Project 3: Calculating Franck-Condon Factors

June 30, 2020

Motivation

Spectroscopy is the study of how light and matter (atoms and molecules) interact. Light can be absorbed by matter (*absorption*) or matter can emit light (*emission*). It turns out that spectroscopy is scientists' main tool for discovering properties of molecules (e.g. their molecular structure, bond strengths, etc.) and for chemical identification. Picture for instance an astronomer taking spectroscopic measurements from a gas cloud located millions of light years away from the Earth. To determine what chemicals this gas cloud comprises of, they certainly cannot travel there and take a physical sample of the gas cloud. The astronomer is tasked with utilizing spectroscopic theory (i.e. models wherein numerical studies can be carried out efficiently) to explain what they see.

Countless other applications like drug discovery, magnetic-resonance imaging (MRI) and climate science rely heavily on spectroscopic methods and theory. This week, you'll familiarize yourself with calculating Franck Condon Factors (FCFs), which are useful in studying *vibronic* transitions in molecules. You'll also get to compare your calculations to real experiments.

Your Tasks

Task #1

In this task, you will calculate Franck-Condon Factors for $H_2 - H_2^+$ using the harmonic oscillator approximation and compare to a real experiment! In a real experiment, we can excite many different vibronic transitions. We would therefore be able to calculate many FCFs that describe different vibronic transitions. For example, it could be that we see excitations corresponding to an H_2 molecule in its $n = 0$ vibrational state to H_2^+ in its $n = 2$ vibrational state (green line in Fig.) and its $n = 4$ vibrational state. In this task, we will look at only transitions that have a high FCF (i.e. the corresponding transition is very intense).

You are provided with a `python` notebook called `Task1.ipynb` which calculates all of the information you require. The `FCF_helper.py` file contains all of the calculations done under the hood. [1] Currently, the `spectrum_analysis` function in `FCF_helper.py` only outputs the following.

- `n_0` and `n_p`: The vibrational state numbers of H_2 and H_2^+, respectively, involved in the vibronic transition
- `FCF`: The corresponding FCF associated to the vibronic transition

[1] Calculating FCFs comes down to calculating the overlap between the wavefunctions before and after the vibronic transition. The overlap calculation is an integral which we chose to evaluate numerically. We emphasize that molecular parameters like the reduced mass of H_2 and fundamental frequencies of H_2 and H_2^+ are hard-coded in `FCF_helper.py`

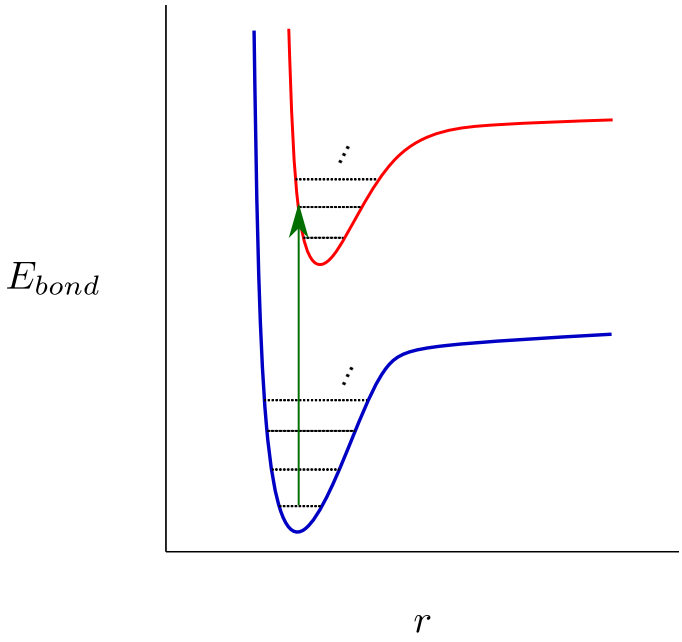

Figure 1: A visualization of vibronic transitions. The blue and red curves represent H_2 and H_2^+, respectively.

Here's what we'd like you to do:

1. Open up `FCF_helper.py` and navigate to the `spectrum_analysis` function. Modify the `data` variable so that it also includes the spectral intensity (`Ep - E0`).

2. Plot the corresponding FCF versus spectral intensity (i.e. plot `FCF` versus `Ep - E0`) and show the results. Make sure you have at least 10 points.[2]

Congratulations, you have now successfully predicted the Franck-Condon Factors of H_2–H_2^+! Figure 2 shows the photoionization spectrum for H_2. Does it look like the real data in Fig. 2?

Task #2

You are provided with a `C++` code `FC.cxx` created by P.-N. Roy [2], which calculates the photoionization spectrum for any molecule up to triple excitations and goes beyond the harmonic oscillator approximation. The theory is based on the paper by Ref [3]. The molecule you will be investigating is V_3. This code takes as input a file which requires the results of diagonalizing the mass-weighted hessian/force-constant matrix (2nd derivative of the Hamiltonian with respect to position). This input file is provided for you (V3).

Browse the following references to understand how the code works, as you will need a basic understanding of this for the next task, but it's not necessary to fully understand it. Compile and run the code `./FC_quick V3`. This code outputs the spectrum `V3.spec.out`. Plot it in your favourite plotting program.

[2]You may need to adjust the input bounds on the maximum vibrational state numbers. For now, start with both being 2.

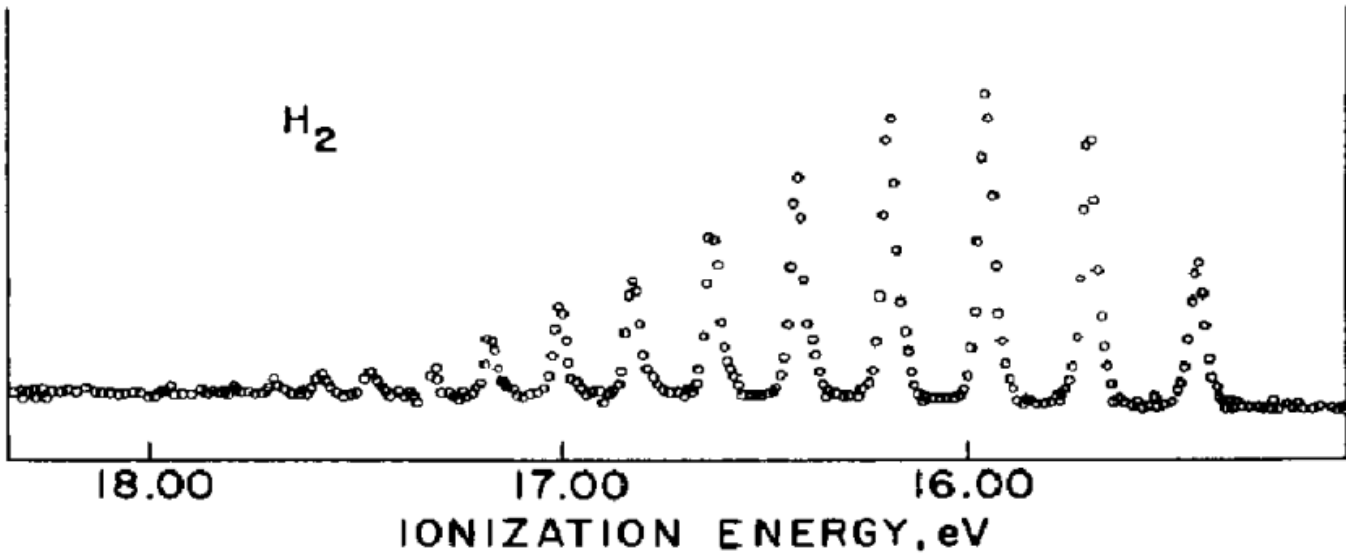

Figure 2: Experimental photoionization spectrum of H_2-H_2^+ from Ref. [1]

Task #3

You are provided with a `python` notebook code Sample_Vibronic.py which calculates all of the information you require. This code takes as input a file which requires the following information:

1. Number of atoms in the molecule
2. Vibrational frequencies of the molecule in the ground electronic state
3. Vibrational frequencies of the molecule in the excited electronic state
4. Duschinsky Matrix (encodes information on transformation between ground and excited electronic states)
5. Displacement vector

This code outputs the spectrum in HTML format.

However, to be able to use this code, you require an input file. To create this input file, you will need to generate results from another code, `FC.cxx`. This code calculates the Franck-Condon Factors using matrix elements and recursive Hermite polynomial relations. Feel free to look around this code, but it is not necessary to completely understand it to achieve this task (the reference(s) noted in this code are Refs [2, 3, 4]. Each piece of information that you need to output has been clearly marked in the code and your task is to write that information to a file, which will then be used as your input file to `Sample_Vibronic.py`. Once you have that input file, you should be able to produce the spectrum for V_3. Compare this spectrum to the previous method. What happens if you decrease the number of samples to 10? 100? 1000? At what number of samples do you feel the spectrum is converged?

Challenges

1. An alternative and analogous method to calculating these Franck-Condon Factors using matrix elements is to use a loop hafnian approach. This loop hafnian approach uses Gauss Boson Sampling which would allow these Factors to be calculated using a quantum circuit. Use the result of Task 3 to provide data to a skeleton code provided that uses loop hafnians to calculate the Franck-Condon Factors.

2. Explain briefly the similarities and differences between these three methods.

Possible Business Outcomes

1. Explain to a layperson what theoretical chemistry/physics is, in the general context of Franck-Condon Factors

2. What is the importance of theoretical chemistry/physics from an economic point of view

3. Explain to a layperson what a quantum circuit is and it's relationship to theoretical chemistry/physics

4. What are advantages and disadvantages of codes licensed for the public domain and those that are licensed for private use

References

[1] J Berkowitz and R Spohr. Comparison of photoelectron intensities and franck-condon factors in the photoionization of h2, hd and d2. *Journal of Electron Spectroscopy and Related Phenomena*, 2(2):143–152, 1973.

[2] Dong-Sheng Yang, Marek Z Zgierski, David M Rayner, Peter A Hackett, Ana Martinez, Dennis R Salahub, Pierre-Nicholas Roy, and Tucker Carrington Jr. The structure of nb3o and nb3o+ determined by pulsed field ionization–zero electron kinetic energy photoelectron spectroscopy and density functional theory. *The Journal of chemical physics*, 103(13):5335–5342, 1995.

[3] EV Doktorov, IA Malkin, and VI Man'ko. Dynamical symmetry of vibronic transitions in polyatomic molecules and the franck-condon principle. *Journal of Molecular Spectroscopy*, 64(2):302–326, 1977.

[4] Nicolás Quesada. Franck-Condon factors by counting perfect matchings of graphs with loops. *J. Chem. Phys.*, 150(16):164113, April 2019.