

Lab 5: Excited States and Spectroscopy
CHE 525/PHY 567, Spring 2021, Stony Brook University

1 Introduction

Molecules spend most of their time in their electronic ground states. Furthermore, most of the time molecules only explore small regions of their ground-state potential energy surfaces near equilibrium. A chemical reaction is a “rare event” where the molecules involved make an occasional foray over a transition state, but still on the ground electronic state potential energy surface. It is then entirely appropriate and not surprising that electronic structure methods are formulated as a search for the ground state using the variational principle. Put another way, quantum chemistry is (mostly) a race to the bottom!

However, even if most of chemistry happens on the ground state, the ways we interrogate molecules to find out what they are doing relies heavily on *spectroscopy* which inherently involves promoting molecules to excited states. Furthermore, many important chemical reactions only occur in excited states after molecules are excited by light (i.e. photochemistry). The electronic device you used to download this writeup is a fine example. The integrated circuits inside of your device are produced using photolithography, in which organic polymers are exposed to UV light to drive photochemistry that results in nm-scale patterns on a silicon wafer. Furthermore, the UV light used in photolithography comes from so-called excimer lasers that use excited states of diatomic molecules. In this lab, we will investigate the potential energy surfaces of the ArF excimer laser, which emits light with a wavelength of 193 nm and is most probably the laser used to make the computer chips in the device you are using right now!

Although ArF is not a large molecule, the calculations on this system will present a number of new challenges for you:

- **Open-Shell Methods:** Calculations on open-shell systems are generally more complicated than closed-shell systems. One can see this even at the Hartree-Fock level. For a closed-shell system, a single Slater determinant is both good for solving the Hartree-Fock problem and an eigenstate of the total spin \hat{S}^2 with eigenvalue $s(s+1) = 0$ and multiplicity $2s+1 = 1$ (a singlet state). The (canonical) orbitals found with the self-consistent field method give a unique set of orbitals. This scenario, resulting from so-called “restricted Hartree-Fock” (RHF), provides a nice and tidy starting point for post-Hartree Fock methods to deal with electron correlation and excited states.

In contrast, for an open-shell system, one must make compromises. If one uses a single Slater determinant for the starting point (unrestricted Hartree-Fock, UHF), the wave function is in general not an eigenstate of \hat{S}^2 since the eigenstates of \hat{S}^2 for a multi-electron system will generally involve superpositions of different spin configurations. Since the true eigenstates of the system are eigenstates of \hat{S}^2 (since \hat{S}^2 commutes with the Hamiltonian), the ground state in unrestricted Hartree-Fock is effectively *contaminated* with contributions from excited states. One can try and solve this problem using “restricted open-shell Hartree-Fock” (ROHF), in which the determinant is forced to maintain proper spin symmetry, but then one has the problem that the orbitals found are not unique, forming a more difficult starting point for post-Hartree-Fock methods. In practice, both ROHF and UHF methods can be used as the starting point (i.e. the “reference”) for post-Hartree-Fock methods and converge to the same result with appropriate care, but it is not always straightforward to accomplish this.

- **Symmetry:** Molecules have only one ground state, but many excited states. It is thus useful to classify excited states by their symmetry in order to keep them straight. This can also be very useful for understanding spectroscopy, since selection rules governing light-driven transitions between the states can be deduced from symmetry considerations. Furthermore, symmetry can also be useful in speeding up quantum chemistry calculations since similar rules can restrict the types of orbitals and configurations that need to be considered in a calculation, and most quantum chemistry codes (including Psi4) allow one to exploit symmetry. However, the number of possible symmetry groups is formally infinite and also some symmetry groups (e.g. the $C_{\infty v}$ group of the ArF molecule) contain an infinite number of symmetry operations! Computers don’t deal with infinity well, and thus quantum chemistry codes are usually restricted to using a finite abelian subgroup of a molecule’s full symmetry group (e.g. C_{2v} for the case of ArF).
- **Excited States:** Molecules often have many excited states that are close in energy. This means that these states are generally very poorly described by a single configuration and thus static electron

correlation is a larger effect in excited states than ground states. Dynamic correlation is also important for excited states as they tend to be more polarizable as well. A key challenge is providing a balanced treatment of the various states of interest. For example, the ground state may have the least dynamic correlation, a local excited state may have more, and a charge transfer excited state may have yet more. Excited states can be more diffuse than ground states, requiring that all electrons “relax” in the excited state, even if the excited state of interest is formally a single excitation. Finally, most excited states are also open shell, so all of the aforementioned complications of open-shell calculations apply as well. These factors generally make excited-state calculations much harder than ground-state calculations, and errors in excited-state energies tend to be much larger than for the ground-state.

2 Procedure

1. Pull down and run the starter code `Lab5starter.dat` which performs an open shell excited-state calculation for the OH radical for a range of internuclear distances. After running this calculation you will see several output files giving results of the calculation at various stages. Run `Lab5starter_plots.py` to plot the potential energy surface data saved in `OHpotentials.csv`.
2. Inspect the output files `EquilibriumSpectrum.dat` and `OscStrength.dat`. Here you will see data regarding the states of the OH radical and the transition dipole moments (and corresponding oscillator strengths and Einstein A coefficients) between the manifold of states. Unfortunately, the way Psi4 presents this data can be somewhat confusing, especially if your molecule’s ground state does not belong to the totally symmetric representation (Σ^+ in $C_{\infty v}$ and A_1 in C_{2v}). So be careful! When reporting states, it is the symmetry of the state that is listed. When reporting transitions instead it is the symmetry of the product of the two states involved in the transition (or the irreducible representation of the relevant component of the dipole operator connecting the two states).
For example, for transition between the $X^2\Pi$ (B_1 or B_2 in C_{2v}) and $A^2\Sigma^+$ (A_1 in C_{2v}) states of the OH radical at $h\nu \approx 4$ eV, in `OscStrength.dat` the *transition* is listed as having B_1 symmetry, even though it says “state” in the output file. Note also that the ordering of the states you see in the output file also may not correspond to the ordering of the states found in the starter code with the `psi4.core.variables('CC ROOT ENERGY')` command in the starter code. Such are the idiosyncrasies that tend to persist in software that is free and/or has a user base consisting predominantly of experts!
3. Now do the calculation for ArF using the `eom-ccsd` method with an `aug-cc-pvdz` basis set, using the starter code as a starting point. Scan the potential energy curves to see where there might be bound states and make a plot similar to that generated by the starter codes.
4. In an ArF excimer laser, the excited states are generated by striking an electrical discharge in a gas consisting of a mixture of Ar and F_2 . Thus a wide range of excited states are generated. Use your data from step 3 to identify the transition responsible for the ArF laser emission. *Hint 1: In a laser, you want the upper state to have a much longer lifetime than the ground state such that one can more easily attain a population inversion, with more population in the upper state than the lower state. Hint 2: If the excited state is also short-lived (e.g. because it is reactive) one would also desire a large oscillator strength for the laser transition.*
5. Identify the equilibrium geometry of the upper state of the laser transition. You can do this by geometry optimization, but optimizing geometries in excited states in Psi4 is tricky. For this 1D problem, it is sufficient to just “eyeball it” - i.e. judge from your potential curves the approximate internuclear distance for which the upper state has the lowest energy.
6. Calculate the transition dipoles/oscillator strengths near the equilibrium geometry of the excited state. These are not easily returned via the Psi4 API as variables, but they are printed to the output file after running a `psi4.properties(...properties = ['oscillator_strength'])` command. You will use this data to calculate some of the deliverables below.

3 Deliverables

- Plot the potential curves for the ground state and the first 4 four excited states over a range that clearly illustrates any important minima in the two states involved in the laser transition. Clearly label the states by symmetry (you can use the C_{2v} labels spit out by Psi4 or the true $C_{\infty v}$ labels, whichever you prefer).
- What are the two states involved in the laser transition. At what internuclear distance does the transition mostly likely happen? Explain the reasoning behind your answers.
- What is the transition frequency for the ArF excimer laser at the eom-cc/aug-cc-pvdz level?
- Discuss the chemical nature of the two states involved in the laser transition. Are both states bound? What do the molecular orbitals involved look like?
- Is the transition dipole moment (dipole matrix element) between the two states involved in the laser transition parallel or perpendicular to the molecular axis connecting the two nuclei? You can find this in the output file. You can also deduce this from the symmetries of the states involved and/or from the chemical nature of the two states. Discuss your result in terms of *both*.
- Estimate the lifetime of the upper state involved in the laser transition due to radiative decay (i.e. spontaneous emission) using the results of your calculation.
- What do you think is responsible for the decay of the lower state involved in the laser transition? Make an estimate for the lifetime and compare your result to that of the upper state.