

Project 3: Calculating Franck-Condon factors using a variety of methods including quantum circuits

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1 Introduction

You've probably wondered how scientists in labs are able to determine extremely small quantities like the distance between atoms that are chemically bonded. Spectroscopy is the field of study that has provided techniques to measure such quantities with ease. Not only is its importance in academic settings unprecedented, industry relies on spectroscopic theory and techniques for countless applications. This week, you'll learn:

1. introductory physics and chemistry behind spectroscopy
2. what a Franck Condon Factor is
3. how to calculate Franck Condon Factors for simple molecules

For further reading, you may consult the following references among many others: Ref. [1, 2, 3]

If you come from a physics or chemistry background, you will have probably learned material that will be covered in the the next few subsections. Feel free to skip them! This is intended for an audience that is entirely unfamiliar with these concepts.

1.1 What is spectroscopy?

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*). However, it turns out that atoms and molecules can only emit / absorb certain wavelengths of light and not all wavelengths. The wavelengths of light that atoms and molecules can emit / absorb is dictated by the *energy levels* of a molecule. Think of a molecule's energy levels as a set of stairs, where each stair represents one energy level and the vertical distance separating stairs is the difference in energy between stairs. For a molecule to absorb or emit light, the light must have *exactly* the amount of energy between two stairs. If stairs # 1 and # 2 have energy E_1 and E_2 respectively, then the light's energy, E_{light} , must satisfy

$$E_2 - E_1 = E_{\text{light}}. \quad (1)$$

Therefore, a molecule can only absorb or emit light that has a specific energy, and therefore wavelength since the energy of light is inversely proportional to its wavelength (λ).

$$E_{\text{light}} \propto \frac{1}{\lambda} \quad (2)$$

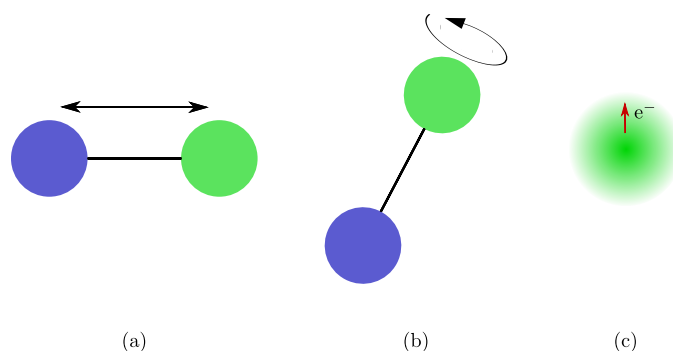


Figure 1: (a) Molecular vibration, (b) rotation, and (c) exciting an electron in an atom / molecule.

It is from the pattern of light that a molecule can emit / absorb – its *spectrum* – that we can determine all sorts of properties (e.g. bond strengths, positions of atoms in molecules, etc.)

1.2 Molecular energy levels

So, the energy levels of molecules give us the key to its structural properties. What are these energy levels? Energy in a molecule can be stored in a few ways: vibration, rotation and the energy of electrons (e^-) surrounding the molecule (see Fig. 1). For now, let's only worry about harnessing vibrational energy and energy from exciting electrons within a molecule.

The chemical bond is what forces atoms in a molecule to stay close enough together. If we were to try and take two atoms that are chemically bonded and rip them apart, we would be met with incredible resistance from the retaliation of the bond. On the flip side, there is a repulsive force between atoms that are bonded that ensures that the atoms don't get too close to each other. This balance between the repulsive and attractive forces determines the distance that separates atoms in a chemical bond (called *bond length*). If we were to plot the potential energy stored in a molecule, E_{bond} , as a function of the two atoms' separation, r , it would look something like the blue or red curve in Fig. 2. It's at the very minimum point on the curves in Fig. 2 where the attractive and repulsive forces are in equilibrium with each other.

Vibrations affect the distance between the atoms, r , in the molecule. It turns out that the laws of quantum mechanics only allow for *discrete* vibrational energies, and that the lowest vibrational energy that can be obtained (dubbed the “ground” vibrational state) is actually slightly above the minimum point on the blue/red curve. The allowed vibrational energy levels of the molecule are the horizontal lines within the blue curve in Fig. 2.

We can also think about exciting the molecule's electrons. If we were to do this, this can drastically change the interplay between the attractive and repulsive forces. Therefore, E_{bond} as a function of r changes significantly. The red and blue curves in Fig. 2 are meant to represent the molecule in an excited electronic state and in its ground (lowest energy) electronic state, respectively. Note that the excited electronic state of the molecule also vibrates and therefore has its own discrete vibrational energy levels.

1.3 Wavefunctions

We need knowledge of one more thing before we can accomplish our goal of calculating Franck Condon Factors: wavefunctions. The wavefunction of a system, often denoted by the Greek letter ψ ,

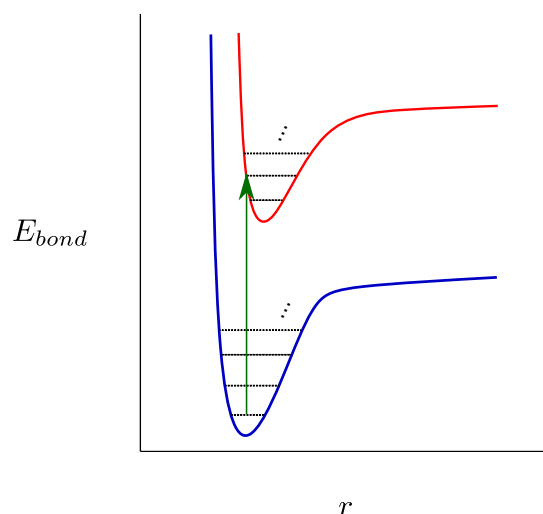


Figure 2: The general form of a molecule’s potential energy curve as a function of bond length. The blue curve represents a molecule in its ground electronic state and the red curve represents the same molecule in an excited electronic state.

is essentially the key to being able to calculate anything and everything about said system. In our spectroscopy language, the wavefunction of a molecule that we are interested in can be extremely complicated to fully determine. However, for our purposes we can “separate” the wavefunction of our molecule into parts describing its vibration (v), rotation (R) and electrons (e).

$$\psi_{molecule} = \psi_e \psi_R \psi_v \quad (3)$$

1.4 Franck Condon Factors

Armed with this conceptual knowledge of molecular vibrational energy levels and wavefunctions, we can now learn about Franck Condon Factors (FCFs). Picture the following scenario. We have a molecule in its ground state (both vibrationally and electronically), and we excite it electronically (i.e. move from the blue curve to the red curve in Fig. 2). To a very good approximation, it turns out that electronic transitions are so fast that the distance separating atoms in a molecule does not have time to adjust (this is the Franck Condon Principle). Diagrammatically, we are looking at the vertical green line in Fig. 2 (it is vertical because the atoms in the molecule stays at the same distance apart during the transition). This specific “vertical” transition from the ground electronic and vibrational state to the excited electronic state and its second vibrational state will have a *transition intensity* that is related to the vibrational part of the wavefunctions describing the system before and after the transition. More specifically, the transition intensity is proportional to the square *overlap* (think of a vector dot product) between the two vibrational wavefunctions.

$$\text{Transition intensity} \propto \text{overlap}(\psi_{v,\text{before}}, \psi_{v,\text{after}})^2 \quad (4)$$

The square of this overlap is precisely the Franck Condon Factor!

$$\text{FCF} = \text{overlap}(\psi_{v,\text{before}}, \psi_{v,\text{after}})^2 \quad (5)$$

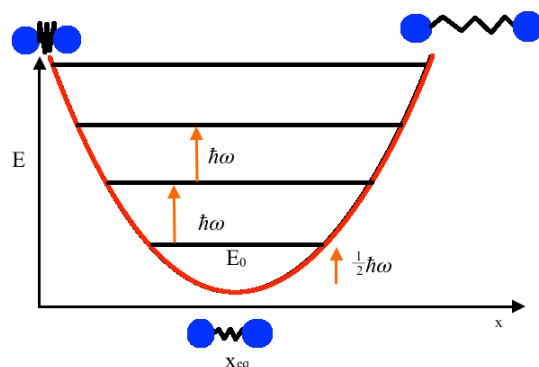


Figure 3: A representation of a diatomic and its vibrational energy levels in the harmonic oscillator approximation. The properties of this diatomic are its equilibrium geometry, x_{eq} , its frequency, ω , and its reduced mass, μ . The ground state energy (E_0) is $\frac{1}{2}\hbar\omega$ from the potential minimum and vibrational energy differences between adjacent levels is $\hbar\omega$.

1.5 A simplified model for vibrations of diatomic molecules (2-atom molecules)

One of the simplest ways to represent vibrations of diatomic molecules is to consider they are connected by a spring. The frequency of the vibration is a property of the molecule (and remains the same regardless of the energy the system has) and can be easily calculated using the masses of the atoms and the stiffness of the spring. This “spring system” is denoted a harmonic oscillator.

Refer to Fig. 3 for the energy levels associated with a harmonic oscillator system. If a molecule is in its ground vibrational state, it will “stretch” and “contract” about its natural (or equilibrium) bond length. As it gains energy and moves into excited vibrational states, it can stretch and contract further and further from its equilibrium bond length, however it continues to vibrate at the same natural frequency.

The harmonic oscillator is a simplified model, since it ignores all repulsive effects of the 2 atoms within the molecule (the steep wall at small r denoted by a more realistic potential energy curve in Fig. 2). As well, the harmonic oscillator potential has no dissociation (or bond-breaking) as is denoted by the flat portion at large r in the potential energy curve in Fig. 2 meaning at higher excited states, the atoms will continue to stretch further and further without the “spring snapping.”

However, the harmonic oscillator has a unique feature, in that the energy levels are equally spaced and the wavefunction takes an analytic form, allowing for simple calculations.

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \cdot \left(\frac{\mu\omega}{\pi\hbar}\right)^{1/4} \cdot \exp\left(-\frac{\mu\omega(x-x_{eq})^2}{2\hbar}\right) \cdot H_n\left(\sqrt{\frac{\mu\omega}{\hbar}}(x-x_{eq})\right), n=0,1,2,\dots$$

where μ is the reduced mass of the molecule, ω is its vibrational frequency, x is the bond length, x_{eq} is the equilibrium bond length, n is the vibrational state of the system, and H_n is the Hermite polynomial.

2 Initial Tasks

2.1 Task 1: Calculate Franck-Condon Factors for $H_2-H_2^+$ using the harmonic oscillator approximation and compare to experiment

You are provided with a Python code FCF-H2-H2+.py which calculates all of the information you require.

This code takes as input:

1. Number of allowed ground and excited vibrational states for transitions
2. Reduced mass of H_2 molecule (same as H_2^+)
3. Frequency of the H_2 molecule (ground state, 0)
4. Frequency of the H_2^+ molecule (excited state, p)
5. Equilibrium bond lengths (the difference is the displacement)
6. Difference between potential minima of the electronic states (ionization energy)

This code outputs:

1. Franck-Condon Factors for each pair of ground and excited vibrational states up to a threshold, using the $n_{H_2} = 0, n_{H_2^+} = 0$ Franck-Condon factor as the reference.

Your task will be to attempt to reproduce Figure 4, which shows the experimental photoionization spectrum for H_2 . To do this, you must plot the spectra of the first 10 transitions, keeping the vibrational level of the ground electronic state $n_{H_2} = 0$ and only changing the vibrational levels of the excited electronic state. The spectral position is calculated as:

$$\text{Spectral Position} = IE + E_{H_2^+} - E_{H_2}.$$

All of these energies are calculated for you (E_0 and E_p). You will need to store the Franck-Condon Factors and plot them. You may also need to adjust the bounds of allowed ground and excited vibrational states to reach 10 transitions.

Congratulations, you have now successfully predicted the Franck-Condon Factors and calculated a spectrum for the photoionization of $H_2 - H_2^+$! How does it compare to your calculation using the harmonic oscillator approximation? Can you explain the differences using what you know about the harmonic oscillator approximation?

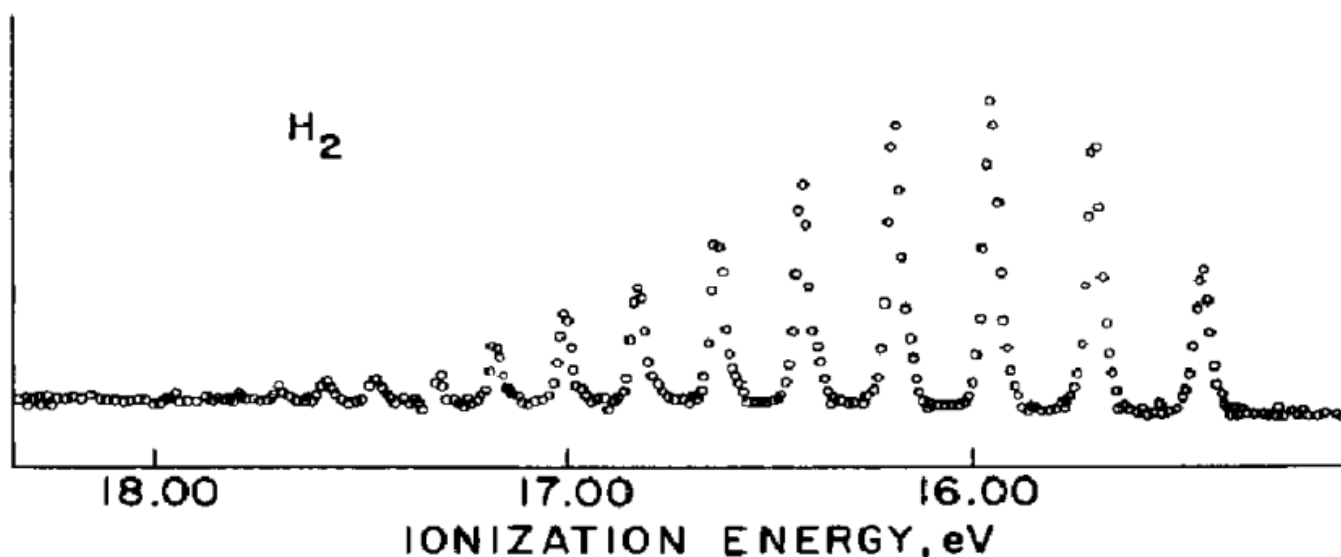


Figure 4: Experimental photoionization spectrum of $\text{H}_2\text{-H}_2^+$ from Ref. [4]

2.2 Task 2: Calculate the Franck-Condon Factors (and spectra) of V_3 using matrix elements (Hermite polynomial recursion relations).

You are provided with a C++ code `FC.cxx` created by P.-N. Roy ([5]), 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 [6]. 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.

2.3 Task 3: Calculate the Franck-Condon Factors (and spectra) of V_3 using Gaussian Boson Sampling.

You are provided with a Python 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 [6, 5, 1]. 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?

3 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 harnians to calculate the Franck-Condon Factors.
2. Explain briefly the similarities and differences between these three methods.

4 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

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