triplet state and confirm your predictions. To do this, you need to set the multiplicity to 3 in the QUI:



Job Section: Job 1
Calculate: Geometry
Method: HF
Basis: 6-31G
Exchange: HF
Charge: 0
Multiplicity: 3
ECP: None
Correlation: None

8. Compute the energy of the singlet at your optimized *triplet* geometry. You will need this to compute the phosphorescence energy.

III. EXERCISES

You report should include tables containing the following for each molecule:

- The optimized energies and nuclear repulsion energies for the lowest singlet and triplet states. Also include the ground state singlet energy at the triplet geometry. Report total energies in hartree, with 6 decimals.

- Energies of the intense transitions (in eV), along with their intensities and leading configurations involved in the transition.

Also answer the following questions:

1. Why are all the bright transitions are singlets?
2. For each molecule, what energy do you predict for phosphorescence from the lowest triplet to the ground state?
3. What geometric effects did you observe going from the singlet to the triplet states? Include any relevant MO pictures to help explain these changes.
4. What is the magnitude of Stokes shift?