



Electronic Spectroscopy Outside of the Condon Approximation

Permanent link

<http://nrs.harvard.edu/urn-3:HUL.InstRepos:39987957>

Terms of Use

This article was downloaded from Harvard University's DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at <http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA>

Share Your Story

The Harvard community has made this article openly available.
Please share how this access benefits you. [Submit a story](#).

[Accessibility](#)

Electronic Spectroscopy Outside of the Condon Approximation

A DISSERTATION PRESENTED

BY

JOSEPH SEAN CAHILL GOODKNIGHT

TO

THE DEPARTMENT OF CHEMISTRY AND CHEMICAL BIOLOGY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN THE SUBJECT OF

CHEMICAL PHYSICS

HARVARD UNIVERSITY

CAMBRIDGE, MASSACHUSETTS

NOVEMBER 2017

©2017 – JOSEPH SEAN CAHILL GOODKNIGHT

ALL RIGHTS RESERVED.

Electronic Spectroscopy Outside of the Condon Approximation

ABSTRACT

Biological and artificial light-harvesting systems as well as ion-trap quantum computing all have physics which are highly dependent on electron-nuclear interactions, so it is important to be precise in how we treat these interactions. People very commonly, however, invoke the approximation that molecules do not absorb or emit light differently, no matter what the state is of their nuclear geometry is; put more technically, that the molecular dipoles do not change with respect to nuclear coordinate. The first person to make this approximation was E.U. Condon (in 1928), and so it is named after him. Now, however, that state-of-the-art spectroscopy has short-enough pulses to isolate nuclear motion, this approximation is being shown to have limitations in the context of modern investigations of the interactions between electronic and nuclear degrees of freedom.

We start with an example of how a variation in the transition dipole moment can completely change the interpretation of an entire class of experiment by confusing one physical effect for another when investigating the mechanism of photosynthetic energy transfer. Recognizing that having a non-Condon transition dipole moment can be a problem, we investigate a method for estimating the functional form of the transition dipole as a function of the nuclear coordinate through a linear electronic absorption spectroscopy experiment. Then, we look at how a variation in the transition dipole moment actually causes a molecule to heat during the operation of an ultrafast laser spectroscopy and how that heating would manifest as an isotropic infrared signal. Then, finally, we look at how relaxing the Condon approximation both heating up and causes loss of fidelity in a trapped-ion Molmer-Sorenson gate: a ubiquitous architecture in the field of trapped ion quantum computing.

Contents

| | | |
|----------|--|-----------|
| 1 | INTRODUCTION | 1 |
| 1.1 | Electric Field Interactions with Quantum Systems | 1 |
| 1.1.1 | What are we trying to learn? | 1 |
| 1.1.2 | What is physically going on? | 2 |
| 1.1.3 | The Dipole Matrix | 5 |
| 1.1.4 | Putting it all together | 7 |
| 1.2 | Time-Dependent Quantum Mechanics | 8 |
| 1.3 | Perturbation Treatment | 8 |
| 1.4 | Electric Field Emissions from Quantum Systems | 12 |
| 1.4.1 | What is Actually Being Measured | 13 |
| 1.4.2 | Adding together multiples orders of perturbation | 14 |
| 1.5 | Phase-Matching Conditions: or, Whither my Signal's direction? | 15 |
| 1.6 | Absorption Spectra | 18 |
| 1.6.1 | Bringing it all together | 22 |
| 1.6.2 | Real Data | 22 |
| 1.7 | Pump Probe Experiments | 25 |
| 1.8 | Higher Order Experiments | 25 |
| 1.9 | Representations of the Nuclear Coordinate | 26 |
| 1.9.1 | What Happens when you apply a ladder operator to the wrong eigenstate? | 30 |
| 1.10 | Nuclear Structure of the Electronic Transition Dipole Moment and the Condon Approximation | 31 |
| 1.10.1 | Different Potential Energy Wells | 32 |
| I | Non-Condon Effects in Dynamic Spectroscopy | 36 |
| 2 | PROBLEMS WITH DETECTION OF ELECTRONIC COHERENCES IN SYSTEMS WITH COORDINATE-VARYING TRANSITION DIPOLE | 38 |
| 2.1 | Introduction | 39 |
| 2.2 | Methods | 41 |
| 2.3 | Results and Discussion | 47 |
| 2.4 | Conclusion | 56 |
| 2.5 | Acknowledgments | 56 |
| 3 | DETECTING NON-CONDON TRANSITION DIPOLE MOMENTS WITH ABSORPTION SPECTROSCOPY | 57 |
| 3.1 | Introduction | 58 |
| 3.2 | System Setup | 58 |
| 3.3 | Effects on Linear Absorption Spectroscopy | 60 |
| 3.4 | Corrections to Tetracene | 63 |
| 3.5 | Conclusion | 74 |
| 3.6 | Acknowledgments | 74 |
| 3.7 | Supplementary Information | 75 |
| 3.7.1 | Absorption Harmonic Oscillator Model | 75 |

| | | |
|-----------|---|------------|
| 4 | NON-CONDON HEATING DURING LASER SPECTROSCOPY | 82 |
| 4.1 | Introduction | 82 |
| 4.2 | System Setup | 83 |
| 4.3 | Mode Heating | 85 |
| 4.3.1 | Resonance Raman | 86 |
| 4.3.2 | Simulations of Non Condon Heating | 89 |
| 4.4 | Results | 91 |
| 5 | DECOHERENCE AND HEATING IN MOLMER SORENSON GATES BECAUSE OF NON-CONDON TRANSITION DIPOLES | 95 |
| 5.1 | Introduction | 95 |
| 5.2 | Typical values for $c^{(i)}$ | 103 |
| 5.3 | Conclusion | 103 |
| 5.4 | Supplemental Material | 103 |
| 5.4.1 | Rabi Frequency | 103 |
| 5.4.2 | Proper Unitary Dynamics | 105 |
| II | Other Electronic Spectroscopy Tools | 109 |
| 6 | GETTING DOWN TO THE HEART OF MATTER | 111 |
| 7 | OTHER METHODS OF ELECTRONIC SPECTROSCOPY | 115 |
| 7.1 | Transient Grating as a Witness for Electronic Coherence | 115 |
| 7.1.1 | Pump Probe | 115 |
| 7.1.2 | Transient Grating | 116 |
| 7.1.3 | Pump Probe Equivalence with Transient Grating | 119 |
| 7.1.4 | Pump Probe Facsimiles | 119 |
| 7.1.5 | Experimental Considerations | 122 |
| 7.1.6 | Delta-Function Pulse Limit for a two level system with one vibrational coordinate | 125 |
| 7.1.7 | Transient Grating for a Coherent Monomer | 129 |
| 7.1.8 | TG of a Coherent Dimer | 134 |
| 7.2 | Quantum Process Tomography | 144 |
| 7.2.1 | Quick Introduction to Quantum Process Tomography | 145 |
| 7.2.2 | Experimental Determination of χ | 146 |
| 7.2.3 | The Goal | 147 |
| 7.2.4 | Initial Equations | 147 |
| 7.2.5 | Simplifications | 152 |
| 7.2.6 | Initial Conditions | 159 |
| 7.2.7 | More Correct Forms for Laser Amplitude | 170 |
| 7.2.8 | Ancilla | 171 |
| 7.2.9 | Experimental Considerations | 175 |
| 7.2.10 | Conclusion | 177 |
| 7.3 | Investigating Conical Intersections Using Pulse-width Dependent Dynamics | 177 |
| 7.3.1 | Adiabatic Representation | 181 |
| 7.3.2 | Detecting A Conical Intersection | 182 |

| | | |
|------------|---|------------|
| 8 | COMPUTATIONAL METHODS USED | 184 |
| 8.1 | Working with Natural Units: or, Why Mess with SI? | 184 |
| 8.1.1 | Setting Constants equal to 1 | 185 |
| 8.1.2 | Setting units equal to 1 or: Finding the “Natural” units | 186 |
| 8.1.3 | Setting other things equal to 1 | 187 |
| 8.1.4 | Conclusion on Units | 189 |
| 8.2 | Discrete Fourier Transform | 189 |
| 8.3 | Choosing the Parameters of Space | 190 |
| 8.3.1 | Momentum-Space Considerations | 191 |
| 8.3.2 | One-Interaction | 192 |
| 8.3.3 | Two-Interactions | 192 |
| 8.3.4 | Summarize | 193 |
| 8.4 | Applying $U(t)$ Numerically: the Split Operator Method | 194 |
| 8.5 | Trapezoidal Integration for Perturbation Theory Calculations with Smaller Time Discretization | 196 |
| 8.6 | Calculation Method For Heating Calculations | 198 |
| 8.7 | Notorious RWA: the Rotating Wave Approximation | 202 |
| III | Conclusion | 204 |
| 9 | CONCLUSION | 206 |

*For Mom and Dad,
who always made me answer my own questions, instead of just telling me the answer
...this is what you get...*

Acknowledgments

It seems standard to have a sappy acknowledgments section in every thesis so this will be no exception. Many tears went into writing this section so please read it.

My grad school story starts after orientation when a kind first-year graduate student who had been a Harvard undergrad offers me a tour of campus beyond the department. Jacob Sanders' initial kindness turned into a great friendship that got us through many boring seminars, teaching together and an exciting trip 20 hour to Paris after a 3 day layover at a conference on Quantum Effects in Biology.

My co-hort had many other special people whose constant friendship helped me get through grad school and the particularly tough first year. Especially Ryan Babbush, Amy Gilson, Katherine Phillips and Denise Alfonso.

The classes that came after mine weren't so bad either, actually, and I'm particularly grateful for the stoic realism of Thomas Markovich and the free hugs of Jennifer Wei; they were both great friends in Grad School.

Then of course, there are the awesome older grad students to whom I owe a great deal. Jarrod McClean is by far the most intellectually impressive person I have ever met and I had some incredibly eye-opening conversations with him as I was starting out in the research group. Roberto Olivares was also so kind as to take me on during my rotation in the research group even though I'm reasonably confident I actively slowed him down. Joel Yuen, who started basically all of the work that my PhD was on, also helped me a great deal. Jon Welch was also a constant friend and colleague who I owe a lot to.

I also owe a tremendous debt to many of the fantastic postdocs that have been in the group while I've been here. Starting with the most important: Jacob Krich. My PhD would probably not have happened if he hadn't offered to mentor me as if he was still a postdoc from his new faculty job in Ottawa, as I was lost and adrift as a third year student. I will forever be grateful to him.

I also want to mention Johannes Hachman, John Parkhill, David Tempel, Man Hong Yung, Xavier Andrade, Joonsuk Huh, Dmitriy Rappoport, and Sule Atahan-Evrenk who all taught me little bits here and there and who I all owe a debt of gratitude for making grad school a much more interesting experience.

Outside of the lab I have many people to thank! Starting close to the lab, I have to thank the former department administrator Allen Aloise for helping me through some difficult and more bureaucratic parts of

grad school.

Stepping a bit further away from lab, I always greatly enjoyed my teaching obligations, and Gregg Tucci was always an incredible resource for teaching and navigating the department. But I also have to particularly thank Pia Sorenson for hiring me to teach the most awesome course possibly in Harvard's History: "Science and the Physical Universe 27: Science and Cooking" not once but twice. Still sorry I couldn't have taught it even more times, but finishing this document took some precedence, alas.

I also must admit to spending a lot of time outside of lab engaged in the most fulfilling music and theatrical performance opportunities I have ever had—and likely will ever have.

Each show with the Harvard-Radcliffe Gilbert and Sullivan players was an absolute joy and gave me reasons to laugh and to sing and the people were amazing to work with; there are far too many to mention them all.

Then, 4 years in the Harvard University Choir gave me the constant feeling that I was a terrible musician but I loved every minute of it; I particularly want to thank Laszlo Seress for being such a good friend and literally dragging me to auditions, and also Edward Elwyn Jones (Gund University Choirmaster and Organist in the Memorial Church at Harvard University: a Space of Grace@in Harvard Yard) who was an inspirationally patient leader, wonderful parent and outstanding musician.

Working as a resident tutor in Pforzheimer House has also been an immense joy and honor. That would never have happened without Emily Stokes-Rees, Anne Harrington and John Durant. And it would have been a lot more boring without Gabe Katsch and David Francis! I have learned from all of my students in the house, and there are once again too many to mention.

Then there was the UC Berkeley Alumni Club of New England which I got myself involved with when I went with my good friend Michael Chang, to a football watching party near Fenway and eventually ended up leading it after my other good friend Chad Smith left for California. I too left this last year, and want to thank Geoffrey Liou for helping me not worry; I know the group is in great hands!

The more science I learned, the more I realized the whole Universe is mind-bogglingly complex, wonderful, and mysterious. Contrary to what one might expect, I think I came out of grad school more Catholic than I started, and I want to thank Fr. George Salzmann (who is also a scientist with a PhD in biochemistry) for being such a great friend and intellectual conversationalist these 4 years. I never thought a friendly but unexpected lunch invitation after mass one Sunday would turn into such a long friendship.

Coming back to science, I have to thank Keith Nelson and Dudley Herschbach for being on my Graduate

Advising Committee. I chose them both, as much for their reputation as scientists, as for their reputations as decent human beings. That being said, the handful of chances I got to present my research and ideas to them, I was constantly blown away by their scientific insight and probing questions. One of my biggest regrets in grad school is not meeting with these amazing scientists more often. I also owe a tremendous debt of gratitude to Rick Heller for stepping in to be on my dissertation defense committee.

Then there's the people who got me in to science in the first place. OF many professors at my undergrad UC Berkeley, there's the late, great David Chandler who introduced me to the beauty of statistical mechanics; then Marcin Majda who was a great general advisor and gave me countless pieces of invaluable advice over the 4 years there. Then, last but not least, Rich Saykally whose lab I worked in for 3 years and who allowed me to learn so many cool things I never would have otherwise. His vouching for me gave me an embarrassingly good choice of where to study for graduate school. I will always remember his kindness and especially his sense for drama; he was who taught me scientists could actually be funny and theatrical instead of the stereotypical. I also have to mention Rich's grad students Paul Peng, Neil Switz, Rob Onorato and Dale Otten who all certainly prolonged their PhDs dealing with undergrad-Joey but whose help and encouragement was invaluable to me as well.

My family has been incredibly important to me throughout this whole experience. My Dad (Greg Goodknight) in particular has always been there to talk with me when I needed and been very patient about not seeing me as much as he did when I was in college in California. I know my dear mother (Teri Cahill) would be just as helpful had we not lost her over 15 years ago to cancer. I wish more than anything she was here to read this acknowledgement in person, but I have faith she may now have other means of reading it now. My amazing step-mother (Rosie Stephenson-Goodknight) has been there for me and so supportive. As have her two sons, my amazing stepbrothers Sean and John who were always both so excited to hear me describe my research at Christmas and Thanksgiving.

Then there is the person who has made the last year+ of grad school the best year of my life despite being stressed out of my mind. Tess Brooks: the love of my life has made my life full in a way I never knew before. If you're reading this at some point in the future because some dude named "Joseph Knightbrook" claimed he wrote it; he's not lying. He just got married to the most amazing woman in the world and changed his name from what is on the front. I can't wait to spend the rest of my life with her.

Then there's the man who's second in line behind me for fault on this PhD: my advisor Alán Aspuru-Guzik. Many graduate students have to go through graduate school constantly wondering if their bosses actually care about them as a person as opposed to caring about them as a citation-producing machine, but I never had that problem. Alán cultivates the most friendly and healthy atmosphere in his lab and never says no to a crazy new idea. I thank my advisor Alán from the bottom of my heart for taking a chance on a kid from Berkeley with no theory experience at all and for helping me through a wild ride.

Further Acknowledgements by Chapter

CHAPTER 2 contains content that has been previously published in the following article:

- Joseph Goodknight, Peter Rose, Jacob Krich, Alán Aspuru-Guzik “Coordinate-varying transition dipole effects on the witness for electronic coherences.” (To Be Submitted).

CHAPTER 3 contains content that has been previously published in the following article:

- Joseph Goodknight, Jacob Krich, Alán Aspuru-Guzik “ Detecting Non-Condon Transition Dipole Moments with Absorption Spectroscopy.” (To Be Submitted).

CHAPTER 6 contains content that has been previously published in the following article:

- Joseph Goodknight, Alán Aspuru-Guzik “Taking six-dimensional spectra in finite time.” *Science* 356 (2017): 1333.

1

Introduction

As a young graduate student, I was incredibly disappointed by the resources available to me to learn the physics about what is going on in electronic spectroscopy. Thus, I am going to use the opportunity here to attempt to write a useful and pedagogical introduction to the physics behind Electronic Spectroscopy in the hopes that future students can hit the ground running faster than I was able to.

1.1 ELECTRIC FIELD INTERACTIONS WITH QUANTUM SYSTEMS

Let's imagine that we have in our possession a two-level Quantum System with a Hamiltonian like so:

$$H = \begin{pmatrix} 0 & 0 \\ 0 & E_1 \end{pmatrix} \quad (1.1.1)$$

We don't have to assume a two level system and indeed, most of the time we won't know the exact nature of the system before we begin the experiment. For the purposes of explaining what's going on, however, the two level system more than suffices and is much easier to type (for me) and write (for you) so we will stick with it for now.

Anyway, we have decided that we want to see what happens when we hit this guy with light. Why? What are we going to learn?

1.1.1 WHAT ARE WE TRYING TO LEARN?

When we hit the system with light, we can learn about the structure of the system and the dynamics of how that structure evolves.

This happens because when the system is excited with light, it will, itself, emit light. The light that comes forth from our system will encode very basic information about the system and our theory here can predict what it will say.

1.1.2 WHAT IS PHYSICALLY GOING ON?

We have in our possession a femtosecond laser which can output electric fields of the following Gaussian form:

$$\vec{E}(t) = \vec{e} \frac{A}{\sqrt{2\pi\sigma^2}} e^{-(t-T)^2/2\sigma^2} \left(e^{i\vec{k}\cdot\vec{r}-i\omega_c t+i\phi} + e^{-i\vec{k}\cdot\vec{r}+i\omega_c t-i\phi} \right) \quad (1.1.2)$$

Where the parameters are as follows:

| | | |
|------------|--|--------------------------------------|
| \vec{e} | | the polarization and of the beam |
| σ | | spread parameter of the beam in time |
| ω_c | | the frequency of the carrier wave |
| \vec{k} | | the wave-vector of the beam |
| T | | the center-time of the pulse |
| ϕ | | the phase of the pulse |

What's that you say? The magnetic field? We're going to assume it's negligible since $|B| \propto |E|/c$ and c is generally assumable to be a big number.

You may be rightfully asking at this point: how is this electric field going to interact with our quantum system? For that answer, we must appeal to electrodynamics and, specifically, the electrodynamic quantum mechanical Hamiltonian (which we will refrain from deriving or otherwise generating).

$$H = \sum_i \frac{\left| \vec{p}_i - \frac{q_i}{c} \vec{A}(\vec{r}_i, t) \right|^2}{2m_i} + q_i \phi(\vec{r}_i, t) \quad (1.1.3)$$

Where the sum is over all particles in the system. Theoretically, this is all we need to begin simulations. Just define a vector potential for the input field and then a vector and scalar potential for the system and you're done.

Unfortunately, that's not going to work. While in theory a simulation like that is possible, the scaling would be awful and even with a modern supercomputer, there's not way we could treat anything more than a small system. Furthermore, we were talking about our system in terms of energy states, not particles, so we need to find a way to get this Hamiltonian to look like it will play well with energy states. To do this, let's expand out the Hamiltonian.

$$H = \sum_i \left[\frac{\vec{p}_i^2}{2m_i} + q_i \phi(\vec{r}_i, t) \right] - \frac{q_i}{2mc} \left(\vec{p}_i \cdot \vec{A}(\vec{r}_i, t) + \vec{A}(\vec{r}_i, t) \cdot \vec{p}_i \right) + \frac{q_i^2}{2m_i c^2} \vec{A}(\vec{r}_i, t)^2 \quad (1.1.4)$$

Let's now assume that we're in the Coulomb gauge and the following are true:

$$\nabla \cdot \vec{A} = 0 \quad (1.1.5)$$

$$\vec{E} = -\frac{\partial \vec{A}}{\partial t} \quad (1.1.6)$$

$$\vec{B} = \nabla \times \vec{A} \quad (1.1.7)$$

Since the momentum operator is the gradient, that gives us our first simplification:

$$H = \sum_i \left[\frac{\vec{p}_i^2}{2m_i} + q_i \phi(\vec{r}_i, t) \right] - \frac{q_i}{2mc} \vec{A}(\vec{r}_i, t) \cdot \vec{p}_i + \frac{q_i^2}{2m_i c^2} \vec{A}(\vec{r}_i, t)^2 \quad (1.1.8)$$

Now the trick we want here is to make yet another gauge transformation like so:

$$f = \vec{A} \cdot \vec{r} \quad (1.1.9)$$

$$(1.1.10)$$

Which will affect \vec{A} like so

$$\begin{aligned} \vec{A} &\rightarrow \vec{A} + \nabla f \\ &= \vec{A} + \nabla \cdot \vec{A} \\ \nabla (\vec{A} \cdot \vec{r}) &= \vec{A} \times (\nabla \times \vec{r}) + \vec{r} \times (\nabla \times \vec{A}) + (\vec{A} \cdot \nabla) \vec{r} + (\vec{r} \cdot \nabla) \vec{A} \\ &= \vec{r} \times \vec{B} + \vec{A} + (\vec{r} \cdot \nabla) \vec{A} \\ \vec{A} &\rightarrow 2\vec{A} + \vec{r} \times \vec{B} + (\vec{r} \cdot \nabla) \vec{A} \end{aligned}$$

and ϕ like so:

$$\begin{aligned} \phi &\rightarrow \phi - \frac{\partial}{\partial t} f \\ &\rightarrow \phi - \frac{\partial}{\partial t} \vec{A} \cdot \vec{r} \\ &\rightarrow \phi + \vec{E} \cdot \vec{r} \end{aligned}$$

Alright, now the electric field appears. Going back to the Hamiltonian:

$$\begin{aligned}
 H = \sum_i & \left[\frac{\vec{p}_i^2}{2m_i} + q_i \phi(\vec{r}_i, t) \right] \\
 & + q_i \vec{E}(t, \vec{r}_i) \cdot \vec{r}_i \\
 & - \frac{q_i}{2mc} \left(2\vec{A}(\vec{r}_i, t) + \vec{r}_i \times \vec{B}(\vec{r}_i, t) + \vec{r}_i \cdot \nabla_i \right) \cdot \vec{p}_i \\
 & + \frac{q_i^2}{2m_i c^2} \left(2\vec{A}(\vec{r}_i, t) + \vec{r}_i \times \vec{B}(\vec{r}_i, t) + \vec{r}_i \cdot \nabla_i \right)^2
 \end{aligned}$$

This looks workable, does it not? OK, so given that in molecular systems, the Hamiltonian is just a collection of Coulomb terms with no time dependence, we will say that the first line of the above equation is the system Hamiltonian and all the time dependence of ϕ is just manifest in the Electric field of the incoming light.

We now make the famous **Electric Dipole Approximation** which basically says that since c is large, the only term that matters in the above expression is the Electric field. Why do we call it the electric dipole approximation? Because it involves the dipole operator:

$$H'(t) = \sum_i q_i \vec{E}(t, \vec{r}_i) \cdot \vec{r}_i$$

Which, if we assume the electric field is constant across all the particles in the system (another big part of the electric dipole approximation), we can calculate matrix elements,

$$H'_{ab}(t) = \vec{E}(t, \vec{r}) \cdot \langle a | \sum_i q_i \vec{r}_i | b \rangle$$

$$H'_{ab}(t) = \vec{E}(t, \vec{r}) \cdot \vec{\mu}_{ab} \tag{1.1.11}$$

We now have a way of describing the interaction of light with an electronic system.

1.1.3 THE DIPOLE MATRIX

The dipole matrix we have just derived is a very useful thing. The first claim I want to make is that it is a completely off-diagonal matrix.

1.1.3.1 OFF-DIAGONAL

To explain this, let's go to one dimension and assume some position space form for the energy eigenfunctions of the system:

$$\mu_{aa} = \int_{-\infty}^{\infty} a^\dagger(x) x a(x) dx \quad (1.1.12)$$

If the claim is that this is equal to zero, I can prove this simply by proving that

$a^\dagger(-x) - xa(-x) = -a^\dagger(x)xa(x)$ which is equivalent to determining $a^\dagger(-x)a(-x) = a^\dagger(x)a(x)$ because of our friend the x operator. This itself is equivalent to determining that the function for a and its hermitian conjugate have the same parity (\pm behavior under coordinate mirroring).

$$a^\dagger(-x) = \pm a^\dagger(x) \quad (1.1.13)$$

$$a(-x) = \pm a(x) \quad (1.1.14)$$

To do this, let's assume that they have the opposite behavior:

$$a^\dagger(-x) = -a^\dagger(x) \quad (1.1.15)$$

$$a(-x) = a(x) \quad (1.1.16)$$

And try to normalize the wavefunction

$$1 = \int_{-\infty}^{\infty} a^\dagger(x)a(x)dx \quad (1.1.17)$$

$$= \int_{-\infty}^0 a^\dagger(x)a(x)dx + \int_0^{\infty} a^\dagger(x)a(x)dx \quad (1.1.18)$$

$$= - \int_{\infty}^0 a^\dagger(-x)a(-x)dx + \int_0^{\infty} a^\dagger(x)a(x)dx \quad (1.1.19)$$

$$= - \int_0^{\infty} a^\dagger(x)a(x)dx + \int_0^{\infty} a^\dagger(x)a(x)dx = 0 \quad (1.1.20)$$

Clearly then, our original assumption is false and they have the same parity behavior and the dipole matrix is off-diagonal

1.1.3.2 PHYSICAL MEANING OF THE DIPOLE MATRIX

But what does the Dipole Matrix represent? To understand this, let's look at the matrix representation:

$$\vec{\mu} = \begin{pmatrix} 0 & \vec{\mu}_{01} \\ \vec{\mu}_{10} & 0 \end{pmatrix} \quad (1.1.21)$$

Let's imagine a wavefunction in the ground state:

$$|\Psi\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (1.1.22)$$

What happens when we act the dipole operator on the wavefunction?

$$\vec{\mu}|\Psi\rangle = \begin{pmatrix} 0 & \vec{\mu}_{01} \\ \vec{\mu}_{10} & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (1.1.23)$$

$$= \begin{pmatrix} 0 \\ \vec{\mu}_{10} \end{pmatrix} \quad (1.1.24)$$

It induces a transition from the ground state to the excited state, which corresponds to the Absorption of a photon. It is for this reason that it is sometimes called the "Transition Dipole Operator". Just for fun, let's act it on the excited state as well.

$$|\Psi\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (1.1.25)$$

$$\vec{\mu}|\Psi\rangle = \begin{pmatrix} 0 & \vec{\mu}_{01} \\ \vec{\mu}_{10} & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (1.1.26)$$

$$= \begin{pmatrix} \vec{\mu}_{01} \\ 0 \end{pmatrix} \quad (1.1.27)$$

It just brought it down to the excited state. This corresponds to the "Stimulated Emission" of a photon.

Given that this operator induces transition, the following notation makes it easier to understand what's going

on:

$$\vec{\mu} = \begin{pmatrix} 0 & \vec{\mu}_{0 \leftarrow 1} \\ \vec{\mu}_{1 \leftarrow 0} & 0 \end{pmatrix} \quad (1.1.28)$$

1.1.3.3 TRANSITION DIPOLE MATRIX NOTATION

The transition Dipole Matrix has a dual role as an operator and a vector in space. Which makes the notation of $\vec{\mu}$ seem incomplete. Therefore, I propose the following notation instead:

$$\vec{\mu}\boldsymbol{\mu} = \begin{pmatrix} 0 & \vec{\mu}_{0 \leftarrow 1} \\ \vec{\mu}_{1 \leftarrow 0} & 0 \end{pmatrix} \quad (1.1.29)$$

Pronounced ‘‘Double-mu’’ for hopefully obvious reasons, each ‘mu’ represents a part of the nature of the object: either operator or vector. I hope you will like it.

Furthermore, there may also come a day when we need a non-matrix representation of the dipole operator for convenience’s sake.

$$\vec{\mu}\boldsymbol{\mu} = \sum_{i \neq j} \vec{\mu}_{j \leftarrow i} |j\rangle \langle i| \quad (1.1.30)$$

1.1.4 PUTTING IT ALL TOGETHER

After some algebra we can now go back to the physics of the situation. Recall that we’re dealing with a two-level system like this:

$$H = \begin{pmatrix} 0 & 0 \\ 0 & E_1 \end{pmatrix} \quad (1.1.31)$$

And now we have a Hamiltonian which describes how this system interacts with radiation:

$$H'(t) = \vec{E}(r,t) \cdot \vec{\mu}\boldsymbol{\mu} \quad (1.1.32)$$

$$\vec{E}(\vec{r},t) = \vec{e} \frac{A}{\sqrt{2\pi\sigma^2}} e^{-(t-T)^2/2\sigma^2} \left(e^{i\vec{k}\cdot\vec{r}-i\omega_c t-i\phi} + e^{-i\vec{k}\cdot\vec{r}+i\omega_c t-i\phi} \right) \quad (1.1.33)$$

We now know fully how light interacts with a quantum system but only at a very high level of the Hamiltonian. We just have this weird object which we know nothing about how to manipulate yet. Furthermore, how does this system emit light? First let's tackle how to incorporate this Hamiltonian into a wavefunction.

1.2 TIME-DEPENDENT QUANTUM MECHANICS

With any Hamiltonian you can just go about solving the Quantum-Mechanical differential equation

$$\frac{d}{dt} |\Psi(t)\rangle = -\frac{i}{\hbar} H |\Psi(t)\rangle$$

in any way you desire. If H is time-independent and you can precisely identify the wavefunction at an initial time t_0 , this is super easy since you just solve a dead-simple differential equation to get:

$$|\Psi(t)\rangle = e^{-\frac{i}{\hbar} H_0(t-t_0)} |\Psi(t_0)\rangle$$
$$|\Psi(t)\rangle = U(t, t_0) |\Psi(t_0)\rangle$$

Where $U(t, t_0)$ is the "Time-Evolution Operator".

We can not, however, do something quite this simple for a generalized time-dependent Hamiltonian

1.3 PERTURBATION TREATMENT

To treat a time-dependent Hamiltonian, we have to go back to the initial equation:

$$\frac{d}{dt} |\Psi(t)\rangle = -\frac{i}{\hbar} H(t) |\Psi(t)\rangle$$

Rearrange it to get the beginning of the solution to the differential equation:

$$d|\Psi(t)\rangle = -\frac{i}{\hbar} H(t) |\Psi(t)\rangle dt$$

Now let's integrate both sides from t_0 to a general time t :

$$|\Psi(t)\rangle - |\Psi(t_0)\rangle = -\frac{i}{\hbar} \int_{t_0}^t H(\tau) |\Psi(\tau)\rangle d\tau$$

$$|\Psi(t)\rangle = |\Psi(t_0)\rangle - \frac{i}{\hbar} \int_{t_0}^t H(\tau) |\Psi(\tau)\rangle d\tau$$

And there we have solved it ... Oh wait, shoot, this equation is self-referential. No matter, we'll just plug it in again,

$$|\Psi(t)\rangle = |\Psi(t_0)\rangle - \frac{i}{\hbar} \int_{t_0}^t H(\tau) |\Psi(t_0)\rangle d\tau + \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^t H(\tau) \int_{t_0}^{\tau} H(\tau') |\Psi(\tau')\rangle d\tau' d\tau$$

Since this seems to be going on for infinity (spoiler alert: it is), it seems best to define then a series of wavefunctions like so:

$$|\Psi(t)\rangle = \sum_i |\Psi^{(i)}(t)\rangle \quad (1.3.1)$$

$$|\Psi^{(0)}(t)\rangle = |\Psi(t_0)\rangle \quad (1.3.2)$$

$$|\Psi^{(n)}(t)\rangle = -\frac{i}{\hbar} \int_{t_0}^t H(\tau) |\Psi^{(n-1)}(\tau)\rangle d\tau \quad (1.3.3)$$

What is happening here? The first perturbation term is the Hamiltonian acting on the system once. In our case, it's almost always a photon so what is happening, here, is the first order term is one photon interacting, the second two photons etc.

The integral, it will soon become clear, is taking every time that the light beam is "on" and could interact with the system once, and interfering together, all the possible times that the interaction could happen. This is more clear, ironically, when we shift around these equations into what is called the "interaction picture":

1.3.0.1 THE INTERACTION PICTURE

The perturbation integrals are probably going to be rather difficult to calculate and, since the integrand is never going to equal zero, we won't be able to cut any corners to save time. You will recall, however, that the Gaussian pulses we are looking to hit our system with do approach zero. For that reason, let's start by

splitting the Hamiltonian into a time-independent and time-dependent part:

$$H(t) = H_0 + H'(t) \quad (1.3.4)$$

For the time-independent part, we know we can define the propagator $U_0(t, t_0) = e^{-i(t-t_0)H_0/\hbar}$ which is how the system evolves in time if there is no time-dependent interaction term. Note that because this is merely the evolution when there is not time-dependent perturbation, if we are working in a density matrix formalism, this could easily include dephasing.

To spare an awkward derivation I'll cut right to the chase: for any operator and for the actual, true wavefunction, we define the “interaction” operator and wavefunctions:

$$|\Psi_I(t)\rangle = U_0^\dagger(t, t_0) |\Psi(t)\rangle \quad (1.3.5)$$

$$A_I(t) = U_0^\dagger(t, t_0) A(t) U_0(t, t_0) \quad (1.3.6)$$

Why did we do that? Just wait, all will be revealed. I will leave it up to you to confirm that:

$$\frac{d}{dt} |\Psi_I(t)\rangle = \frac{i}{\hbar} H_I(t) |\Psi_I(t)\rangle \quad (1.3.7)$$

Huh, OK so that means that our perturbation series stays the same as well with the addition of I subscripts:

$$|\Psi_I(t)\rangle = \sum_i |\Psi_I^{(i)}(t)\rangle \quad (1.3.8)$$

$$|\Psi_I^{(0)}(t)\rangle = |\Psi_I(t_0)\rangle \quad (1.3.9)$$

$$|\Psi_I^{(n)}(t)\rangle = -\frac{i}{\hbar} \int_{t_0}^t H_I'(\tau) |\Psi_I^{(n-1)}(\tau)\rangle d\tau \quad (1.3.10)$$

Let's begin by examining the zero order term and bringing it back into the actual wavefunction picture:

$$|\Psi_I^{(0)}(t)\rangle = |\Psi_I(t_0)\rangle \quad (1.3.11)$$

$$U_0^\dagger(t, t_0) |\Psi^{(0)}(t)\rangle = U_0^\dagger(t_0, t_0) |\Psi(t_0)\rangle \quad (1.3.12)$$

$$|\Psi^{(0)}(t)\rangle = U_0(t, t_0) |\Psi(t_0)\rangle \quad (1.3.13)$$

This means that after our interaction picture transformation, zero-order estimate for the wavefunction's evolution is just how the wavefunction would evolve without a perturbation, which hopefully makes a lot of

sense. Now let's look at the first order correction:

$$U_0^\dagger(t, t_0) \left| \Psi^{(1)}(t) \right\rangle = -\frac{i}{\hbar} \int_{t_0}^t U_0^\dagger(\tau, t_0) H'(\tau) U_0(\tau, t_0) \left| \Psi^{(0)}(t_0) \right\rangle d\tau \quad (1.3.14)$$

$$\left| \Psi^{(1)}(t) \right\rangle = -\frac{i}{\hbar} \int_{t_0}^t U_0(t, \tau) H'(\tau) \left| \Psi^{(0)}(\tau) \right\rangle d\tau \quad (1.3.15)$$

Here we have the system evolving, minding its own business until time τ when it decides to interact with the perturbation which in this case is also interacting with a photon: absorbing or emitting. After it has interacting with the photon, it goes again on its merry way, evolving in time without the perturbation. The system can 'decide' to interact with a photon at any time the perturbation is 'on', so the integral serves to average over all possible time the photon can interact with the system.

It should further be clear that the 0th order correction is 0 photons interacting with the system, the first order is one photon, second two photons, ad nauseum. So from now on, we take the interaction picture derivation as moot and use the following equations to do all of our time-dependent Quantum Mechanics:

$$\left| \Psi_0(t) \right\rangle = U_0(t, t_0) \left| \Psi(t_0) \right\rangle \quad (1.3.16)$$

$$\left| \Psi^{(n)}(t) \right\rangle = -\frac{i}{\hbar} \int_{t_0}^t \hat{H}(\tau) \left| \Psi^{(n-1)}(\tau) \right\rangle d\tau \quad (1.3.17)$$

1.3.0.2 MULTIPLE HAMILTONIANS

Whenever you can express the perturbation Hamiltonian as a sum of other Hamiltonians (like in a multiple laser beam spectroscopy experiment), you may want to talk about applying them in a certain order in which case the above notation is far too simplistic,

$$H'(t) = \hat{H}'_1(t) + \hat{H}'_2(t) + \hat{H}'_3(t) \quad (1.3.18)$$

$$\left| \Psi_1(t) \right\rangle = -\frac{i}{\hbar} \int_{t_0}^t \hat{H}_1(\tau) \left| \Psi_0(\tau) \right\rangle d\tau \quad (1.3.19)$$

$$\left| \Psi_{1,2}(t) \right\rangle = -\frac{i}{\hbar} \int_{t_0}^t \hat{H}_2(\tau) \left| \Psi_1(\tau) \right\rangle d\tau \quad (1.3.20)$$

Where the interactions can be read from left to right. So for example, that last equation represents one interaction of the first perturbation, followed by another interaction of the second Hamiltonian

1.4 ELECTRIC FIELD EMISSIONS FROM QUANTUM SYSTEMS

We're still missing a huge piece, though. Sure, we could now go on to calculate how the wavefunction evolves in time... but how we measure this? Fear not, for our savior comes in the form of the dipole operator. Recall from your Electricity and Magnetism courses that an oscillating dipole will produce radiation. So let's plan on doing that: on taking the time-expectation value of the dipole operator:

$$\vec{D}_i(t) = \langle \Psi(t) | \vec{\mu} \mu | \Psi(t) \rangle \quad (1.4.1)$$

That is for the dipole on one molecule or one system. For multiple systems, you sum the dipoles together to get the macroscopic "Polarization". For our General case, we use Mukamel³⁷ Equation 4.75 but ignore the term for phase matching, assuming that it's always fulfilled for the systems we will treat.

$$\vec{E}_{\text{emission}}(t) = i \frac{2\pi}{n(\omega_s)} \frac{\omega_s}{c} I P(t) = i \sum_j D_j(t) \quad (1.4.2)$$

This number is actually dimensionless so in the interest of accuracy, we want to know what the prefactor is. According to Griffith's¹⁵, the form of the electric field for a simple oscillating dipole (form given below) and far away from the source is:

$$\vec{p}(t) = q_0 d \hat{z} \cos \omega t = \vec{p}_0 \cos \omega t \quad (1.4.3)$$

$$\vec{E}(t) = -\frac{p_0}{4\pi\epsilon_0} \frac{\omega^2}{c^2} \cos \omega \left(t - \frac{r}{c} \right) (\hat{r} \cos \theta - \hat{z}) \quad (1.4.4)$$

The prefactor constants are not terribly important for our purposes, but the ω^2 could very important as it will be different for different signals. Generally, however, we can ignore it, except in some cases, especially where I compare to experiment. So I will then take a hybrid approach in those cases where we keep the imaginary factor as it is a result of Quantum Mechanics but establish the pre-factor of $\frac{1}{4\pi\epsilon_0} \frac{\omega^2}{c^2}$. The factor r/c retarding the dipole does not concern us here, neither does the direction of the dipole. The direction would also matter if we were investigating systems where there were multiple dipoles at different directions, but we do not have that in any of the systems of interest in this thesis.

1.4.1 WHAT IS ACTUALLY BEING MEASURED

Imagine you have an input pulse $\vec{E}_{\text{in}}(t)$ and then some molecular output $\vec{E}_{\text{out}}(t)$. Most detectors actually detect the intensity of light which is the mod squared of the electric field. So that detector is actually measuring:

$$I_{\text{total}}(t) = \left| \vec{E}_{\text{in}}(t) + \vec{E}_{\text{out}}(t) \right|^2 \quad (1.4.5)$$

$$= \left(\vec{E}_{\text{in}}(t) + \vec{E}_{\text{out}}(t) \right) \left(\vec{E}_{\text{in}}(t) + \vec{E}_{\text{out}}(t) \right)^* \quad (1.4.6)$$

$$= I_{\text{in}}(t) + I_{\text{out}}(t) + \vec{E}_{\text{out}}^*(t) \cdot \vec{E}_{\text{in}}(t) + \vec{E}_{\text{out}}(t) \cdot \vec{E}_{\text{in}}^*(t) \quad (1.4.7)$$

We now have a simple complex number arithmetic problem in front of us

$$\mathbf{a} = a_r + ia_i$$

$$\mathbf{b} = b_r + ib_i$$

$$\mathbf{ab}^* = a_r b_r + a_i b_i + i(-a_r b_i + a_i b_r)$$

$$\mathbf{a}^* \mathbf{b} = a_r b_r + a_i b_i + i(a_r b_i - a_i b_r)$$

$$\mathbf{ab}^* + \mathbf{a}^* \mathbf{b} = 2(a_r b_r + a_i b_i)$$

$$\mathbf{ab}^* + \mathbf{a}^* \mathbf{b} = 2\text{Re}[\mathbf{ab}^*] = 2\text{Re}[\mathbf{a}^* \mathbf{b}]$$

which bringing it back:

$$I_{\text{total}}(t) = I_{\text{in}}(t) + I_{\text{out}}(t) + 2\text{Re} \left[\vec{E}_{\text{out}}(t) \cdot \vec{E}_{\text{in}}^*(t) \right] \quad (1.4.8)$$

OK, so there first term here is big (we are using a laser after all) and most likely known (although not necessarily always). Then the second term is interesting but is going to be much smaller than the next term which describes the interference between the input pulse and the output emission. This third term will be what we measure most of the time, since it provides a way to make it easier to measure the small signal we care about, since it's attached to a large signal we know [almost] everything about.

1.4.2 ADDING TOGETHER MULTIPLES ORDERS OF PERTURBATION

OK, given we have two different perturbations added together which we will call 1 and 2, the overall wavefunction will look like so:

$$|\Psi\rangle(t) = |\psi_0(t)\rangle + |\psi_1(t)\rangle + |\psi_2(t)\rangle + |\psi_{1,2}(t)\rangle + |\psi_{2,1}(t)\rangle + |\psi_{1,1}(t)\rangle + |\psi_{2,2}(t)\rangle + \dots \quad (1.4.9)$$

and that will go on infinitely. I call this the Grand Electric Field Expansion (GEFE) The molecule's electric field output will then have many different terms

$$\begin{aligned} -i\vec{E} &= \langle\Psi(t)|\vec{\mu}\mu|\Psi(t)\rangle \\ &= \langle\psi_0(t)|\vec{\mu}\mu|\psi_0(t)\rangle \\ &\quad + \langle\psi_0(t)|\vec{\mu}\mu|\psi_1(t)\rangle + \langle\psi_1(t)|\vec{\mu}\mu|\psi_0(t)\rangle + \langle\psi_2(t)|\vec{\mu}\mu|\psi_0(t)\rangle + \langle\psi_0(t)|\vec{\mu}\mu|\psi_2(t)\rangle \\ &\quad + \langle\psi_0(t)|\vec{\mu}\mu|\psi_{1,2}(t)\rangle + \langle\psi_1(t)|\vec{\mu}\mu|\psi_1(t)\rangle + \dots \end{aligned}$$

which will similarly go on infinitely. As is done with all perturbation calculations, you can truncate the expansion to a specific order in perturbation order and approximate all further to be zero. Still, even if we said we only cared about the first order, there are 4 signals in just this one case of two perturbations.

Thankfully there are a few more tricks to simplify this expansion.

Take the zero order electric field:

$$-i\vec{E} = \langle\Psi(t)|\vec{\mu}\mu|\Psi(t)\rangle + \dots$$

One often works in electronic spectroscopy with something like $\vec{\mu}\mu = \vec{m}u_0 (|g\rangle\langle e| + |e\rangle\langle g|)$ indicating light can excite the system from the ground to an excited state. Ignoring any time dependence for now, the zero order signal in a system with that dipole and starting off in $|g\rangle$ will be:

$$\begin{aligned} -i\vec{E} &= \vec{m}u_0 \langle g|(|g\rangle\langle e| + |e\rangle\langle g|)|g\rangle + \dots \\ &= \vec{m}u_0 \langle g|e\rangle = 0 \end{aligned}$$

So in systems with an off-diagonal $\vec{\mu}\mu$, all terms in the Grand Electric Field Expansion for which the bra and ket interact with the perturbation an odd number of times will be zero.

There's one last trick and it's the biggest so it gets its own section.

1.5 PHASE-MATCHING CONDITIONS: OR, WHITHER MY SIGNAL'S DIRECTION?

With a theoretical framework in place now for how to calculate the polarization and thus the emitted electric field, we are in a position, now, to ask: what does this light look like and what direction is the light going to come out of? We haven't thought about this yet at all. How to we figure this out? Let's look at the perturbation we're applying generally applying in all ultrafast laser spectroscopy experiments:

$$\vec{E}(\vec{r}, t) = \vec{e} \frac{A}{\sqrt{2\pi\sigma^2}} e^{-(t-T)^2/2\sigma^2} \left(e^{i\vec{k}\cdot\vec{r} - i\omega_c t + i\phi} + e^{-i\vec{k}\cdot\vec{r} + i\omega_c t - i\phi} \right) \quad (1.5.1)$$

The \vec{k} vector represents the direction of the light is propagating. There is, you can plainly see, a positive and a negative term, here. What do those physically represent: is there a wave going backwards? Kind of. It is helpful to think here of splitting up the real electric field into two imaginary (complex to be strictly mathematical) beam components:

$$\vec{E}(\vec{r}, t) = \vec{E}^{(-)}(\vec{r}, t) + \vec{E}^{(+)}(\vec{r}, t) \quad (1.5.2)$$

$$\vec{E}(t) = \vec{e} \frac{A}{\sqrt{2\pi\sigma^2}} e^{-(t-T)^2/2\sigma^2} \quad (1.5.3)$$

$$\vec{E}^{(-)}(\vec{r}, t) = \vec{E}(t) e^{-i\vec{k}\cdot\vec{r} + i\omega_c t - i\phi} \quad (1.5.4)$$

$$\vec{E}^{(+)}(\vec{r}, t) = \vec{E}(t) e^{i\vec{k}\cdot\vec{r} - i\omega_c t + i\phi} \quad (1.5.5)$$

and we can then learn something by applying the energy operator to both:

$$\hat{H} = i\hbar \frac{d}{dt} \quad (1.5.6)$$

$$\hat{H}\vec{E}^{(\pm)}(\vec{r}, t) = \pm\hbar\omega\vec{E}^{(\pm)}(\vec{r}, t) \quad (1.5.7)$$

So the positive k vector can be thought of as a positive energy component which will excite a system, and the negative part as being a negative energy component which will relax the system via stimulated emission.

But let's imagine we have a two beam setup and we interact the positive part of each beam once:

$$|\Psi_{1+,2+}(t)\rangle \quad (1.5.8)$$

1.5. Phase-Matching Conditions: or, Whither my Signal's direction?

and let's pick out the component of electric field with just those two interactions:

$$E(t) = i \langle \Psi_0(t) | \vec{\mu} \mu | \Psi_{1+,2+}(t) \rangle \quad (1.5.9)$$

That's all fine and good but what direction is this electric field going to be coming out? We haven't looked at that yet.

To think about that, imagine that our molecules, in the approximation we're looking at, are simply radiating dipoles. The derivation is complicated but you can prove that the emitted electric field for an oscillating dipole looks something very roughly like this:

$$\vec{E} \approx \vec{\mu} \frac{e^{i|\vec{k}|r}}{r} \quad (1.5.10)$$

meaning that any given dipole is radiating out in all directions (note that the numerator of the above fraction has no vectors in it, so it is emitting in all directions) indiscriminately. Does that all signals are coming out in all direction?

The short answer is no: the laser has a finite focal point and every molecule within that focal point will be emitting dipole radiation. Imagine you're a molecule at \vec{r}_i within the laser spot. Because the incoming laser beams have defined k-vectors, when laser 1 hits you, it will have a phase based on **your** location:

$$\vec{E} \propto e^{i\vec{k}_1 \cdot \vec{r}_i} \quad (1.5.11)$$

Which will then be imparted onto your dipole emission like so:

$$\vec{E}_i \approx \vec{\mu} \frac{e^{i|\vec{k}_1||\vec{r}-\vec{r}_i|}}{|\vec{r}-\vec{r}_i|} e^{i\vec{k}_1 \cdot \vec{r}_i} \quad (1.5.12)$$

Then in the case when the molecule interacts with the $+\vec{k}_2$ part of the next beam, you will get another phase:

$$\vec{E}_i \approx \vec{\mu} \frac{e^{i|\vec{k}_1+\vec{k}_2||\vec{r}-\vec{r}_i|}}{|\vec{r}-\vec{r}_i|} e^{i(\vec{k}_1+\vec{k}_2) \cdot \vec{r}_i} \quad (1.5.13)$$

In this case, once you've added up all of the molecules within the spot of your laser, you will only get light emitting in the $\vec{k}_1 + \vec{k}_2$ direction also called the "phase matching" direction because the wavevector of the emitted light matches the phase given to each of the individual dipoles. It is easier to show than to prove so check out `phaseMatchingDemo.py` on my GitHub or just look below and trust me that I'm a good

programmer:

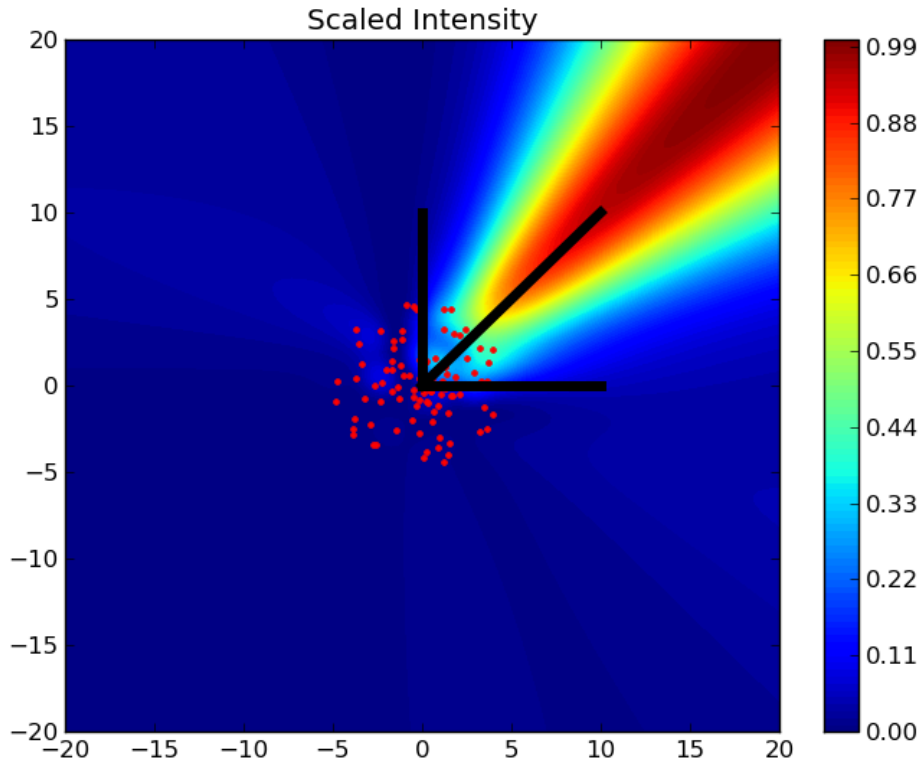


Figure 1.1: An example of how phase matching actually works. The red dots are all emitting molecules and the black bar pointing up and the black bar pointing to the right are the k-vectors of the input beams. The Emissions are then all added up and I've plotted the intensity, along with the addition of the two k-vectors to show they are both most definitely going in the same direction.

The vertical and horizontal black bars are the input k-vectors and the skewed black bar is the phase matching direction which you can see significant intensity of light coming out of. Red dots are the individual dipoles used in this simulation (100 in this case).

You will often hear the argument that phase matching is just a product of conservation of momentum. You had a photon with momentum k_1 coming in and then another with k_2 coming in: of course the output will have a k-vector of $k_1 + k_2$. That intuition will actually never lead you astray, so feel free to use it, but know that it's not physical. When the molecule absorbs the photon, the momentum conservation happens right then and there: there's recoil in the molecule once the photon hits it. The later-emitting dipole radiation is going out in all directions, but interfering with all the neighboring dipoles

1.5.0.1 DETERMINING THE DIRECTION OF A TERM IN THE GRAND ELECTRIC FIELD EXPANSION

Phase matching comes from the imprinting of a k phase on a molecule but the above derivation was done, implicitly, only considering phases applied to a bra term. What if you care about the following term from the Grand Electric Field Expansion:

$$\langle \psi_{1+,2-}(t) | \vec{\mu} \mu | \psi_{1+,3+}(t) \rangle$$

the bra will contribute phase of $k_1 + k_3$ but the bra is less obvious. The physics of excitation by pulse one, followed by relaxation of pulse 2 is still there, so it's counter-intuitive, but the phase is flipped from the notation in the argument of the bra. You'll have to watch out, though, as you go out into the real world as some authors prefer the opposite convention: keeping the intuition for phases and leaving behind the intuition of + exciting and - relaxing. Also if you ever see a thing called a double-sided Feynman diagram, they are just another tool to make sense of the Grand Electric Field Expansion*. I prefer the latter because it's more physical and intuitive in my mind. So then in what direction does the above term radiate in? The answer is $k_3 + k_2$.

1.6 ABSORPTION SPECTRA

An absorption/emission spectrum is the most basic of spectroscopies we will cover here. The setup in question is a light source comes into a system and excites it: only one interaction although multiple interactions will occur, as we will see, the most important interaction is just one absorption.

This process of light interaction provides lots of information about a molecule's structure through the energy transitions allowed by the method of spectroscopy. The method can be tuned to tell you more about electrons absorbing energy or the nucleus absorbing energy either through vibrations (Infrared/Raman spectroscopy) or the nuclear spin state through Nuclear Magnetic Resonance (NMR) spectroscopy and its variants.

The different forms of absorption spectroscopy are the oldest form of spectroscopy. Indeed, the first absorption experiment could be said to have taken place in 1802 when Wollaston first noticed odd dark bands in sunlight he had just separated by his improved version of Newton's prism⁵⁷. It turns out the

*Double-sided Feynman diagrams also aid in the understanding of de-phasing when one is doing calculations which involve the density matrix of a system but we are not treating that here.

gaps Wollaston observed in the spectrum were molecules between the sun and the experimenter. Spectroscopy like that eventually proved indispensable to detecting molecules and learning about their structure. Today there's not a working scientist whose work doesn't benefit from absorption spectroscopy whether they directly use it or not.

I will focus on electronic absorption but the techniques are quite interchangeable.

But what does absorption mechanistically look like? After the system absorbs a photon, the system then proceeds to emit light. If the incoming beam had a k-vector k_1 then the emission will also be in the same direction. Mathematically this looks like this:

$$E_{\text{Abs}}(t) = i \frac{1}{4\pi\epsilon_0} \frac{\omega^2}{c^2} \langle \Psi_0(t) | \vec{\mu} \mu | \Psi_{1+}(t) \rangle \quad (1.6.1)$$

For the basic example of a vibrational monomer, what will this signal look like? First a little Housekeeping/definitions. We start with a two-level system.

$$H_0 = \hbar\omega_e |e\rangle \langle e| \quad (1.6.2)$$

$$U_0(t, \tau) = |g\rangle \langle g| + e^{-i\omega_e(t-\tau)} |e\rangle \langle e| \quad (1.6.3)$$

but we want a vibrational coordinate on both electronic sites as well for our purposes, so we introduce one,

$$H_0 = \sum_n \hbar\omega_\gamma \left(n + \frac{1}{2} \right) |n_\gamma\rangle |g\rangle \langle g| \langle n_\gamma| + \sum_m \left(\hbar\omega_\epsilon \left(m + \frac{1}{2} \right) + \omega_e \right) |m_\epsilon\rangle |e\rangle \langle e| \langle m_\epsilon| \quad (1.6.4)$$

$$U_0(t, \tau) = \sum_n e^{-i\omega_\gamma(n+\frac{1}{2})(t-\tau)} |n_\gamma\rangle |g\rangle \langle g| \langle n_\gamma| + \sum_m e^{-i(\omega_\epsilon(m+\frac{1}{2})+\omega_e)(t-\tau)} |m_\epsilon\rangle |e\rangle \langle e| \langle m_\epsilon| \quad (1.6.5)$$

and it interacts with an electric field thusly to get the first order term

$$|\Psi_{1+}(t)\rangle = -\frac{i}{\hbar} \int_{-\infty}^t U(t, \tau) \hat{H}'_{1+}(\tau) |\Psi_0(\tau)\rangle d\tau \quad (1.6.6)$$

$$= -\frac{i}{\hbar} \int_{-\infty}^t U(t, \tau) E_{1+}(\tau) \hat{\mu} e^{-i\omega_0\tau} |0_\gamma\rangle |g\rangle d\tau \quad (1.6.7)$$

$$= -\frac{i}{\hbar} \int_{-\infty}^t U(t, \tau) E_{1+}(\tau) e^{-i\omega_0\tau} \mu(x) |0_\gamma\rangle |e\rangle d\tau \quad (1.6.8)$$

where we now must change the vibrational basis

$$|\Psi_{1+}(t)\rangle = -\frac{i}{\hbar} \int_{-\infty}^t U(t, \tau) E_{1+}(\tau) e^{-i\omega_0\tau} \sum_n |n_\epsilon\rangle \langle n_\epsilon| \mu(x) |0_\gamma\rangle |e\rangle d\tau \quad (1.6.9)$$

where we let $\langle n_\varepsilon | \mu(x) | 0_\gamma \rangle = \mu_0^n$

$$|\psi_{1+}(t)\rangle = -\frac{i}{\hbar} \sum_n \int_{-\infty}^t U(t, \tau) E_{1+}(\tau) e^{-i\omega_0 \tau} \mu_0^n |n_\varepsilon\rangle |e\rangle d\tau \quad (1.6.10)$$

and the time-evolution operator can now be applied

$$|\psi_{1+}(t)\rangle = -\frac{i}{\hbar} \sum_n \mu_0^n \int_{-\infty}^t E_{1+}(\tau) e^{-i\omega_0 \tau} e^{-i\omega'_{e,n}(t-\tau)} |n_\varepsilon\rangle |e\rangle d\tau \quad (1.6.11)$$

where $\omega'_{e,n}$ is the energy of the excited state in the n th vibrational level. We simplify:

$$|\psi_{1+}(t)\rangle = -\frac{i}{\hbar} \sum_n \mu_0^n e^{-i\omega'_{e,n} t} \int_{-\infty}^t E_{1+}(\tau) e^{i(\omega'_{e,n} - \omega_0)\tau} |n_\varepsilon\rangle |e\rangle d\tau \quad (1.6.12)$$

If we now assume we primarily care about the time after which the pulse or perturbation has turned off, then we can extend the limit out to positive infinity and define $\Delta\omega_{e,n} = \omega'_{e,n} - \omega_0$

$$|\psi_{1+}(t)\rangle = -\frac{i}{\hbar} \sum_n \mu_0^n e^{-i\omega'_{e,n} t} \int_{-\infty}^{\infty} E_{1+}(\tau) e^{i\Delta\omega_{e,n} \tau} |n_\varepsilon\rangle |e\rangle d\tau \quad (1.6.13)$$

Now this looks an awful lot like a Fourier transform and it is. Now we need a specific form for the electric field envelope:

$$E_{1+}(\tau) = \frac{A}{\sqrt{2\pi\sigma^2}} e^{-\frac{(\tau-t_1)^2}{2\sigma^2}} e^{-i\omega_c(\tau-t_1)} \quad (1.6.14)$$

$$\int_{-\infty}^{\infty} E_{1+}(\tau) e^{i\omega t} d\tau = A e^{i\omega t_1} e^{-\frac{\sigma^2}{2}(\omega - \omega_c)^2} = \tilde{E}_{1+}(\omega) \quad (1.6.15)$$

which we can then put into the expression:

$$|\psi_{1+}(t)\rangle = -\frac{i}{\hbar} \sum_n e^{-i\omega'_{e,n} t} \mu_0^n \tilde{E}_{1+}(\Delta\omega_{e,n}) |n_\varepsilon\rangle |e\rangle \quad (1.6.16)$$

As a side note, this is an incredibly versatile trick. If you ever have a perturbation $E_a(t)$ which effectively turns off at a certain time, the perturbed wavefunction will always look like a sum of all the accessible energy states multiplied by the transition dipole moment, multiplied by the amplitude of the electric field at the relevant energy level transition so long as the time you are interested in is after the perturbation turns off. I will use that a lot going forward.

1.6.0.1 2 VIBRATIONAL COORDINATES

What if we were to instead look at a 2-dimensional vibrational coordinate? Then we have to go back to the beginning

$$|\psi_{1+}(t)\rangle = -\frac{i}{\hbar} \int_{-\infty}^t U(t, \tau) E_{1+}(\tau) \hat{\mu} e^{-i\omega_0 \tau} |0, 0_\gamma\rangle |g\rangle d\tau \quad (1.6.17)$$

$$= -\frac{i}{\hbar} \int_{-\infty}^t U(t, \tau) E_{1+}(\tau) e^{-i\omega_0 \tau} \mu(x) |0, 0_\gamma\rangle |e\rangle d\tau \quad (1.6.18)$$

and this time, the basis change will be more difficult. We have to multiply in a 2D identity:

$$I = \sum_{n,m} |n, m_\epsilon\rangle \langle n, m_\epsilon|$$

$$|\psi_{1+}(t)\rangle = -\frac{i}{\hbar} \int_{-\infty}^t U(t, \tau) E_{1+}(\tau) e^{-i\omega_0 \tau} \sum_{n,m} |n, m_\epsilon\rangle \langle n, m_\epsilon| \mu(x) |0, 0_\gamma\rangle |e\rangle d\tau \quad (1.6.19)$$

$$= -\frac{i}{\hbar} \sum_{n,m} \int_{-\infty}^t U(t, \tau) E_{1+}(\tau) e^{-i\omega_0 \tau} |n, m_\epsilon\rangle \mu_{0,0}^{n,m} |e\rangle d\tau \quad (1.6.20)$$

at this point, it's clear we will end up with an incredibly similar situation as before:

$$|\psi_{1+}(t)\rangle = -\frac{i}{\hbar} \sum_{n,m} e^{-i\omega'_{e,n,m} t} \mu_{0,0}^{n,m} \tilde{E}_{1+}(\Delta\omega_{e,n,m}) |n, m_\epsilon\rangle |e\rangle \quad (1.6.21)$$

1.6.1 BRINGING IT ALL TOGETHER

With all the relevant perturbations collected, we return to calculating the signal.

$$|\psi_{1+}(t)\rangle = -\frac{i}{\hbar} \sum_n e^{-i\omega'_{e,n}t} \mu_0^n \tilde{E}_{1+}(\Delta\omega_{e,n}) |n_\epsilon\rangle |e\rangle \quad (1.6.22)$$

$$|\psi_0(t)\rangle = e^{-i\omega'_{g,0}t} |0_\gamma\rangle |e\rangle \quad (1.6.23)$$

$$P_{\text{Abs}}(t) = -\frac{i}{\hbar} \sum_n e^{-i(\omega'_{e,n}-\omega'_{g,0})t} \mu_0^{*n} \mu_0^n \tilde{E}_{1+}(\Delta\omega_{e,n}) \quad (1.6.24)$$

$$E_{\text{Abs}}(t) = \frac{1}{\hbar} \frac{1}{4\pi\epsilon_0 c^2} \sum_n (\omega'_{e,n} - \omega'_{g,0})^2 e^{-i(\omega'_{e,n}-\omega'_{g,0})t} \mu_0^{*n} \mu_0^n \tilde{E}_{1+}(\Delta\omega_{e,n}) \quad (1.6.25)$$

$$\tilde{E}_{\text{Abs}}(\omega) = \frac{1}{\hbar} \frac{1}{4\pi\epsilon_0 c^2} \sum_n (\omega'_{e,n} - \omega'_{g,0})^2 \mu_0^{*n} \mu_0^n \tilde{E}_{1+}(\Delta\omega_{e,n}) \frac{\delta\left[\omega - (\omega'_{e,n} - \omega'_{g,0})\right]}{d\tau} \quad (1.6.26)$$

$$= \frac{1}{\hbar} \frac{1}{4\pi\epsilon_0 c^2} \omega^2 \sum_n \mu_0^{*n} \mu_0^n \tilde{E}_{1+}(\Delta\omega_{e,n}) \frac{\delta\left[\omega - (\omega'_{e,n} - \omega'_{g,0})\right]}{d\tau} \quad (1.6.27)$$

$$= C\omega^2 \sum_n \mu_0^{*n} \mu_0^n \tilde{E}_{1+}(\Delta\omega_{e,n}) \delta[\omega - \Delta\omega_{e,n}] \quad (1.6.28)$$

As one might expect from the name absorption spectrum, we see an oscillation at all the frequency transitions from the ground state to all possible excited vibrational states. This is tempered by the amplitude of the excitation pulse at the relevant transition energy and the dipole element, often referred to as the Franck-Condon factor $\mu_0^n \mu_0^n$.

1.6.2 REAL DATA

Experimentalists will often give us the the molar extinction constant, what do we do with that and what is it?

It's ϵ below:

$$A = cI\epsilon(\omega) = \log\left(\frac{I_0(\omega)}{I(\omega)}\right)$$

$$cI\epsilon(\omega) = \log\left(\frac{I_0(\omega)}{I_0(\omega) + \delta I(\omega)}\right)$$

$$cI\epsilon(\omega) = \log\left(\frac{1}{1 + \frac{\delta I(\omega)}{I_0(\omega)}}\right)$$

let's then investigate this dimensionless parameter:

$$\frac{\delta I(\omega)}{I_0(\omega)}$$

but what is $\delta I(\omega)$? Well in reality, we are putting the light source exciting the molecule into the system, at the same time that it is emitting light. So what we're actually measuring is:

$$\begin{aligned} I(\omega) &= |\tilde{E}_{1+}(\omega) + E_{\text{abs}}(\omega)|^2 \\ &= |\tilde{E}_{1+}(\omega)|^2 + 2\Re [E_{\text{Abs}}(\omega)\tilde{E}_{1+}^*(\omega)] + |E_{\text{Abs}}(\omega)|^2 \\ &= I_0(\omega) + 2\Re [E_{\text{Abs}}(\omega)\tilde{E}_{1+}^*(\omega)] + |E_{\text{abs}}(\omega)|^2 \\ \delta I(\omega) &= 2\Re [E_{\text{Abs}}(\omega)\tilde{E}_{1+}^*(\omega)] + |E_{\text{Abs}}(\omega)|^2 \end{aligned}$$

Starting with the first term using our previous model:

$$\begin{aligned} \Re [E_{\text{Abs}}(\omega)\tilde{E}_{1+}^*(\omega)] &= \Re \left[C\omega^2 \sum_n \mu_0^{*n} \mu_0^n \tilde{E}_{1+}(\Delta\omega_{e,n}) \delta[\omega - \Delta\omega_{e,n}] \tilde{E}_{1+}^*(\omega) \right] \\ &= \Re \left[C\omega^2 \sum_n \mu_0^{*n} \mu_0^n \delta[\omega - \Delta\omega_{e,n}] \tilde{E}_{1+}(\Delta\omega_{e,n}) \tilde{E}_{1+}^*(\Delta\omega_{e,n}) \right] \\ &= \Re \left[C\omega^2 \sum_n \mu_0^{*n} \mu_0^n \delta[\omega - \Delta\omega_{e,n}] |\tilde{E}_{1+}(\Delta\omega_{e,n})|^2 \right] \\ &= C\omega^2 \sum_n \mu_0^{*n} \mu_0^n \delta[\omega - \Delta\omega_{e,n}] I_0(\omega) = \Xi(\omega) I_0(\omega) \end{aligned}$$

The delta-function doing a lot there to make the calculations simpler. This is a cool result, here, showing that there is a dimensionless function we'll call $\Xi(\omega)$ that is multiplied by the input laser source intensity to get the first term of δI . Now we check out the second term

$$\begin{aligned} |E_{\text{Abs}}(\omega)|^2 &= \left| C\omega^2 \sum_n \mu_0^{*n} \mu_0^n \tilde{E}_{1+}(\Delta\omega_{e,n}) \delta[\omega - \Delta\omega_{e,n}] \right|^2 \\ &= \left| C\omega^2 \sum_n \mu_0^{*n} \mu_0^n \delta[\omega - \Delta\omega_{e,n}] \right|^2 I_0(\omega) \end{aligned}$$

I'm about to do something a lot of people won't like... and that is to take the square of the delta function to be delta. Close your eyes if you don't like that sort of mathematical liberty:

$$\begin{aligned} |E_{\text{Abs}}(\omega)|^2 &= C^2 \omega^4 \sum_n (\mu_0^{*n} \mu_0^n)^2 \delta[\omega - \Delta\omega_{e,n}] I_0(\omega) \\ &= \Xi^2(\omega) I_0(\omega) \end{aligned}$$

Ξ has turned out to be very useful as here we see it again being squared. We can now go back to our dimensionless intensity ratio which is:

$$\frac{\delta I(\omega)}{I_0(\omega)} = 2\Xi(\omega) + \Xi^2(\omega)$$

bringing this back to the measured molar extinction coefficient

$$\begin{aligned} c l \mathcal{E}(\omega) &= \log \left(\frac{1}{1 + \frac{\delta I(\omega)}{I_0(\omega)}} \right) \\ &= \log \left(\frac{1}{1 + 2\Xi(\omega) + \Xi^2(\omega)} \right) \\ &= \log \left(\frac{1}{(1 + \Xi(\omega))^2} \right) \\ &= -2 \log(1 + \Xi(\omega)) \\ &= -2 \sum_n \sum_i (-1)^i \frac{(\Xi(\omega))^{i+1}}{i+1} \\ &\approx -2\Xi(\omega) \\ c l \mathcal{E}(\omega) &\approx C \omega^2 \sum_n \mu_0^{*n} \mu_0^n \delta[\omega - \Delta\omega_{e,n}] \end{aligned}$$

The last approximation is justified by noting this is essentially a series in the fine structure constant:

$$\begin{aligned} C \omega^2 * \mu^2 &\propto C \omega^2 * e^2 l^2 \\ &\propto \left(\frac{1}{4\pi\epsilon_0 c^2 \hbar} \right) \omega^2 e^2 l^2 \\ &= \left(\frac{e^2}{4\pi\epsilon_0 c^2 \hbar} \right) \omega^2 l^2 \\ &= \alpha \omega^2 l^2 \end{aligned}$$

1.7 PUMP PROBE EXPERIMENTS

With absorption spectroscopy, we put one laser beam, but why not put in more? Pump Probe is what happens when we put two laser beams in and instead of measuring how much of the first beam is absorbed, we look at how much of the second beam is absorbed. Then, because we only care about the signal which will come out in the direction of the probe beam, we have to only consider terms in the Grand Electric Field Expansion which will output in the probe direction. There are 4 and they have names based on the physical phenomenon they are measuring.

| Signal | Ket Interactions | Bra Interactions | Name |
|--------|------------------|------------------|--------------------------|
| 1 | pu+, pu-, pr+ | none | Ground State Bleach 1 |
| 2 | pu+, pr+ | pu+ | Excited State Absorption |
| 3 | pu+ | pu+, pr- | Stimulated Emission |
| 4 | pr+ | pu+, pu- | Ground State Bleach 2 |

and then the output electric fields look like so:

$$E_1(t) = i \langle \psi_0(t) | \hat{\mu} | \psi_{pu+, pu-, pr+}(t) \rangle \quad (1.7.1)$$

$$E_2(t) = i \langle \psi_{pu+}(t) | \hat{\mu} | \psi_{pu+, pr+}(t) \rangle \quad (1.7.2)$$

$$E_3(t) = i \langle \psi_{pu+, pr-}(t) | \hat{\mu} | \psi_{pu+}(t) \rangle \quad (1.7.3)$$

$$E_4(t) = i \langle \psi_{pu+, pu-}(t) | \hat{\mu} | \psi_{pr+}(t) \rangle \quad (1.7.4)$$

$$E_{pp}(t) = E_1(t) + E_2(t) + E_3(t) + E_4(t) \quad (1.7.5)$$

$$S_{pp}(T) = 2\text{Re} \left[\int E_{pp}^*(t) E_{pr+}(t) dt \right] \quad (1.7.6)$$

1.8 HIGHER ORDER EXPERIMENTS

There are many types of higher-order experiments and not terribly hard to concoct a new spectroscopy scheme. The most common as 2-D techniques where instead of just one pump beam, there are two pump beams, and the same for the probe. Then by scanning not just the middle gap between the pump pair and the probe pair, you also scan the two gaps between the pump/pairs. Then by Fourier transforming the gap between the pairs, you can get a picture of the energy input and the energy output of the system under investigation. That's just a high level explanation; I won't be going into detail as my PhD did not include much work on 2D spectroscopy.

As mentioned, you can go even higher than 4 pulses and I recently had the honor of providing a

perspective for an article on a 6th order laser spectrum which I reproduce in Chapter 6.

1.9 REPRESENTATIONS OF THE NUCLEAR COORDINATE

For the rest of this thesis, we will be very interested in forms of the transition dipole which are not just constant numbers but exist as functions. In particular, the science I have worked on has all involved vibrational coordinate dependence of the transition dipole moment. In order to understand how to do algebra with operators that are proportional to vibrational coordinates, it is worthwhile to understand the raising and lowering operator formulation of the Harmonic oscillator.

The Harmonic oscillator Hamiltonian looks like so:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 (\hat{x} - \bar{x}_0)^2$$

which has eigenstates $|n\rangle$ for which:

$$\hat{H}|n\rangle = \left(n\omega + \frac{1}{2}\right)|n\rangle \quad (1.9.1)$$

And it is useful to define operators:

$$\begin{aligned} \hat{a} &= \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - \bar{x}_0 + \frac{i}{m\omega} \hat{p} \right) \\ \hat{a}^\dagger &= \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - \bar{x}_0 - \frac{i}{m\omega} \hat{p} \right) \end{aligned}$$

such that

$$\hat{a}^\dagger \hat{a} = \frac{m\omega}{2\hbar} \left(\hat{x} - \bar{x}_0 - \frac{i}{m\omega} \hat{p} \right) \left(\hat{x} - \bar{x}_0 + \frac{i}{m\omega} \hat{p} \right) \quad (1.9.2)$$

$$= \frac{m\omega}{2\hbar} \left[(\hat{x} - \bar{x}_0)^2 + \frac{1}{m^2\omega^2} \hat{p}^2 - \frac{i}{m\omega} (\hat{p}\hat{x} - \hat{x}\hat{p}) \right] \quad (1.9.3)$$

we know, however, that:

$$[\hat{x}, \hat{p}] = \hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar \quad (1.9.4)$$

$$\hat{a}^\dagger \hat{a} = \frac{m\omega}{2\hbar} \left[(\hat{x} - \bar{x}_0)^2 + \frac{1}{m^2 \omega^2} \hat{p}^2 + \frac{i}{m\omega} i\hbar \right] \quad (1.9.5)$$

$$= \frac{m\omega}{2\hbar} \left[(\hat{x} - \bar{x}_0)^2 + \frac{1}{m^2 \omega^2} \hat{p}^2 - \frac{\hbar}{m\omega} \right] \quad (1.9.6)$$

$$= \frac{m\omega}{2\hbar} (\hat{x} - \bar{x}_0)^2 + \frac{m\omega}{2\hbar} \frac{1}{m^2 \omega^2} \hat{p}^2 - \frac{m\omega}{2\hbar} \frac{\hbar}{m\omega} \quad (1.9.7)$$

$$= \frac{m\omega}{2\hbar} (\hat{x} - \bar{x}_0)^2 + \frac{1}{2\hbar} \frac{1}{m\omega} \hat{p}^2 - \frac{1}{2} \quad (1.9.8)$$

we now note that with a little manipulation:

$$\hat{H} = \hbar\omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right) \quad (1.9.9)$$

So we define the product of those two operators in that manner as the number operator:

$$\hat{N} = \hat{a}^\dagger \hat{a} \quad (1.9.10)$$

because when you act it on an eigenstate:

$$\hat{N} |n\rangle = n |n\rangle \quad (1.9.11)$$

We can now note that because the ladder operators are made of position and momentum operators that they themselves will have commutators as well

$$[\hat{a}^\dagger, \hat{a}] = 1 \quad (1.9.12)$$

$$[\hat{N}, \hat{a}] = -\hat{a} \quad (1.9.13)$$

$$[\hat{N}, \hat{a}^\dagger] = \hat{a}^\dagger \quad (1.9.14)$$

Now we might ask what happens when we act the number operator on an eigenstate for which the operator \hat{a}^\dagger has been appended:

$$\begin{aligned} \hat{N} \hat{a}^\dagger |n\rangle &= (\hat{N} \hat{a}^\dagger + \hat{a}^\dagger \hat{N} - \hat{a}^\dagger \hat{N}) |n\rangle \\ &= ([N, \hat{a}^\dagger] + \hat{a}^\dagger \hat{N}) |n\rangle \\ &= (\hat{a}^\dagger + \hat{a}^\dagger \hat{N}) |n\rangle \\ &= (1+n) \hat{a}^\dagger |n\rangle \end{aligned}$$

implying that the operator \hat{a}^\dagger adds a quanta of energy. Similarly:

$$\begin{aligned}\hat{N}\hat{a}|n\rangle &= (\hat{N}\hat{a} + \hat{a}\hat{N} - \hat{a}\hat{N})|n\rangle \\ &= ([N, \hat{a}] + \hat{a}\hat{N})|n\rangle \\ &= (-\hat{a} + \hat{a}\hat{N})|n\rangle \\ &= (n-1)\hat{a}|n\rangle\end{aligned}$$

and that \hat{a} operator takes away a quanta. But what exactly does an application of one of these operators look like?

$$\begin{aligned}\hat{a}|n\rangle &= \sqrt{n}|n-1\rangle \\ \hat{a}^\dagger|n\rangle &= \sqrt{n+1}|n+1\rangle\end{aligned}$$

Because I don't feel like deriving them right now.

1.9.0.1 POSITION AND MOMENTUM OPERATORS

We can take the ladder operators and turn them into position and momentum operators,

$$\begin{aligned}\hat{a} &= \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - \bar{x}_0 + \frac{i}{m\omega} \hat{p} \right) \\ \hat{a}^\dagger &= \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - \bar{x}_0 - \frac{i}{m\omega} \hat{p} \right)\end{aligned}$$

say we add them together:

$$\begin{aligned}\hat{a}^\dagger + \hat{a} &= 2\sqrt{\frac{m\omega}{2\hbar}} (\hat{x} - \bar{x}_0) \\ (\hat{x} - \bar{x}_0) &= \sqrt{\frac{\hbar}{2m\omega}} (\hat{a}^\dagger + \hat{a})\end{aligned}$$

which gives us as a final answer:

$$\hat{x} = \bar{x}_0 + \sqrt{\frac{\hbar}{2m\omega}} (\hat{a}^\dagger + \hat{a}) \tag{1.9.15}$$

similarly when we subtract the ladder operators:

$$\begin{aligned}\hat{a}^\dagger - \hat{a} &= -2\sqrt{\frac{m\omega}{2\hbar}} \frac{i}{m\omega} \hat{p} \\ &= -i\sqrt{\frac{2}{\hbar m\omega}} \hat{p}\end{aligned}$$

giving us:

$$\hat{p} = i\sqrt{\frac{\hbar m\omega}{2}} (\hat{a}^\dagger - \hat{a}) \quad (1.9.16)$$

1.9.0.2 THE HUANG-RHYS PARAMETER

Say we want a dimensionless quantity that will tell us something about the difference between two potential energy wells. This would mean we have two Hamiltonians:

$$\hat{H}_\gamma = \frac{\hat{p}^2}{2m_\gamma} + \frac{1}{2}m_\gamma\omega_\gamma^2(\hat{x} - \bar{x}_\gamma)^2 + E_\gamma$$

and

$$\hat{H}_\epsilon = \frac{\hat{p}^2}{2m_\epsilon} + \frac{1}{2}m_\epsilon\omega_\epsilon^2(\hat{x} - \bar{x}_\epsilon)^2 + E_\epsilon$$

We could look at the value of one potential energy surface (ignoring any constant offset) at the difference between the two center points:

$$\begin{aligned}V_\epsilon(\bar{x}_\gamma) &= \frac{1}{2}m_\epsilon\omega_\epsilon^2(\Delta\bar{x})^2 \\ \Delta\bar{x} &= \bar{x}_\epsilon - \bar{x}_\gamma\end{aligned}$$

this is called the reorganization energy, because it is the amount of energy that would be “lost” or “gained” to go from one equilibrium point to another. This is not, however, dimensionless but it will be if we divide it by a quanta of energy:

$$\frac{V_\epsilon(\bar{x}_\gamma)}{\hbar\omega_\epsilon} = \frac{m_\epsilon\omega_\epsilon}{2\hbar} (\Delta\bar{x})^2 = S$$

Which is called the Huang-Rhys Parameter or S in our notation and characterizes the change in equilibrium position between two harmonic potential energy wells. Now, at this point, you should be asking: Isn't this an equally valid measure of the difference between two potential energy wells?

$$\frac{V_\gamma(\bar{x}_\varepsilon)}{\hbar\omega_\gamma} = \frac{m_\gamma\omega_\gamma}{2\hbar} (\Delta\bar{x})^2 = S$$

and I think you would be right but I do not know how to resolve this paradox... What you COULD do is note that these dimensionless parameters suggest the existence of dimensionless units of measurement of distance.

$$\begin{aligned} S_\varepsilon &= \frac{m_\varepsilon\omega_\varepsilon}{2\hbar} (\Delta\bar{x})^2 \\ &= \frac{1}{2} \left(\sqrt{\frac{m_\varepsilon\omega_\varepsilon}{\hbar}} \Delta\bar{x} \right)^2 \end{aligned}$$

and then just take the square of the difference between the two dimensionless locations of the center of the potential energy wells:

$$S = \frac{1}{2} \left(\sqrt{\frac{m_\varepsilon\omega_\varepsilon}{\hbar}} \bar{x}_\varepsilon - \sqrt{\frac{m_\gamma\omega_\gamma}{\hbar}} \bar{x}_\gamma \right)^2$$

but apparently the proper convention (citation needed) is

$$S = \frac{m_\varepsilon\omega_\varepsilon m_\gamma\omega_\gamma (\Delta\bar{x})^2}{m_\varepsilon\omega_\varepsilon + m_\gamma\omega_\gamma}$$

Which would reduce to the previous formula is both the masses and both the frequencies were the same.

1.9.1 WHAT HAPPENS WHEN YOU APPLY A LADDER OPERATOR TO THE WRONG EIGEN-STATE?

For the purposes of this thesis, we will often encounter two different potential energy wells on the same molecule (one for its ground state, γ , and the other for its excited state, ε). Does it matter if we apply a ladder operator from γ to ε ? Let's see.

$$\hat{a}_\gamma^\dagger |n_\varepsilon\rangle$$

but we only know for sure how the operator works in its own basis so we transform to that basis using the identity operator $\sum_i |i_\gamma\rangle \langle i_\gamma|$ and my shorthand for the frank-Condon factor $\langle a_\gamma | b_\epsilon \rangle = O_a^b$:

$$\begin{aligned} \hat{a}_\gamma^\dagger |n_\epsilon\rangle &= \hat{a}_\gamma^\dagger \sum_i O_i^n |i_\gamma\rangle \\ &= \sum_i O_i^n \hat{a}_\gamma^\dagger |i_\gamma\rangle \\ &= \sum_i O_i^n \sqrt{i+1} |i+1_\gamma\rangle \end{aligned}$$

Now what if we bring it back into the original basis?

$$\hat{a}_\gamma^\dagger |n_\epsilon\rangle = \sum_{i,j} O_i^n O_{i+1}^j \sqrt{i+1} |j_\epsilon\rangle$$

If we had mistakenly assumed the ladder operators were the same, we would have gotten:

$$\hat{a}_\gamma^\dagger |n_\epsilon\rangle \neq \sqrt{n+1} |n+1_\epsilon\rangle$$

But what is the amplitude that really ends up in the $|n+1_\epsilon\rangle$ state?

$$\begin{aligned} \langle n+1_\epsilon | \hat{a}_\gamma^\dagger |n_\epsilon\rangle &= \sum_{i,j} O_i^n O_{i+1}^j \sqrt{i+1} \delta_{j,n+1} \\ &= \sum_i O_i^n O_{i+1}^{n+1} \sqrt{i+1} \end{aligned}$$

So one must be very, very careful to apply the correct ladder operators to the correct state.

1.10 NUCLEAR STRUCTURE OF THE ELECTRONIC TRANSITION DIPOLE MOMENT AND THE CONDON APPROXIMATION

One of the more common transition dipole moments to see looks like this,

$$\vec{\mu} \mu = \vec{\mu}_0 (|e\rangle \langle g| + |g\rangle \langle e|) \quad (1.10.1)$$

where $\vec{\mu}_0$ is just a constant vector which does not depend on any other variable. Edward Condon in 1928 made with surprisingly little justification the above approximation that the electronic transition dipole did not depend on the nuclear position at all. But that should seem wrong, because shouldn't a molecule be

1.10. Nuclear Structure of the Electronic Transition Dipole Moment and the Condon Approximation

more likely to transition when it's in a nuclear configuration that is more similar to the state it's not in?

There is no reason that instead of $\vec{\mu}_0$, we can substitute an arbitrary function of the nuclear position $\vec{\mu}(\vec{R})$.

For the purposes of illustration, we will always collapse this object into a scalar which is only a function of one coordinate $\mu(x)$. We also then expand it into a polynomial basis,

$$\mu(x) = \mu_0 \sum_i \kappa_i x^i \quad (1.10.2)$$

but we know from above that this can be expressed in terms of creation and annihilation operators,

$$\mu(x) = \mu_0 \sum_i c_i (\hat{a} + \hat{a}^\dagger)^i \quad (1.10.3)$$

To keep things as simple as possible in analytic expressions, we normally will only work with the linear correction.

$$\mu(x) = \mu_0 + \mu' x \quad (1.10.4)$$

1.10.1 DIFFERENT POTENTIAL ENERGY WELLS

If we take the above operator, we realize we need it to be able to act it on two potential energy wells γ and ϵ with their own sets of eigenstates: $\{|n_\gamma\rangle\}$ and $\{|n_\epsilon\rangle\}$. What will that operator look like in terms of the ladder operators for each well? We'll start with the γ state:

$$\mu(x) = \mu_0 + \mu' \left(\bar{x}_\gamma + \sqrt{\frac{\hbar}{2m_\gamma\omega_\gamma}} (\hat{a}_\gamma^\dagger + \hat{a}_\gamma) \right) \quad (1.10.5)$$

$$= (\mu_0 + \mu' \bar{x}_\gamma) + \mu' \sqrt{\frac{\hbar}{2m_\gamma\omega_\gamma}} (\hat{a}_\gamma^\dagger + \hat{a}_\gamma) \quad (1.10.6)$$

and the epsilon will look frightfully similar:

$$\mu(x) = (\mu_0 + \mu' \bar{x}_\epsilon) + \mu' \sqrt{\frac{\hbar}{2m_\epsilon\omega_\epsilon}} (\hat{a}_\epsilon^\dagger + \hat{a}_\epsilon) \quad (1.10.7)$$

but we want them to look neat, so we define a few more variables:

$$\mu(x) = \bar{\mu}_\gamma + \mu'_\gamma (\hat{a}_\gamma^\dagger + \hat{a}_\gamma) \quad (1.10.8)$$

$$= \bar{\mu}_\varepsilon + \mu'_\varepsilon (\hat{a}_\varepsilon^\dagger + \hat{a}_\varepsilon) \quad (1.10.9)$$

$$\bar{\mu}_\gamma = (\mu_0 + \mu' \bar{x}_\gamma) \quad (1.10.10)$$

$$\bar{\mu}_\varepsilon = (\mu_0 + \mu' \bar{x}_\varepsilon) \quad (1.10.11)$$

$$\mu'_\gamma = \mu' \sqrt{\frac{\hbar}{2m_\gamma \omega_\gamma}} \quad (1.10.12)$$

$$\mu'_\varepsilon = \mu' \sqrt{\frac{\hbar}{2m_\varepsilon \omega_\varepsilon}} \quad (1.10.13)$$

Then if we wanted to make the operator exceedingly simple in one basis, γ , what would the constants look like for ε ?

$$\mu(x) = 1 + c (\hat{a}_\gamma^\dagger + \hat{a}_\gamma)$$

$$\bar{\mu}_\gamma = 1 = \mu_0 + \mu' \bar{x}_\gamma$$

$$\mu'_\gamma = c = \mu' \sqrt{\frac{\hbar}{2m_\gamma \omega_\gamma}}$$

$$\mu(x) = d + c_\varepsilon (\hat{a}_\varepsilon^\dagger + \hat{a}_\varepsilon)$$

$$\bar{\mu}_\varepsilon = d = \mu_0 + \mu' \bar{x}_\varepsilon$$

$$\mu'_\varepsilon = c_\varepsilon = \mu' \sqrt{\frac{\hbar}{2m_\varepsilon \omega_\varepsilon}}$$

we can now do some algebra:

$$1 - d = \mu' \bar{x}_\gamma - \mu' \bar{x}_\varepsilon$$

$$d = 1 - \mu' (\bar{x}_\varepsilon - \bar{x}_\gamma)$$

or in terms of c :

$$d = 1 - c \sqrt{\frac{2m_\gamma \omega_\gamma}{\hbar}} \Delta x$$

and some more algebra:

$$\begin{aligned}\frac{c_{\mathcal{E}}}{c} &= \sqrt{\frac{\hbar}{2m_{\mathcal{E}}\omega_{\mathcal{E}}}} \sqrt{\frac{2m_{\gamma}\omega_{\gamma}}{\hbar}} \\ \frac{c_{\mathcal{E}}}{c} &= \sqrt{\frac{m_{\gamma}\omega_{\gamma}}{m_{\mathcal{E}}\omega_{\mathcal{E}}}} \\ c_{\mathcal{E}} &= c \sqrt{\frac{m_{\gamma}\omega_{\gamma}}{m_{\mathcal{E}}\omega_{\mathcal{E}}}}\end{aligned}$$

1.10.1.1 GETTING A DIMENSIONLESS c

We initially defined the transition dipole function as

$$\mu(x) = \mu_0 + \mu'x \quad (1.10.14)$$

but suppose we want a dimensionless number to describe the slope, let's construct one:

$$\mu(x) = \mu_0 \left(1 + \frac{\mu'}{\mu_0}x \right) \quad (1.10.15)$$

$$= \mu_0 \left(1 + \Delta x \frac{\mu'}{\mu_0} \frac{x}{\Delta x} \right) \quad (1.10.16)$$

where $\Delta x = \bar{x}_{\mathcal{E}} - \bar{x}_{\gamma}$. We can then define $\lambda = \Delta x \frac{\mu'}{\mu_0}$ as a completely dimensionless way to describe how much variation in the transition dipole a wavepacket would experience when traversing the potential energy wells

$$\mu(x) = \mu_0 \left(1 + \lambda \frac{x}{\Delta x} \right) \quad (1.10.17)$$

1.10.1.2 A NATURAL ESTIMATE OF λ

Looking at the paper “Vibronic effects in the spectroscopy and dynamics of C-phycocyanin”⁵⁸, and, specifically, figure 9c, the black line represents the author’s worst (most non-Condon) transition dipole that they calculated. The transition dipole is roughly linear, with a value of -3 Debye at $x=0$ and decreasing .5 Debye in .5 distance units giving a slope of 1 Debye per dimensionless distance unit . They quote the

dimensionless displacement as being .4 which we can then use to extract an estimate for λ in a real system.

$$\begin{aligned}\mu(x) &\approx -3 - \frac{.5}{.5}x \\ &= -3 \left(1 + \frac{x}{3}\right) \\ &= -3 \left(1 + \frac{x d}{3 d}\right) \\ &= -3 \left(1 + \frac{d x}{3 d}\right) \\ \lambda &= \frac{d}{3} = \frac{.4}{3} = .1\bar{3}\end{aligned}$$

Part I

Non-Condon Effects in Dynamic Spectroscopy

This page intentionally left blank.

2

Problems with Detection of Electronic Coherences in Systems with Coordinate-Varying Transition Dipole

Apart from minor modifications, this chapter originally appeared as:

“Coordinate-varying transition dipole effects on the witness for electronic coherences”. Joseph Goodknight, Peter Rose, Jacob Krich, Alán Aspuru-Guzik, (To Be Submitted)

ABSTRACT

Frequency-integrated pump-probe experiments with ultrafast pump and probe have been previously proposed to provide a witness for electronic coherence. That is, given a coherent oscillation of interest, such an experiment can distinguish whether the coherence has electronic character or is solely a vibrational effect. That proposal assumed the Condon approximation, that the transition dipole moments are independent of the nuclear coordinates. We consider the effects of non-Condon transition dipoles on the witness protocol and show that for systems with small Huang-Rhys factor, the witness protocol will give false positives even with very small non-Condon effects. For larger Huang-Rhys factors, we show that a modified interpretation of the pump probe data continues to give a functioning witness protocol, up to a limiting strength of non-Condonicity, which we quantify.

Revised Saturday 5th August, 2017, at 13:40

2.1 INTRODUCTION

Since the discovery of long-lived oscillations in cross peaks of the two-dimensional electronic spectrum of the Fenna-Matthews-Olsen (FMO) complex¹², there has been a great deal of interest because the observed oscillations could mean that photosynthetic chlorophylls were keeping a stable superposition of electronic-excited-states for much longer than a chaotic biological environment was expected to allow^{19,31,43}. A long-lived electronic superposition (coherence) can have positive consequences for energy transfer rates and efficiencies¹², so biological protection against electronic decoherence would be a profoundly interesting result of natural selection—one that we might hope to emulate. There is further suggestion that the FMO and other photosynthetic complexes may have an optimal dephasing rate for energy transfer efficiency between perfect coherence and strong dephasing, both of which are sub-optimal^{35 8,13,43}. There is also great interest in being able to mimic these evolution-tuned efficiencies for artificial designs¹¹.

The assignment of the off-diagonal oscillations to electronic effects is, however, disputed, as vibrations can cause similar signatures. While much useful work has been done to pinpoint the unique signatures of electronic coherence and the unique signatures of vibrational coherence in a two-dimensional electronic spectroscopy experiment^{7,17,19,29,30,42,52}, such signatures remain disputed, and a simpler, unambiguous tool to distinguish electronic from vibrational coherences is valuable.

Yuen-Zhou et al. proposed such an experiment⁶⁰, which aims to give a concrete yes or no answer (called a witness in the language of quantum information⁴¹) to the question of whether a given coherent oscillation has electronic character. That work proposed using only a one dimensional pump-probe experiment in the impulsive (i.e., ultrashort pulse) limit. They showed that for impulsive pulses, there are no oscillations in the frequency-integrated pump probe signal when a system has only vibrational coherences. Oscillations in the pump-probe signal are a

witness for electronic coherence. Thus for the rest of this paper, we will refer to the proposed procedure as “The Witness”.

The effects of pulse widths on pump-probe spectroscopy had been studied previously²⁵ but the proposed witness uniquely suggested using pulse width as an independent variable in an experiment, which should be feasible given developments in two-dimensional spectroscopy using pulse-shaping devices^{1,49,50,54}.

Johnson et al.²³ showed that the witness procedure works for finite-duration pulses and proposed to use several such pulse durations to extrapolate to the impulsive limit. Generally speaking, if the oscillations in a pump probe experiment approach zero as the pulse duration approaches 0, then there is no electronic coherence. If, however, the oscillations increase as the pulse duration approaches 0, then there is an electronic coherence.

An essential assumption of Refs.^{23,60} is the Condon approximation, that transition dipoles have no variation with respect to nuclear coordinate^{9,10}. This approximation is widely used in molecular spectroscopy, and there are also well-known systems in which non-Condon effects are highly important^{20,21,33,58}. In this work, we show how well the witness protocol can tolerate a violation of the Condon approximation. We show that for systems with small electron-vibration coupling, quantified by the Huang-Rhys factor S , the witness protocol can give false-positive results even with small non-Condon effects. For larger values of S , where the vibrational coherence is more visible in optical experiments, the witness protocol is robust to larger non-Condon effects, with a small modification to the interpretation of the data. We quantify the parameter range in which the protocol is expected to work.

To test the effect of transition dipole variation on the witness experiment, we construct the simplest possible system with vibrational effects but no electronic coherence and then simulate pump probe experiments. Our system of choice has two electronic levels and a single harmonic

vibrational level. This system is the same as that studied in Refs.^{23,60}, with the addition of non-Condon effects in the transition dipole.

2.2 METHODS

We study a model system with two electronic levels, labelled $|g\rangle$ and $|e\rangle$, coupled to a single harmonic vibrational mode. The frequency of the vibration is ω_γ , ω_ϵ when the system is in the state $|g\rangle$, $|e\rangle$, respectively, giving a Hamiltonian

$$H_0 = \sum_n \hbar\omega_\gamma \left(n + \frac{1}{2} \right) |n_\gamma\rangle |g\rangle \langle g| \langle n_\gamma| \quad (2.2.1)$$

$$+ \sum_m \left(\hbar\omega_\epsilon \left(m + \frac{1}{2} \right) + \omega_e \right) |m_\epsilon\rangle |e\rangle \langle e| \langle m_\epsilon|. \quad (2.2.2)$$

Greek indices correspond to the vibrational states and the roman indices correspond to the electronic states. The ground-state vibrational wavefunctions $\langle x | n_\gamma \rangle$ are centered at vibrational coordinate $x = 0$ while the excited-state vibrational wavefunctions $\langle x | m_\epsilon \rangle$ are centered at $x = \delta x$, giving a Huang-Rhys factor of $S = \frac{\omega_\gamma \omega_\epsilon (\delta x)^2}{\hbar(\omega_\gamma + \omega_\epsilon)}$.

We consider the transition dipole to be aligned with the optical pulse polarizations, for simplicity, with a transition dipole

$$\hat{\mu}(x) = \mu(x) (|e\rangle \langle g| + |g\rangle \langle e|). \quad (2.2.3)$$

In the Condon approximation, $\mu(x) = \mu_0$ is a constant. In the spirit of keeping things as simple as possible to demonstrate the effect of transition dipole variations, we consider a linear form of $\mu(x)$:

$$\mu(x) = \mu_0 (1 + \kappa x) \quad (2.2.4)$$

To make κ comparable for different values of δx , we define also the dimensionless quantity $\lambda = \delta x \kappa$. The quantity λ has the useful property that above $\lambda = 1$, the variation of μ as the system moves from the ground- to excited-state equilibrium position becomes larger than the mean value μ_0 . As a reference, in C-phycoerythrin, κ has been calculated to be approximately 0.3 and λ to be approximately 0.1⁵⁸.

We simulate Pump Probe spectroscopy using ideal Gaussian laser pulses, which differ only in their pulse durations and arrival times. This means that both of our pulses (labeled pu for pump and pr for probe) will have the form:

$$E_{\text{pu}} = \frac{E_0}{\sqrt{2\pi\sigma^2}} e^{-\frac{t^2}{2\sigma^2}} [e^{-i\omega_c t} + e^{i\omega_c t}] \quad (2.2.5)$$

$$E_{\text{pr}} = \frac{E_0}{\sqrt{2\pi\sigma^2}} e^{-\frac{(t-T)^2}{2\sigma^2}} [e^{-i\omega_c(t-T)} + e^{i\omega_c(t-T)}] \quad (2.2.6)$$

We normalize the pulses as in Ref.²³ to keep the integral of the absolute value of the electric field constant across with varying pulse widths. The pulse's central frequency ω_c is always tuned to the strongest absorption transition in the simulated system and the pulse width σ is our main experimental independent variable.

In the rotating wave approximation, it is helpful to further split the laser pulses into positive frequency excitation pulses:

$$E_{\text{pu}+}(t) = \frac{E_0}{\sqrt{2\pi\sigma^2}} e^{-\frac{t^2}{2\sigma^2}} e^{-i\omega_c t} \quad (2.2.7)$$

$$E_{\text{pr}+}(t) = \frac{E_0}{\sqrt{2\pi\sigma^2}} e^{-\frac{(t-T)^2}{2\sigma^2}} e^{-i\omega_c(t-T)} \quad (2.2.8)$$

and negative frequency relaxation pulses:

$$E_{\text{pu-}}(t) = \frac{E_0}{\sqrt{2\pi\sigma^2}} e^{-\frac{t^2}{2\sigma^2}} e^{i\omega_c t} \quad (2.2.9)$$

$$E_{\text{pr-}}(t) = \frac{E_0}{\sqrt{2\pi\sigma^2}} e^{-\frac{(t-T)^2}{2\sigma^2}} e^{i\omega_c(t-T)} \quad (2.2.10)$$

Assuming that the system begins in state $|\psi_0\rangle$, the first order perturbative wavepacket after one interaction with pulse Q is

$$|\psi_Q(t)\rangle = -\frac{i}{\hbar} \int_{-\infty}^t U(t, \tau) E_Q(\tau) \hat{\mu}(x) |\psi_0(\tau)\rangle d\tau. \quad (2.2.11)$$

A subsequent interaction with pulse P , which could be the same pulse, gives the second-order perturbative wavepacket

$$|\psi_{Q,P}(t)\rangle = -\frac{i}{\hbar} \int_{-\infty}^t U(t, \tau) E_P(\tau) \hat{\mu}(x) |\psi_Q(\tau)\rangle d\tau. \quad (2.2.12)$$

Assuming an ensemble of identical systems distributed over a volume larger than the pulse wavelength, contributions to the pump-probe signal require phase matching. In the rotating wave approximation, these perturbative wavepackets allow construction of the pump probe signal

$S_{PP}(T)$ as

$$E_{GSB1}(t, T) = i \langle \psi_0(t) | \hat{\mu}(x) | \psi_{\text{pu}+, \text{pu}-, \text{pr}+}(t, T) \rangle$$

$$E_{ESA}(t, T) = i \langle \psi_{\text{pu}+}(t) | \hat{\mu}(x) | \psi_{\text{pu}+, \text{pr}+}(t, T) \rangle$$

$$E_{GSB2}(t, T) = i \langle \psi_{\text{pu}+, \text{pr}+}(t, T) | \hat{\mu}(x) | \psi_{\text{pu}+}(t) \rangle$$

$$E_{SE}(t, T) = i \langle \psi_{\text{pu}+, \text{pu}+}(t) | \hat{\mu}(x) | \psi_{\text{pr}+}(t, T) \rangle$$

$$S_i(T) = 2\text{Re} \left[\int E_{\text{pr}+}^*(t) E_i(t, T) dt \right]$$

$$S_{PP}(T) = S_{GSB1}(T) + S_{GSB2}(T) + S_{ESA}(T) + S_{SE}(T)$$

$$\tilde{S}(\Omega) = \int S_{PP}(T) e^{i\Omega T} dT,$$

$$\Gamma = \int |S_{PP}(T) - \bar{S}_{PP}|^2 dT$$

where t is the laboratory time, T is the time delay between the pump and probe pulses. The main object investigated in this work is $\tilde{S}(\Omega)$, the Fourier transform of $S_{PP}(T)$. When Ω is chosen equal to the vibrational frequency, we explore the changing amplitude of $\tilde{S}(\Omega)$ with pulse duration σ for a range of systems with varying Huang-Rhys factors S and non-Condonicities κ .

We calculate these quantities using time-domain wavepacket propagation, as described previously^{37,38,51,61}. In this work, we consider only systems with a single electronic excited state, so they have no excited-state electronic coherence. All oscillatory effects in the pump-probe signal are vibrational, so we want to show when the modified witness successfully characterizes these oscillations as vibrational in origin. In all simulations, we choose the central frequency of the optical pulses to be resonant with the strongest transition in the calculated absorption spectrum. We begin with initial states in the lowest-energy vibrational state of the ground state manifold and do not consider thermal or orientational averaging effects, which we do not believe are important for the present study. We do not consider dephasing or inhomogeneous broadening processes.

If we consider the impulsive limit, then we can show that the Pump-Probe signals simplify to:

$$S_{GSB2} = E_0^4 \sum_k \cos [\omega_\gamma (k - \eta) T] (\langle \eta_\gamma | \mu^2(x) | k_\gamma \rangle)^2 \quad (2.2.13)$$

$$S_{SE} = E_0^4 \sum_{j,l} \cos [\omega_\epsilon (j - l) T] \quad (2.2.14)$$

$$\times \langle \eta_\gamma | \mu(x) | j_\epsilon \rangle \langle j_\epsilon | \mu^2(x) | l_\epsilon \rangle \langle l_\epsilon | \mu(x) | \eta_\gamma \rangle \quad (2.2.15)$$

$$S_{ESA} = 0 \quad (2.2.16)$$

$$S_{GSB1} = E_0^4 \sum_k \cos [\omega_\gamma (k - \eta) T] (\langle \eta_\gamma | \mu^2(x) | k_\gamma \rangle)^2 \quad (2.2.17)$$

which because the vibrational states are eigenfunctions, this will be zero unless $\mu(x)$ is non-constant. So we do expect oscillations at the impulsive limit for non-Condon systems, but we will address the question of how they approach the impulsive limit numerically.

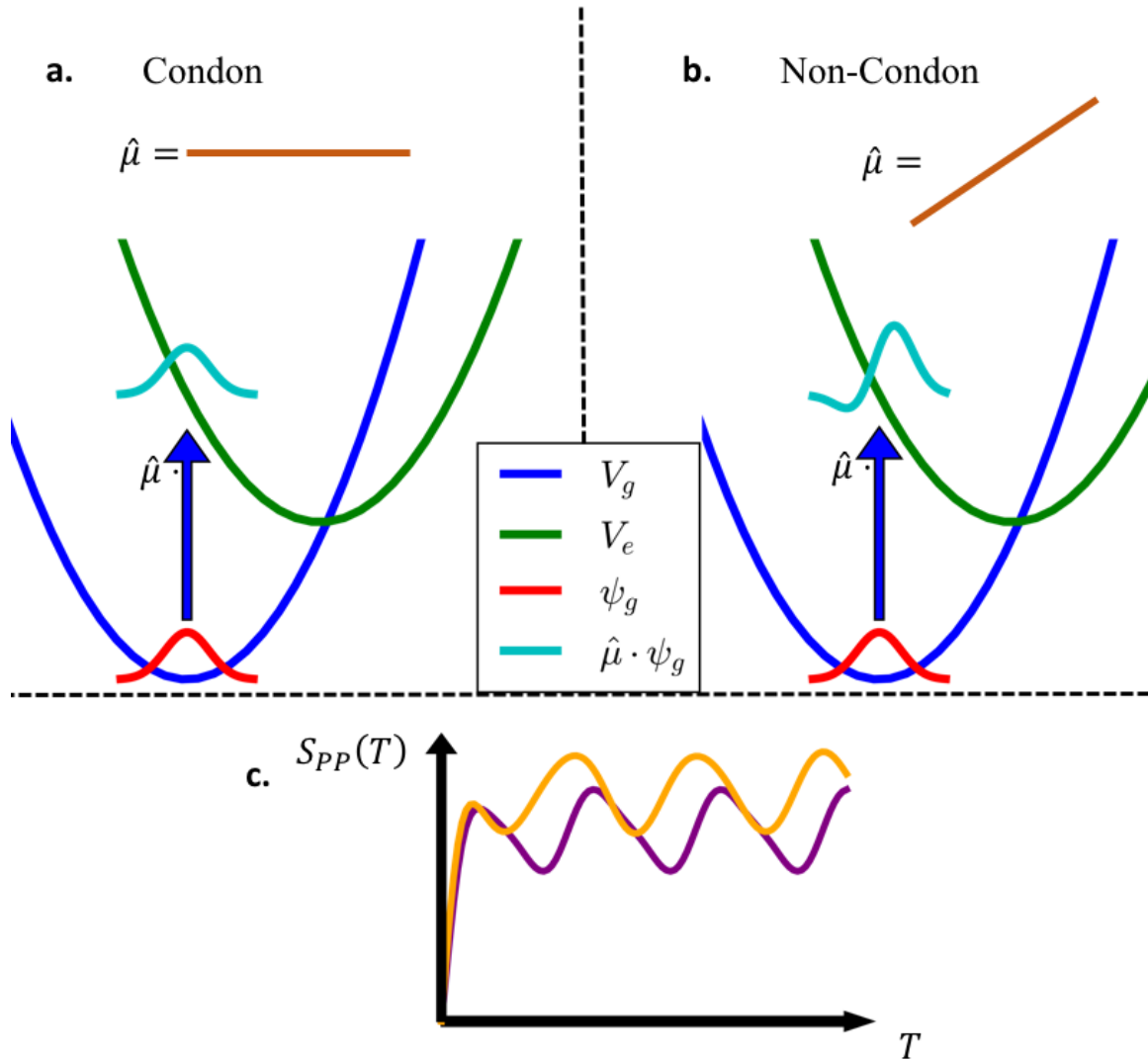


Figure 2.1: In the case where there is no transition dipole variation, when the transition dipole operator is applied (with an impulsive pulse), the ground state wavepacket's shape is perfectly replicated as seen in a. If, however, we introduce a linear variation, the wavepacket's shape is distorted as we see in b. This distortion is, in itself, a change in the vibrational coherence which manifests as a demonstrable difference in the pump probe signal as seen in c and could. What is not clear is how the the signal changes as the pulse width changes for different transition dipole slopes, so we set out to investigate and see if this change keeps the protocol for electronic coherence detection proposed in ^{23,60} from working properly.

2.3 RESULTS AND DISCUSSION

We can consider a variety of model systems, characterized by their vibrational frequencies ω_γ , ω_ϵ , Huang-Rhys factor S , and non-Condonicity λ . For the commonly considered case with $\omega_\gamma \approx \omega_\epsilon$, we show that the witness protocol breaks down for the smallest values of S but is robust for a larger range of λ when S is larger. We begin by considering the smallest values of S , where the witness is broken, and then consider larger values of S and propose a modified protocol that remains robust even in the presence of some non-Condonicity. For strongly non-Condon transition dipoles, the witness does not work at any S . For specificity, we consider $\omega_\gamma = \omega_\epsilon = 640\text{cm}^{-1}$, but all timescales can be easily scaled for any other vibrational frequency of interest.

The worst case scenario for the witness protocol occurs when $S = 0$. In that limit, in the Condon-approximation with $\omega_\gamma = \omega_\epsilon$, the only allowed optical transition is the 0-0 transition, from the lowest vibrational state of the ground state to the lowest vibrational state of the excited state. There is no coherence of any variety, so there is no oscillation in the pump-probe signal, and $\tilde{S}_{PP}(\omega_\epsilon) = 0$ always. Even in the Condon approximation, this case is difficult for the witness protocol, as the signal is independent of pulse duration σ , rather than monotonically decreasing as σ is decreased. This case does, however, illustrate the effects of a non-Condon transition dipole.

In the non-Condon case, the 0-0 and 0-1 transitions are both allowed, producing a vibrational coherence in the singly-excited manifold and a nonzero $\tilde{S}_{PP}(\omega_\epsilon)$. This oscillatory pump-probe signal becomes stronger as σ becomes smaller, which looks qualitatively similar to the case of a Condon electronic coherence, as shown for several values of κ in Fig. 2.2. That is, this witness technique cannot distinguish an electronic coherence from a non-Condon vibrational-only system.

We now consider $S = 0.005$, which is close to photosynthetic Huang-Rhys factors⁴⁴, with results in Fig. 2.3. For this small S , the witness protocol essentially does not work for any $\lambda > 10^{-3}$.

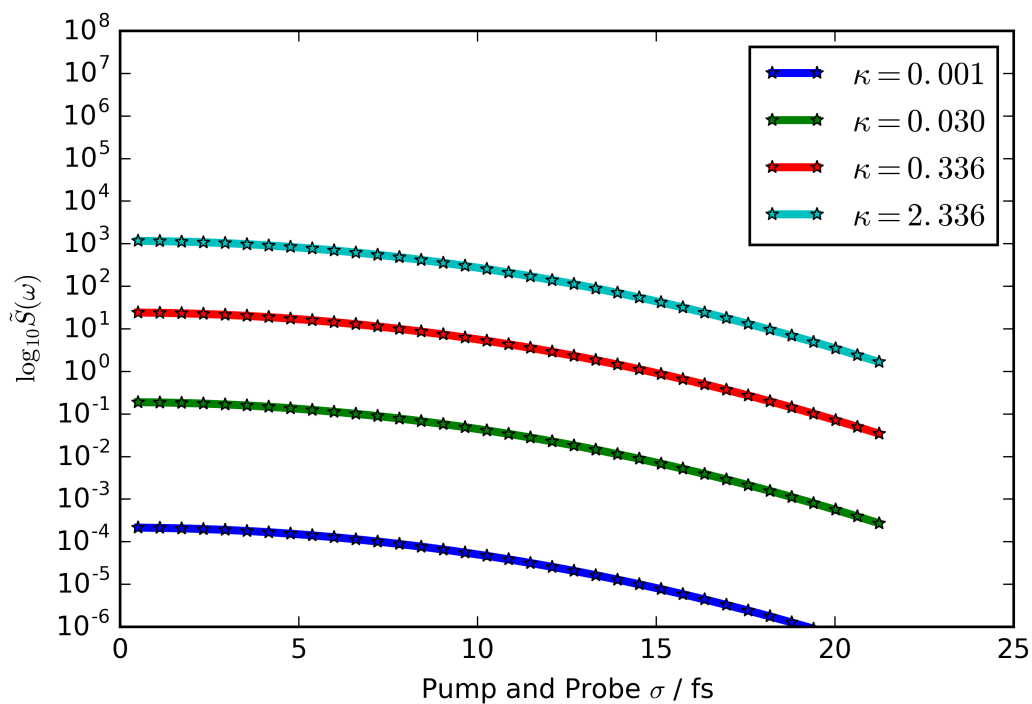


Figure 2.2: Pump-probe oscillations at the vibrational frequency, $\tilde{S}_{PP}(\omega)$, for a system with $S = 0$ and $\omega_\gamma = \omega_e = \omega = 640 \text{ cm}^{-1}$, for various values of κ . The signal is log scaled due to the signal's fourth-order dependence on $\mu(x)$; small differences in κ make very large differences in signal. In all of these systems, an experimenter using the proposed protocol would conclude that an electronic coherence exists in the system when there's not even a vibrational coherence in the ground state, absent a non-constant transition dipole.

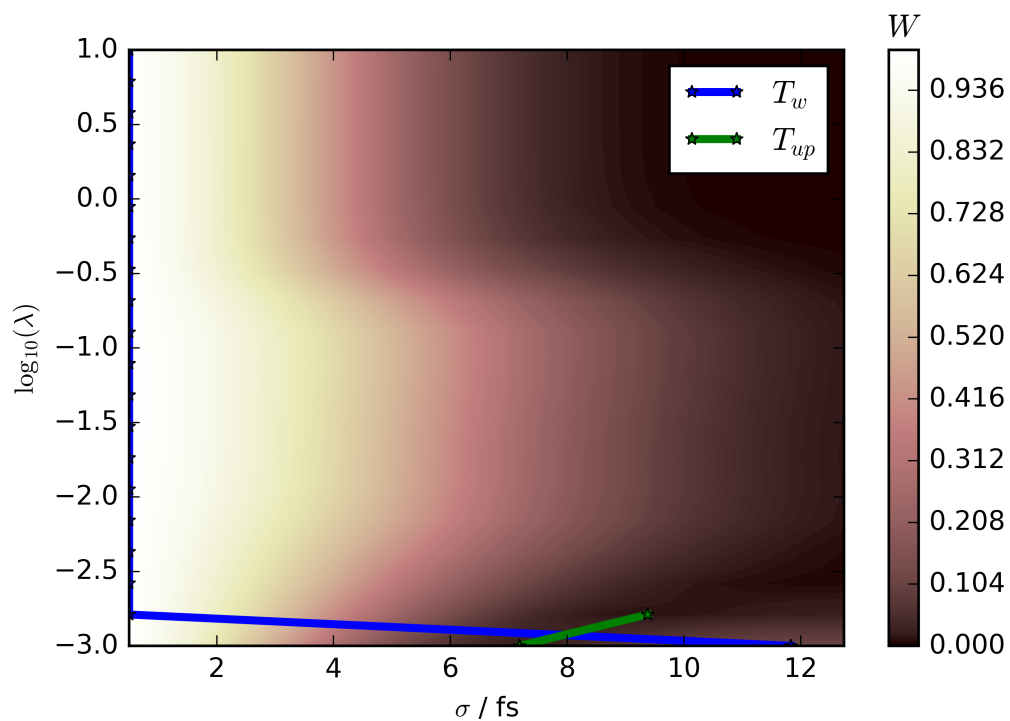


Figure 2.3: Γ as a function of λ and the pulse width σ in a system where $S = 0.005$, $\omega_e = .9\omega_g$, and $\omega_g = 640\text{cm}^{-1}$. T_w is the same as defined in reference²³: the peak of the signal before it goes down again. Some traces in λ have local minima as well when the signal goes up and we plot those as σ_{up} . In the case where the signal just goes up as the pulse width goes down, then T_w is set as $\sigma = 0$.

We now consider $S = 0.2$, with results in Fig. 2.5. For this larger value of S , for $\lambda < 0.1$, the witness signature is apparent in the data, with a declining pump-probe signal as σ is reduced, until the pulse duration σ_{up} is reached. For $\sigma < \sigma_{up}$, the signal again increases, due to the non-Condonicity. This upturn occurs at short pulse durations, after the usual peak structure of a negative witness is well established, coming from large σ to T_w down to σ_{up} .

We propose a modified witness protocol that declares a negative witness (i.e., vibrational-only coherence) in experiments that observe a peak at T_w and a short-duration upturn at σ_{up} . We consider such a structure to be observed if the signal $\tilde{S}_{PP}(\omega)$ at T_w is more than twice the value of the signal at σ_{up} , and we call this ratio w . In such a case, the experiment has determined both the vibrational character of the relevant coherence as well as the presence of a non-Condon contribution to the transition dipole. Further methods for detecting and measuring non-Condon transition dipoles can be found in Ref. ²⁷.

With this modified protocol in mind, we construct figure 2.4 where we show the ratio w for 5 values of S . With our criteria that $w \leq 0.5$ there are quite a few regions where the proposed protocol will still work, but even more where it will give false positives.

Reference²³ proposed using the entire frequency-integrated pump-probe signal $\Gamma = \int |S_{PP}(T) - \bar{S}_{PP}|^2 dT$, where \bar{S}_{PP} is the average value of the pump-probe signal and the integral is taken only for $T > 3\sigma_{max}$, to avoid pulse-overlap effects, where σ_{max} is the largest pulse duration studied in the experiment. In this work we have considered the frequency-resolved pump-probe signal $\tilde{S}_{PP}(\omega)$, but the analysis for Γ is similar and gives the same regions of (S, λ) where the modified witness protocol functions.

To investigate the dips in signal seen in figures 2.3 and , we introduce figure 2.8, where we look at $S = .2$ and $\kappa = .037$. When the nonzero κ is turned off and set to zero, we get a decreasing oscillatory signal approaching zero as the laser pulse width approaches zero just as predicted by ²³.

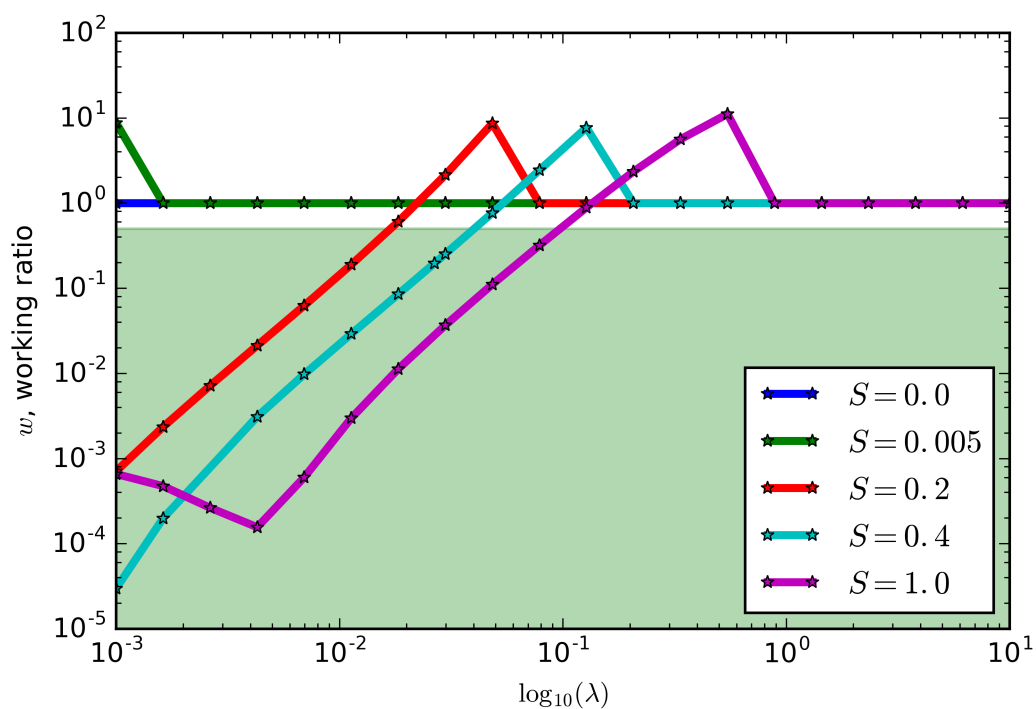


Figure 2.4: The ratio w of the oscillation amplitude at the minimum pulse width to the oscillation amplitude at the local maxima (or witness time T_w) for various values of S . The region shaded in green is where our modified protocol does not produce a false-positive.

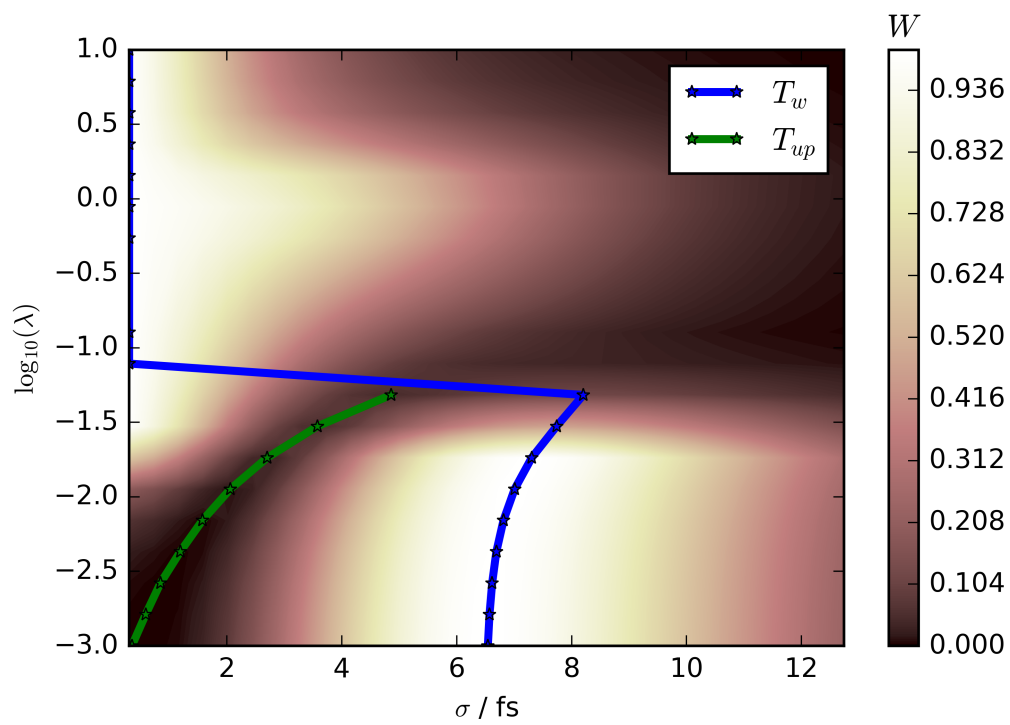


Figure 2.5: Γ as a function of λ and the pulse width σ in a system where $S=0.2$, $\omega_e = .9\omega_g$. and $\omega_g = 640\text{cm}^{-1}$.

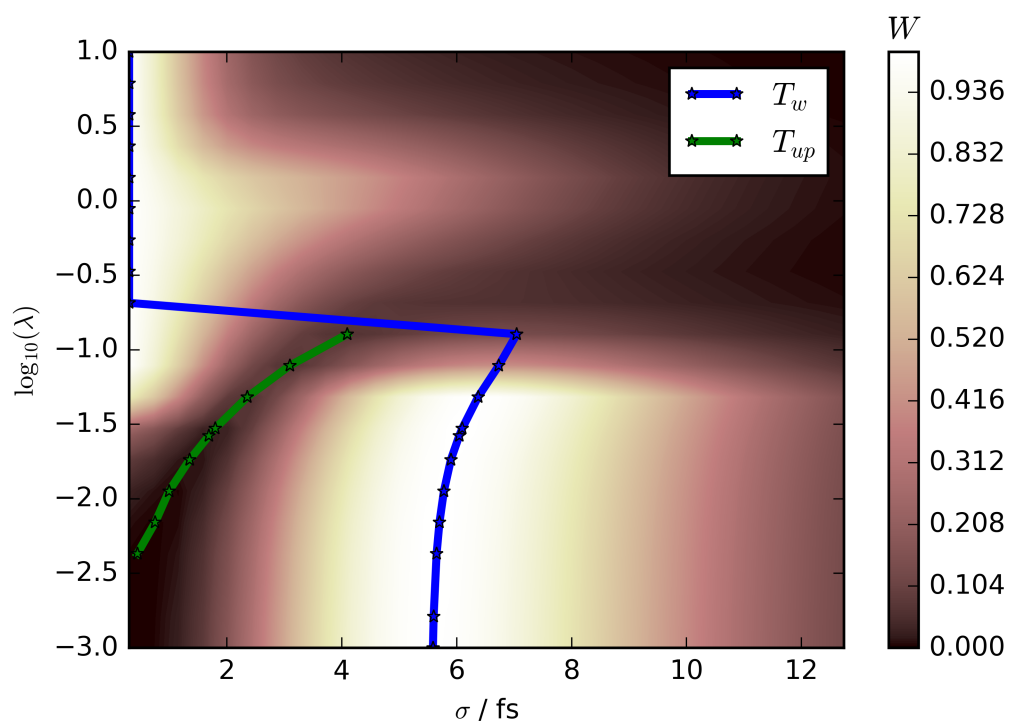


Figure 2.6: Γ as a function of λ and the pulse width σ in a system where $S = 0.4$. $\omega_e = .9\omega_g$. and $\omega_g = 640\text{cm}^{-1}$.

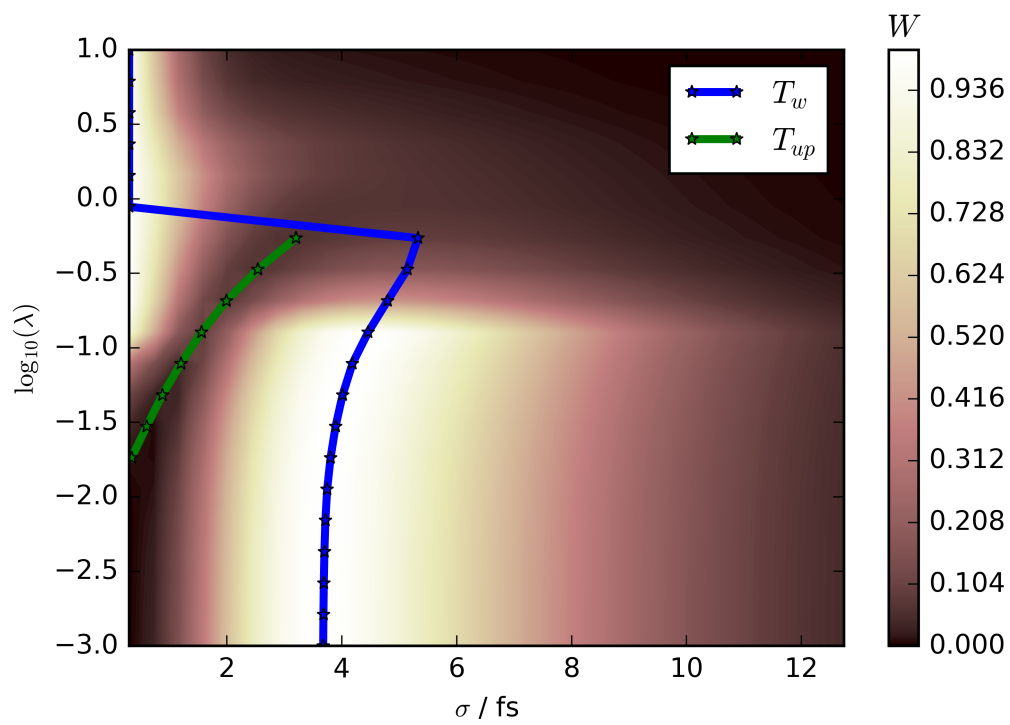


Figure 2.7: dT as a function of λ and the pulse width σ in a system where $S = 1.0$, $\omega_e = .9\omega_g$, and $\omega_g = 640\text{cm}^{-1}$.

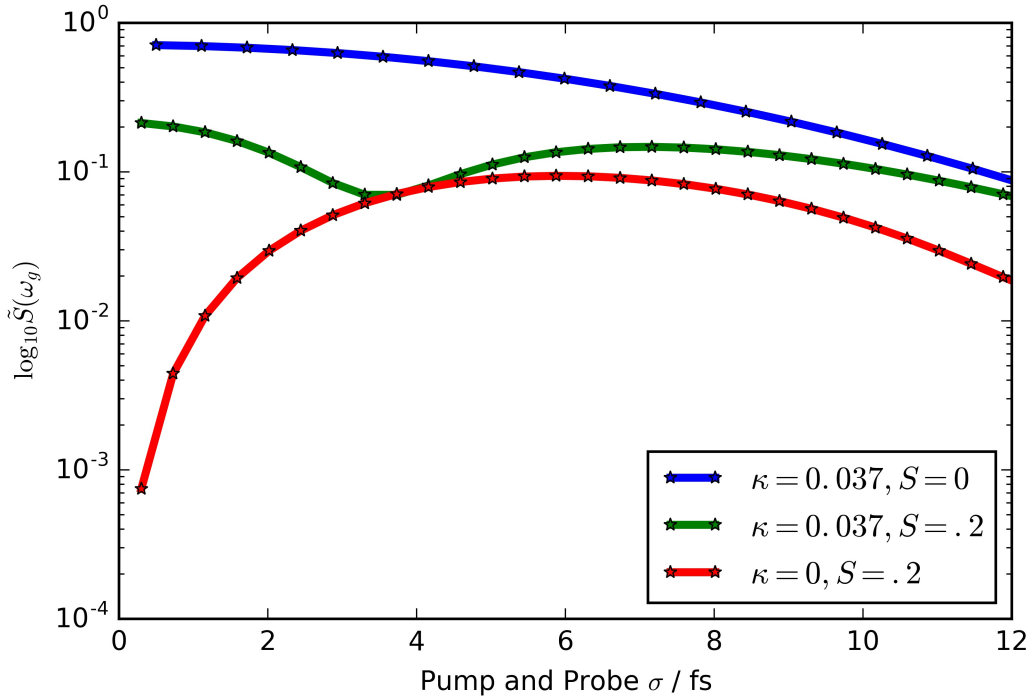


Figure 2.8: $\tilde{S}_{pp}(\omega_\gamma)$ Here we have plotted the ground state oscillations for 3 systems: $\kappa = .037, S = 0$; $\kappa = .037, S = 0.2$; and $\kappa = 0.0, S = 0.2$. This shows roughly that the effects of a non-Condon monomer without vibrational displacement add together with the effects of a Condon monomer to get the result for a non-Condon monomer with a vibrational displacement

If, however, we turn on the nonzero κ , we see the while there is a dip at a certain point in the signal, it increases as the pulse width approaches zero. Indeed, even if we set $S = 0.0$ but keep the same value of κ , and thus have a system that should have almost no oscillations, there is still an increasing oscillation signal. The shape of these three curves suggests that there is an interference interplay between the tendency of a vibrational coherence to go down as the pulse width approaches zero and the tendency of an oscillation induced by a linear transition dipole variation to increase as the pulse width gets toward zero.

2.4 CONCLUSION

The proposed witness for electronic coherences^{23,60} relied on the Condon approximation. We have found that in vibrational systems with very small Huang-Rhys factors S , small non-Condon effects can give false-positive effects, where a system with no electronic coherence is incorrectly determined to have an electronic coherence. For larger S , the witness protocol can be successfully used for larger values of λ . It is possible that modified experimental procedures could increase the domain of (S, κ) in which the witness protocol will function. In order to apply the witness protocol, one must be able to estimate or measure the non-Condon effects to be sufficiently small. Methods to measure non-Condonicity are proposed in Ref.²⁷.

2.5 ACKNOWLEDGMENTS

We acknowledge support from the Center for Excitonics, an Energy Frontier Research Center funded by the U.S. Department of Energy under award DE-SC0001088 (Solar energy conversion process) and the Natural Sciences and Engineering Research Council of Canada. The authors also wish to thank Doran Bennet for his useful commentary on this manuscript.

3

Detecting Non-Condon Transition Dipole Moments with Absorption Spectroscopy

Apart from minor modifications, this chapter originally appeared as:

“Detecting Non-Condon Transition Dipole Moments with Absorption Spectroscopy”. Joseph Goodknight, Jacob Krich, Alán Aspuru-Guzik, (In Preparation)

ABSTRACT

The Condon approximation assumes that transition dipole moments do not vary with nuclear coordinates. It is often employed in physical chemistry and spectroscopy settings without fully verifying if the approximation is justified. Recent scholarship shows both that such variation non-trivially affects spectroscopic observables and that many systems do indeed exhibit significant variation in their electronic transition dipole moments. The most striking recent example is the work of Heller and co-workers²⁰ where non-varying transition dipole moments were essential to understand the spectra of polyacetylene and graphene. Thus a better understanding of how such phenomenon affects even basic spectroscopic variables would be useful, as would a tool to measure the extent to which a system has a variation in its transition dipole moment. We discuss how polynomial variation with respect to the nuclear coordinate in the electronic transition dipole moment affects the interpretation of the electronic absorption spectrum and use the result to investigate the transition dipole structure of tetracene.

3.1 INTRODUCTION

In 1928, Edward Condon introduced the useful approximation that the transition dipole moment does not depend on variations of nuclear coordinates ⁹. Deviations from the approximation are crucial for the explanation of Raman Spectroscopy ³⁹.

The Condon approximation is often employed without verifying what are the effects of lifting it. Recently, Heller and co-workers have shown that the variation in transition dipole moment is crucial to explain the Raman spectrum of graphene ²⁰. Furthermore, recent studies suggest a highly noticeable transition dipole moment in photosynthetic pigments ⁵⁸. Van Voorhis and co-workers have recently stressed the role of non-Condon effects in electron transfer ³³. Finally, our own work indicates that non-Condon effects may make the application of witnesses of electronic spectroscopy ^{23,60} harder than originally thought²⁸.

In this work, we examine the role of non-Condon effects in one of the simplest forms of spectroscopy, linear absorption spectroscopy.

3.2 SYSTEM SETUP

For the purposes of this work, we will employ a simple model that consists of a one-mode vibrational monomer with a ground electronic state $|g\rangle$ and an excited electronic state $|e\rangle$ and assume the vibrational frequency is the same in both states. In principle, however, this method is extensible to more vibrational degrees of freedom. Using this assumption, we can write the Hamiltonian for the system as,

$$H_0 = \sum_n \hbar\omega \left(n + \frac{1}{2} \right) |n_\gamma\rangle |g\rangle \langle g| \langle n_\gamma| \quad (3.2.1)$$

$$+ \sum_m \left(\hbar\omega \left(m + \frac{1}{2} \right) + \omega_e \right) |m_\varepsilon\rangle |e\rangle \langle e| \langle m_\varepsilon| \quad (3.2.2)$$

Here, the Greek indices corresponding to the vibrational states and the roman indices corresponding to the electronic states. The ground and excited electronic states are represented by $|g\rangle$ and $|e\rangle$, and the set of $|i_\gamma\rangle$ is the set of vibrational eigenstates in the ground electronic state manifold, and $|i_\epsilon\rangle$ is the set of vibrational eigenstates in the electronic excited state. The vibrational quanta is ω and ω_e is the electronic energy gap. The electronic transition dipole moment $\hat{\mu}$ varies spatially as a function of the x coordinate in an object $\mu(x)$,

$$\hat{\mu} = \mu(x) (|e\rangle \langle g| + |g\rangle \langle e|) \quad (3.2.3)$$

For the purposes of this study, we construct a generic polynomial transition dipole moment, which one can be expressed as ladder operators for easier calculation,

$$\mu(x) = \mu_0 \sum_{i=0} \kappa_i x^i \quad (3.2.4)$$

$$= \mu_0 \sum_{i=0} c_i (\hat{a} + \hat{a}^\dagger)^i \quad (3.2.5)$$

or as a vibrational matrix element,

$$\mu_{a,b} = \langle a_\gamma | \mu(x) | b_\gamma \rangle \quad (3.2.6)$$

Going forward, we will use the a notation of $(\{i\})$ to indicate the polynomial orders of x we included. In a simple linear variation setting would be,

$$\mu_{a,b}^{(1)} = \mu_0 \left[\delta_{a,b} + c \left(\sqrt{b-1} \delta_{a,b-1} + \sqrt{b} \delta_{a,b+1} \right) \right] \quad (3.2.7)$$

but for a cubic variation would be,

$$\mu_{a,b}^{(3)} = \mu_0 \left(\delta_{a,b} + c_3 \left(2\delta_{a+1,b} + \sqrt{6}\delta_{a+3,\lambda} \right) \right)$$

and so on for higher orders.

3.3 EFFECTS ON LINEAR ABSORPTION SPECTROSCOPY

The change in transition dipole moment from the Condon approximation will not affect the frequency of the transitions in our model, so instead we look only at peak heights: specifically the absorptivity normalized to the frequency squared

$$\frac{\varepsilon(\omega)}{\omega^2} = K(\omega) = \sum_{\eta,i} h_{\eta,i} f_L(\omega, \sigma, \Delta\omega_{\eta,i}) \quad (3.3.1)$$

where f_L is a line-shape function which integrates to unity, sigma σ is the width parameter(s) for the line-shape. Finally and most importantly, $h_{\eta,i}$ and $\Delta\omega_{\eta,i}$ are the strength and frequency, respectively, of the transition from the ground vibrational state η to the excited vibrational state i .

Normally a researcher can compare the k th and $k + 1$ th transition strengths to ascertain the Huang Rhys Parameter S :

$$\frac{h_{\eta,k+1}}{h_{\eta,k}} = \frac{\sum_{\lambda,v} \mu_{\eta,\lambda} \mu_{\eta,v} O_{\lambda}^{k+1} O_v^{k+1}}{\sum_{l,n} \mu_{\eta,l} \mu_{\eta,n} O_l^k O_n^k} = H(\eta, k) \quad (3.3.2)$$

Where O_{λ}^k is the Franck-Condon overlap factor between a electronic ground vibrational energy state λ and an electric excited vibrational energy state k . If one starts out in the 0th state and assumes constant transition dipole moment(0th order as indicated in the subscript to H), the

relation is quite simple:

$$H_{(0)}(0, k) = \frac{S}{k+1} \quad (3.3.3)$$

But going one step further to a linear-only transition dipole variation, one obtains the relation between subsequent peak heights of

$$H_{(1)}(0, k) = \frac{S}{k+1} \frac{|1 + c\sqrt{S}(1 - \frac{k+1}{S})|^2}{|1 + c\sqrt{S}(1 - \frac{k}{S})|^2} \quad (3.3.4)$$

Of crucial relevance to our argument is that if one only employs the ratio of the $0 \rightarrow 1$ peak to the $0 \rightarrow 0$ peak under the assumption of linear variation of the transition dipole moment, one is not extracting a pristine Huang-Rhys parameter, but rather an effective Huang-Rhys parameter S_{eff} ,

$$S_{\text{eff}} = S \frac{|1 + c\sqrt{S}(1 - \frac{1}{S})|^2}{|1 + c\sqrt{S}|^2} \quad (3.3.5)$$

In Figure 3.1, we plot the potential error in the estimation of the Huang-Rhys parameter as a function of the variation of the linear dependence of the transition dipole moment.

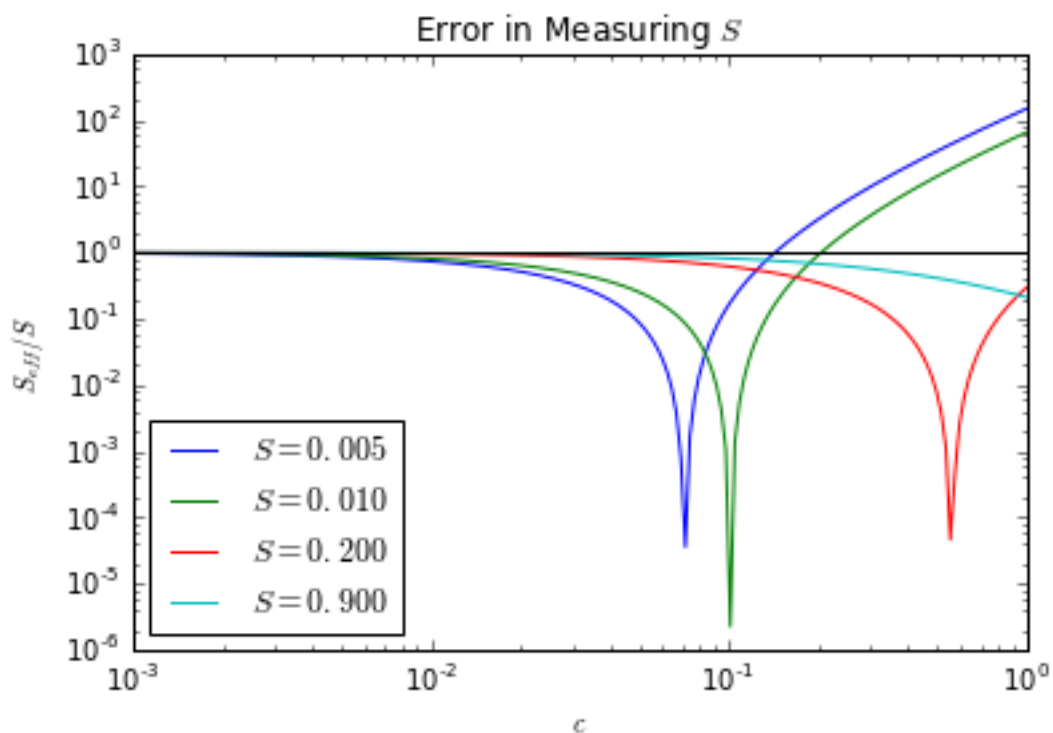


Figure 3.1: The relative measurement error as the ratio of the effective Huang-Rhys parameter over the actual Huang-Rhys parameter (S_{eff}/S) as a function of S for the ratio of the $0 \rightarrow 1$ peak to the $0 \rightarrow 0$ peak, for various values of S and an entirely real linear-variation in the transition dipole moment: c . If the Huang-Rhys parameter is small, even small linear variations of the transition dipole moment with coordinate can induce large errors in its estimation.

3.4 CORRECTIONS TO TETRACENE

The use of the peak heights in absorption spectra to determine the coordinate dependence of transition dipole moments has been employed for more than 60 years. In 1954, Fraser described how to map out the precise coordinate dependence of transition dipoles in high-resolution electronic-vibrational absorption spectra of diatomics¹⁴. But in solution, one often has far fewer peaks so a full map is not possible. Here we describe a method to find an approximate low-order polynomial transition dipole variation for just one mode in a molecule in solution.

To demonstrate this, we take the absorption spectrum of tetracene in dichloromethane⁴⁰ and in toluene⁴. We chose tetracene because of its important role in organic electronics and recently in singlet-fission studies⁶ and because it has a sufficiently large Huang-Rhys parameter S that results in a spectrum with multiple line-shapes.

We fit Equation 3.3.1 to the addition of 5 Voigt line-shape for the Toluene spectrum and 6 Voigt line-shapes for the DCM spectrum. The Voigt profile allows peaks to have varying amount of Gaussian and Lorentzian line-shape character. The results of this fit are shown in Figures 3.2 and 3.3. We then employed the centers of the line-shapes and fit a Morse oscillator model, the results of which are summarized in Table 3.1 which allowed us to conclude that the harmonic approximation is sufficient for an accurate description of this system.

Then to fit to Equation 3.3.2, we employed a trust region reflective algorithm least-squares fitting procedure as implemented in the Scipy package by fitting to the^{26,55}. Because there are

| Parameter | DCM | Toluene |
|------------------------------------|----------|----------|
| V_0 / cm^{-1} | 20421.87 | 20420.06 |
| $\omega_e / \text{cm}^{-1}$ | 1404.74 | 1388.87 |
| $\chi_e \omega_e / \text{cm}^{-1}$ | -.9501 | -1.5 |
| r^2 | 0.9999 | 1.0000 |

Table 3.1: Fit of the calculated peak heights to a Morse potential model. Because of the small value of $\chi_e \omega_e$ relative to ω_e , we conclude that the harmonic approximation is reasonable for this system.

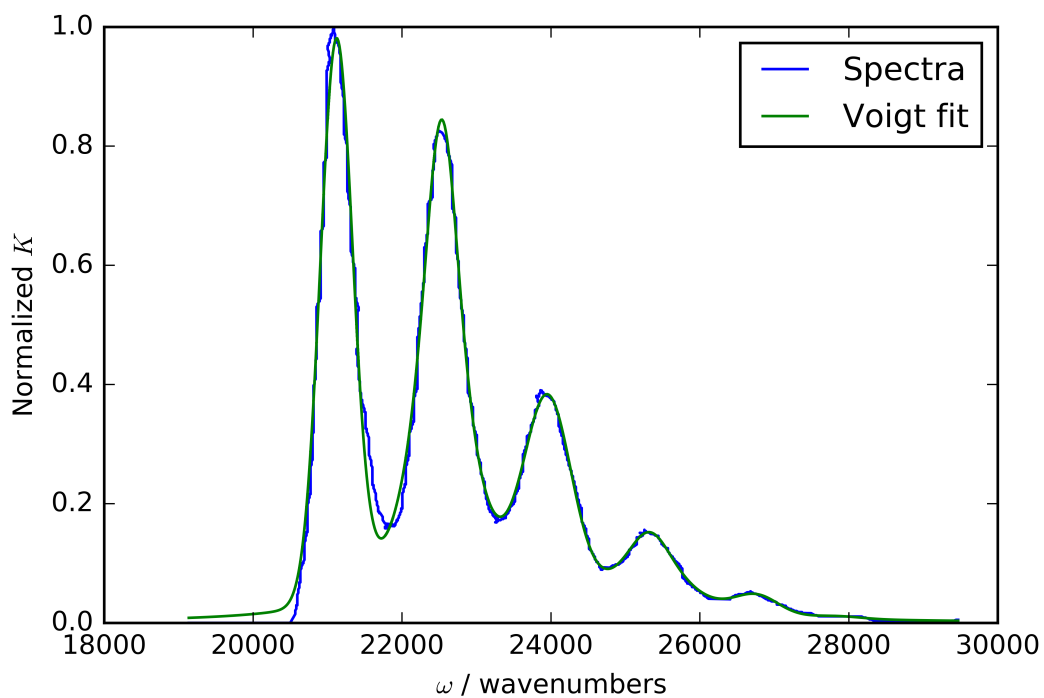


Figure 3.2: The fit for Voigt line-shapes to the spectra of tetracene in dichloromethane from Ref. ⁴⁰

| Parameter | DCM | Toluene |
|-----------------------|------------|----------------|
| S_{Condon} | 1.52 | 1.185 |
| r_{Condon}^2 | .743 | .829 |
| $S_{(2)}$ | 1.263 | 1.201 |
| c_2 | -0.063 | 0.006 |
| $r_{(2,)}^2$ | 0.833 | 0.830 |
| $S_{(3)}$ | 1.245 | 1.064 |
| c_3 | -0.021 | -0.011 |
| $r_{(3,)}^2$ | 0.806 | 0.838 |
| $S_{(9)}$ | 1.082 | 0.994 |
| c_9 | -3.31e-5 | -1.82e-5 |
| $r_{(9,)}^2$ | 0.985 | 0.965 |
| $S_{(9,7)}$ | 1.202 | 1.110 |
| c_9 | -5.05e-5 | -3.35e-5 |
| c_7 | 3.72e-4 | 3.31e-4 |
| $r_{(9,7)}^2$ | 0.990 | 0.976 |

Table 3.2: Fit of certain parameters

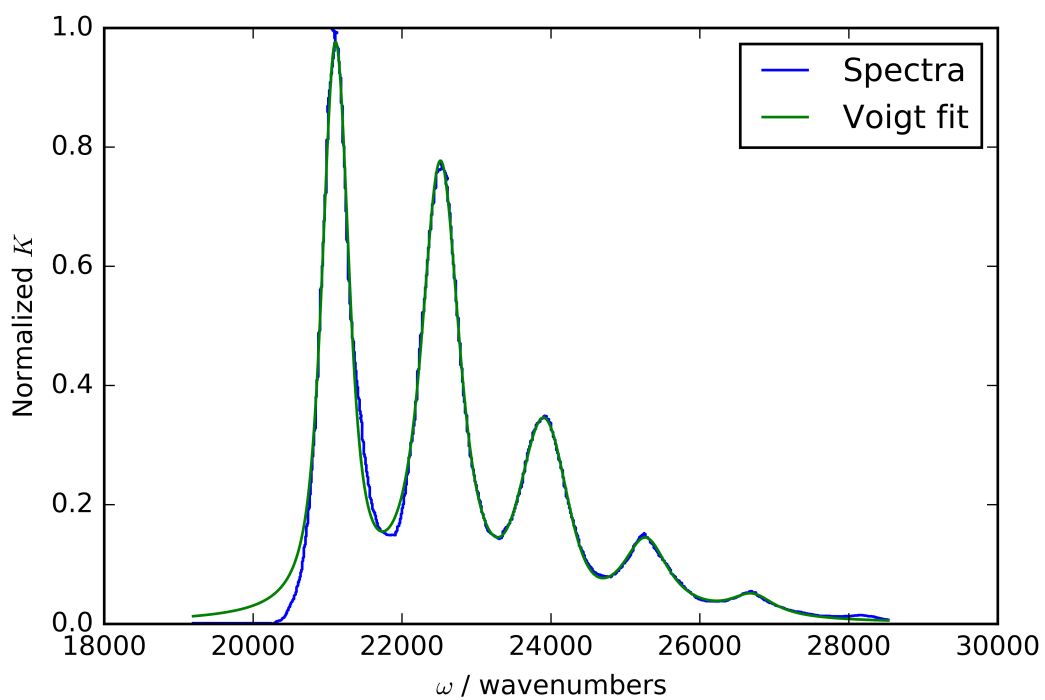


Figure 3.3: The fit for Voigt line-shapes to the spectra of tetracene in toluene from Ref.⁴

multiple solutions for c and θ for all orders, we include a small regularization term in the fitting procedure to keep the solutions close to the Condon value of S .

Our method was unable to find a better fit than the Condon solution for for the (1) model, but fitting the second order, $H_{(2)}(k, 0)$, improved the fit slightly. The fit for an order 2 correction, however, is barely better than the Condon fit as evidenced in Figures 3.5 and 3.4.

We do, however, expect odd-order-polynomials to be the most physically relevant because of the broken symmetry when the molecule gets excited; we expect the molecule to preferentially absorb to the excited state when the nuclear configuration is closer to the shape of the excited state. We tried many models and found that the best fits were around order 9, suggesting that in addition to having small coefficients, the non-Condon corrections in this system are high-order polynomials. In Figures 3.7 and 3.6, we see that the 9th order really matches the experimental data very well.

Then, because we have enough data points to fit more than just two parameters, we go ahead and fit $H_{(9,7)}(k, 0)$ and find that this model fits the data even better. Figures 3.7 and 3.6 show that the fit, while only marginally better than order 9, is much better. Table 3.2 summarizes the parameters found for all the investigated orders.

We can also look at the functional form of $\mu(x)$. The result of this for (9,7) is shown in Figure 3.10. Despite the slightly different values found for c_9 , c_7 and S for the Toluene and DCM for the (9,7) correction, the derived transition dipole moments seem roughly similar, at least up until $x = 2x_0$, given that we are only able to discern information about the transition dipole moment where it overlaps with $|0_\gamma\rangle$, we do expect more uncertainty about the transition dipole as x gets large compared to x_0 .

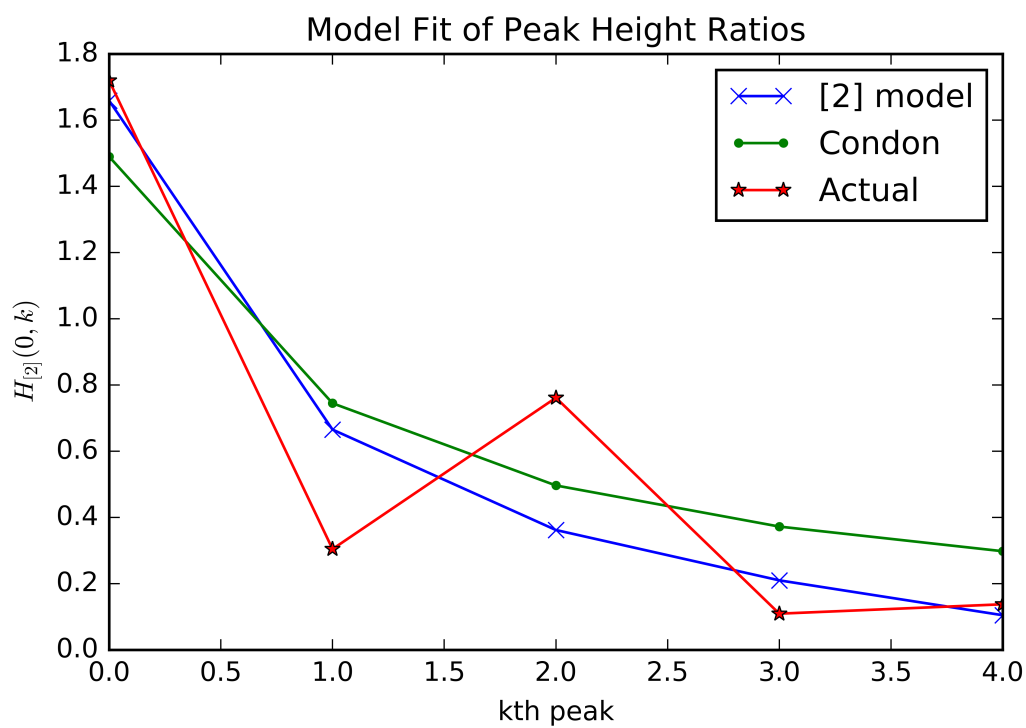


Figure 3.4: The Voigt-derived values of $H(0, k)$ from tetracene in DCM, fit to the model for $H_{(2)}(0, k)$ and a purely Condon model. Note that the Condon model does not fit the trend very well at all whereas the non-Condon model tracks the trend very well.

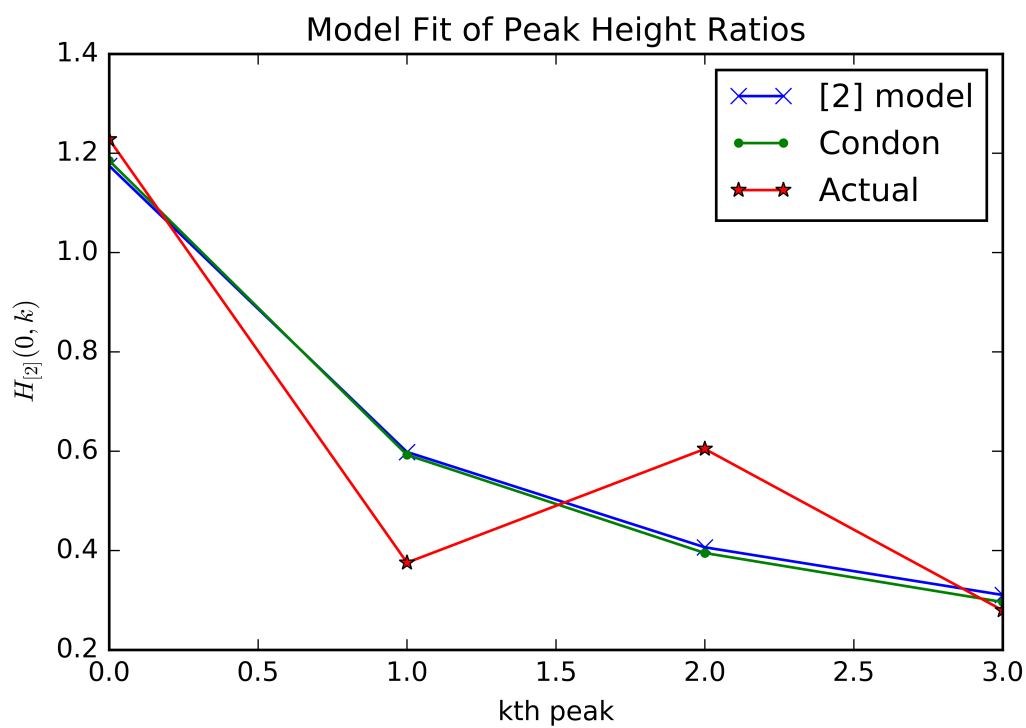


Figure 3.5: The Voigt-derived values of $H(0, k)$ from tetracene in toluene, fit to the model for $H_{(2)}(0, k)$ and a purely Condon model. Note that the Condon model does not fit the trend very well at all whereas the non-Condon model tracks the trend very well.

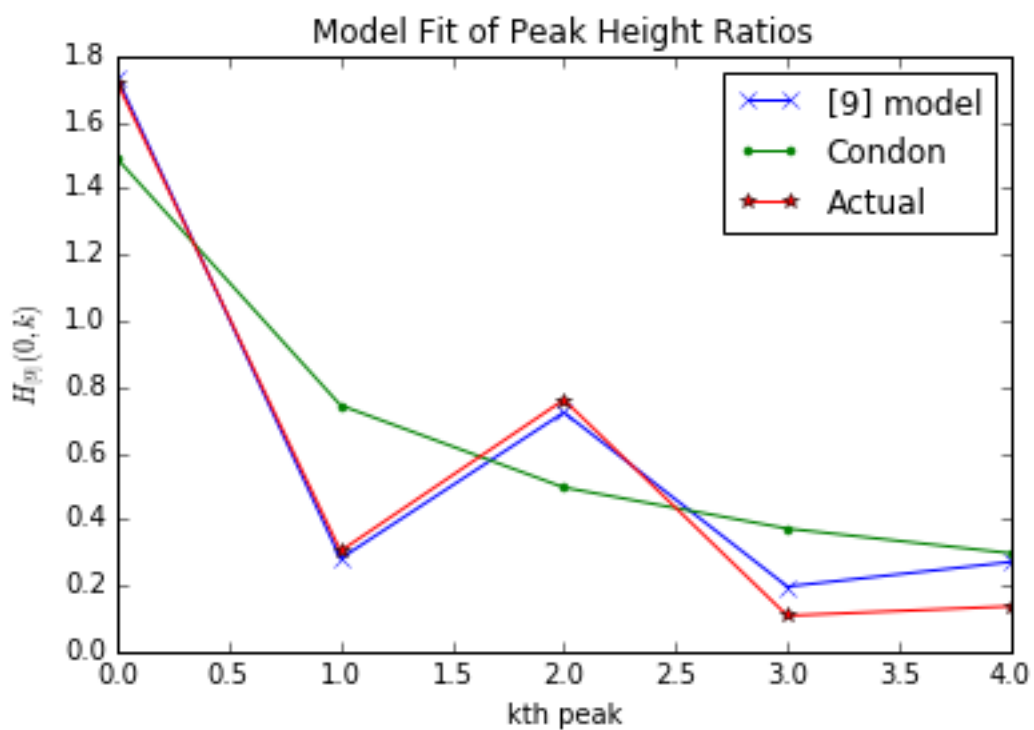


Figure 3.6: The Voigt-derived values of $H(0,k)$ from tetracene in DCM, fit to the model for $H_{(9)}(0,k)$ and a purely Condon model. Note that the Condon model does not fit the trend very well at all whereas the non-Condon model tracks the trend very well.

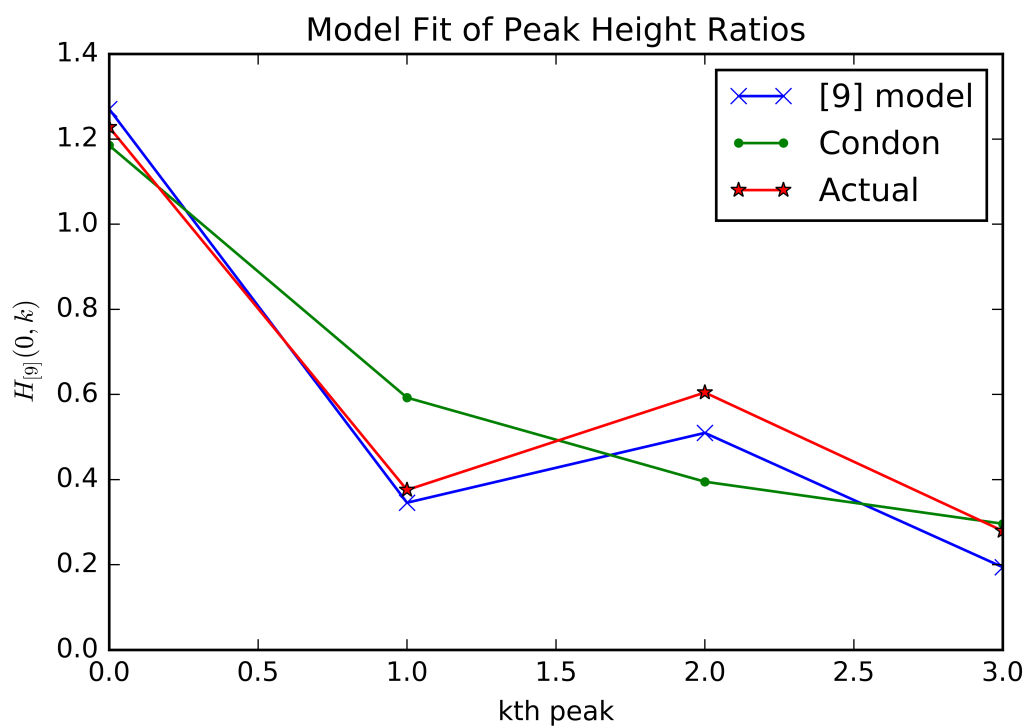


Figure 3.7: The Voigt-derived values of $H(0, k)$ from tetracene in toluene, fit to the model for $H_{(9)}(0, k)$ and a purely Condon model. Note that the Condon model does not fit the trend very well at all whereas the non-Condon model tracks the trend very well.

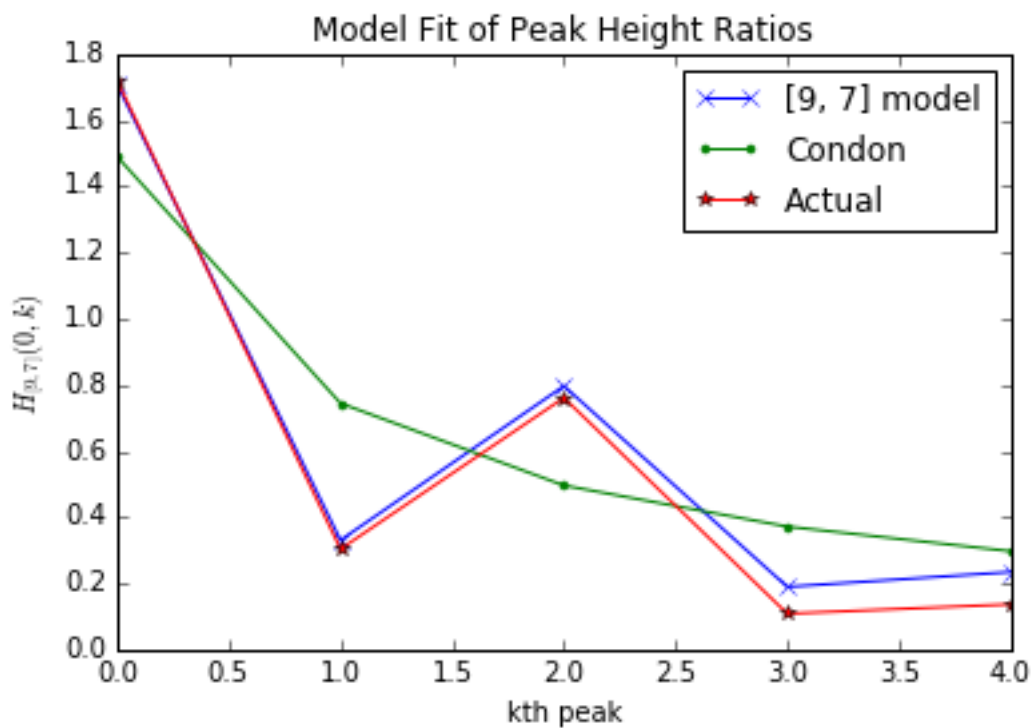


Figure 3.8: The Voigt-derived values of $H(0, k)$ from tetracene in DCM, fit to the model for $H_{(9,7)}(0, k)$ and a purely Condon model. Note that the Condon model does not fit the trend very well at all whereas the non-Condon model tracks the trend very well.

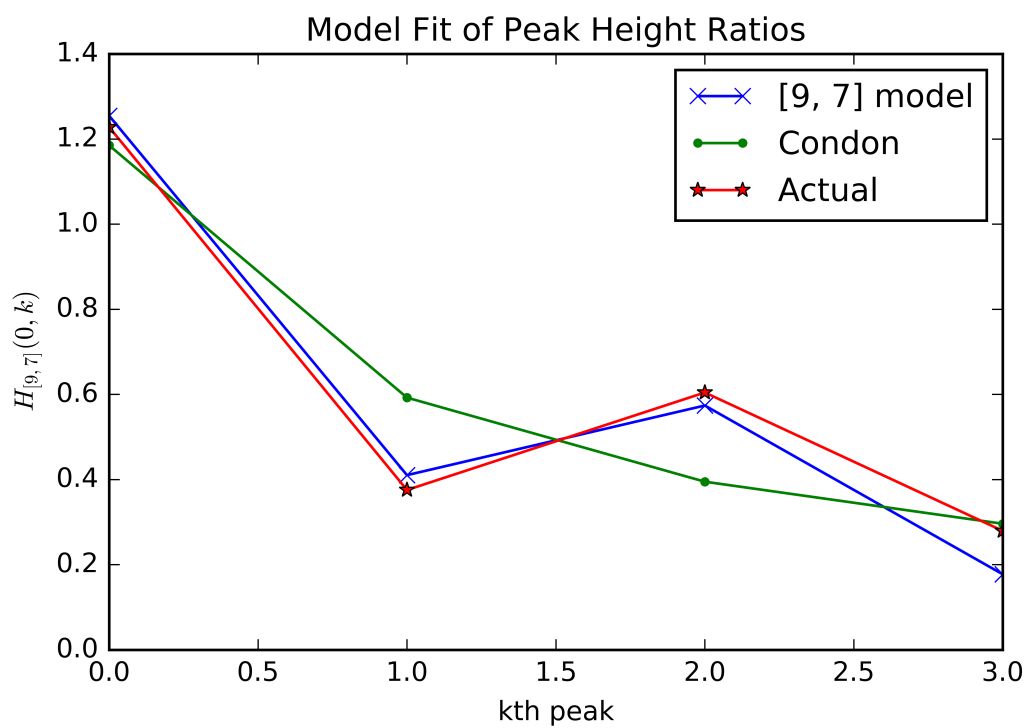


Figure 3.9: The Voigt-derived values of $H(0,k)$ from tetracene in toluene, fit to the model for $H_{[9,7]}(0,k)$ and a purely Condon model. Note that the Condon model does not fit the trend very well at all whereas the non-Condon model tracks the trend very well.

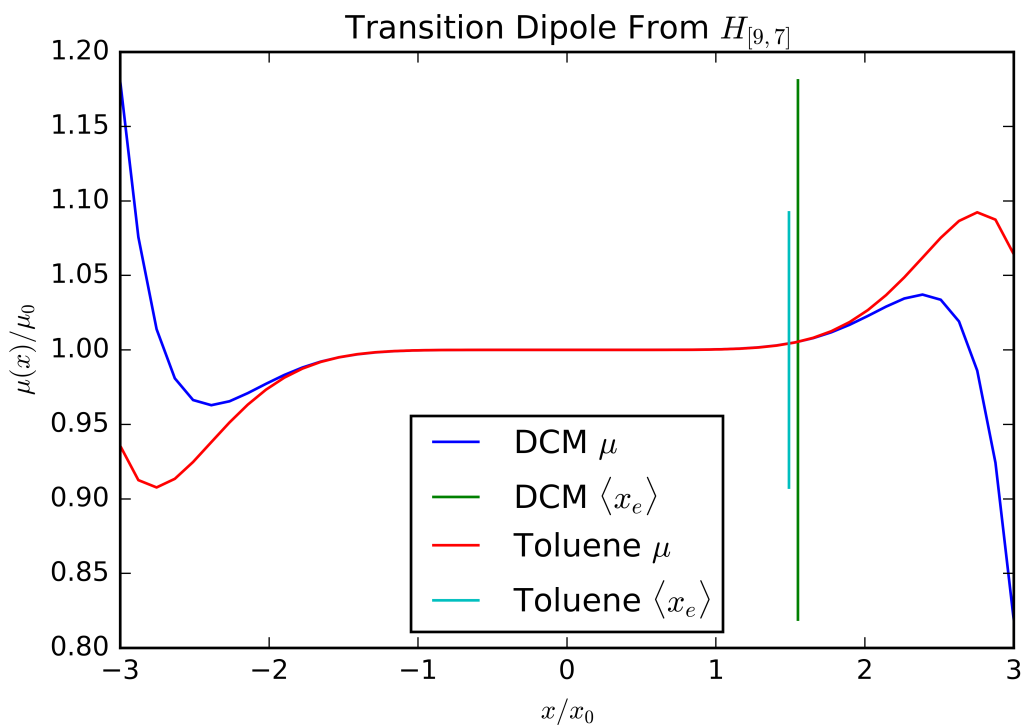


Figure 3.10: The fitted functional form for the transition dipole moment calculated for the Voigt-derived values of $H(0,k)$ to the model for $H_{(9,7)}(0,k)$. The units of the x axis are the characteristic distance of the ground electronic state harmonic oscillator x_0 .

3.5 CONCLUSION

We have developed a method to provide estimates of the vibrational structure of an electronic transition dipole moment by fitting the linear electronic absorption spectrum to lineshape profiles and then fitting the transition strengths to a polynomial non-Condon model. We then applied this method to tetracene in two different solvents. This method can make it clear—when a system is highly harmonic—that the system has a non-constant transition dipole moment with respect to nuclear coordinates. We caution against using this method to precisely define the functional form of the transition dipole without more peak heights. More peak heights removes the need to assume that certain orders are zero and thus means the modeller does not have to pick a model to fit the data, which is not on the most solid statistical footing. Further work on data from sources such as molecular spectroscopic databases will be useful to further explore the magnitude of the corrections studied in this work.

3.6 ACKNOWLEDGMENTS

We acknowledge the support from the Center for Excitonics, an Energy Frontier Research Center funded by the U.S. Department of Energy under award DE-SC0001088 (Solar energy conversion process). The authors also wish to thank Jacob Krich for discussions and Alex Eisfeld for his commentary on this manuscript.

3.7 SUPPLEMENTARY INFORMATION

3.7.1 ABSORPTION HARMONIC OSCILLATOR MODEL

We will find useful here the generic form of the Franck Condon Overlap factor for a displaced harmonic oscillator with the same curvature in the ground and excited states:

$$O_m^n = (-1)^n \sqrt{\frac{e^{-S} S^{m+n}}{m!n!}} \sum_{j=0}^{\min(m,n)} \frac{m!n!(-1)^j S^{-j}}{j!(m-j)!(n-j)!} \quad (3.7.1)$$

3.7.1.1 LINEAR CORRECTION

To calculate the electric field ratio for a linear non-Condon correction for a system starting in the 0th state:

$$\begin{aligned} \mu_{0,\lambda} &= \mu_0 \langle 0 | (1 + c_1 (\hat{a} + \hat{a}^\dagger)) | \lambda \rangle \\ &= \mu_0 (\delta_{0,\lambda} + c_1 \delta_{1,\lambda}) \end{aligned}$$

$$H_{(1)}(0, k) = \frac{\sum_{\lambda,v} [\delta_{0,\lambda} + c^* \delta_{\lambda,1}] [\delta_{0,v} + c \delta_{v,1}] O_\lambda^{k+1} O_v^{k+1}}{\sum_{l,n} [\delta_{0,l} + c^* \delta_{l,1}] [\delta_{0,n} + c \delta_{n,1}] O_l^k O_n^k} \quad (3.7.2)$$

$$= \frac{[O_0^{k+1} + c^* O_1^{k+1}] [O_0^{k+1} + c O_1^{k+1}]}{[O_0^k + c^* O_1^k] [O_0^k + c O_1^k]} \quad (3.7.3)$$

$$= \frac{|O_0^{k+1} + c O_1^{k+1}|^2}{|O_0^k + c O_1^k|^2} \quad (3.7.4)$$

$$= \left(\frac{O_0^{k+1}}{O_0^k} \right)^2 \frac{\left| 1 + c \frac{O_1^{k+1}}{O_0^{k+1}} \right|^2}{\left| 1 + c \frac{O_1^k}{O_0^k} \right|^2} \quad (3.7.5)$$

For this, several quantities can be computed

$$\mathcal{O}_0^{k+1} = (-1)^{k+1} \sqrt{\frac{e^{-S} S^{k+1}}{(k+1)!}} \quad (3.7.6)$$

$$\mathcal{O}_1^{k+1} = (-1)^{k+1} \sqrt{\frac{e^{-S} S^{1+k+1}}{(k+1)!}} \sum_{j=0}^{\min(1,k+1)} \frac{(k+1)!(-1)^j S^{-j}}{j!(1-j)!(k+1-j)!} \quad (3.7.7)$$

$$= (-1)^{k+1} \sqrt{\frac{e^{-S} S^{1+k+1}}{(k+1)!}} \left[\frac{(k+1)!}{(k+1)!} - \frac{(k+1)! S^{-1}}{k!} \right] \quad (3.7.8)$$

$$= (-1)^{k+1} \sqrt{\frac{e^{-S} S^{1+k+1}}{(k+1)!}} \left[1 - \frac{(k+1)}{S} \right] \quad (3.7.9)$$

then the desired ratio is

$$\frac{\mathcal{O}_1^{k+1}}{\mathcal{O}_0^{k+1}} = \frac{(-1)^{k+1} \sqrt{\frac{e^{-S} S^{1+k+1}}{(k+1)!}} \left[1 - \frac{(k+1)}{S} \right]}{(-1)^{k+1} \sqrt{\frac{e^{-S} S^{k+1}}{(k+1)!}}} \quad (3.7.10)$$

$$= \frac{\sqrt{\frac{e^{-S} S^{1+k+1}}{(k+1)!}}}{\sqrt{\frac{e^{-S} S^{k+1}}{(k+1)!}}} \left[1 - \frac{(k+1)}{S} \right] \quad (3.7.11)$$

$$= \sqrt{S} \left[1 - \frac{(k+1)}{S} \right] \quad (3.7.12)$$

as for the other ratio:

$$\mathcal{O}_0^k = (-1)^k \sqrt{\frac{e^{-S} S^k}{k!}} \quad (3.7.13)$$

$$\mathcal{O}_1^k = (-1)^k \sqrt{\frac{e^{-S} S^{1+k}}{k!}} \sum_{j=0}^{\min(1,k)} \frac{k!(-1)^j S^{-j}}{j!(1-j)!(k-j)!} \quad (3.7.14)$$

first we start with the case where $k \geq 1$

$$\mathcal{O}_1^k = (-1)^k \sqrt{\frac{e^{-S} S^{1+k}}{k!}} \left[\frac{k!}{k!} - \frac{k! S^{-1}}{(k-1)!} \right] \quad (3.7.15)$$

$$= (-1)^k \sqrt{\frac{e^{-S} S^{1+k}}{k!}} \left[1 - \frac{k}{S} \right] \quad (3.7.16)$$

if $k = 0$ then the summation above will be unity and the same equation will thus work for both.

Now when we bring it back into the ratio:

$$\frac{O_1^k}{O_0^k} = \frac{(-1)^k \sqrt{\frac{e^{-S} S^{1+k}}{k!}} \left[1 - \frac{k}{S}\right]}{(-1)^k \sqrt{\frac{e^{-S} S^k}{k!}}} \quad (3.7.17)$$

$$= \sqrt{S} \left[1 - \frac{k}{S}\right] \quad (3.7.18)$$

Which after substitution leads to

$$H_{(1)}(0, k) = \frac{S}{k+1} \frac{|1 + c\sqrt{S}(1 - \frac{k+1}{S})|^2}{|1 + c\sqrt{S}(1 - \frac{k}{S})|^2} \quad (3.7.19)$$

3.7.1.2 QUADRATIC CORRECTION

but for a quadratic correction:

$$\begin{aligned} \mu_{0,\lambda}^{(2)} &= \mu_0 \langle 0 | \left(1 + c_2 (\hat{a} + \hat{a}^\dagger)^2\right) | \lambda \rangle \\ &= \mu_0 \langle 0 | \left(1 + c_2 (\hat{N} + 1 + \hat{a}\hat{a} + \hat{a}^\dagger\hat{a}^\dagger)\right) | \lambda \rangle \\ &= \mu_0 \left((1 + c_2) \delta_{0,\lambda} + c_2 \sqrt{2} \delta_{2,\lambda} \right) \\ &= \frac{\mu_0}{(1 + c_2)} \left(\delta_{0,\lambda} + \frac{c_2 \sqrt{2}}{(1 + c_2)} \delta_{2,\lambda} \right) \\ &= \mu'_0 (\delta_{0,\lambda} + c'_2 \delta_{2,\lambda}) \end{aligned}$$

which gives us for the peak ratios instead

$$H_{(2)}(0, k) = \frac{|O_0^{k+1} + c'_2 O_2^{k+1}|^2}{|O_0^k + c'_2 O_2^k|^2} \quad (3.7.20)$$

$$= \left(\frac{O_0^{k+1}}{O_0^k} \right)^2 \frac{\left| 1 + c'_2 \frac{O_2^{k+1}}{O_0^{k+1}} \right|^2}{\left| 1 + c'_2 \frac{O_2^k}{O_0^k} \right|^2} \quad (3.7.21)$$

Instead of getting algebraic expressions for $O_{n \geq 2}^k$ as we did for O_1^k , we instead implement Equation 3.7.1 directly in our solver.

3.7.1.3 3 CORRECTION

The cubic correction looks like so:

$$\begin{aligned} \mu_{0,\lambda}^{(3)} &= \mu_0 \langle 0 | \left(1 + c_3 (\hat{a} + \hat{a}^\dagger)^3 \right) | \lambda \rangle \\ &= \mu_0 \langle 0 | \left(1 + c_3 (\hat{a} + \hat{a}^\dagger) (\hat{N} + 1 + \hat{a}\hat{a} + \hat{a}^\dagger\hat{a}^\dagger) \right) | \lambda \rangle \\ &= \mu_0 \left(\langle 0 | + c_3 \langle 1 | (\hat{N} + 1 + \hat{a}\hat{a} + \hat{a}^\dagger\hat{a}^\dagger) \right) | \lambda \rangle \\ &= \mu_0 \left(\langle 0 | + c_3 \left(2 \langle 1 | + \sqrt{6} \langle 3 | \right) \right) | \lambda \rangle \\ &= \mu_0 \left(\delta_{0,\lambda} + c_3 \left(2\delta_{1,\lambda} + \sqrt{6}\delta_{3,\lambda} \right) \right) \end{aligned}$$

which indicates it makes more sense to treat (1,3) and not just (3):

$$\begin{aligned}
 \mu_{0,\lambda}^{(1,3)} &= \mu_0 \left(\delta_{0,\lambda} + \delta_{1,\lambda} (2c_3 + c_1) + c_3 \sqrt{6} \delta_{3,\lambda} \right) \\
 &= \mu_0 \left(\delta_{0,\lambda} + c'_1 \delta_{1,\lambda} + c_3 \sqrt{6} \delta_{3,\lambda} \right) \\
 c'_1 &= (2c_3 + c_1) \\
 c'_3 &= c_3 \sqrt{6} \\
 c_1 &= \left(c'_1 - 2 \frac{c'_3}{\sqrt{6}} \right)
 \end{aligned}$$

3.7.1.4 4 CORRECTION

Looking at a quadratic correction:

$$\begin{aligned}
 \mu_{0,\lambda}^{(4)} &= \mu_0 \langle 0 | \left(1 + c_4 (\hat{a} + \hat{a}^\dagger)^4 \right) | \lambda \rangle \\
 &= \mu_0 \langle 0 | \left(1 + c_4 (\hat{N} + 1 + \hat{a}\hat{a} + \hat{a}^\dagger\hat{a}^\dagger)^2 \right) | \lambda \rangle \\
 &= \mu_0 \left(\delta_{0,\lambda} + c_4 \langle 0 | (1 + \hat{a}\hat{a}) (\hat{N} + 1 + \hat{a}\hat{a} + \hat{a}^\dagger\hat{a}^\dagger) | \lambda \rangle \right) \\
 &= \mu_0 \left(\delta_{0,\lambda} + c_4 \left[3\delta_{0,\lambda} + 4\sqrt{2}\delta_{2,\lambda} + 2\sqrt{6}\delta_{4,\lambda} \right] \right) \\
 &= \mu_0 \left(\delta_{0,\lambda} (1 + 3c_4) + 4\sqrt{2}c_4\delta_{2,\lambda} + 2\sqrt{6}c_4\delta_{4,\lambda} \right) \\
 &= \mu'_0 \left(\delta_{0,\lambda} + \frac{4\sqrt{2}c_4}{1 + 3c_4} \delta_{2,\lambda} + \frac{2\sqrt{6}c_4}{1 + 3c_4} \delta_{4,\lambda} \right)
 \end{aligned}$$

much like for (3) we had to consider (1,3) to be more accurate, it makes no sense to consider (4) on its own; we'll need to introduce (2) as well to get (2,4):

$$\begin{aligned}
 \mu_{0,\lambda}^{(2,4)} &= \mu_0 \left(\delta_{0,\lambda} (1 + c_2 + 3c_4) + (\sqrt{2}c_2 + 4\sqrt{2}c_4) \delta_{2,\lambda} + 2\sqrt{6}c_4 \delta_{4,\lambda} \right) \\
 &= \mu'_0 \left(\delta_{0,\lambda} + \frac{\sqrt{2}c_2 + 4\sqrt{2}c_4}{1 + c_2 + 3c_4} \delta_{2,\lambda} + \frac{2\sqrt{6}c_4}{1 + c_2 + 3c_4} \delta_{4,\lambda} \right) \\
 c'_2 &= \frac{\sqrt{2}c_2 + 4\sqrt{2}c_4}{1 + c_2 + 3c_4} \\
 c'_4 &= \frac{2\sqrt{6}c_4}{1 + c_2 + 3c_4}
 \end{aligned}$$

which when inverted turns into:

$$\begin{aligned}
 c_2 &= -\frac{2 \left(\sqrt{6}c'_2 - 2\sqrt{2}c'_4 \right)}{2\sqrt{6}c'_2 - \sqrt{2}c'_4 - 4\sqrt{3}} \\
 c_4 &= \frac{c'_4 \left(3\sqrt{2}c'_4 - 4\sqrt{3} \right)}{\left(2\sqrt{6} - 3c'_4 \right) \left(2\sqrt{6}c'_2 - \sqrt{2}c'_4 - 4\sqrt{3} \right)}
 \end{aligned}$$

3.7.1.5 GENERIC CORRECTION

It becomes clear that we should be able to define an arbitrary-order correction (at least for $\eta = 0$) rather simply by adding together generic x^n operator

$$\mu_{0,\lambda} = \sum_n c_n \mu_{0,\lambda}^{(n)} = \sum_n c_n \langle 0 | (\hat{a} + \hat{a}^\dagger)^n | \lambda \rangle$$

this would then feed in to our expression for H :

$$H_{(\{i\})}(0, k) = \frac{S}{k+1} \frac{\left| 1 + \sum_{l=\{i\}} c'_l \frac{\sigma_l^{k+1}}{\sigma_0^{k+1}} \right|^2}{\left| 1 + \sum_{l=\{i\}} c'_l \frac{\sigma_l^k}{\sigma_0^k} \right|^2} \quad (3.7.22)$$

where the transformation from c' back into c would have to be calculated for any individual $H_{\{i\}}$ but is non-trivial. We saw above that the squared operator brought amplitude back to zero and in general, all even operators will bring back amplitude to all even operators in order below and the same with odd operators.

4

Non-Condon Heating during Laser Spectroscopy

ABSTRACT

The Condon approximation that off-diagonal electronic transition dipole moments do not vary with nuclear coordinates, is not as solid an approximation in the world of ultrafast, dynamic spectroscopies as it was in the days of gas-phase rovibrational spectroscopy when Condon first made the approximation. Recent scholarship shows both that such variation non-trivially effects spectroscopic observables and that many systems do indeed exhibit variation in their transition dipole moments. Thus a better understanding of how such phenomenon affects even basic spectroscopic variables would be useful, as would a tool to measure the extent to which a system has a variation in its transition dipole moment. We discuss the effects of a simple, linear transition dipole moment variation on the vibrational state of the molecule during laser excitation and predict that for an IR-active vibrational mode, one would see isotropic signal at the fundamental vibrational frequency if and only if there is a non-trivial transition dipole moment in the impulsive pulse limit. We then look at this IR effect for real pulses and conclude that it would not be a useful discriminator between Condon and non-Condon moments.

4.1 INTRODUCTION

Edward Condon in 1928⁹ made with surprisingly little justification the approximation that the electronic transition dipole did not depend on the nuclear position at all. That approximation has

stood in great stead until recently its effects, particularly in dynamic spectroscopy, have become particularly clear.

There are no doubt many more, but among the recent work include invoking a nontrivial transition dipole to explain graphene's anomalous Raman spectrum²⁰. Furthermore, recent calculations also predict a highly noticeable transition dipole moment in photosynthetic systems⁵⁸. There is also most probably a noticeable effect in some electron-transfer systems of a varying transition dipole moment³³. Lastly, the introduction of a linear variation in transition dipole, completely broke a proposed detection scheme for electronic versus vibrational coherence.

Thus, as more and more scholarship begins to make clear the importance of variation of the transition dipole to the field of dynamic spectroscopy, it would seem to be eminently useful to have a tool to measure these variations. While experiments can infer the presence of a nontrivial transition dipole, we believe it is important to work towards an experiment which definitively can determine the structure of a transition dipole moment.

4.2 SYSTEM SETUP

For our purposes we construct the simplest system for which transition dipole variation can affect its spectra: a vibrational monomer with a ground electronic state $|g\rangle$ and an excited electronic state $|e\rangle$ with a different harmonic vibration in both the ground and excited state such that the Hamiltonian looks like this:

$$H_0 = \sum_n \hbar\omega_\gamma \left(n + \frac{1}{2} \right) |n_\gamma\rangle |g\rangle \langle g| \langle n_\gamma| \quad (4.2.1)$$

$$+ \sum_m \left(\hbar\omega_\epsilon \left(m + \frac{1}{2} \right) + \omega_e \right) |m_\epsilon\rangle |e\rangle \langle e| \langle m_\epsilon| \quad (4.2.2)$$

With the Greek indices corresponding to the vibrational states and the roman indices corresponding to the electronic states. We give this system an electronic transition dipole:

$$\hat{\mu}(x) = \mu(x) (|e\rangle \langle g| + |g\rangle \langle e|) \quad (4.2.3)$$

Where we put all the nuclear variation of the transition dipole moment into the function $\mu(x)$. Considering what a varying transition dipole may look like, we construct the simplest possible variation: a linear-varying moment, which one can transform into ladder operators for easier calculation:

$$\mu(x) = \mu_0 [1 + c (\hat{a}_\gamma + \hat{a}_\gamma^\dagger)] \quad (4.2.4)$$

where \hat{a}_γ and \hat{a}_γ^\dagger are ladder operators in the ground state vibrational potential. One can imagine a more general form of the transition dipole for more than just linear variation:

$$\mu(x) = \mu_0 \sum_{i=0} \kappa_i x^i \quad (4.2.5)$$

$$= \mu_0 \sum_{i=0} c_i (\hat{a} + \hat{a}^\dagger)^i \quad (4.2.6)$$

but we will concern ourselves exclusively with the linear variation here. Depending on the context, it can be useful to transition dipole of the transition dipole as more of a vibrational matrix element:

$$\mu_{a,b} = \langle a_\gamma | \mu(x) | b_\gamma \rangle \quad (4.2.7)$$

This equation shows that a nonzero c will cause an application of $\mu_{a,b}$ to deform the wavefunction, but how?

4.3 MODE HEATING

We instead want to work with an object which only exhibits interesting dynamics when there is an interesting transition dipole, like $|\psi_{+,-}(t)\rangle$.

If you imagine hitting our monomer with the positive energy delta-function laser pulse, and then hitting it again immediately after (really at the same time) with the negative energy part of the laser pulse to get a second order perturbation. Without a transition dipole that varies, one would expect to have a perfect copy of the original vibrational wavepacket, back in the ground electronic state after an instantaneous trip to the excited state. If, however, there is a variation in the transition dipole, then you would no longer have a perfect copy, but you would have induced a ground-state vibrational coherence. Putting this mathematically, we would only expect interesting or novel effects from $|\psi_{+,-}(t)\rangle$, if the transition dipole varies, but it's boring if there is no variation. Putting it yet another way, a non-trivial transition dipole moment causes a vibrational coherence in the ground state of $|\psi_{+,-}(t)\rangle$ where there would be none if the transition dipole moment is constant.

Mathematically, it would look like this assuming a delta-function laser beam at $t = 0$ and starting in the 0th state:

$$|\psi_{+,-}(0)\rangle = \tag{4.3.1}$$

$$= \mu_0^2 [1 + c(\hat{a}_\gamma + \hat{a}_\gamma^\dagger)] [1 + c^*(\hat{a}_\gamma + \hat{a}_\gamma^\dagger)] |0_\gamma\rangle |g\rangle \tag{4.3.2}$$

$$= \mu_0^2 [1 + (c + c^*)(\hat{a}_\gamma + \hat{a}_\gamma^\dagger) + |c|^2(\hat{a}_\gamma + \hat{a}_\gamma^\dagger)^2] |0_\gamma\rangle |g\rangle \tag{4.3.3}$$

$$= \mu_0^2 [(1 + |c|^2)|0_\gamma\rangle + (c + c^*)|1_\gamma\rangle + \sqrt{2}|c|^2|2_\gamma\rangle] |g\rangle \tag{4.3.4}$$

So for the case of a delta function pulse, the wavefunction is either trivially the same ground state if the transition dipole is constant ($c = 0$) or it can be a vibrational coherence for nonzero c . That

vibrational coherence implies that the ground state has heated up; the average vibrational quantum number is now higher. We set out to find a way to make a signal out of that.

4.3.1 RESONANCE RAMAN

The simplest signal that could be constructed for this would be

$$E(t) = -i\omega^2 \langle \psi_0(t) | \hat{\mu} | \psi_{+,-}(t) \rangle$$

but the transition dipole we introduced earlier would mean this is zero as both the bra and ket are in the ground electronic state, and the transition dipole operator is off-diagonal in the electronic basis. If, however, the vibrational mode is IR-active, it will have a transition dipole that is diagonal in the electronic basis:

$$\hat{\mu}_{IR} = d_g |g\rangle \langle g| (\hat{a}_\gamma^\dagger + \hat{a}_\gamma) + d_e |e\rangle \langle e| (\hat{a}_\epsilon^\dagger + \hat{a}_\epsilon) \quad (4.3.5)$$

which will give us a signal like so:

$$E_{IR}(t) = i\omega^2 \langle \psi_0(t) | \hat{\mu}_{IR} | \psi_{+,-}(t) \rangle \quad (4.3.6)$$

which due to phase matching will be isotropic. This is very similar to the phenomenon of resonance Raman³⁹ but we are predicting an additional isotropic signal as opposed to

To generalize this to real pulses, we treat a more general laser pulse perturbation of the form:

$$H'(\tau) = E(\tau)\mu(x)(|e\rangle \langle g| + |g\rangle \langle e|) \quad (4.3.7)$$

and a starting wavefunction of

$$|\psi_0(0)\rangle = |\eta_\gamma\rangle |g\rangle \quad (4.3.8)$$

If we consider times t only after the pulse has turned off, and let $\tilde{E}_\pm(\omega)$ be the positive and negative frequency parts of the Fourier transform of $E(\tau)$, we get first as the excitation perturbation:

$$|\psi_+(t)\rangle = \sum_{\lambda,k} \tilde{E}_+ \left(\Omega_e^{(k)} - \Omega_g^{(\eta)} \right) \mu_{\eta,\lambda} O_\lambda^k e^{-i\Omega_e^{(k)} t} |k_\epsilon\rangle |e\rangle$$

Going forward we define $\Omega_e^{(k)} - \Omega_g^{(\eta)} = \Delta\Omega_{(\eta)}^{(k)}$

$$|\psi_+(t)\rangle = \sum_{\lambda,k} \tilde{E}_+ \left(\Delta\Omega_{(\eta)}^{(k)} \right) \mu_{\eta,\lambda} O_\lambda^k e^{-i\Omega_e^{(k)} t} |k_\epsilon\rangle |e\rangle$$

then we bring in the relaxation or negative frequency part of the perturbation and apply again to get:

$$|\psi_{+,-}(t)\rangle = \sum_{\lambda,k,a,b} \tilde{E}_+ \left(\Delta\Omega_{(\eta)}^{(k)} \right) \tilde{E}_- \left(-\Delta\Omega_{(b)}^{(k)} \right) \mu_{\eta,\lambda} \mu_{a,b} O_\lambda^k O_a^k e^{-i\Omega_g^{(b)} t} |b_\gamma\rangle |g\rangle$$

Now we apply the IR transition dipole to the ground state

$$\hat{\mu}_{IR} |\psi_0(t)\rangle = d_g e^{-i\Omega_g^{(\eta)} t} \left(\sqrt{\eta} |\eta - 1_\gamma\rangle + \sqrt{\eta + 1} |\eta + 1_\gamma\rangle \right) |g\rangle$$

which we then combine together with the perturbed wavefunction to get:

$$\begin{aligned}
\frac{1}{\omega_\gamma^2 d_g} E_{IR}(t) = & \\
& \sqrt{\eta} \sum_{\lambda,k,a} \tilde{E}_+ \left(\Delta\Omega_{(\eta)}^{(k)} \right) \tilde{E}_- \left(-\Delta\Omega_{(\eta-1)}^{(k)} \right) \mu_{\eta,\lambda} \mu_{a,\eta-1} \\
& \times O_\lambda^k O_a^k e^{i\omega_\gamma t} \\
& + \sqrt{\eta+1} \sum_{\lambda,k,a} \tilde{E}_+ \left(\Delta\Omega_{(\eta)}^{(k)} \right) \tilde{E}_- \left(-\Delta\Omega_{(\eta+1)}^{(k)} \right) \mu_{\eta,\lambda} \mu_{a,\eta+1} \\
& \times O_\lambda^k O_a^k e^{-i\omega_\gamma t}
\end{aligned}$$

if we assume the 0th state initially it gets a little simpler:

$$\begin{aligned}
\frac{1}{\omega_\gamma^2 d_g} E_{IR}(t) = & \\
& \sum_{\lambda,k,a} \tilde{E}_+ \left(\Delta\Omega_{(0)}^{(k)} \right) \tilde{E}_- \left(-\Delta\Omega_{(1)}^{(k)} \right) \mu_{0,\lambda} \mu_{a,1} \\
& \times O_\lambda^k O_a^k e^{-i\omega_\gamma t}
\end{aligned}$$

which is certainly more complicated than before. What does this signal look like in the Condon approximation?

$$\begin{aligned}
\frac{1}{\mu_0^2 \omega_\gamma^2 d_g} E_{IR}(t) = & \\
& \sum_k \tilde{E}_+ \left(\Delta\Omega_{(0)}^{(k)} \right) \tilde{E}_- \left(-\Delta\Omega_{(1)}^{(k)} \right) \\
& \times O_0^k O_1^k e^{-i\omega_\gamma t}
\end{aligned}$$

which in the impulsive limit $\tilde{E}(\omega) = E_0$ reduces to:

$$\begin{aligned} E_{IR}(t) &= \mu_0^2 \omega_\gamma^2 d_g E_0^2 \sum_k O_0^k O_1^k e^{-i\omega_\gamma t} \\ &= \mu_0^2 \omega_\gamma^2 d_g E_0^2 \langle 0_\gamma | 1_\gamma \rangle e^{-i\omega_\gamma t} = 0 \end{aligned}$$

So in the impulsive limit and with a non-Condon transition dipole moment, there is no IR emission on resonant excitation.

4.3.2 SIMULATIONS OF NON CONDON HEATING

We now have three relevant parameters. Assuming we're working with Gaussian moments, we can call the first the pulse width but measured here by the ratio of amplitude for the $0 \rightarrow 1$ to the $0 \rightarrow 0$ transition. Then, the ratio of the laser's energy in the $0 \rightarrow 0$ transition to the vibrational energy:

$$\tau = \frac{\tilde{E}_- \left(-\Delta\Omega_{(1)}^{(0)} \right)}{\tilde{E}_+ \left(\Delta\Omega_{(0)}^{(0)} \right)} \quad (4.3.9)$$

$$\kappa = \frac{\mu_0 \tilde{E}_+ \left(-\Delta\Omega_{(0)}^{(0)} \right)}{\hbar \omega_\gamma} \quad (4.3.10)$$

and then of course c .

We decide to integrate Schrodinger's equation directly because all orders of perturbation that end up in the ground electronic state will give IR signal. We want to explore an experimental protocol for determining whether there is a linear transition dipole as discussed above.

We want to describe how the ground state of vibrational system can be heated up through the continuous application of a varying transition dipole moment. We showed above that to second order in perturbation theory, there is a definitive heating of the ground state mode. We will

mathematically show heating as being the average of the vibrational quanta:

$$\bar{n}(t) = \sum_n n |\langle g | \langle n_\gamma | \Psi(t) \rangle|^2$$

But then what does the time-dependent wavefunction look like? We're interested in the exact picture. The interaction Hamiltonian is

$$\hat{H}'(t) = E(t) (|g\rangle \langle e| + |e\rangle \langle g|) \mu(x)$$

and the time-independent Hamiltonian is as above:

$$H_0 = \sum_n \hbar \omega_\gamma \left(n + \frac{1}{2} \right) |n_\gamma\rangle |g\rangle \langle g| \langle n_\gamma| \quad (4.3.11)$$

$$+ \sum_m \left(\hbar \omega_\epsilon \left(m + \frac{1}{2} \right) + \omega_e \right) |m_\epsilon\rangle |e\rangle \langle e| \langle m_\epsilon| \quad (4.3.12)$$

If we turn the electronic degrees of freedom, putting it into Matrix form, we then have:

$$\hat{H}(t) = \begin{bmatrix} H_\gamma(x) & E(t)\mu(x) \\ E(t)\mu(x) & H_\epsilon(x) \end{bmatrix}$$

no that won't work since the coefficients of the Pauli matrices won't commute...

Let's think about this in terms of time-dependent coefficients. We assume the following form of the time-varying wavefunction:

$$|\Psi(t)\rangle = \sum_a G_a(t) |a_\gamma\rangle |g\rangle + \sum_b E_b(t) |b_\epsilon\rangle |e\rangle$$

This can be re-cast as a matrix problem,

$$\frac{d}{dt} \begin{bmatrix} G_a(t) \\ E_b(t) \end{bmatrix} = -\frac{i}{\hbar} \begin{bmatrix} \Omega_{(a)} & E(t)\mu_a^b \\ E(t)\mu_a^b & \Omega^b \end{bmatrix} \cdot \begin{bmatrix} G_a(t) \\ E_b(t) \end{bmatrix}$$

Let's look, now at μ_a^b . In the Condon approximation it's

$$\mu_0 O_a^b$$

If instead we have

$$\begin{aligned} \mu(x) &= \mu_0 (1 + \lambda x) \\ &= \mu_0 (1 + c (a + a^\dagger)) \\ \mu_a^b &= \mu_0 \left(O_a^b + c \left(\sqrt{a} O_{a-1}^b + \sqrt{a+1} O_{a+1}^b \right) \right) \end{aligned}$$

4.4 RESULTS

So we look at two cases: $c = 0.0001$ as effectively zero and $c = .1$ for a Huang Rhys Parameter of 0.8.

Unfortunately, there is no qualitative difference, here, between the two Figures 4.2 and 4.3 despite the fact that they are 5 orders of magnitude in c away from each other, so we conclude that there is likely not a way to discriminate between these two situations using IR spectroscopy. We suspect it would be more fruitful to look into resonance Raman³⁹ as a distinguishing method.

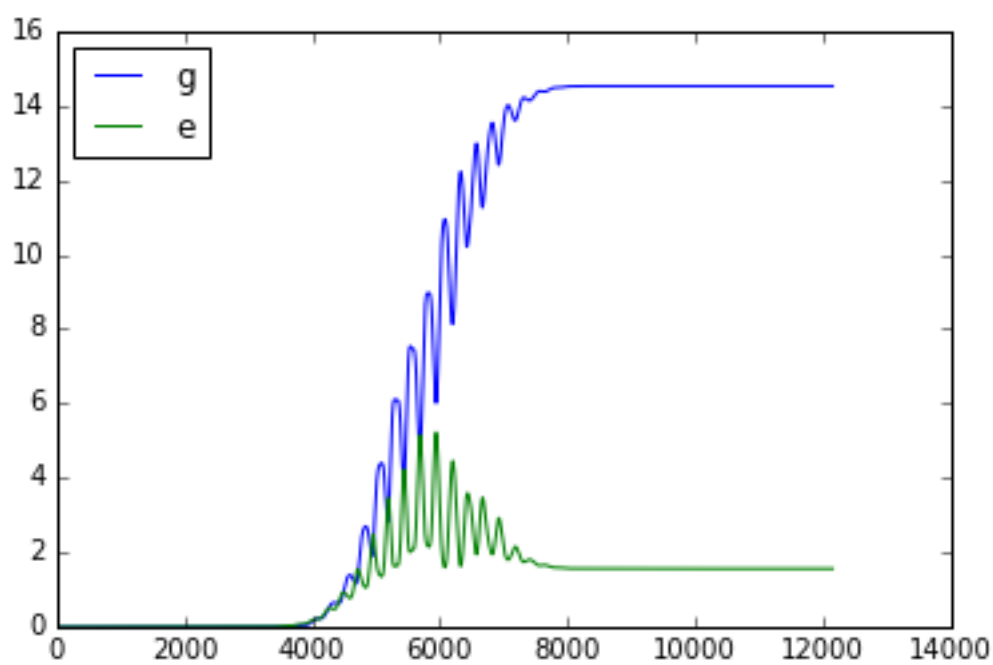


Figure 4.1: This is a representative plot of the average value of the ground and excited state vibrational quantum number of a system with $S=0.8$ and a nonzero c , while a laser interacts with it. The heating is notable in both wells and we'd expect to be able to see signatures of this heating.

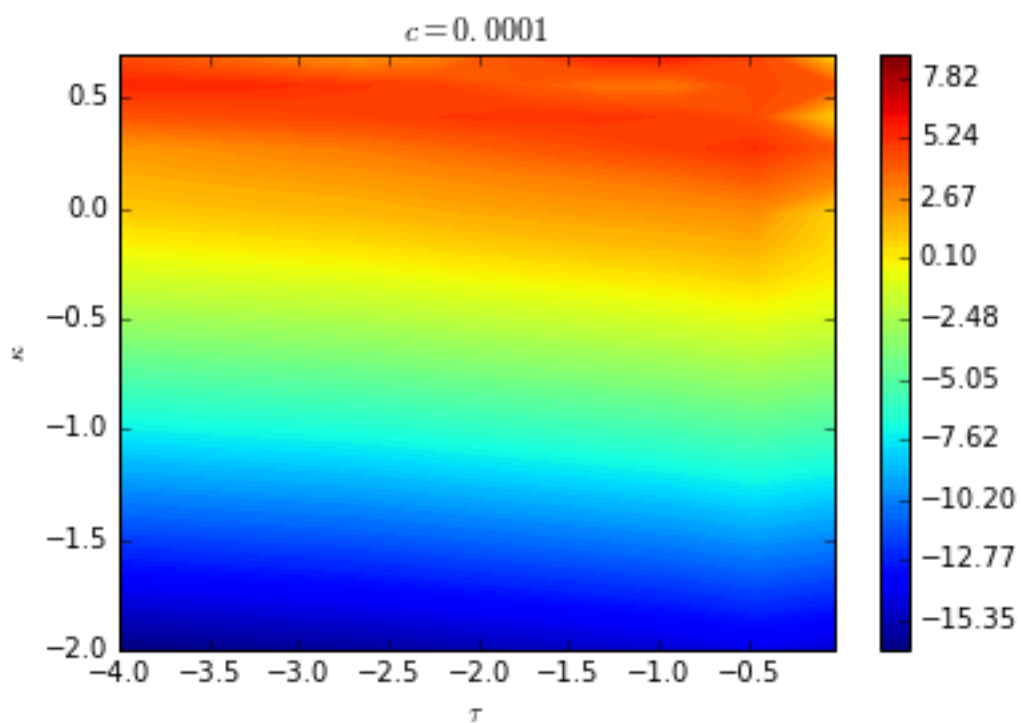


Figure 4.2: This is a plot of the spectral power at the frequency of the ground vibrational state for $c = 0.0001$ as a function of τ and κ for $S = 0.8$

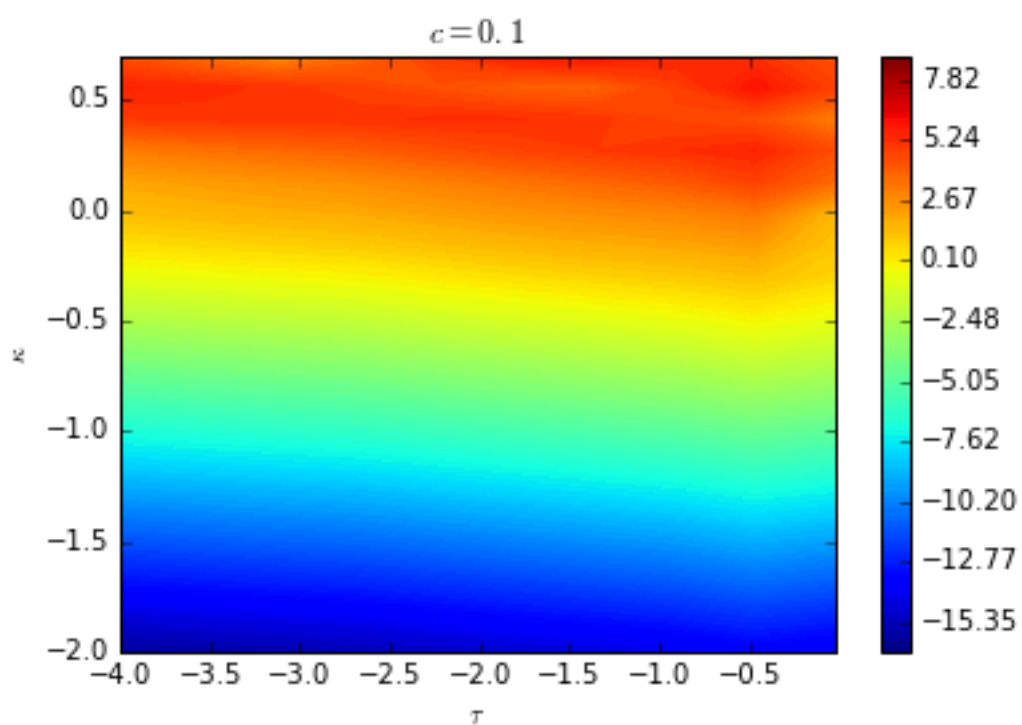


Figure 4.3: This is a plot of the spectral power at the frequency of the ground vibrational state for $c = 0.1$ as a function of τ and κ for $S = 0.8$

5

Decoherence and Heating in Molmer Sorenson Gates because of Non-Condon Transition Dipoles

ABSTRACT

Molmer Sorenson gates have emerged as a promising architecture for Quantum computing in recent years. Theoretical treatments of the architecture implicitly make the approximation that transitions between electronic states do not alter the nuclear state. This approximation, sometimes called the Condon approximation, is very often valid but recent scholarship suggests that non-trivial transition dipole moments are important for physics in many different systems. We investigate here the effect such a perturbation would have on a Molmer-Sorenson gate and estimate its effect.

5.1 INTRODUCTION

The idea of using trapped ions for quantum computing has been around for a long time^{34,46} but one of the most promising turned out to be the architecture proposed by Molmer and Sorenson in 1999⁴⁷ which then began to be achieved experimentally soon after^{36,56}.

One of the problems turned out, however, to be heating during the operation of the gate^{2,16,24}. The ability of the gate to perform universal quantum computation depends on the system's vibrational quantum number staying reasonably constant. Much work looked at possible

mechanisms for observed heating including r.f. heating⁵³ and micromotion.

The basic Hamiltonian is, as laid out by Molmer and Sorenson⁴⁷.

$$\begin{aligned}\hat{H} &= \hat{H}_0 + \hat{H}_{\text{int}} \\ \hat{H}_0 &= \hbar\nu \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right) + \frac{\hbar\omega_{eg}}{2} \sum_i \sigma_{zi} \\ \hat{H}_{\text{int}} &= \sum_i \frac{\hbar\Omega_i}{2} \left(\sigma_{+i} e^{i[\eta_i(\hat{a}^\dagger + \hat{a}) - \omega_i t]} + \sigma_{-i} e^{-i[\eta_i(\hat{a}^\dagger + \hat{a}) - \omega_i t]} \right)\end{aligned}$$

To which we will focus on \hat{H}_{int} . The form supplied in these equations makes the tacit assumption that the transition strength is constant with respect to the nuclear configuration of the system; the only nuclear component of the transition comes from the recoil operator ($e^{-i\eta_i(\hat{a}^\dagger + \hat{a})}$) coming from the laser momentum projected onto the direction of the trap. Put another way, the actual Rabi frequency Ω_i approximately does not change with vibrational state. Condon first articulated this approximation⁹ for molecular spectra in 1928 but recent scholarship has shown lots of ways this approximation can lead to incorrect interpretation of experiments involving electronic transitions^{20,33,58}. In particular, because (if one thinks of things in the position basis) a transition dipole variation such as this will deform the wavefunction upon application, this does imply that the system is heated upon laser excitation if this is indeed the case. Since Heating is a constant problem for the operation of any quantum computer, we take it upon ourselves to investigate the effect a variation in transition dipole will have on a Molmer-Sorenson type System.

Mathematically, this means we are taking Ω_i and adding a position dependence which can then

be decomposed into creation and annihilation operators

$$\Omega_i \rightarrow \Omega_i \mu(x) \quad (5.1.1)$$

$$\mu(x) = \mu_0 \sum_{i=0} \kappa^{(i)} x^i \quad (5.1.2)$$

$$= \mu_0 \sum_{i=0} c^{(i)} (\hat{a} + \hat{a}^\dagger)^i \quad (5.1.3)$$

We assume that $c^{(1)} = 0$ and all odd numbered corrections because the excited vibrational manifold is no different than the excited vibrational manifold so only symmetric orders in x should physically be present. Furthermore, and linear dependence would directly effect the calculated Rabi Frequency $\tilde{\Omega}$ but we are looking for an insipid effect to explain heating, not a major effect that should have been noticed by now.

We then explore a rather drastic shift and set $c^{(2)} = .1$ and explore the effect it would have on the dynamics of the system. To wit, we recreate Figure 2 in ⁴⁷ with this system in our Figure 5.2. This is a very large effect which would doubtless make a system completely unusable.

We next look at the Fidelity³ of the state compared to the ideal, unitary dynamics for multiple values of $c^{(2)}$ from $10^{-5} \rightarrow 1$ and plot the result in Figure 5.3. As would be expected, small corrections don't induce much of a problem at all, but larger correction have the potential to affect the fidelity a great deal.

Another way of looking at this would be the average quantum number of the gate during operation and we plot that for the same values of $c^{(2)}$ in Figure 5.4. The laser beam appears to impart some heat at the beginning based on the value of $c^{(2)}$ but the value is not much. What is increasing is the variation in the expected quantum number. If we calculate, instead, the standard deviation of the vibrational quantum number, there is a clear trend up as $c^{(2)}$ goes up as seen in Figure 5.5

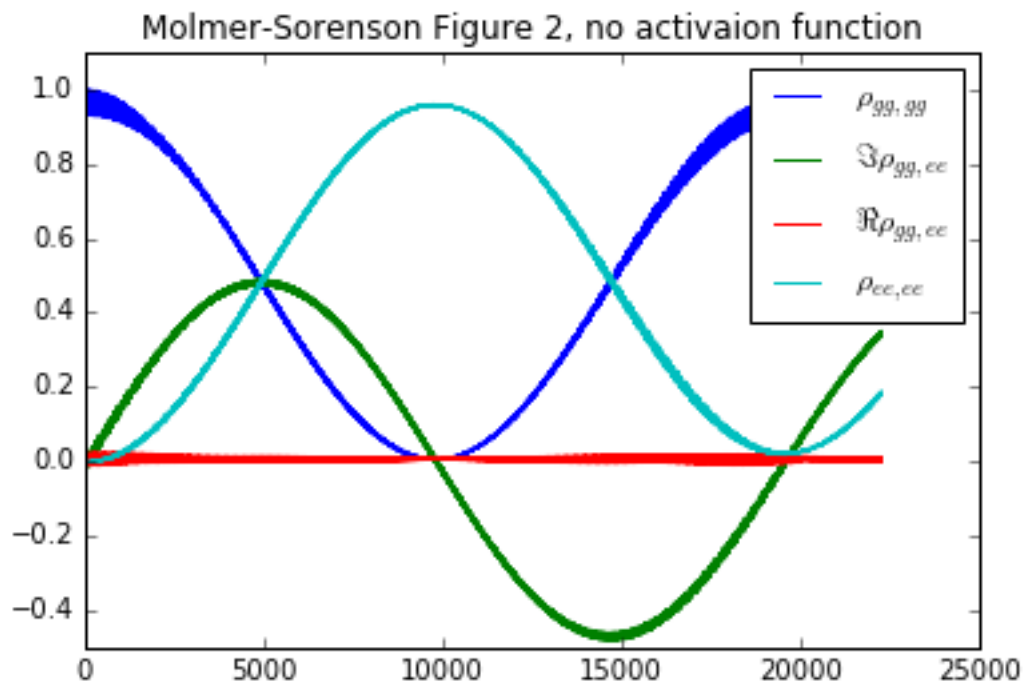


Figure 5.1: This is a reproduction of Figure 2 from the original paper by Molmer and Sorenson where they proposed using a gate which operates like this to perform quantum computations. Any needed state is accessible by turning off the excitation lasers at a given time during operation.

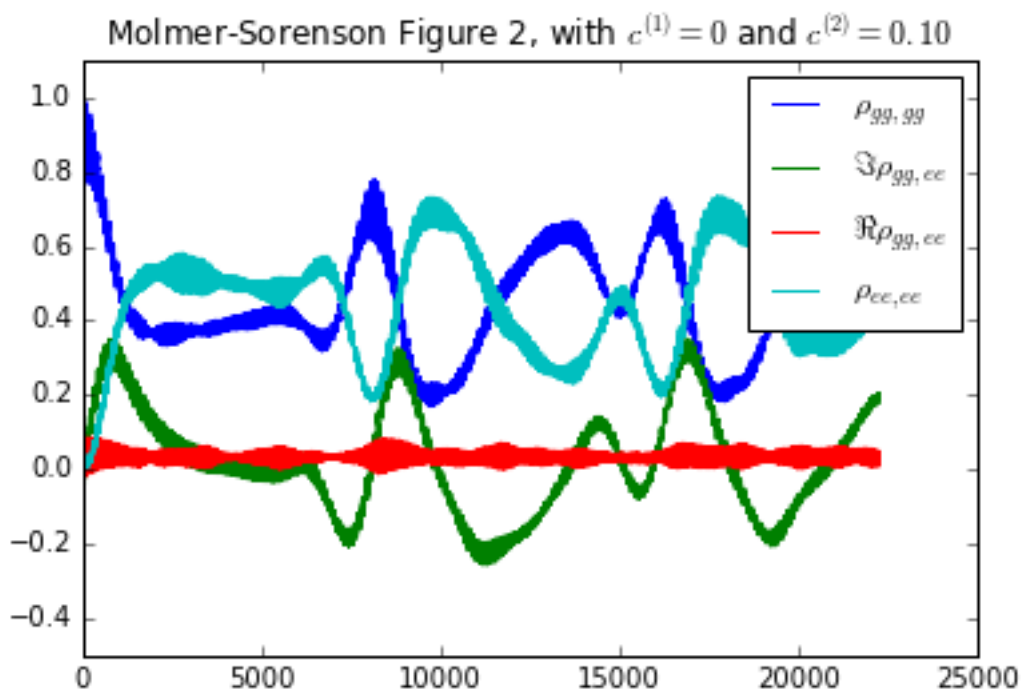


Figure 5.2: This is what Figure 2 from the original paper by Molmer and Sorenson would have looked like with a large quadratic term in the transition dipole $\mu(x)$. Note that the nice unitary dynamics are almost completely gone. This is not due, however, to heating but tot he

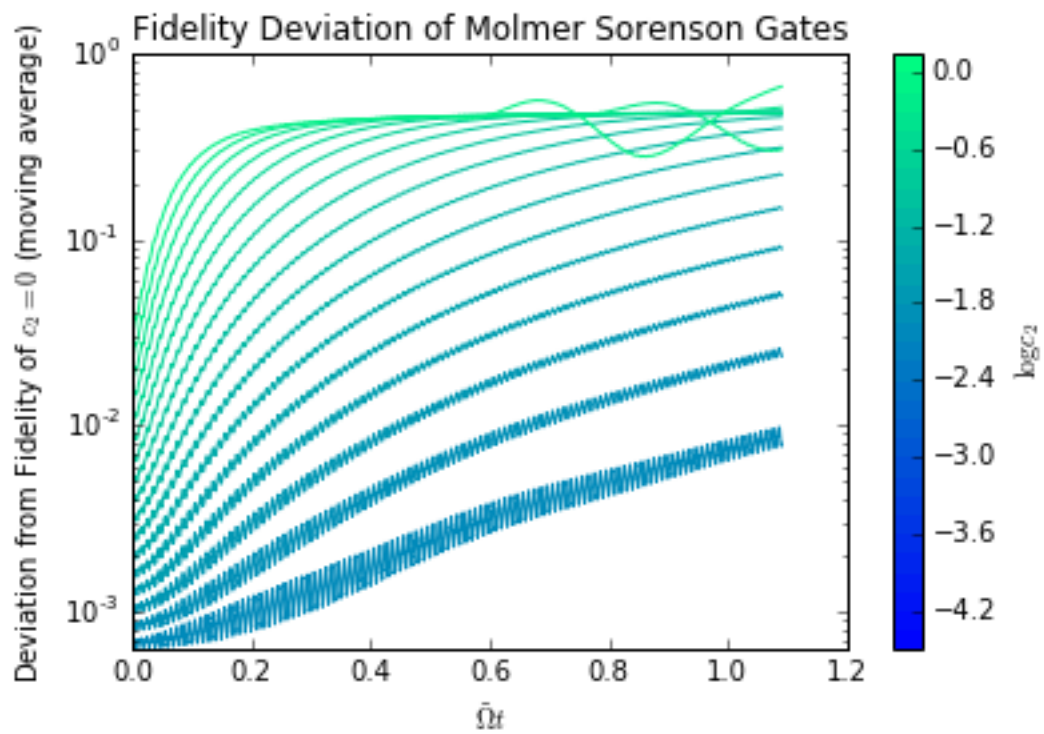


Figure 5.3: This show on a log scale the deviation from the ideal unitary dynamics for various values of $c^{(2)}$. Notably, the larger the value of $c^{(2)}$, the greater the deviation. The effect is still not very big.

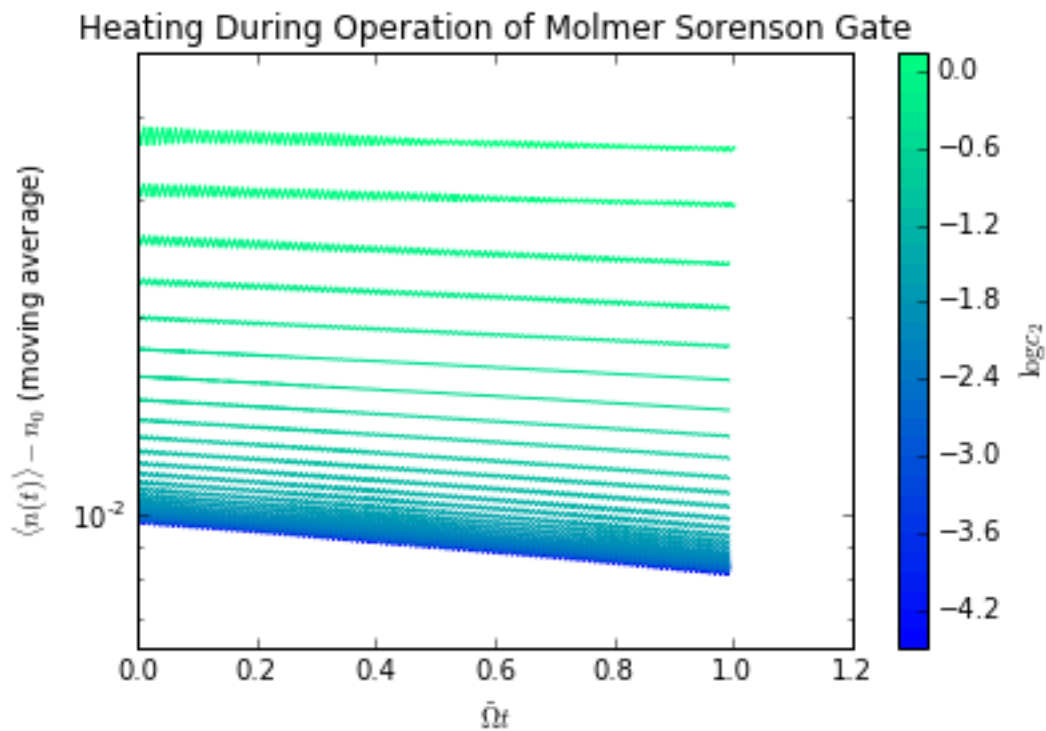


Figure 5.4: This show on a log scale the expected value of the vibrational quantum number during gate operation, for various values of $c^{(2)}$. Once again, the larger the value of $c^{(2)}$, the greater the amount of heating but oddly, compared to such effects in ultrafast systems, the system very quickly reaches the higher level of heat, and then very slowly declines as the laser continues operation. This effect is also not terribly large

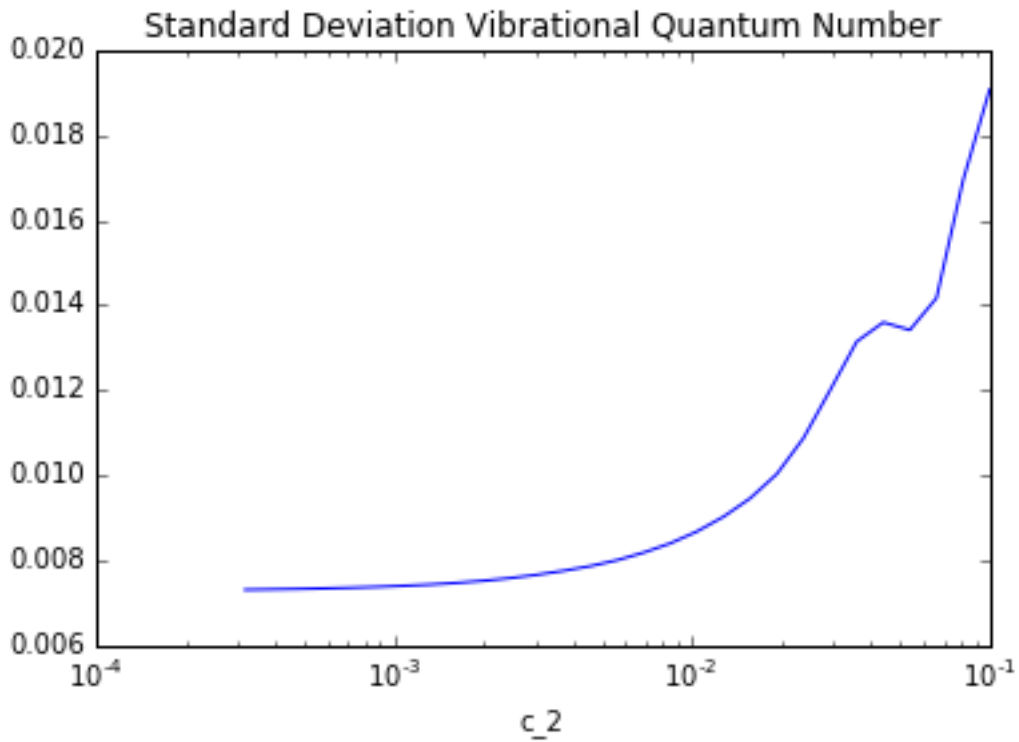


Figure 5.5: This show on a linear scale the standard deviation of the vibrational quantum number during gate operation, for various values of $c^{(2)}$. There is a very clear increasing relationship between this variation and $c^{(2)}$. This increases uncertainty in the state of the gate when the laser is turned off.

5.2 TYPICAL VALUES FOR $c^{(i)}$

If we take Yb+, and do a back of the envelope calculation. The

5.3 CONCLUSION

We have shown the effect that a term quadratic in the nuclear position on the transition operator, can do to the fidelity of a Molmer-Sorenson gate. Values of this term are, however, likely not large enough to be of any concern to experimentalists as they are very small. As trap frequencies get higher and traps begin to include more and more atoms, this effect could potentially cascade and cause problems for future implementations of trapped-ion quantum computers.

5.4 SUPPLEMENTAL MATERIAL

5.4.1 RABI FREQUENCY

We want to see how this will nuclear dependence of the transition dipole will affect the calculated Rabi Frequency (to second order). The formula in the original paper is

$$\left(\frac{\tilde{\Omega}}{2}\right)^2 = \frac{1}{\hbar^2} \left| \sum_m \frac{\langle e e n | H_{\text{int}} | m \rangle \langle m | H_{\text{int}} | g g n \rangle}{E_{ggn} + \hbar \omega_i - E_m} \right|^2$$

Our H_{int} for this derivation will assume $\eta = \eta_i = \eta_2$ and $\Omega = \Omega_1 = \Omega_2$ and has the added vibrational transition dipole moment $f(z)$

$$\hat{H}_{\text{int}} = \frac{\hbar \Omega}{2} \sum_i \left(f(z) \sigma_{+i} e^{i[\eta(\hat{a}^\dagger + \hat{a}) - \omega_i t]} + f^*(z) \sigma_{-i} e^{-i[\eta(\hat{a}^\dagger + \hat{a}) - \omega_i t]} \right)$$

now we act this on the appropriate states:

$$\begin{aligned}\hat{H}_{\text{int}}|ggn\rangle &= \frac{\hbar\Omega}{2}f(z)e^{i\eta(\hat{a}^\dagger+\hat{a})}(|egn\rangle e^{-i\omega_1 t} + |gen\rangle e^{-i\omega_2 t}) \\ \hat{H}_{\text{int}}|een\rangle &= \frac{\hbar\Omega}{2}f^*(z)e^{-i\eta(\hat{a}^\dagger+\hat{a})}(|egn\rangle e^{i\omega_2 t} + |gen\rangle e^{i\omega_1 t})\end{aligned}$$

if we do as the paper does and restrict m to be $|egn+1\rangle, |gen-1\rangle$

$$\begin{aligned}\langle gen-1|\hat{H}_{\text{int}}|ggn\rangle &= \frac{\hbar\Omega}{2}\langle gen-1|f(z)e^{i\eta(\hat{a}^\dagger+\hat{a})}(|egn\rangle e^{-i\omega_1 t} + |gen\rangle e^{-i\omega_2 t}) \\ &= \frac{\hbar\Omega}{2}\langle n-1|f(z)e^{i\eta(\hat{a}^\dagger+\hat{a})}|n\rangle e^{-i\omega_2 t} \\ \langle egn+1|\hat{H}_{\text{int}}|ggn\rangle &= \frac{\hbar\Omega}{2}\langle egn+1|f(z)e^{i\eta(\hat{a}^\dagger+\hat{a})}(|egn\rangle e^{-i\omega_1 t} + |gen\rangle e^{-i\omega_2 t}) \\ &= \frac{\hbar\Omega}{2}\langle n+1|f(z)e^{i\eta(\hat{a}^\dagger+\hat{a})}|n\rangle e^{-i\omega_1 t}\end{aligned}$$

then the de-excitations from the doubly excited state

$$\begin{aligned}\langle gen-1|\hat{H}_{\text{int}}|een\rangle &= \frac{\hbar\Omega}{2}\langle gen-1|f^*(z)e^{-i\eta(\hat{a}^\dagger+\hat{a})}(|egn\rangle e^{i\omega_2 t} + |gen\rangle e^{i\omega_1 t}) \\ &= \frac{\hbar\Omega}{2}\langle n-1|f^*(z)e^{-i\eta(\hat{a}^\dagger+\hat{a})}|n\rangle e^{i\omega_1 t} \\ \langle egn+1|\hat{H}_{\text{int}}|een\rangle &= \frac{\hbar\Omega}{2}\langle egn+1|f^*(z)e^{-i\eta(\hat{a}^\dagger+\hat{a})}(|egn\rangle e^{i\omega_2 t} + |gen\rangle e^{i\omega_1 t}) \\ &= \frac{\hbar\Omega}{2}\langle n+1|f^*(z)e^{-i\eta(\hat{a}^\dagger+\hat{a})}|n\rangle e^{i\omega_2 t}\end{aligned}$$

Now is the time to think. Our vibrational correction to the electronic transition moment, should only have even corrections to it. And Molmer and Sorenson only expanded the laser recoil operator out to first order, meaning a typical matrix element from above will look like:

$$\langle n+1|f^*(z)e^{-i\eta(\hat{a}^\dagger+\hat{a})}|n\rangle \approx -i\eta \langle n+1|f^*(z)(\hat{a}^\dagger+\hat{a})|n\rangle$$

and since f will look like this:

$$\begin{aligned} f(z) &= 1 + c^{(2)} (\hat{a}^\dagger + \hat{a})^2 \\ &= 1 + c^{(2)} (\hat{a}^\dagger \hat{a}^\dagger + \hat{a} \hat{a}^\dagger + \hat{a}^\dagger \hat{a} + \hat{a} \hat{a}) \end{aligned}$$

quick math aside:

$$\begin{aligned} [\hat{a}, \hat{a}^\dagger] &= 1 \\ \hat{a} \hat{a}^\dagger - \hat{a}^\dagger \hat{a} &= 1 \\ \hat{a} \hat{a}^\dagger - \hat{N} &= 1 \\ \hat{a} \hat{a}^\dagger &= 1 + \hat{N} \end{aligned}$$

$$\begin{aligned} f(z) &= 1 + c^{(2)} (\hat{a}^\dagger \hat{a}^\dagger + (1 + \hat{N}) + \hat{N} + \hat{a} \hat{a}) \\ &= 1 + c^{(2)} + 2c^{(2)} \hat{N} + c^{(2)} (\hat{a}^\dagger \hat{a}^\dagger + \hat{a} \hat{a}) \end{aligned}$$

So this indicates that we must be very careful when adding an $f(z)$ term as we're trying to imply an effect that hasn't been seen before, so we ought to renormalize and keep the Rabi Frequency the same as what we saw before we knew there was a polynomial transition dipole.

$$f(z) = 1 - c^{(2)}(1 + 2\bar{n}_0) + c^{(2)} (\hat{a}^\dagger + \hat{a})^2$$

5.4.2 PROPER UNITARY DYNAMICS

According to Molmer and Sorenson's original paper, when you input both detunings to both ions, you get the following dynamics which are essentially a quantum process matrix... after a little bit

of algebra

$$\begin{aligned}
 |gg\rangle &\rightarrow \cos\left(\frac{\tilde{\Omega}T}{2}\right)|gg\rangle + i\sin\left(\frac{\tilde{\Omega}T}{2}\right)|ee\rangle \\
 |ee\rangle &\rightarrow \cos\left(\frac{\tilde{\Omega}T}{2}\right)|ee\rangle + i\sin\left(\frac{\tilde{\Omega}T}{2}\right)|gg\rangle \\
 |ge\rangle &\rightarrow \cos\left(\frac{\tilde{\Omega}T}{2}\right)|ge\rangle - i\sin\left(\frac{\tilde{\Omega}T}{2}\right)|eg\rangle \\
 |eg\rangle &\rightarrow \cos\left(\frac{\tilde{\Omega}T}{2}\right)|eg\rangle - i\sin\left(\frac{\tilde{\Omega}T}{2}\right)|ge\rangle
 \end{aligned}$$

If we want to know what the density matrix elements are, this requires some more work: being a bit more mathematically precise we get:

$$\begin{aligned}
 U(T)|gg\rangle &= \cos\left(\frac{\tilde{\Omega}T}{2}\right)|gg\rangle + i\sin\left(\frac{\tilde{\Omega}T}{2}\right)|ee\rangle \\
 U(T)|ee\rangle &= \cos\left(\frac{\tilde{\Omega}T}{2}\right)|ee\rangle + i\sin\left(\frac{\tilde{\Omega}T}{2}\right)|gg\rangle \\
 U(T)|ge\rangle &= \cos\left(\frac{\tilde{\Omega}T}{2}\right)|ge\rangle - i\sin\left(\frac{\tilde{\Omega}T}{2}\right)|eg\rangle \\
 U(T)|eg\rangle &= \cos\left(\frac{\tilde{\Omega}T}{2}\right)|eg\rangle - i\sin\left(\frac{\tilde{\Omega}T}{2}\right)|ge\rangle
 \end{aligned}$$

which will give us the elements of $U(T)$,

$$\begin{aligned}
 \langle gg|U(T)|gg\rangle &= \cos\left(\frac{\tilde{\Omega}T}{2}\right) \\
 \langle ee|U(T)|gg\rangle &= i\sin\left(\frac{\tilde{\Omega}T}{2}\right) \\
 \langle ee|U(T)|ee\rangle &= \cos\left(\frac{\tilde{\Omega}T}{2}\right) \\
 \langle gg|U(T)|ee\rangle &= i\sin\left(\frac{\tilde{\Omega}T}{2}\right) \\
 \langle ge|U(T)|ge\rangle &= \cos\left(\frac{\tilde{\Omega}T}{2}\right) \\
 \langle eg|U(T)|ge\rangle &= -i\sin\left(\frac{\tilde{\Omega}T}{2}\right) \\
 \langle eg|U(T)|eg\rangle &= \cos\left(\frac{\tilde{\Omega}T}{2}\right) \\
 \langle ge|U(T)|eg\rangle &= -i\sin\left(\frac{\tilde{\Omega}T}{2}\right)
 \end{aligned}$$

so there are all the nonzero elements of the time-evolution operator.

$$U(T) = \begin{bmatrix} \cos\left(\frac{\tilde{\Omega}T}{2}\right) & 0 & 0 & i\sin\left(\frac{\tilde{\Omega}T}{2}\right) \\ 0 & \cos\left(\frac{\tilde{\Omega}T}{2}\right) & -i\sin\left(\frac{\tilde{\Omega}T}{2}\right) & 0 \\ 0 & -i\sin\left(\frac{\tilde{\Omega}T}{2}\right) & \cos\left(\frac{\tilde{\Omega}T}{2}\right) & 0 \\ i\sin\left(\frac{\tilde{\Omega}T}{2}\right) & 0 & 0 & \cos\left(\frac{\tilde{\Omega}T}{2}\right) \end{bmatrix}$$

You can see from above that $U^\dagger U = I$ as we would expect. And we can use this operator to calculate the time-dependent density matrix through:

$$\begin{aligned}\rho(T) &= |\Psi(T)\rangle \langle \Psi(T)| \\ &= U(T) |\Psi(0)\rangle \langle \Psi(0)| U^\dagger(T) \\ &= U(T) \rho(0) U^\dagger(T)\end{aligned}$$

Part II

Other Electronic Spectroscopy Tools

This page intentionally left blank.

6

Getting Down to the Heart of Matter

Apart from minor modifications, this chapter originally appeared as:

“Getting Down to the Heart of Matter”. Goodknight, Joseph and Aspuru-Guzik Alan, *Science* (In Press)

ABSTRACT

Spectroscopy exploits the electromagnetic field to interrogate the properties of matter. If laser pulses are employed, in general, one can gain more information about matter the more laser pulses involved. Therefore, one of the main goals of the field has been the detection of signals involving many light-matter interaction events. Spencer et. al. report in *Nature Communications*⁴⁸ on the newest form of laser spectroscopy on the block: GAMERS (gradient-assisted multidimensional electronic Raman spectroscopy) and its application to several dye molecules. GAMERS uses 6 pulses to measure perhaps the most complex multidimensional spectroscopic signals yet obtained. GAMERS allows for the possibility of obtaining intricate detail on the coupling of electronic states to nuclear vibrational motion. Through this newly-gained insight into electron-nuclear coupling, GAMERS is poised to provide new information related to quantum dynamics involving perovskite solar cells⁶⁴, singlet fission materials⁶, quantum nanostructures⁵, and photosynthetic complexes¹². All of these systems exhibit details of the electronic-vibrational interactions that require further exploration and that have been the subject of several discussions in the literature.

Once pulsed lasers became available in the mid-20th century, the movement of molecules was

subject to scrutiny. The most basic spectroscopies which accomplishes this are those in the family of pump-probe methods. Pump probe techniques employ one laser beam to excite the molecule and then another which comes in after some time to probe what has happened since the pump. Pump probe gave many insights into chemical dynamics, and culminated in the 1999 Nobel Prize to Ahmed Zewail for his work in the field⁶³.

As pulses become shorter, so does the energy range they have to cover owing to the time-energy uncertainty principle $\Delta E \Delta t \geq \frac{\hbar}{2}$. Once ultra-fast pulses became commonplace, experimentalists began to replace the one pump (and probe) beam with two beams which, through controlling the spacing and careful data analysis, allowed different initial states to be created, and different final states detected.

These 4-pulse techniques are called 2D spectroscopies because of the two time-dimensions scanned: one in between the two pumps and the other between the two probes. This process generates a “map” of the energy that flows in, to the energy output detected as a function of the time gap between the pairs, providing great amounts of detail to study energy transfer during that gap. 2D techniques were first used in NMR, but eventually were employed in the Infrared to learn about many things about chemical vibrations³² and eventually in electronic spectroscopy to learn about electronic energy transfer in many different systems, including photosynthetic light harvesting systems^{12,22,45}.

The experiments on photosynthetic complexes discussed above generated a lot of discussion as they suggested that in certain cases, electronic excited states might be in a quantum coherent superposition that lasted long enough to transport like a wave, instead of like a particle—which would be slower—through an array of chromophores. If true, biomolecular engineering for sustaining wavelike transport, would be a of interest for basic and applied research. A use that would hopefully begat better light collection devices. Other groups, however, have emphasized the

role of molecular vibrations⁵². Enter the group of Prof. Elad Harel who we hope may have developed the methodology for finally settling this matter⁴⁸.

Austin Spencer, William Hudson and Prof. Harel have managed the complicated task of adding yet another pulse to a 2D Electronic spectroscopy. This additional pulse controls the initial vibrational state of the molecule. During the time between between the first and the second pulse, the vibrational state changes. By looking at the subsequent changes to the electronic coupling based on the starting vibrational state, Harel's team can determine how vibrations change the electronic coupling, which is not generally possible with other spectroscopies.

If one were to use traditional setups, a full set of data collection for a GAMERS experiment would require over a week to collect all necessary data points. That is technically very challenging because state of the art lasers are not guaranteed to be stable enough for that period of time. Therefore, a 6-pulse spectroscopy would be out of the question, if not for the ingenious GRAPES method developed by Harel, Engel and co-authors in 2011¹⁸ for 4 pulse spectroscopy. Instead of delaying two beams by physically changing the beam path and measuring in the same location, GRAPES tilts the two beams relative to each other (see beam 2 and 3 in Fig. 1) and takes the detection as a 2D image, thus performing all the necessary experiments at once and drastically reducing the time to solution. GAMERS uses the GRAPES technique for the delay between the middle two pulses, thus reducing the acquisition time from a week to mere hours.

There are some drawbacks, however. The GAMERS protocol requires a molecular vibration which is Raman-active. A Raman active vibration is one that allows light to scatter, losing energy to the vibration but not every vibration can accomplish this with a strong-enough signal. Furthermore, while there is no doubt that this is an experimental tour-de-force and some very useful information will come out, there is work to be done on the theory front to understand precisely what information GAMERS encodes. It may be particularly useful to consider GAMERS

in the context of Quantum-Process Tomography⁶² as the addition of more pulses makes the experiment probe more elements of the Quantum Process matrix.

The real power of GAMERS will be, as mentioned before, in its application for the understanding of several photophysical processes involved in systems related to light-harvesting processes and optoelectronics. We hope those experiments are forthcoming soon.

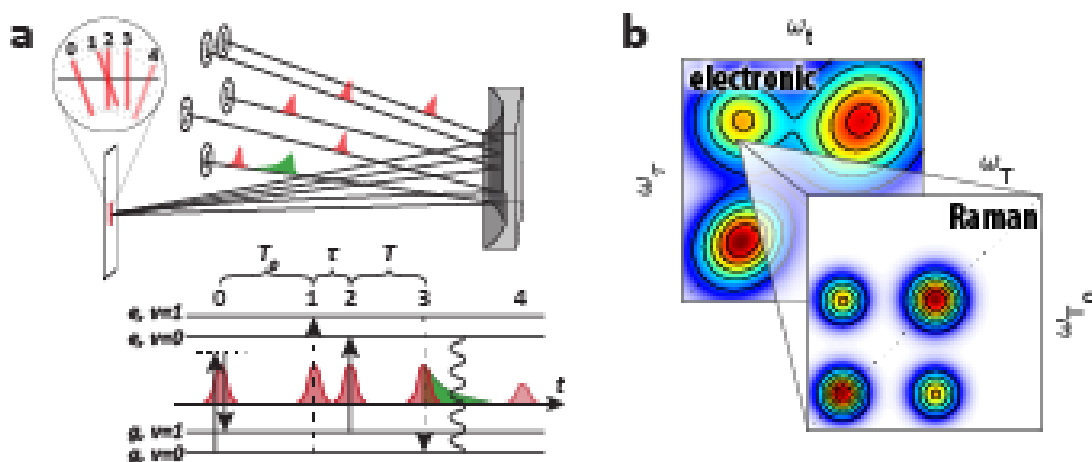


Figure 6.1: Reprinted and adapted from the original paper⁴⁸. **a** The top is a diagram of the 5 separate laser pulses focusing in to the target. The bottom part of the figure showing pulse the pulses coming in to the system; it also gives a sense for the experimental complexity involved: at minimum, T_0 , τ and T all have to be scanned without GRAPES¹⁸. Note the tilt between beams 1 and 2 in the circular inset, which is GRAPES' hallmark. Also note that the 0th pulse interacts with the system twice, which is why GAMERS is considered a 6-pulse experiment. **b** An example of the kind of 4-dimensional data they get, showing correlations between energy levels wherever there is signal where the pump(x) frequency is different from the probe(y) frequency.

7

Other Methods of Electronic Spectroscopy

7.1 TRANSIENT GRATING AS A WITNESS FOR ELECTRONIC COHERENCE

The work which came before me in References ^{23,60} was all using Pump-Probe Spectroscopy as the Tool. But then Juergen Hauer came to my collaborator Jacob Krich and wanted to know if he could perform the suggested electronic coherence witness with transient grating instead? WE then worked to see if it was possible.

7.1.1 PUMP PROBE

First a review on Pump Probe. Two beams coming at a target from different directions, separated by a time T , the signal comes out in the same direction as the second (or probe, pr) beam.

| Signal | Ket Interactions | Bra Interactions | Name |
|--------|------------------|------------------|--------------------------|
| 1 | pu+, pu-, pr+ | none | Ground State Bleach 1 |
| 2 | pu+, pr+ | pu+ | Excited State Absorption |
| 3 | pu+ | pu+, pr- | Stimulated Emission |
| 4 | pr+ | pu+, pu- | Ground State Bleach 2 |

$$E_1(t) = i \langle \psi_0(t) | \hat{\mu} | \psi_{pu+, pu-, pr+}(t) \rangle \quad (7.1.1)$$

$$E_2(t) = i \langle \psi_{pu+}(t) | \hat{\mu} | \psi_{pu+, pr+}(t) \rangle \quad (7.1.2)$$

$$E_3(t) = i \langle \psi_{pu+, pr-}(t) | \hat{\mu} | \psi_{pu+}(t) \rangle \quad (7.1.3)$$

$$E_4(t) = i \langle \psi_{pu+, pu-}(t) | \hat{\mu} | \psi_{pr+}(t) \rangle \quad (7.1.4)$$

$$E_{pp}(t) = E_1(t) + E_2(t) + E_3(t) + E_4(t) \quad (7.1.5)$$

$$S_{pp}(T) = 2\text{Re} \left[\int E_{pp}^*(t) E_{pr+}(t) dt \right] \quad (7.1.6)$$

7.1.2 TRANSIENT GRATING

There are three input beams all at different directions. The signal is then measured in the $k_1 - k_2 + k_3$ direction via means of a spectrometer or a 4th local oscillator beam. This allows a spectrum to be taken for every value of T because in a pump probe experiment, generally the local oscillator beam would be too intense to place a spectrometer in the path of the probe beam. The same effect can be had, however, by scanning the 4th local oscillator beam in time to get a signal in t_3 and then Fourier transforming. Thus what comes out is essentially a different absorption spectrum for every value of T . The terms in the grand electric field expansion are pretty much the same as pump probe with 1/2 substituting for pump and 3 substituting for probe and, if used, also the local oscillator 4 beam.

| Signal | Ket Interactions | Bra Interactions | Name |
|--------|------------------|------------------|--------------------------|
| a | 1+, 2-, 3+ | none | Ground State Bleach 1 |
| b | 1+, 3+ | 2+ | Excited State Absorption |
| c | 1+ | 2+, 3- | Stimulated Emission |
| d | 3+ | 2+, 1- | Ground State Bleach 2 |

$$E_a(t) = i \langle \psi_0(t) | \hat{\mu} | \psi_{1+, 2-, 3+}(t) \rangle \quad (7.1.7)$$

$$E_b(t) = i \langle \psi_{1+}(t) | \hat{\mu} | \psi_{2+, 3+}(t) \rangle \quad (7.1.8)$$

$$E_c(t) = i \langle \psi_{2+, 3-}(t) | \hat{\mu} | \psi_{1+}(t) \rangle \quad (7.1.9)$$

$$E_d(t) = i \langle \psi_{1+, 2-}(t) | \hat{\mu} | \psi_{3+}(t) \rangle \quad (7.1.10)$$

$$E_{TG}(T, t) = E_a(t) + E_b(t) + E_c(t) + E_d(t) \quad (7.1.11)$$

$$S_{TG}(T, \omega) = \left| \int E_{TG}(T, t) e^{-\omega t} dt \right|^2 \quad (7.1.12)$$

The last line or signal can differ based on the implementation of the experiment. Sometimes a local oscillator in the TG direction gets used to smooth out the signal although this comes at a considerable cost to acquisition time.

But say we do want a smooth signal, and use a local oscillator in the form of a fourth pulse and translate it's center forward from the location of the third pulse by an amount τ but while integrating the emitted electric field along laboratory time t to smooth out the signal:

$$S_{TG}(T, \tau) = \int E_4(t - \tau) \cdot E_{TG}(t) dt \quad (7.1.13)$$

If, however, we have a spectrometer in front of the signal we'd be measuring the Fourier transform:

$$\tilde{S}_{\text{TG}}(T, \omega) = \int e^{i\omega\tau} \int E_4(t - \tau) \cdot E_{\text{TG}}(T, t) dt d\tau \quad (7.1.14)$$

which we can manipulate to our advantage:

$$\tilde{S}_{\text{TG}}(T, \omega) = \int \left(\int e^{i\omega\tau} E_4(t - \tau) d\tau \right) \cdot E_{\text{TG}}(T, t) dt \quad (7.1.15)$$

substitute $u = t - \tau$

$$\tilde{S}_{\text{TG}}(T, \omega) = - \int \left(\int e^{i\omega(u+t)} \int E_4(u) du \right) \cdot E_{\text{TG}}(t) dt \quad (7.1.16)$$

$$= - \left(\int e^{i\omega u} E_4(u) du \right) \cdot \left(\int e^{i\omega t} E_{\text{TG}}(t) dt \right) \quad (7.1.17)$$

$$= -\tilde{E}_4(T, \omega) \cdot \tilde{E}_{\text{TG}}(T, \omega) \quad (7.1.18)$$

Notice we left out the dependence on T until the end: sorry about that. But what is the form of this Fourier transform? Assuming a standard Gaussian beam

$$E_4(t) = \frac{A}{\sqrt{2\pi\sigma^2}} e^{-i\omega_c(t-T)} e^{-\frac{(t-T)^2}{2\sigma^2}} \quad (7.1.19)$$

$$\tilde{E}_4(\omega) = \int_{-\infty}^{\infty} E_4(t) e^{i\omega t} dt \quad (7.1.20)$$

$$= \frac{A}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} e^{-i\omega_c(t-T)} e^{-\frac{(t-T)^2}{2\sigma^2}} e^{i\omega t} dt \quad (7.1.21)$$

$$= A e^{i\omega T} e^{-\frac{1}{2}\sigma^2(\omega - \omega_c)^2} \quad (7.1.22)$$

but if for whatever reason, we were to have defined the Fourier Transform integral as being using

$e^{-i\omega t}$, we'd get something different

$$\tilde{E}'_4(\omega) = Ae^{-i\omega T} e^{-\frac{1}{2}\sigma^2(\omega+\omega_c)^2} \quad (7.1.23)$$

So what are the relationships between these two different methods?

$$\tilde{E}'_4(-\omega) = \tilde{E}_4(\omega) \quad (7.1.24)$$

7.1.3 PUMP PROBE EQUIVALENCE WITH TRANSIENT GRATING

It is often said that we could integrate the transient grating signal to get the pump probe signal.

How is that?

$$S_{\text{TG}}(T, \omega) = \int e^{i\omega\tau} \int E_4(t - \tau) \cdot E_{\text{TG}}(t) dt d\tau \quad (7.1.25)$$

$$\int S_{\text{TG}}(T, \omega) d\omega = \int \int e^{i\omega\tau} \int E_4(t - \tau) \cdot E_{\text{TG}}(t) dt d\tau d\omega \quad (7.1.26)$$

$$= \int \int \left[\int e^{i\omega\tau} d\omega \right] E_4(t - \tau) \cdot E_{\text{TG}}(t) dt d\tau \quad (7.1.27)$$

$$= \int \int 2\pi\delta(\tau) E_4(t - \tau) \cdot E_{\text{TG}}(t) dt d\tau \quad (7.1.28)$$

$$= 2\pi \int E_4(t) \cdot E_{\text{TG}}(t) dt \quad (7.1.29)$$

7.1.4 PUMP PROBE FACSIMILES

There may come a time when you do not have access to the full, phased transient grating signal: you may be performing a transient grating experiment with just a spectrometer in the direction of

the signal output.

$$S_J(T, \omega) = |\tilde{E}_{TG}(\omega, T)|^n \quad (7.1.30)$$

$$= \left| \int e^{i\omega t} E_{TG}(t, T) dt \right|^n \quad (7.1.31)$$

$$= \left| \int e^{i\omega t} E_{TG}(t, T) dt \int e^{-i\omega t'} E_{TG}^*(t', T) dt' \right|^{\frac{n}{2}} \quad (7.1.32)$$

$$= \left| \int \int e^{i\omega(t-t')} E_{TG}(t, T) E_{TG}^*(t', T) dt dt' \right|^{\frac{n}{2}} \quad (7.1.33)$$

$$= |\tilde{E}_{TG}(\omega, T) \tilde{E}_{TG}^*(\omega, T)|^{\frac{n}{2}} \quad (7.1.34)$$

Now we would take an integral over the frequency space to try and understand this. I use Σ instead of S for this pump probe because it's kind of like S , but not quite.

$$\Sigma_{PP}(T) = \int S_J(T, \omega) d\omega \quad (7.1.35)$$

$$= \int |\tilde{E}_{TG}(\omega, T)|^n d\omega \quad (7.1.36)$$

$$= \int (\tilde{E}_{TG}(\omega, T) [\tilde{E}_{TG}(\omega, T)]^*)^{\frac{n}{2}} d\omega \quad (7.1.37)$$

$$= \int \left(\Re [\tilde{E}_{TG}(\omega, T)]^2 - \Im [\tilde{E}_{TG}(\omega, T)]^2 \right)^{\frac{n}{2}} d\omega \quad (7.1.38)$$

$$= \int \left[(\Re [\tilde{E}_{TG}(\omega, T)] + \Im [\tilde{E}_{TG}(\omega, T)]) (\Re [\tilde{E}_{TG}(\omega, T)] - \Im [\tilde{E}_{TG}(\omega, T)]) \right]^{\frac{n}{2}} d\omega \quad (7.1.39)$$

Let's simplify by making the simplification $E_{TG}(t, T) = f(t, T)$

$$\Sigma_{PP}(T) = \int \left[(\Re [\tilde{f}(\omega, T)] + \Im [\tilde{f}(\omega, T)]) (\Re [\tilde{f}(\omega, T)] - \Im [\tilde{f}(\omega, T)]) \right]^{\frac{n}{2}} d\omega \quad (7.1.40)$$

Let's look at these separately since things are getting crowded

$$(\Re [\tilde{f}(\omega, T)] + \Im [\tilde{f}(\omega, T)]) \quad (7.1.41)$$

$$= \frac{1}{\sqrt{2\pi}} \int (\cos(\omega t) \Re [f(t)] - \sin(\omega t) \Im [f(t)] + \cos(\omega t) \Im [f(t)] + \sin(\omega t) \Re [f(t)]) dt \quad (7.1.42)$$

$$= \frac{1}{\sqrt{2\pi}} \int ((\cos(\omega t) + \sin(\omega t)) \Re [f(t)] + (\cos(\omega t) - \sin(\omega t)) \Im [f(t)]) dt \quad (7.1.43)$$

$$= \frac{1}{\sqrt{2\pi}} \int \left(\sqrt{2} \sin \left(\omega t + \frac{\pi}{4} \right) \Re [f(t)] - \sqrt{2} \sin \left(\omega t - \frac{\pi}{4} \right) \Im [f(t)] \right) dt \quad (7.1.44)$$

$$= \frac{1}{\sqrt{\pi}} \int \left(\sin \left(\omega t + \frac{\pi}{4} \right) \Re [f(t)] - \sin \left(\omega t - \frac{\pi}{4} \right) \Im [f(t)] \right) dt \quad (7.1.45)$$

and the other one:

$$(\Re [\tilde{f}(\omega, T)] - \Im [\tilde{f}(\omega, T)]) \quad (7.1.46)$$

$$= \frac{1}{\sqrt{2\pi}} \int (\cos(\omega t) \Re [f(t)] - \sin(\omega t) \Im [f(t)] - \cos(\omega t) \Im [f(t)] - \sin(\omega t) \Re [f(t)]) dt \quad (7.1.47)$$

$$= \frac{1}{\sqrt{2\pi}} \int ((\cos(\omega t) - \sin(\omega t)) \Re [f(t)] - (\cos(\omega t) + \sin(\omega t)) \Im [f(t)]) dt \quad (7.1.48)$$

$$= \frac{1}{\sqrt{2\pi}} \int \left(-\sqrt{2} \sin \left(\omega t - \frac{\pi}{4} \right) \Re [f(t)] - \sqrt{2} \sin \left(\omega t + \frac{\pi}{4} \right) \Im [f(t)] \right) dt \quad (7.1.49)$$

$$= \frac{-1}{\sqrt{\pi}} \int \left(\sin \left(\omega t - \frac{\pi}{4} \right) \Re [f(t)] + \sin \left(\omega t + \frac{\pi}{4} \right) \Im [f(t)] \right) dt \quad (7.1.50)$$

$$= \frac{-1}{\sqrt{\pi}} \int \left(\sin \left(\omega t' - \frac{\pi}{4} \right) \Re [f(t')] + \sin \left(\omega t' + \frac{\pi}{4} \right) \Im [f(t')] \right) dt' \quad (7.1.51)$$

with that last step just being so we can recombine the two integrals

$$(\Re [\tilde{f}(\omega, T)] + \Im [\tilde{f}(\omega, T)]) (\Re [\tilde{f}(\omega, T)] - \Im [\tilde{f}(\omega, T)]) \quad (7.1.52)$$

$$= \frac{-1}{\pi} \int \int \left(\sin \left(\omega t' - \frac{\pi}{4} \right) \Re [f(t')] + \sin \left(\omega t' + \frac{\pi}{4} \right) \Im [f(t')] \right) \times \quad (7.1.53)$$

$$\left(\sin \left(\omega t + \frac{\pi}{4} \right) \Re [f(t)] - \sin \left(\omega t - \frac{\pi}{4} \right) \Im [f(t)] \right) dt dt' \quad (7.1.54)$$

$$= \frac{-1}{2\pi} \int \int \Re [f(t')] \Re [f(t)] (\sin(\omega(t-t')) - \cos(\omega(t+t'))) + \quad (7.1.55)$$

$$\Re [f(t')] \Im [f(t)] (\sin(\omega(t+t')) - \cos(\omega(t-t'))) + \quad (7.1.56)$$

$$\Im [f(t')] \Re [f(t)] (-\sin(\omega(t-t')) - \cos(\omega(t+t'))) + \quad (7.1.57)$$

$$\Im [f(t')] \Im [f(t)] (\sin(\omega(t+t')) - \cos(\omega(t-t'))) dt dt' \quad (7.1.58)$$

7.1.5 EXPERIMENTAL CONSIDERATIONS

If an experimentalist puts the output of a TG experiment into a spectrometer AND include a local oscillator beam at the same time as the third pulse, you would then be measuring:

$$I(\omega) = I_{LO}(\omega) + 2\Re [E_{TG}^*(\omega)E_{LO}(\omega)] + I_{TG}(\omega)$$

It is easy to measure $I_{LO}(\omega)$ by just putting it in the spectrometer by itself. Then, we can assume that $I_{TG}(\omega) \ll 2\Re [E_{TG}^*(\omega)E_{LO}(\omega)]$ because we expect the power of the laser to be very high.

Which means the experimenter will be measuring just the interference term:

$$I(\omega) = 2\Re E_{TG}^*(\omega)E_{LO}(\omega)$$

But is there a way to extract the magnitude of the transient grating electric field from just this measured intensity? Generally the Local oscillator signal will look like a very general Gaussian:

$$E_{LO}(t) = E_0 e^{-\frac{(t-T)^2}{2\sigma^2}} e^{-i(\omega_c(t-T) + \phi_{LO}(\omega))}$$

$$\tilde{E}_{LO}(\omega) = E'_0 e^{i\omega T} e^{-i\phi(\omega)} e^{-\frac{\sigma^2}{2}(\omega - \omega_c)^2}$$

or more generally, if all we know is that the laser beam is centered at a specific time T :

$$E_{LO}(t) = V(t - T)$$

$$\tilde{E}_{LO}(\omega) = \tilde{V}(\omega) e^{i\omega T}$$

$$= |\tilde{E}_{LO}(\omega)| e^{i\omega T - i\phi_{LO}(\omega)}$$

But we don't want that constant phase factor as we don't really know what it is; it is rather hard to measure. We can, however, get rid of it. If we take the frequency signal and Fourier transform it into the time-domain (we'll call the resultant function B), we'll get:

$$B(t) = 2 \int e^{-i\omega t} \Re [E_{TG}^*(\omega) E_{LO}(\omega)] d\omega$$

$$= 2 \int e^{-i\omega t} \Re \left[|E_{TG}(\omega)| e^{-i\phi_{TG}(\omega)} |E_{LO}(\omega)| e^{i(\omega T - \phi_{LO}(\omega))} \right] d\omega$$

$$= 2 \int e^{-i\omega t} |E_{TG}(\omega)| |E_{LO}(\omega)| \Re \left[e^{-i\phi_{TG}(\omega)} e^{i(\omega T - \phi_{LO}(\omega))} \right] d\omega$$

$$= 2 \int e^{-i\omega t} |E_{TG}(\omega)| |E_{LO}(\omega)| \cos(\omega T + \phi(\omega)) d\omega$$

where $\phi(\omega) = \phi_{TG}(\omega) - \phi_{LO}(\omega)$ to make things easier to write, I will define

$$A(\omega) = |E_{TG}(\omega)| |E_{LO}(\omega)|$$

$$\begin{aligned} B(t) &= 2 \int e^{-i\omega t} A(\omega) \cos(\omega T + \phi(\omega)) d\omega \\ &= \int e^{-i\omega t} A(\omega) \left(e^{-i(\omega T + \phi(\omega))} + e^{i(\omega T + \phi(\omega))} \right) d\omega \\ &= \int A(\omega) \left(e^{-i(\omega(t+T) + \phi(\omega))} + e^{-i(\omega(t-T) - \phi(\omega))} \right) d\omega \\ &= \int \left(A(\omega) e^{-i(\omega(t+T) + \phi(\omega))} + A(\omega) e^{-i(\omega(t-T) - \phi(\omega))} \right) d\omega \\ &= \int \left(A(\omega) e^{-i\phi(\omega)} e^{-i\omega(t+T)} + A(\omega) e^{i\phi(\omega)} e^{-i\omega(t-T)} \right) d\omega \\ &= \tilde{A}_-(t+T) + \tilde{A}_+(t-T) \end{aligned}$$

which we can then filter out one of these terms numerically to get $B'(t)$:

$$B'(t) = \tilde{A}_+(t-T)$$

This does assume that there will be two distinct humps of signal centered at the positive and negative time of the Local oscillator. Assuming this is true, then we Fourier transform back into frequency space:

$$\begin{aligned} C(\omega) &= \int e^{i\omega t} \tilde{A}_+(t-T) dt \\ &= A(\omega) e^{-i(\omega T + \phi(\omega))} \end{aligned}$$

Which we can then take the absolute value of:

$$|C(\omega)| = A(\omega) = |E_{TG}(\omega)| |E_{LO}(\omega)|$$

and divide by the relatively easily measurable $|E_{LO}(\omega)|$

$$\frac{|C(\omega)|}{|E_{LO}(\omega)|} = |E_{TG}(\omega)|$$

and we now have the transient grating intensity without the effect of the phase of the pulse messing it up at all.

7.1.6 DELTA-FUNCTION PULSE LIMIT FOR A TWO LEVEL SYSTEM WITH ONE VIBRATIONAL COORDINATE

We now want to ask ourselves, what is the precise form of $E_{TG}(\omega)$ when the pulses used to generate it are delta-functions. Let us remember what goes into the delta function pulses:

| Signal | Ket Interactions | Bra Interactions | Name |
|--------|------------------|------------------|------|
| a | 1+, 2-, 3+ | none | GSB |
| b | 1+, 3+ | 2+ | ESA |
| c | 1+ | 2+, 3- | SE |
| d | 3+ | 2+, 1- | GSB |

$$E_a(t) = i \langle \psi_0(t) | \hat{\mu} | \psi_{1+, 2-, 3+}(t) \rangle \quad (7.1.59)$$

$$E_b(t) = i \langle \psi_{1+}(t) | \hat{\mu} | \psi_{2+, 3+}(t) \rangle \quad (7.1.60)$$

$$E_c(t) = i \langle \psi_{2+, 3-}(t) | \hat{\mu} | \psi_{1+}(t) \rangle \quad (7.1.61)$$

$$E_d(t) = i \langle \psi_{1+, 2-}(t) | \hat{\mu} | \psi_{3+}(t) \rangle \quad (7.1.62)$$

$$E_{TG}(T, t) = E_a(t) + E_b(t) + E_c(t) + E_d(t) \quad (7.1.63)$$

We can borrow liberally from our earlier work on pump probe.

$$|\psi_0(t)\rangle = e^{-i\omega_{(\eta)}t} |\eta_\gamma\rangle |g\rangle \quad (7.1.64)$$

$$|\psi_{1+}(t)\rangle = -\frac{i}{\hbar} E_0 \mu \sum_j O_\eta^j e^{-i\omega^{(j)}t} |j_\epsilon\rangle |e\rangle = |\psi_{2+}(t)\rangle \quad (7.1.65)$$

$$|\psi_{3+}(t)\rangle = -\frac{i}{\hbar} E_0 \mu e^{-i\omega_{(\eta)}T} H(t-T) \sum_j O_\eta^j e^{-i\omega^{(j)}(t-T)} |j_\epsilon\rangle |e\rangle \quad (7.1.66)$$

$$|\psi_{1+,2-}(t)\rangle = -\frac{1}{\hbar^2} E_0^2 \mu^2 e^{-i\omega_{(\eta)}t} |\eta_\gamma\rangle |g\rangle \quad (7.1.67)$$

$$|\psi_{1+,3-}(t)\rangle = -\frac{1}{\hbar^2} E_0^2 \mu^2 H(t-T) \sum_{j,k} O_\eta^j O_k^j e^{-i\omega^{(j)}T} e^{-i\omega^{(k)}(t-T)} |k_\gamma\rangle |g\rangle \quad (7.1.68)$$

$$|\psi_{1+,2-,3+}(t)\rangle = \frac{i}{\hbar^3} E_0^3 \mu^3 e^{-i\omega_{(\eta)}T} H(t-T) \sum_j O_\eta^j e^{-i\omega^{(j)}(t-T)} |j_\epsilon\rangle |e\rangle \quad (7.1.69)$$

Now we can begin to calculate the components.

$$E_a(T, t) = i \langle \psi_0(t) | \hat{\mu} | \psi_{1+, 2-, 3+}(t) \rangle \quad (7.1.70)$$

$$= i \left(e^{-i\omega_{(\eta)}t} |\eta_\gamma\rangle |g\rangle \right)^\dagger \hat{\mu} \left(\frac{i}{\hbar^3} E_0^3 \mu^3 e^{-i\omega_{(\eta)}T} H(t-T) \sum_j O_\eta^j e^{-i\omega^{(j)}(t-T)} |j_\epsilon\rangle |e\rangle \right) \quad (7.1.71)$$

$$= -\frac{1}{\hbar^3} E_0^3 \mu^4 e^{i\omega_{(\eta)}t} e^{-i\omega_{(\eta)}T} H(t-T) \sum_j O_\eta^j O_\eta^j e^{-i\omega^{(j)}(t-T)} \quad (7.1.72)$$

$$= -\frac{1}{\hbar^3} E_0^3 \mu^4 H(t-T) \sum_j O_\eta^j O_\eta^j e^{-i\omega_{(\eta)}(t-T)} \quad (7.1.73)$$

on to the b signal... except it's zero because this is two level system. Instead we continue with c:

$$E_c(t) = i \langle \psi_{2+, 3-}(t) | \hat{\mu} | \psi_{1+}(t) \rangle \quad (7.1.74)$$

$$= i \left(-\frac{1}{\hbar^2} E_0^2 \mu^2 H(t-T) \sum_{j,k} O_\eta^j O_k^j e^{-i\omega^{(j)}T} e^{-i\omega_{(k)}(t-T)} |k_\gamma\rangle |g\rangle \right)^\dagger \hat{\mu} \left(-\frac{i}{\hbar} E_0 \mu \sum_l O_\eta^l e^{-i\omega^{(l)}t} |l_\epsilon\rangle |e\rangle v \right) \quad (7.1.75)$$

$$= -\frac{1}{\hbar^3} E_0^3 \mu^4 H(t-T) \sum_{j,k,l} O_\eta^j O_k^j e^{i\omega^{(j)}T} e^{i\omega_{(k)}(t-T)} O_\eta^l e^{-i\omega^{(l)}t} O_k^l \quad (7.1.76)$$

$$= -\frac{1}{\hbar^3} E_0^3 \mu^4 H(t-T) \sum_{j,k,l} O_\eta^j O_k^j O_\eta^l O_k^l e^{i\omega_{(k)}^{(j)}T} e^{-i\omega_{(k)}^{(l)}t} \quad (7.1.77)$$

Well... THAT is not pretty but it is what it is. Now for the final signal:

$$E_d(t) = i \langle \psi_{1+, 2-}(t) | \hat{\mu} | \psi_{3+}(t) \rangle \quad (7.1.78)$$

$$= i \left(-\frac{1}{\hbar^2} E_0^2 \mu^2 e^{-i\omega_{(\eta)}t} |\eta_\gamma\rangle |g\rangle \right)^\dagger \hat{\mu} \left(-\frac{i}{\hbar} E_0 \mu e^{-i\omega_{(\eta)}T} H(t-T) \sum_j O_\eta^j e^{-i\omega^{(j)}(t-T)} |j_\epsilon\rangle |e\rangle \right) \quad (7.1.79)$$

$$= -\frac{1}{\hbar^3} E_0^3 \mu^4 H(t-T) \sum_j O_\eta^j O_\eta^j e^{-i\omega_{(\eta)}^{(j)}(t-T)} \quad (7.1.80)$$

OK, we are all set and ready to continue. I do think it will be good to work in the Fourier domain instead.

$$\tilde{f}(\Omega, \omega) = \int \int e^{i\Omega T} e^{i\omega t} H(t-T) e^{\omega_a t} e^{\Omega_a T} dT dt \quad (7.1.81)$$

$$= \sqrt{2\pi} \delta(\Omega + \Omega_a + \omega + \omega_a) \left[\frac{-i}{\Omega + \Omega_a} + \pi \delta(\Omega + \Omega_a) \right] \quad (7.1.82)$$

We have two options here. We can consider the effect of the Heaviside theta function or just assume that we don't care about it for the time being and assume a nice, clean Fourier Transform

with two delta functions. We will employ the latter strategy at this point:

$$\tilde{E}_{SE}(\Omega, \omega) = -\frac{1}{\hbar^3} E_0^3 \mu^4 \sum_{j,k,l} O_\eta^j O_k^j O_\eta^l O_k^l \delta(\Omega - \omega_{(k)}^{(j)}) \delta(\omega + \omega_{(k)}^{(l)}) \quad (7.1.83)$$

This is interesting

$$\tilde{E}_{GSB}(\Omega, \omega) = -\frac{2}{\hbar^3} E_0^3 \mu^4 \sum_j O_\eta^j O_\eta^j \delta(\Omega - \omega_{(\eta)}^{(j)}) \delta(\omega + \omega_{(\eta)}^{(j)}) \quad (7.1.84)$$

We are looking for cancellations so we will start with the GSB terms and see if there are matches in the SE term. Considering that the GSB term is only nonzero when the population and laboratory time frequencies are the negative of each other, that simplifies things:

$$\tilde{E}_{GSB}(\omega_{(\eta)}^{(j)}, -\omega_{(\eta)}^{(j)}) = -\frac{2}{\hbar^3} E_0^3 \mu^4 O_\eta^j O_\eta^j [\delta(0)]^2 \quad (7.1.85)$$

so we look at similar terms in the stimulated emission signal:

$$\tilde{E}_{SE}(\omega_{(\eta)}^{(j)}, -\omega_{(\eta)}^{(j)}) = -\frac{1}{\hbar^3} E_0^3 \mu^4 O_\eta^j O_\eta^j O_\eta^j O_\eta^j [\delta(0)]^2 \quad (7.1.86)$$

7.1.7 TRANSIENT GRATING FOR A COHERENT MONOMER

Using our previous definitions for the Transient Grating signal, we can begin to calculate the components.

$$E_a(T, t) = i \langle \psi_0(t) | \hat{\mu} | \psi_{1+, 2-, 3+}(t) \rangle \quad (7.1.87)$$

$$= i \left(e^{-i\omega(\eta)t} | \eta_\gamma \rangle | g \rangle \right)^\dagger \hat{\mu} \left(\frac{i}{\hbar^3} E_0^3 \mu^3 e^{-i\omega(\eta)T} H(t-T) H(t) \sum_j O_\eta^j e^{-i\omega^{(j)}(t-T)} | j_\epsilon \rangle | e \rangle \right) \quad (7.1.88)$$

$$= -\frac{1}{\hbar^3} E_0^3 \mu^4 e^{i\omega(\eta)t} e^{-i\omega(\eta)T} H(t-T) H(t) \sum_j O_\eta^j O_\eta^j e^{-i\omega^{(j)}(t-T)} \quad (7.1.89)$$

$$= -\frac{1}{\hbar^3} E_0^3 \mu^4 H(t-T) H(t) \sum_j O_\eta^j O_\eta^j e^{-i\omega^{(j)}(t-T)} \quad (7.1.90)$$

on to the b signal... except it's zero because this is two level system. Instead we continue with c:

$$E_c(t) = i \langle \psi_{2+, 3-}(t) | \hat{\mu} | \psi_{1+}(t) \rangle \quad (7.1.91)$$

$$= i \left(-\frac{1}{\hbar^2} E_0^2 \mu^2 H(t-T) H(t) \sum_{j,k} O_\eta^j O_k^j e^{-i\omega^{(j)}T} e^{-i\omega^{(k)}(t-T)} | k_\gamma \rangle | g \rangle \right)^\dagger \hat{\mu} \left(-\frac{i}{\hbar} E_0 \mu \sum_l O_\eta^l e^{-i\omega^{(l)}t} | l_\epsilon \rangle | e \rangle \nu \right) \quad (7.1.92)$$

$$= -\frac{1}{\hbar^3} E_0^3 \mu^4 H(t-T) H(t) \sum_{j,k,l} O_\eta^j O_k^j e^{i\omega^{(j)}T} e^{i\omega^{(k)}(t-T)} O_\eta^l e^{-i\omega^{(l)}t} O_k^l \quad (7.1.93)$$

$$= -\frac{1}{\hbar^3} E_0^3 \mu^4 H(t-T) H(t) \sum_{j,k,l} O_\eta^j O_k^j O_\eta^l O_k^l e^{i\omega^{(j)}T} e^{-i\omega^{(k)}t} \quad (7.1.94)$$

Well... THAT is not pretty but it is what it is. Now for the final signal:

$$E_d(t) = i \langle \psi_{1+, 2-}(t) | \hat{\mu} | \psi_{3+}(t) \rangle \quad (7.1.95)$$

$$= i \left(-\frac{1}{\hbar^2} E_0^2 \mu^2 H(t) e^{-i\omega(\eta)t} | \eta_\gamma \rangle | g \rangle \right)^\dagger \hat{\mu} \left(-\frac{i}{\hbar} E_0 \mu e^{-i\omega(\eta)T} H(t-T) \sum_j O_\eta^j e^{-i\omega^{(j)}(t-T)} | j_\epsilon \rangle | e \rangle \right) \quad (7.1.96)$$

$$= -\frac{1}{\hbar^3} E_0^3 \mu^4 H(t-T) H(t) \sum_j O_\eta^j O_\eta^j e^{-i\omega^{(j)}(t-T)} \quad (7.1.97)$$

7.1.7.1 ANALYZING THE SIGNAL WITHOUT DECAY CONSTANTS: LIMITED COLLECTION TIME

if instead we keep out the step of introducing decay constants, we will get a different expression:

$$S_{obs}(\omega, T) = F \left| \int_{-\infty}^{\infty} e^{i\omega t} \sum_{a,b} C_{a,b} H(t-T) H(t) e^{i\omega_a t} e^{i\Omega_b T} dt \right|^n$$

But this won't do much either. We need to recognize, here, that the spectrometer will only be measuring the modes for a certain amount of time, making this expression more correct:

$$S_{obs}(\omega, T) = F \left| \int_0^{T_D} e^{i\omega t} \sum_{a,b} C_{a,b} H(t-T) e^{i\omega_a t} e^{i\Omega_b T} dt \right|^n$$

where T_D is the amount of time the detector is on for. We can now simplify from here:

$$\begin{aligned} S_{PP}(T) &= F' \int_{-\infty}^{\infty} \left| \sum_{a,b} C_{a,b} \frac{e^{i\Omega_b T}}{\omega + \omega_a} \left(e^{i(\omega + \omega_a)T} - e^{i(\omega + \omega_a)T_D} \right) \right|^n d\omega \\ &= F' \int_{-\infty}^{\infty} \left[\sum_{a,b,c,d} C_{a,b} C_{c,d}^* \frac{e^{i(\Omega_b - \Omega_d)T}}{(\omega + \omega_a)(\omega + \omega_c)} \left(e^{i(\omega + \omega_a)T} - e^{i(\omega + \omega_a)T_D} \right) \left(e^{-i(\omega + \omega_c)T} - e^{-i(\omega + \omega_c)T_D} \right) \right]^{n/2} d\omega \\ &= F' \int_{-\infty}^{\infty} \left[\sum_{a,b,c,d} C_{a,b} C_{c,d}^* \frac{e^{i(\Omega_b - \Omega_d)T}}{(\omega + \omega_a)(\omega + \omega_c)} \left(e^{i(\omega_a - \omega_c)T} - e^{i(\omega_a - \omega_c)T_D} + \dots \right) \right]^{n/2} d\omega \end{aligned}$$

7.1.7.2 ANALYZING THE SIGNAL WITH DECAY CONSTANTS

Now that the signal is all put together, we are left with how to deal with it. In general, we now have this object:

$$E_{TG}(t, T) = \sum_{a,b} C_{a,b} H(t-T) H(t) e^{i\omega_a t} e^{i\Omega_b T} \quad (7.1.98)$$

but our experimentalist friends are actually only getting the Fourier transform of the laboratory time variable and on top of that, only the absolute value of the entire thing and then applying some power to it in processing. So we define the observed signal as

$$S_{obs}(\omega, T) = F \left| \int_{-\infty}^{\infty} e^{i\omega t} \sum_{a,b} C_{a,b} H(t-T) H(t) e^{i\omega_a t} e^{i\Omega_b T} dt \right|^n \quad (7.1.99)$$

$$= F \left| \sum_{a,b} C_{a,b} e^{i\Omega_b T} \left[\pi \delta(\omega + \omega_a) + i \frac{e^{i(\omega + \omega_a)T}}{\omega + \omega_a} \right] dt \right|^n \quad (7.1.100)$$

but this is not true, as all good things must come to an end, every signal will decay and indeed, that fact should make our calculations much easier:

$$S_{obs}(\omega, T) = F \left| \int_{-\infty}^{\infty} e^{i\omega t} \sum_{a,b} C_{a,b} H(t-T) H(t) e^{i\omega_a t - \gamma_a t} e^{i\Omega_b T - \Gamma_b T} dt \right|^n \quad (7.1.101)$$

$$= F \left| \sum_{a,b} C_{a,b} e^{i\Omega_b T - (\Gamma_b + \gamma_a)T} \left[\frac{e^{\gamma_a T} H(-T) - e^{i(\omega + \omega_a)T} (H(-T) - 1)}{\gamma_a - i(\omega + \omega_a)} \right] \right|^n \quad (7.1.102)$$

for the time being, we only consider positive population times because although we can get that data, I don't think experimentalists normally do:

$$S_{obs}(\omega, T) = F \left| \sum_{a,b} C_{a,b} e^{i\Omega_b T - (\Gamma_b + \gamma_a)T} \left[\frac{e^{i(\omega + \omega_a)T}}{\gamma_a - i(\omega + \omega_a)} \right] \right|^n \quad (7.1.103)$$

this seems eminently calculable. We know from our previous calculations that $C_{a,b}$ is entirely real, but may be negative so we proceed with caution of simplifications involving that term. We also note that the facsimile we create for the pump probe signal involves integration over the laboratory time frequency ω :

$$S_{\bar{P}P}(T) = F \int_{-\infty}^{\infty} \left| \sum_{a,b} C_{a,b} \frac{e^{i(\Omega_b + \omega + \omega_a)T - (\Gamma_b + \gamma_a)T}}{\gamma_a - i(\omega + \omega_a)} \right|^n d\omega \quad (7.1.104)$$

$$= F \int_{-\infty}^{\infty} \left[\sum_{a,b,c,d} C_{a,b} \frac{e^{i(\Omega_b + \omega + \omega_a)T - (\Gamma_b + \gamma_a)T}}{\gamma_a - i(\omega + \omega_a)} C_{c,d}^* \frac{e^{-i(\Omega_d + \omega + \omega_c)T - (\Gamma_d + \gamma_c)T}}{\gamma_c + i(\omega + \omega_c)} \right]^{n/2} d\omega \quad (7.1.105)$$

$$= F \int_{-\infty}^{\infty} \left[\sum_{a,b,c,d} C_{a,b} \frac{e^{i(\Omega_b + \omega_a)T - (\Gamma_b + \gamma_a)T}}{\gamma_a - i(\omega + \omega_a)} C_{c,d}^* \frac{e^{-i(\Omega_d + \omega_c)T - (\Gamma_d + \gamma_c)T}}{\gamma_c + i(\omega + \omega_c)} \right]^{n/2} d\omega \quad (7.1.106)$$

$$= F \int_{-\infty}^{\infty} \left[\sum_{a,b,c,d} \Theta_{a,b,c,d} \frac{e^{i(\Omega_b + \omega_a - \Omega_d - \omega_c)T - (\Gamma_b + \gamma_a + \Gamma_d + \gamma_c)T}}{[\gamma_a - i(\omega + \omega_a)][\gamma_c + i(\omega + \omega_c)]} \right]^{n/2} d\omega \quad (7.1.107)$$

so we now find the Fourier transform of this pseudo-pump-probe signal:

$$\tilde{S}_{\bar{P}P}(\Omega) = \int_0^{\infty} e^{i\Omega T} \left(F \int_{-\infty}^{\infty} \left[\sum_{a,b,c,d} \Theta_{a,b,c,d} \frac{e^{i(\Omega_b + \omega_a - \Omega_d - \omega_c)T - (\Gamma_b + \gamma_a + \Gamma_d + \gamma_c)T}}{[\gamma_a - i(\omega + \omega_a)][\gamma_c + i(\omega + \omega_c)]} \right]^{n/2} d\omega \right) dT \quad (7.1.108)$$

OK, well at this point it's painfully clear because of the 4-index summation underneath a possibly fractional power, that anything other than $n = 2$ is going to be very hard if not impossible to calculate so we'll work with just $n = 2$ that going forward.

$$\tilde{S}_{\bar{P}P}^{(2)}(\Omega) = \int_0^{\infty} e^{i\Omega T} \left(F \int_{-\infty}^{\infty} \sum_{a,b,c,d} \Theta_{a,b,c,d} \frac{e^{i(\Omega_b + \omega_a - \Omega_d - \omega_c)T - (\Gamma_b + \gamma_a + \Gamma_d + \gamma_c)T}}{[\gamma_a - i(\omega + \omega_a)][\gamma_c + i(\omega + \omega_c)]} d\omega \right) dT \quad (7.1.109)$$

$$= \int_0^{\infty} e^{i\Omega T} \left(F \sum_{a,b,c,d} \Theta_{a,b,c,d} \frac{2\pi e^{i(\omega_a - \omega_c + \Omega_b - \Omega_d)T - (\Gamma_b + \gamma_a + \Gamma_d + \gamma_c)T}}{\gamma_a + \gamma_c - i(\omega_a - \omega_c)} \right) dT \quad (7.1.110)$$

now we can continue with the second Fourier transform,

$$\tilde{S}_{\bar{P}\bar{P}}^{(2)}(\Omega) = F' \int_0^\infty e^{i\Omega T} \sum_{a,b,c,d} \Theta_{a,b,c,d} \frac{e^{i(\omega_a - \omega_c + \Omega_b - \Omega_d)T - (\Gamma_b + \gamma_a + \Gamma_d + \gamma_c)T}}{\gamma_a + \gamma_c - i(\omega_a - \omega_c)} dT \quad (7.1.111)$$

$$= F' \sum_{a,b,c,d} \frac{\Theta_{a,b,c,d}}{[\gamma_a + \gamma_c - i(\omega_a - \omega_c)] [\Gamma_b + \gamma_a + \Gamma_d + \gamma_c - i(\Omega + \omega_a - \omega_c + \Omega_b - \Omega_d)]} \quad (7.1.112)$$

Now we can indulge in the whole point of this exercise: taking all the decay constants to zero,

$$\tilde{S}_{\bar{P}\bar{P}}^{(2)}(\Omega) = -F' \sum_{a,b,c,d} \frac{\Theta_{a,b,c,d}}{(\omega_a - \omega_c)(\Omega + \omega_a - \omega_c + \Omega_b - \Omega_d)} \quad (7.1.113)$$

7.1.7.3 NO DECAY CONSTANTS: “INFINITE” COLLECTION TIME

We can return to the form of the expression before we introduced the decay constants which had a delta-function term in addition to the sinc-like term.

$$S_{\bar{P}\bar{P}}(T) = F \int_{-\infty}^{\infty} \left| \sum_{a,b} C_{a,b} e^{i\Omega_b T} \left[\pi \delta(\omega + \omega_a) + i \frac{e^{i(\omega + \omega_a)T}}{\omega + \omega_a} \right] \right|^n d\omega \quad (7.1.114)$$

$$= F \int_{-\infty}^{\infty} \left[\sum_{a,b,c,d} C_{a,b} e^{i\Omega_b T} \left[\pi \delta(\omega + \omega_a) + i \frac{e^{i(\omega + \omega_a)T}}{\omega + \omega_a} \right] C_{c,d}^* e^{-i\Omega_d T} \left[\pi \delta(\omega + \omega_c) - i \frac{e^{-i(\omega + \omega_c)T}}{\omega + \omega_c} \right] \right]^{n/2} d\omega \quad (7.1.115)$$

$$= F \int_{-\infty}^{\infty} \left[\sum_{a,b,c,d} C_{a,b} C_{c,d}^* e^{i(\Omega_b - \Omega_d)T} \left[\pi \delta(\omega + \omega_a) + i \frac{e^{i(\omega + \omega_a)T}}{\omega + \omega_a} \right] \left[\pi \delta(\omega + \omega_c) - i \frac{e^{-i(\omega + \omega_c)T}}{\omega + \omega_c} \right] \right]^{n/2} d\omega \quad (7.1.116)$$

But then we're left with the square of a delta function which is formally infinite because of the part of the integral we know to be zero from above. If we set $n = 2$, we can do some more work

$$S_{\bar{P}P}(T) = F \sum_{a,b,c,d} C_{a,b} C_{c,d}^* e^{i(\Omega_b - \Omega_d)T} \left[\pi^2 \int_{-\infty}^{\infty} \delta(\omega + \omega_a) \delta(\omega + \omega_c) d\omega + i\pi \frac{e^{i(\omega_c + \omega_a)T}}{\omega_c + \omega_a} - i\pi \frac{e^{-i(\omega_a + \omega_c)T}}{\omega_a + \omega_c} \right] \quad (7.1.117)$$

$$= F \sum_{a,b,c,d} C_{a,b} C_{c,d}^* e^{i(\Omega_b - \Omega_d)T} \left[\pi^2 \int_{-\infty}^{\infty} \delta(\omega + \omega_a) \delta(\omega + \omega_c) d\omega - 2\pi \frac{\sin[(\omega_c + \omega_a)T]}{\omega_c + \omega_a} \right] \quad (7.1.118)$$

but then we're still seemingly stuck with the delta function integral being infinite always, unless there just happens to be a symmetry such that $C_{a,b} C_{c,d}^* = -C_{c,b} C_{a,d}^*$ which I highly doubt.

7.1.8 TG OF A COHERENT DIMER

We are interested in investigating the form of the Transient Grating spectrum for a coherent dimer: 2 coupled two level systems given a two level system. That will help inform how well a TG would work for a witness as we also need to show what a positive identification of electronic coherence would look like.

Individually, one monomer looks like this:

$$\hat{H}_{M1} = \omega_{M1} |e1\rangle \langle e1|$$

$$\hat{U}(t) = |g1\rangle \langle g1| + e^{-i\omega_{M1}t} |e1\rangle \langle e1|$$

with a simple transition dipole:

$$\hat{\mu}_{M1} = \vec{\mu}_{M1} (|e1\rangle \langle g1| + |g1\rangle \langle e1|)$$

and the other looks like:

$$\hat{H}_{M2} = \omega_{M2} |e2\rangle \langle e2|$$

$$\hat{U}(t) = |g2\rangle \langle g2| + e^{-i\omega_{M2}t} |e2\rangle \langle e2|$$

$$\hat{\mu}_{M2} = \vec{\mu}_{M2} (|e2\rangle \langle g2| + |g2\rangle \langle e2|)$$

After combining the two systems, we get a Hamiltonian like this:

$$\hat{H}_D = \omega_{M1} |ge\rangle \langle ge| + \omega_{M2} |eg\rangle \langle eg| + J(|eg\rangle \langle eg| + |ge\rangle \langle ge|) + (\omega_{M1} + \omega_{M2}) |ee\rangle \langle ee|$$

which we can redefine into energy eigenstates for easier calculation:

$$\hat{H}_D = \omega_\alpha |\alpha\rangle \langle \alpha| + \omega_\beta |\beta\rangle \langle \beta| + \omega_f |f\rangle \langle f|$$

$$\hat{U}_D(t) = |g\rangle \langle g| + e^{-i\omega_\alpha t} |\alpha\rangle \langle \alpha| + e^{-i\omega_\beta t} |\beta\rangle \langle \beta| + e^{-i\omega_f t} |f\rangle \langle f|$$

where the energies are

$$\omega_\alpha = \frac{\omega_{M1} + \omega_{M2}}{2} + \frac{1}{2} \sqrt{(\omega_{M1} - \omega_{M2})^2 + J^2} \quad (7.1.119)$$

$$\omega_\beta = \frac{\omega_{M1} + \omega_{M2}}{2} - \frac{1}{2} \sqrt{(\omega_{M1} - \omega_{M2})^2 + J^2} \quad (7.1.120)$$

and the wavefunctions are able to be defined thusly::

$$\theta = \arctan\left(\frac{J}{\omega_{M1} - \omega_{M2}}\right) \quad (7.1.121)$$

$$|\alpha\rangle = -\sin(\theta)|eg\rangle + \cos(\theta)|ge\rangle \quad (7.1.122)$$

$$|\beta\rangle = \cos(\theta)|eg\rangle + \sin(\theta)|ge\rangle \quad (7.1.123)$$

$$|eg\rangle = -\sin(\theta)|\alpha\rangle + \cos(\theta)|\beta\rangle \quad (7.1.124)$$

$$|ge\rangle = \cos(\theta)|\alpha\rangle + \sin(\theta)|\beta\rangle \quad (7.1.125)$$

The transition dipole is a bit more complex:

$$\begin{aligned} \hat{\mu}_D = & \vec{\mu}_{M2} (|gg\rangle \langle ge| + |ge\rangle \langle gg| + |eg\rangle \langle ee| + |ee\rangle \langle eg|) \\ & + \vec{\mu}_{M1} (|gg\rangle \langle eg| + |eg\rangle \langle gg| + |ge\rangle \langle ee| + |ee\rangle \langle ge|) \end{aligned}$$

This recognizes the fact that the transition dipoles are local but it would be convenient to get this in the energy eigenbasis. For now I'm just going to posit that we CAN transform it and leave the details for later or possibly never:

$$\begin{aligned} \hat{\mu}_D = & \vec{\mu}_{\alpha g} (|g\rangle \langle \alpha| + |\alpha\rangle \langle g|) \\ & + \vec{\mu}_{\beta g} (|g\rangle \langle \beta| + |\beta\rangle \langle g|) \\ & + \vec{\mu}_{\alpha f} (|f\rangle \langle \alpha| + |\alpha\rangle \langle f|) \\ & + \vec{\mu}_{\beta f} (|f\rangle \langle \beta| + |\beta\rangle \langle f|) \end{aligned}$$

Crucially, we note that there is no dipole transition between the α and β states

7.1.8.1 SIGNAL CALCULATION

We now can calculate the contributions to the Transient Grating Signal in this system

$$\begin{aligned}
 |\psi_0(t)\rangle &= |g\rangle \\
 |\psi_{1+}(t)\rangle &= c \left(e^{-i\omega_\alpha t} \tilde{E}_{1+}(\omega_\alpha) \vec{\epsilon} \cdot \vec{\mu}_{\alpha g} |\alpha\rangle + e^{-i\omega_\beta t} \tilde{E}_{1+}(\omega_\beta) \vec{\epsilon} \cdot \vec{\mu}_{\beta g} |\beta\rangle \right) \\
 |\psi_{2+}(t)\rangle &= c \left(e^{-i\omega_\alpha t} \tilde{E}_{2+}(\omega_\alpha) \vec{\epsilon} \cdot \vec{\mu}_{\alpha g} |\alpha\rangle + e^{-i\omega_\beta t} \tilde{E}_{2+}(\omega_\beta) \vec{\epsilon} \cdot \vec{\mu}_{\beta g} |\beta\rangle \right) \\
 |\psi_{3+}(t)\rangle &= c \left(e^{-i\omega_\alpha t} \tilde{E}_{3+}(\omega_\alpha) \vec{\epsilon} \cdot \vec{\mu}_{\alpha g} |\alpha\rangle + e^{-i\omega_\beta t} \tilde{E}_{3+}(\omega_\beta) \vec{\epsilon} \cdot \vec{\mu}_{\beta g} |\beta\rangle \right) \\
 |\psi_{1+,2-}(t)\rangle &= c^2 \left[\tilde{E}_{1+}(\omega_\beta) \tilde{E}_{2-}(-\omega_\beta) (\vec{\epsilon} \cdot \vec{\mu}_{\beta g})^2 + \tilde{E}_{1+}(\omega_\alpha) \tilde{E}_{2-}(-\omega_\alpha) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g})^2 \right] |g\rangle \\
 |\psi_{1+,2+}(t)\rangle &= c^2 \left[\tilde{E}_{1+}(\omega_\beta) \tilde{E}_{2+}(\delta\omega_{\beta f}) (\vec{\epsilon} \cdot \vec{\mu}_{\beta g}) (\vec{\epsilon} \cdot \vec{\mu}_{\beta f}) + \tilde{E}_{1+}(\omega_\alpha) \tilde{E}_{2+}(\delta\omega_{\alpha f}) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g}) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha f}) \right] e^{-i\omega_f t} |f\rangle \\
 |\psi_{2+,3+}(t)\rangle &= c^2 \left[\tilde{E}_{2+}(\omega_\beta) \tilde{E}_{3+}(\delta\omega_{\beta f}) (\vec{\epsilon} \cdot \vec{\mu}_{\beta g}) (\vec{\epsilon} \cdot \vec{\mu}_{\beta f}) + \tilde{E}_{2+}(\omega_\alpha) \tilde{E}_{3+}(\delta\omega_{\alpha f}) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g}) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha f}) \right] e^{-i\omega_f t} |f\rangle \\
 |\psi_{2+,3-}(t)\rangle &= c^2 \left(\tilde{E}_{2+}(\omega_\alpha) \tilde{E}_{3-}(-\omega_\alpha) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g})^2 + \tilde{E}_{2+}(\omega_\beta) \tilde{E}_{3-}(-\omega_\beta) (\vec{\epsilon} \cdot \vec{\mu}_{\beta g})^2 \right) |g\rangle \\
 |\psi_{1+,2-,3+}(t)\rangle &= c^3 \left[\tilde{E}_{1+}(\omega_\beta) \tilde{E}_{2-}(-\omega_\beta) (\vec{\epsilon} \cdot \vec{\mu}_{\beta g})^2 + \tilde{E}_{1+}(\omega_\alpha) \tilde{E}_{2-}(-\omega_\alpha) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g})^2 \right] \\
 &\quad \times \left(e^{-i\omega_\alpha t} \tilde{E}_{3+}(\omega_\alpha) \vec{\epsilon} \cdot \vec{\mu}_{\alpha g} |\alpha\rangle + e^{-i\omega_\beta t} \tilde{E}_{3+}(\omega_\beta) \vec{\epsilon} \cdot \vec{\mu}_{\beta g} |\beta\rangle \right) \\
 \hat{\mu} |\psi_0(t)\rangle &= (\vec{\mu}_{\alpha g} |\alpha\rangle + \vec{\mu}_{\beta g} |\beta\rangle) \\
 \hat{\mu} |\psi_{1+}(t)\rangle &= c \left(e^{-i\omega_\alpha t} \tilde{E}_{1+}(\omega_\alpha) \vec{\epsilon} \cdot \vec{\mu}_{\alpha g} (\vec{\mu}_{\alpha g} |g\rangle + \vec{\mu}_{\alpha f} |f\rangle) + e^{-i\omega_\beta t} \tilde{E}_{1+}(\omega_\beta) \vec{\epsilon} \cdot \vec{\mu}_{\beta g} (\vec{\mu}_{\beta g} |g\rangle + \vec{\mu}_{\beta f} |f\rangle) \right) \\
 \hat{\mu} |\psi_{3+}(t)\rangle &= c \left(e^{-i\omega_\alpha t} \tilde{E}_{3+}(\omega_\alpha) \vec{\epsilon} \cdot \vec{\mu}_{\alpha g} (\vec{\mu}_{\alpha g} |g\rangle + \vec{\mu}_{\alpha f} |f\rangle) + e^{-i\omega_\beta t} \tilde{E}_{3+}(\omega_\beta) \vec{\epsilon} \cdot \vec{\mu}_{\beta g} (\vec{\mu}_{\beta g} |g\rangle + \vec{\mu}_{\beta f} |f\rangle) \right)
 \end{aligned}$$

We are now in the business of examining the Transient Grating Signal. WE start with E_a :

$$\begin{aligned}
 E_a(t) &= i \langle \psi_0(t) | \hat{\mu} | \psi_{1+, 2-, 3+}(t) \rangle \\
 &= c^3 \left[\tilde{E}_{1+}(\omega_\beta) \tilde{E}_{2-}(-\omega_\beta) (\vec{\epsilon} \cdot \vec{\mu}_{\beta g})^2 + \tilde{E}_{1+}(\omega_\alpha) \tilde{E}_{2-}(-\omega_\alpha) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g})^2 \right] \\
 &\quad \times \vec{\mu}_{\alpha g} \left(e^{-i\omega_\alpha t} \tilde{E}_{3+}(\omega_\alpha) \vec{\epsilon} \cdot \vec{\mu}_{\alpha g} \right) + \vec{\mu}_{\beta g} \left(e^{-i\omega_\beta t} \tilde{E}_{3+}(\omega_\beta) \vec{\epsilon} \cdot \vec{\mu}_{\beta g} \right)
 \end{aligned}$$

Now we move on to E_b :

$$\begin{aligned}
 E_b(t) &= i \langle \psi_{1+}(t) | \hat{\mu} | \psi_{2+,3+}(t) \rangle \\
 &= ic \left(e^{i\omega_\alpha t} \tilde{E}_{1+}^* (\omega_\alpha) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g}) \vec{\mu}_{\alpha f} + e^{i\omega_\beta t} \tilde{E}_{1+}^* (\omega_\beta) (\vec{\epsilon} \cdot \vec{\mu}_{\beta g}) \vec{\mu}_{\alpha f} \right) \\
 &\times c^2 \left[\tilde{E}_{2+} (\omega_\beta) \tilde{E}_{3+} (\delta\omega_{\beta f}) (\vec{\epsilon} \cdot \vec{\mu}_{\beta g}) (\vec{\epsilon} \cdot \vec{\mu}_{\beta f}) + \tilde{E}_{2+} (\omega_\alpha) \tilde{E}_{3+} (\delta\omega_{\alpha f}) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g}) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha f}) \right] e^{-i\omega_f t} \\
 &= ic^3 \left(e^{-i(\omega_f - \omega_\alpha)t} \tilde{E}_{1+}^* (\omega_\alpha) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g}) \vec{\mu}_{\alpha f} + e^{-i(\omega_f - \omega_\beta)t} \tilde{E}_{1+}^* (\omega_\beta) (\vec{\epsilon} \cdot \vec{\mu}_{\beta g}) \vec{\mu}_{\alpha f} \right) \\
 &\times \left[\tilde{E}_{2+} (\omega_\beta) \tilde{E}_{3+} (\delta\omega_{\beta f}) (\vec{\epsilon} \cdot \vec{\mu}_{\beta g}) (\vec{\epsilon} \cdot \vec{\mu}_{\beta f}) + \tilde{E}_{2+} (\omega_\alpha) \tilde{E}_{3+} (\delta\omega_{\alpha f}) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g}) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha f}) \right] e
 \end{aligned}$$

then E_c :

$$E_c(t) = i \langle \psi_{2+,3-}(t) | \hat{\mu} | \psi_{1+}(t) \rangle \quad (7.1.126)$$

$$= ic^3 \left(\tilde{E}_{2+}^* (\omega_\alpha) \tilde{E}_{3-}^* (-\omega_\alpha) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g})^2 + \tilde{E}_{2+}^* (\omega_\beta) \tilde{E}_{3-}^* (-\omega_\beta) (\vec{\epsilon} \cdot \vec{\mu}_{\beta g})^2 \right) |g\rangle \quad (7.1.127)$$

$$\times \left(e^{-i\omega_\alpha t} \tilde{E}_{1+} (\omega_\alpha) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g}) \vec{\mu}_{\alpha g} + e^{-i\omega_\beta t} \tilde{E}_{1+} (\omega_\beta) (\vec{\epsilon} \cdot \vec{\mu}_{\beta g}) \vec{\mu}_{\beta g} \right) \quad (7.1.128)$$

and lastly the d term:

$$\begin{aligned}
 E_d(t) &= i \langle \psi_{1+,2-}(t) | \hat{\mu} | \psi_{3+}(t) \rangle \\
 &= ic^3 \left[\tilde{E}_{1+}^* (\omega_\beta) \tilde{E}_{2-}^* (-\omega_\beta) (\vec{\epsilon} \cdot \vec{\mu}_{\beta g})^2 + \tilde{E}_{1+}^* (\omega_\alpha) \tilde{E}_{2-}^* (-\omega_\alpha) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g})^2 \right] \\
 &\times \left(e^{-i\omega_\alpha t} \tilde{E}_{3+} (\omega_\alpha) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g}) \vec{\mu}_{\alpha g} + e^{-i\omega_\beta t} \tilde{E}_{3+} (\omega_\beta) (\vec{\epsilon} \cdot \vec{\mu}_{\beta g}) \vec{\mu}_{\beta g} \right)
 \end{aligned}$$

7.1.8.2 JUERGEN'S APPLICATION

What our experimentalist friend Juergen is doing is taking the frequency-resolved TG spectrum and performing an operation But we want the Fourier transform so let's begin by looking at the a term:

$$\begin{aligned}\tilde{E}_a(\omega) &= i \langle \psi_0(t) | \hat{\mu} | \psi_{1+, 2-, 3+}(t) \rangle \\ &= c^3 \left[\tilde{E}_{1+}(\omega_\beta) \tilde{E}_{2-}(-\omega_\beta) (\vec{\epsilon} \cdot \vec{\mu}_{\beta g})^2 + \tilde{E}_{1+}(\omega_\alpha) \tilde{E}_{2-}(-\omega_\alpha) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g})^2 \right] \\ &\quad \times \left[\vec{\mu}_{\alpha g} (\delta(\omega - \omega_\alpha) \tilde{E}_{3+}(\omega_\alpha) \vec{\epsilon} \cdot \vec{\mu}_{\alpha g}) + \vec{\mu}_{\beta g} (\delta(\omega - \omega_\beta) \tilde{E}_{3+}(\omega_\beta) \vec{\epsilon} \cdot \vec{\mu}_{\beta g}) \right]\end{aligned}$$

But those delta functions aren't terribly useful if we're going to perform operations on them. If instead we assume they are decay exponentials then we can get something to work with:

$$\begin{aligned}& \int_{-\infty}^{\infty} e^{-\omega t} e^{-i\omega_a t - \Gamma t} H[t] dt \\ & \frac{C}{2\Gamma - i(\omega - \omega_a)} \\ & \frac{C}{2\Gamma - i(\omega - \omega_a)} \frac{2\Gamma + i(\omega - \omega_a)}{2\Gamma + i(\omega - \omega_a)} \\ & C \frac{2\Gamma + i(\omega - \omega_a)}{4\Gamma^2 + (\omega - \omega_a)^2}\end{aligned}$$

Now we can put this in to our signal work from earlier:

$$\begin{aligned}\tilde{E}_a(\omega) &= i \langle \psi_0(t) | \hat{\mu} | \psi_{1+, 2-, 3+}(t) \rangle \\ &= i^3 C \left[\tilde{E}_{1+}(\omega_\beta) \tilde{E}_{2-}(-\omega_\beta) (\vec{\epsilon} \cdot \vec{\mu}_{\beta g})^2 + \tilde{E}_{1+}(\omega_\alpha) \tilde{E}_{2-}(-\omega_\alpha) (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g})^2 \right] \\ &\quad \times \left[\vec{\mu}_{\alpha g} \left(\frac{2\Gamma + i(\omega - \omega_\alpha)}{4\Gamma^2 + (\omega - \omega_\alpha)^2} \tilde{E}_{3+}(\omega_\alpha) \vec{\epsilon} \cdot \vec{\mu}_{\alpha g} \right) + \vec{\mu}_{\beta g} \left(\frac{2\Gamma + i(\omega - \omega_\beta)}{4\Gamma^2 + (\omega - \omega_\beta)^2} \tilde{E}_{3+}(\omega_\beta) \vec{\epsilon} \cdot \vec{\mu}_{\beta g} \right) \right]\end{aligned}$$

We now are interested in seeing the effect of one of the operators $\mathfrak{K}, \mathfrak{J}$. I represent this generic operator as \mathcal{N} . There are going to be 4 relevant terms

$$\begin{aligned} \tilde{E}_a(\omega)/c^3C = & i\tilde{E}_{1+}(\omega_\beta)\tilde{E}_{2-}(-\omega_\beta)(\tilde{\epsilon}\cdot\tilde{\mu}_{\beta g})^2\tilde{\mu}_{\alpha g}\left(\frac{2\Gamma+i(\omega-\omega_\alpha)}{4\Gamma^2+(\omega-\omega_\alpha)^2}\tilde{E}_{3+}(\omega_\alpha)\tilde{\epsilon}\cdot\tilde{\mu}_{\alpha g}\right) \\ & + i\tilde{E}_{1+}(\omega_\beta)\tilde{E}_{2-}(-\omega_\beta)(\tilde{\epsilon}\cdot\tilde{\mu}_{\beta g})^2\tilde{\mu}_{\beta g}\left(\frac{2\Gamma+i(\omega-\omega_\beta)}{4\Gamma^2+(\omega-\omega_\beta)^2}\tilde{E}_{3+}(\omega_\beta)\tilde{\epsilon}\cdot\tilde{\mu}_{\beta g}\right) \\ & + i\tilde{E}_{1+}(\omega_\alpha)\tilde{E}_{2-}(-\omega_\alpha)(\tilde{\epsilon}\cdot\tilde{\mu}_{\alpha g})^2\tilde{\mu}_{\alpha g}\left(\frac{2\Gamma+i(\omega-\omega_\alpha)}{4\Gamma^2+(\omega-\omega_\alpha)^2}\tilde{E}_{3+}(\omega_\alpha)\tilde{\epsilon}\cdot\tilde{\mu}_{\alpha g}\right) \\ & + i\tilde{E}_{1+}(\omega_\alpha)\tilde{E}_{2-}(-\omega_\alpha)(\tilde{\epsilon}\cdot\tilde{\mu}_{\alpha g})^2\tilde{\mu}_{\beta g}\left(\frac{2\Gamma+i(\omega-\omega_\beta)}{4\Gamma^2+(\omega-\omega_\beta)^2}\tilde{E}_{3+}(\omega_\beta)\tilde{\epsilon}\cdot\tilde{\mu}_{\beta g}\right) \end{aligned}$$

Now we apply the operator:

$$\begin{aligned} \mathcal{N}[\tilde{E}_a(\omega)/c^3C] = & \tilde{\mu}_{\alpha g}(\tilde{\epsilon}\cdot\tilde{\mu}_{\beta g})^2(\tilde{\epsilon}\cdot\tilde{\mu}_{\alpha g})\mathcal{N}\left[i\tilde{E}_{1+}(\omega_\beta)\tilde{E}_{2-}(-\omega_\beta)\frac{2\Gamma+i(\omega-\omega_\alpha)}{4\Gamma^2+(\omega-\omega_\alpha)^2}\tilde{E}_{3+}(\omega_\alpha)\right] \\ & + \tilde{\mu}_{\beta g}(\tilde{\epsilon}\cdot\tilde{\mu}_{\beta g})^2(\tilde{\epsilon}\cdot\tilde{\mu}_{\beta g})\mathcal{N}\left[i\tilde{E}_{1+}(\omega_\beta)\tilde{E}_{2-}(-\omega_\beta)\frac{2\Gamma+i(\omega-\omega_\beta)}{4\Gamma^2+(\omega-\omega_\beta)^2}\tilde{E}_{3+}(\omega_\beta)\right] \\ & + \tilde{\mu}_{\alpha g}(\tilde{\epsilon}\cdot\tilde{\mu}_{\alpha g})^2(\tilde{\epsilon}\cdot\tilde{\mu}_{\alpha g})\mathcal{N}\left[i\tilde{E}_{1+}(\omega_\alpha)\tilde{E}_{2-}(-\omega_\alpha)\frac{2\Gamma+i(\omega-\omega_\alpha)}{4\Gamma^2+(\omega-\omega_\alpha)^2}\tilde{E}_{3+}(\omega_\alpha)\right] \\ & + \tilde{\mu}_{\beta g}(\tilde{\epsilon}\cdot\tilde{\mu}_{\alpha g})^2(\tilde{\epsilon}\cdot\tilde{\mu}_{\beta g})\mathcal{N}\left[i\tilde{E}_{1+}(\omega_\alpha)\tilde{E}_{2-}(-\omega_\alpha)\frac{2\Gamma+i(\omega-\omega_\beta)}{4\Gamma^2+(\omega-\omega_\beta)^2}\tilde{E}_{3+}(\omega_\beta)\right] \end{aligned}$$

Now it would be worthwhile getting out a form for the pulses. The first two pulses will look like so:

$$\begin{aligned} E_{1/2}(t) = & N(\sigma)e^{-\frac{t^2}{2\sigma^2}}[e^{-i\omega_c t} + e^{+i\omega_c t}] \\ E_3(t) = & N(\sigma)e^{-\frac{(t-T)^2}{2\sigma^2}}[e^{-i\omega_c(t-T)} + e^{+i\omega_c(t-T)}] \end{aligned}$$

and the Fourier Transforms:

$$\begin{aligned}\tilde{E}_{\pm 1/2}(\omega) &= \tilde{N}(\sigma) e^{-(\omega \mp \omega_c)^2 \frac{\sigma^2}{2}} \\ \tilde{E}_{\pm 3}(\omega) &= \tilde{N}(\sigma) e^{-(\omega \mp \omega_c)^2 \frac{\sigma^2}{2}} e^{i\omega T}\end{aligned}$$

So if we define an envelope function $V_{\pm}(\omega, \sigma)$ to take away all the strictly real components of the laser fields we get:

$$\begin{aligned}\mathcal{N} [\tilde{E}_a(\omega)/c^3 C] &= \vec{\mu}_{\alpha g} (\vec{\epsilon} \cdot \vec{\mu}_{\beta g})^2 (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g}) V_+(\omega_{\beta}) V_-(-\omega_{\beta}) V_+(\omega_{\alpha}) \mathcal{N} \left[i \frac{2\Gamma + i(\omega - \omega_{\alpha})}{4\Gamma^2 + (\omega - \omega_{\alpha})^2} e^{i\omega_{\alpha} T} \right] \\ &+ \vec{\mu}_{\beta g} (\vec{\epsilon} \cdot \vec{\mu}_{\beta g})^2 (\vec{\epsilon} \cdot \vec{\mu}_{\beta g}) V_+(\omega_{\beta}) V_-(-\omega_{\beta}) V_+(\omega_{\beta}) \mathcal{N} \left[i \frac{2\Gamma + i(\omega - \omega_{\beta})}{4\Gamma^2 + (\omega - \omega_{\beta})^2} e^{i\omega_{\beta} T} \right] \\ &+ \vec{\mu}_{\alpha g} (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g})^2 (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g}) V_+(\omega_{\alpha}) V_-(-\omega_{\alpha}) V_+(\omega_{\alpha}) \mathcal{N} \left[i \frac{2\Gamma + i(\omega - \omega_{\alpha})}{4\Gamma^2 + (\omega - \omega_{\alpha})^2} e^{i\omega_{\alpha} T} \right] \\ &+ \vec{\mu}_{\beta g} (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g})^2 (\vec{\epsilon} \cdot \vec{\mu}_{\beta g}) V_+(\omega_{\alpha}) V_-(-\omega_{\alpha}) V_+(\omega_{\beta}) \mathcal{N} \left[i \frac{2\Gamma + i(\omega - \omega_{\beta})}{4\Gamma^2 + (\omega - \omega_{\beta})^2} e^{i\omega_{\beta} T} \right]\end{aligned}$$

So all we care about when taking the real or imaginary part or some combination of the two for this term at least is the quantity:

$$\mathcal{N} [i(2\Gamma + i(\omega - \omega_a)) e^{i\omega_a T}] \quad (7.1.129)$$

$$\mathcal{N} [(2i\Gamma - (\omega - \omega_a)) e^{i\omega_a T}] \quad (7.1.130)$$

so now we can turn \mathcal{N} into real operators:

$$\Re [(2i\Gamma - (\omega - \omega_a)) e^{i\omega_a T}] = -2\Gamma \sin(\omega_a T) + (\omega - \omega_a) \cos(\omega_a T) \quad (7.1.131)$$

$$\Im [(2i\Gamma - (\omega - \omega_a)) e^{i\omega_a T}] = 2\Gamma \cos(\omega_a T) + (\omega - \omega_a) \sin(\omega_a T) \quad (7.1.132)$$

Back to the full signal expression for a :

$$\begin{aligned}
 \mathcal{N} [\tilde{E}_a(\omega)/c^3 C] &= \vec{\mu}_{\alpha g} (\vec{\epsilon} \cdot \vec{\mu}_{\beta g})^2 (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g}) V_+(\omega_\beta) V_-(-\omega_\beta) V_+(\omega_\alpha) \mathcal{N} \left[i \frac{2\Gamma + i(\omega - \omega_\alpha)}{4\Gamma^2 + (\omega - \omega_\alpha)^2} e^{i\omega_\alpha T} \right] \\
 &+ \vec{\mu}_{\beta g} (\vec{\epsilon} \cdot \vec{\mu}_{\beta g})^2 (\vec{\epsilon} \cdot \vec{\mu}_{\beta g}) V_+(\omega_\beta) V_-(-\omega_\beta) V_+(\omega_\beta) \mathcal{N} \left[i \frac{2\Gamma + i(\omega - \omega_\beta)}{4\Gamma^2 + (\omega - \omega_\beta)^2} e^{i\omega_\beta T} \right] \\
 &+ \vec{\mu}_{\alpha g} (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g})^2 (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g}) V_+(\omega_\alpha) V_-(-\omega_\alpha) V_+(\omega_\alpha) \mathcal{N} \left[i \frac{2\Gamma + i(\omega - \omega_\alpha)}{4\Gamma^2 + (\omega - \omega_\alpha)^2} e^{i\omega_\alpha T} \right] \\
 &+ \vec{\mu}_{\beta g} (\vec{\epsilon} \cdot \vec{\mu}_{\alpha g})^2 (\vec{\epsilon} \cdot \vec{\mu}_{\beta g}) V_+(\omega_\alpha) V_-(-\omega_\alpha) V_+(\omega_\beta) \mathcal{N} \left[i \frac{2\Gamma + i(\omega - \omega_\beta)}{4\Gamma^2 + (\omega - \omega_\beta)^2} e^{i\omega_\beta T} \right]
 \end{aligned}$$

if we're integrating in frequency space and for simplicity we assume we're only looking at signal with the same polarization as the laser, then all of the constants are going to boil down to:

$$\begin{aligned}
 \mathcal{N} [\hat{\epsilon} \cdot \tilde{E}_{TG}(\omega)/c^3 C] &= A \mathcal{N} \left[i \frac{2\Gamma + i(\omega - \omega_\alpha)}{4\Gamma^2 + (\omega - \omega_\alpha)^2} e^{i\omega_\alpha T} \right] \\
 &+ B \mathcal{N} \left[i \frac{2\Gamma + i(\omega - \omega_\beta)}{4\Gamma^2 + (\omega - \omega_\beta)^2} e^{i\omega_\beta T} \right] \\
 &+ C \mathcal{N} \left[i \frac{2\Gamma + i(\omega - (\omega_f - \omega_\alpha))}{4\Gamma^2 + (\omega - (\omega_f - \omega_\alpha))^2} e^{i(\omega_f - \omega_\alpha) T} \right] \\
 &+ D \mathcal{N} \left[i \frac{2\Gamma + i(\omega - (\omega_f - \omega_\beta))}{4\Gamma^2 + (\omega - (\omega_f - \omega_\beta))^2} e^{i(\omega_f - \omega_\beta) T} \right]
 \end{aligned}$$

Where all of the pulse width dependence is in the constants A, B, C, D . Mathematica isn't

budging on doing any of these integrals... but what if I turn it back into a δ -function?

$$\begin{aligned}
 \mathcal{N} [\hat{\epsilon} \cdot \tilde{E}_{TG}(\omega)/c^3 C] &= A \mathcal{N} [i \delta(\omega - \omega_\alpha) e^{i\omega_\alpha T}] \\
 &+ B \mathcal{N} [i \delta(\omega - \omega_\beta) e^{i\omega_\beta T}] \\
 &+ C \mathcal{N} [i \delta(\omega - (\omega_f - \omega_\alpha)) e^{i(\omega_f - \omega_\alpha) T}] \\
 &+ D \mathcal{N} [i \delta(\omega - (\omega_f - \omega_\beta)) e^{i(\omega_f - \omega_\beta) T}]
 \end{aligned}$$

If we integrate over all frequencies to get a pump-probe facsimile, then what we are left with is:

$$\tilde{S}_{PP}(T) = A' \mathcal{N} [ie^{i\omega_\alpha T}] \quad (7.1.133)$$

$$+ B' \mathcal{N} [ie^{i\omega_\beta T}] \quad (7.1.134)$$

$$+ C' \mathcal{N} [ie^{i(\omega_f - \omega_\alpha)T}] \quad (7.1.135)$$

$$+ D' \mathcal{N} [ie^{i(\omega_f - \omega_\beta)T}] \quad (7.1.136)$$

If we were to then take the Fourier transform of this signal: Take just the first term. IF it were real we would get this:

$$\tilde{S}_{PP}(T) = A' \Re [ie^{i\omega_\alpha T}] + \dots \quad (7.1.137)$$

$$= -A' \sin [\omega_\alpha T] + \dots \quad (7.1.138)$$

$$= -A' \frac{1}{2i} (e^{i\omega_\alpha T} - e^{-i\omega_\alpha T}) + \dots \quad (7.1.139)$$

$$\tilde{S}'_{PP}(\Omega) = -A' \frac{1}{2i} [\delta(\Omega - \omega_\alpha) - \delta(\Omega + \omega_\alpha)] + \dots \quad (7.1.140)$$

Note that here $\tilde{S}'_{PP}(\omega_\alpha) = -\tilde{S}'_{PP}(-\omega_\alpha)$. If I chose the imaginary operator instead, we would have:

$$\tilde{S}_{PP}(T) = A' \Im [ie^{i\omega_\alpha T}] + \dots \quad (7.1.141)$$

$$= A' \cos [\omega_\alpha T] + \dots \quad (7.1.142)$$

$$= A' \frac{1}{2} (e^{i\omega_\alpha T} + e^{-i\omega_\alpha T}) + \dots \quad (7.1.143)$$

$$\tilde{S}'_{PP}(\Omega) = -A' \frac{1}{2i} [\delta(\Omega - \omega_\alpha) + \delta(\Omega + \omega_\alpha)] + \dots \quad (7.1.144)$$

Contrasting from taking the real part, when we take the imaginary part, $\tilde{S}'_{PP}(\omega_\alpha) = \tilde{S}'_{PP}(-\omega_\alpha)$. Do either of these relationships change when we realize that we're only getting signal for $T > 0$?

$$\begin{aligned}\mathcal{F}[\sin(\omega_0 t)H[t]] &= \frac{-1/\sqrt{8\pi}}{\omega - \omega_0} + \frac{1/\sqrt{8\pi}}{\omega + \omega_0} + i\sqrt{\frac{\pi}{8}}\delta(\omega - \omega_0) - i\sqrt{\frac{\pi}{8}}\delta(\omega + \omega_0) \\ \mathcal{F}[\cos(\omega_0 t)H[t]] &= \frac{i/\sqrt{8\pi}}{\omega - \omega_0} + \frac{i/\sqrt{8\pi}}{\omega + \omega_0} + \sqrt{\frac{\pi}{8}}\delta(\omega - \omega_0) + \sqrt{\frac{\pi}{8}}\delta(\omega + \omega_0)\end{aligned}$$

The symmetry is broken a little bit but is in general still dominated by the delta functions. Thus it appears that if one constructs Pump-Probe facsimiles from the Transient Grating Signal in this manner, you should get the exact same pulse width dependence of oscillations in the signal regardless of whether one uses a real or imaginary operation to manipulate the transient grating signal. The only thing that *might* cause there to be a difference would be some kind of signal processing which ends up adding together the positive and negative frequency amplitudes, because they sum to zero.

There still might be odd behavior for the absolute value, however. That calculation is more complex.

7.2 QUANTUM PROCESS TOMOGRAPHY

Early on in my graduate school career, I was asked to develop a polarization control Quantum Process Tomography protocol to make it easier to perform QPT on experimental systems where it was not easy to manipulate the laser central frequency. We ended up running into issues with the solubility of the equations generated, despite the fact that they were n equations with n unknowns. The project ended up being dropped but here is a summary of what we did.

7.2.1 QUICK INTRODUCTION TO QUANTUM PROCESS TOMOGRAPHY

Having a time-dependent density matrix for a system does not tell the whole story of what is going on, because you don't know which elements are turning in to which other elements along the way. To use a distinctly classical analogy, the professor may know that his students are going from the no-paper state to the paper state after a certain time T , but he does not know how much time was spent on REPLACE BAD JOKE along the way.

To use a more apt, quantum analogy, at a time T , say we want to know how much amplitude is on coherence ab but we want to be able to distinguish how much came from coherence ba versus came from population bb . How might we do that?

Let's start out by looking at the density matrix time-evolution:

$$\rho(T) = U(T,0)\rho(0)U^\dagger(T,0) \quad (7.2.1)$$

and expand it out for matrix multiplication:

$$\rho_{ij}(T) = \sum_k \sum_l U_{il}(T,0)\rho_{lk}(0)U_{kj}^\dagger(T,0) \quad (7.2.2)$$

$$\rho_{ij}(T) = \sum_{k,l} U_{il}(T,0)U_{kj}^\dagger(T,0)\rho_{lk}(0) \quad (7.2.3)$$

And there we have it. We can then define an object $\chi_{ij \leftarrow lk}(T)$ which maps the initial density matrix element lk to the time T element ij , giving you an exact description of how each element of a density matrix evolves. This matrix is called the Quantum Process Matrix and finding its elements for a set of time points is called Quantum Process Tomography. Showing that such a tensor exists

for open systems is a little more involved and will be included in a later edition but rest assured it does exist. The only occasion for which it would get very complicated is with a time-dependent Hamiltonian.

7.2.2 EXPERIMENTAL DETERMINATION OF χ

With the knowledge that we want to figure out the process matrix for a system, we are now faced with the daunting task of asking an experimentalist to perform the experiment. Why? For an N level system, there are, of course, N^2 elements of the density matrix and each of those N^2 elements which we need to set up experiments for. Each of those experiments, however, can evolve into ANY of the possible N^2 elements. Which means we're asking for someone to do N^4 experiments which for a two-level system is already 16, and that's assuming you don't need to do different experiments for each point in time. Or is it really that much?

The short answer is no. Let's start with one fact: every operator in quantum mechanics (including the density operator) must be hermitian, that means that only half of the off-diagonal elements are unique which means that there are $\frac{N^2+N}{2}$ possible elements for the beginning and end making the total number of required experiments now $\frac{(N^2+N)^2}{4}$ or just 9 experiments for our two-level system. How does this manifest in the process matrix?

$$\rho_{ij}(T) = \sum_{k,l} \chi_{ij\leftarrow kl}(T) \rho_{kl}(0) \quad (7.2.4)$$

$$\chi_{ij\leftarrow kl}(T) = U_{il}(T,0) U_{kj}^*(T,0) \quad (7.2.5)$$

$$= [U_{jk}(T,0) U_{li}^*(T,0)]^* \quad (7.2.6)$$

$$\chi_{ij\leftarrow kl}(T) = \chi_{ji\leftarrow lk}^*(T) \quad (7.2.7)$$

Or physically that the pathway from ab to cd is the same (to within a complex conjugate) as the

pathway taking ba to dc . Which, if you think about it, should make some sense ($\vec{\mu}_{\alpha g} \cdot \vec{e}_1$) We will use these facts in the next subsection to simplify problems significantly.

7.2.3 THE GOAL

Is it possible to get a full or partial Quantum Process Matrix for a dimer, from a 2D electronic spectrum, just by controlling the polarizations? We take Joel's equations for a dimer developed in references ^{59,62}.

7.2.4 INITIAL EQUATIONS

In a marked change from Joel's work in ^{59,62} I am transforming the C

$$C_{\text{Joey}} \rightarrow -iC_{\text{Joel}}$$

$$C_{\text{Joey}} = \lambda \sqrt{2\pi\sigma^2} e^{-\sigma^2(\omega_{pg} - \omega_i)^2/2}$$

$$S_{\text{Joey}} \rightarrow -\mathbf{Im}[S_{\text{Joel}}]$$

Which removes the confusing, unnecessary presence of the imaginary unit i from many of his expressions.

From here, we get the amplitude values of the diagonal and off-diagonal peaks in for different experiments labeled with superscripts indicating the different polarizations. We start with all in the same direction (we use z to denote this direction but because of the isotropic averaging, it does not matter: only the relative directions of the pulses)

$$\begin{aligned}
\langle S_{\alpha\beta} \rangle^{zzzz} &= \frac{1}{5} C_{\alpha\alpha\beta} \mu_{\alpha g}^4 \chi_{\alpha\alpha\leftarrow\alpha\alpha} \\
&\quad - \frac{2}{15} C_{\alpha\beta\alpha} \mu_{\alpha g}^2 \mu_{\beta g}^2 \chi_{\beta\alpha\leftarrow\beta\alpha} \\
&\quad + \frac{1}{15} C_{\alpha\alpha\beta} \mu_{\alpha g}^2 \mu_{\beta g}^2 (\chi_{g g\leftarrow\alpha\alpha} - \chi_{\beta\beta\leftarrow\alpha\alpha} - 1) \\
a_1 &= \frac{1}{5} C_{\alpha\alpha\beta} \mu_{\alpha g}^4 \\
a_2 &= -\frac{2}{15} C_{\alpha\beta\alpha} \mu_{\alpha g}^2 \mu_{\beta g}^2 \\
a_3 &= \frac{1}{15} C_{\alpha\alpha\beta} \mu_{\alpha g}^2 \mu_{\beta g}^2 \\
\langle S_{\alpha\beta} \rangle^{zzzz} &= a_1 \chi_{\alpha\alpha\leftarrow\alpha\alpha} + a_2 \chi_{\beta\alpha\leftarrow\beta\alpha} + a_3 (\chi_{g g\leftarrow\alpha\alpha} - \chi_{\beta\beta\leftarrow\alpha\alpha} - 1)
\end{aligned}$$

$$\begin{aligned}
\langle S_{\alpha\alpha} \rangle^{zzzz} &= \frac{1}{5} C_{\alpha\alpha\alpha} \mu_{\alpha g}^4 (\chi_{g g\leftarrow\alpha\alpha} - \chi_{\alpha\alpha\leftarrow\alpha\alpha} - 1) \\
&\quad - \frac{2}{15} C_{\alpha\beta\beta} \mu_{\alpha g}^2 \mu_{\beta g}^2 \chi_{\alpha\beta\leftarrow\beta\alpha} \\
&\quad + \frac{1}{15} C_{\alpha\alpha\alpha} \mu_{\alpha g}^2 \mu_{\beta g}^2 \chi_{\beta\beta\leftarrow\alpha\alpha} \\
a_4 &= \frac{1}{5} C_{\alpha\alpha\alpha} \mu_{\alpha g}^4 \\
a_5 &= -\frac{2}{15} C_{\alpha\beta\beta} \mu_{\alpha g}^2 \mu_{\beta g}^2 = a_2 \\
a_6 &= \frac{1}{15} C_{\alpha\alpha\alpha} \mu_{\alpha g}^2 \mu_{\beta g}^2 \\
\langle S_{\alpha\alpha} \rangle^{zzzz} &= a_4 (\chi_{g g\leftarrow\alpha\alpha} - \chi_{\alpha\alpha\leftarrow\alpha\alpha} - 1) + a_5 \chi_{\alpha\beta\leftarrow\beta\alpha} + a_6 \chi_{\beta\beta\leftarrow\alpha\alpha}
\end{aligned}$$

$$\begin{aligned}
 \langle S_{\beta\beta} \rangle^{zzzz} &= \frac{1}{15} C_{\beta\beta\beta} \mu_{\alpha g}^2 \mu_{\beta g}^2 \chi_{\alpha\alpha\leftarrow\beta\beta} \\
 &\quad - \frac{2}{15} C_{\beta\alpha\alpha} \mu_{\alpha g}^2 \mu_{\beta g}^2 \chi_{\beta\alpha\leftarrow\alpha\beta} \\
 &\quad + \frac{1}{5} C_{\beta\beta\beta} \mu_{\beta g}^4 (\chi_{g g\leftarrow\beta\beta} - \chi_{\beta\beta\leftarrow\beta\beta} - 1) \\
 a_7 &= \frac{1}{15} C_{\beta\beta\beta} \mu_{\alpha g}^2 \mu_{\beta g}^2 \\
 a_8 &= -\frac{2}{15} C_{\beta\alpha\alpha} \mu_{\alpha g}^2 \mu_{\beta g}^2 \\
 a_9 &= \frac{1}{5} C_{\beta\beta\beta} \mu_{\beta g}^4 \\
 \langle S_{\beta\beta} \rangle^{zzzz} &= a_7 \chi_{\alpha\alpha\leftarrow\beta\beta} + a_8 \chi_{\beta\alpha\leftarrow\alpha\beta} + a_9 (\chi_{g g\leftarrow\beta\beta} - \chi_{\beta\beta\leftarrow\beta\beta} - 1)
 \end{aligned}$$

$$\begin{aligned}
 \langle S_{\beta\alpha} \rangle^{zzzz} &= \frac{1}{15} C_{\beta\beta\alpha} \mu_{\alpha g}^2 \mu_{\beta g}^2 (\chi_{g g\leftarrow\beta\beta} - \chi_{\alpha\alpha\leftarrow\beta\beta} - 1) \\
 &\quad - \frac{2}{15} C_{\beta\alpha\beta} \mu_{\alpha g}^2 \mu_{\beta g}^2 \chi_{\alpha\beta\leftarrow\alpha\beta} \\
 &\quad + \frac{1}{5} C_{\beta\beta\alpha} \mu_{\beta g}^4 \chi_{\beta\beta\leftarrow\beta\beta} \\
 a_{10} &= \frac{1}{15} C_{\beta\beta\alpha} \mu_{\alpha g}^2 \mu_{\beta g}^2 \\
 a_{11} &= -\frac{2}{15} C_{\beta\alpha\beta} \mu_{\alpha g}^2 \mu_{\beta g}^2 \\
 a_{12} &= \frac{1}{5} C_{\beta\beta\alpha} \mu_{\beta g}^4 \\
 \langle S_{\beta\alpha} \rangle^{zzzz} &= a_{10} (\chi_{g g\leftarrow\beta\beta} - \chi_{\alpha\alpha\leftarrow\beta\beta} - 1) + a_{11} \chi_{\alpha\beta\leftarrow\alpha\beta} + a_{12} \chi_{\beta\beta\leftarrow\beta\beta}
 \end{aligned}$$

Now for the other polarization configuration: subsequent pulses at 90 degrees to each other or

$xzxz$:

$$\begin{aligned}
\langle S_{\alpha\beta} \rangle^{xz} &= \frac{1}{15} C_{\alpha\alpha\beta} \mu_{\alpha g}^4 \chi_{\alpha\alpha\leftarrow\alpha\alpha} \\
&\quad - \frac{1}{10} C_{\alpha\beta\alpha} \mu_{\alpha g}^2 \mu_{\beta g}^2 \chi_{\beta\alpha\leftarrow\beta\alpha} \\
&\quad - \frac{1}{30} C_{\alpha\alpha\beta} \mu_{\alpha g}^2 \mu_{\beta g}^2 (\chi_{g g\leftarrow\alpha\alpha} - \chi_{\beta\beta\leftarrow\alpha\alpha} - 1) \\
b_1 &= \frac{1}{15} C_{\alpha\alpha\beta} \mu_{\alpha g}^4 \\
b_2 &= -\frac{1}{10} C_{\alpha\beta\alpha} \mu_{\alpha g}^2 \mu_{\beta g}^2 \\
b_3 &= -\frac{1}{30} C_{\alpha\alpha\beta} \mu_{\alpha g}^2 \mu_{\beta g}^2 \\
\langle S_{\alpha\beta} \rangle^{xz} &= b_1 \chi_{\alpha\alpha\leftarrow\alpha\alpha} + b_2 \chi_{\beta\alpha\leftarrow\beta\alpha} + b_3 (\chi_{g g\leftarrow\alpha\alpha} - \chi_{\beta\beta\leftarrow\alpha\alpha} - 1)
\end{aligned}$$

$$\begin{aligned}
\langle S_{\alpha\alpha} \rangle^{xz} &= \frac{1}{15} C_{\alpha\alpha\alpha} \mu_{\alpha g}^4 (\chi_{g g\leftarrow\alpha\alpha} - \chi_{\alpha\alpha\leftarrow\alpha\alpha} - 1) \\
&\quad + \frac{1}{6} C_{\alpha\beta\beta} \mu_{\alpha g}^2 \mu_{\beta g}^2 \chi_{\alpha\beta\leftarrow\beta\alpha} \\
&\quad - \frac{1}{30} C_{\alpha\alpha\alpha} \mu_{\alpha g}^2 \mu_{\beta g}^2 \chi_{\beta\beta\leftarrow\alpha\alpha} \\
b_4 &= \frac{1}{15} C_{\alpha\alpha\alpha} \mu_{\alpha g}^4 \\
b_5 &= \frac{1}{6} C_{\alpha\beta\beta} \mu_{\alpha g}^2 \mu_{\beta g}^2 \\
b_6 &= -\frac{1}{30} C_{\alpha\alpha\alpha} \mu_{\alpha g}^2 \mu_{\beta g}^2 \\
\langle S_{\alpha\alpha} \rangle^{xz} &= b_4 (\chi_{g g\leftarrow\alpha\alpha} - \chi_{\alpha\alpha\leftarrow\alpha\alpha} - 1) + b_5 \chi_{\alpha\beta\leftarrow\beta\alpha} + b_6 \chi_{\beta\beta\leftarrow\alpha\alpha}
\end{aligned}$$

$$\begin{aligned}
 \langle S_{\beta\beta} \rangle^{xzxz} &= -\frac{1}{30} C_{\beta\beta\beta} \mu_{\alpha g}^2 \mu_{\beta g}^2 \chi_{\alpha\alpha\leftarrow\beta\beta} \\
 &\quad + \frac{1}{6} C_{\beta\alpha\alpha} \mu_{\alpha g}^2 \mu_{\beta g}^2 \chi_{\beta\alpha\leftarrow\alpha\beta} \\
 &\quad + \frac{1}{15} C_{\beta\beta\beta} \mu_{\beta g}^4 (\chi_{g g\leftarrow\beta\beta} - \chi_{\beta\beta\leftarrow\beta\beta} - 1) \\
 b_7 &= -\frac{1}{30} C_{\beta\beta\beta} \mu_{\alpha g}^2 \mu_{\beta g}^2 \\
 b_8 &= \frac{1}{6} C_{\beta\alpha\alpha} \mu_{\alpha g}^2 \mu_{\beta g}^2 \\
 b_9 &= \frac{1}{15} C_{\beta\beta\beta} \mu_{\beta g}^4 \\
 \langle S_{\beta\beta} \rangle^{xzxz} &= b_7 \chi_{\alpha\alpha\leftarrow\beta\beta} - b_8 \chi_{\beta\alpha\leftarrow\alpha\beta} + b_9 (\chi_{g g\leftarrow\beta\beta} - \chi_{\beta\beta\leftarrow\beta\beta} - 1)
 \end{aligned}$$

$$\begin{aligned}
 \langle S_{\beta\alpha} \rangle^{xzxz} &= -\frac{1}{30} C_{\beta\beta\alpha} \mu_{\alpha g}^2 \mu_{\beta g}^2 (\chi_{g g\leftarrow\beta\beta} - \chi_{\alpha\alpha\leftarrow\beta\beta} - 1) \\
 &\quad - \frac{1}{10} C_{\beta\alpha\beta} \mu_{\alpha g}^2 \mu_{\beta g}^2 \chi_{\alpha\beta\leftarrow\alpha\beta} \\
 &\quad + \frac{1}{15} C_{\beta\beta\alpha} \mu_{\beta g}^4 \chi_{\beta\beta\leftarrow\beta\beta} \\
 b_{10} &= -\frac{1}{30} C_{\beta\beta\alpha} \mu_{\alpha g}^2 \mu_{\beta g}^2 \\
 b_{11} &= -\frac{1}{10} C_{\beta\alpha\beta} \mu_{\alpha g}^2 \mu_{\beta g}^2 \\
 b_{12} &= \frac{1}{15} C_{\beta\beta\alpha} \mu_{\beta g}^4 \\
 \langle S_{\beta\alpha} \rangle^{xzxz} &= b_{10} (\chi_{g g\leftarrow\beta\beta} - \chi_{\alpha\alpha\leftarrow\beta\beta} - 1) + b_{11} \chi_{\alpha\beta\leftarrow\alpha\beta} + b_{12} \chi_{\beta\beta\leftarrow\beta\beta}
 \end{aligned}$$

Which then gives us the system of equations:

$$\begin{aligned}
 \langle S_{\beta\alpha} \rangle^{xzxz} &= b_{10} (\chi_{gg\leftarrow\beta\beta} - \chi_{\alpha\alpha\leftarrow\beta\beta} - 1) + b_{11}\chi_{\alpha\beta\leftarrow\alpha\beta} + b_{12}\chi_{\beta\beta\leftarrow\beta\beta} \\
 \langle S_{\beta\beta} \rangle^{xzxz} &= b_7\chi_{\alpha\alpha\leftarrow\beta\beta} - b_8\chi_{\beta\beta\leftarrow\alpha\beta} + b_9 (\chi_{gg\leftarrow\beta\beta} - \chi_{\beta\beta\leftarrow\beta\beta} - 1) \\
 \langle S_{\alpha\alpha} \rangle^{xzxz} &= b_4 (\chi_{gg\leftarrow\alpha\alpha} - \chi_{\alpha\alpha\leftarrow\alpha\alpha} - 1) + b_5\chi_{\alpha\beta\leftarrow\beta\alpha} + b_6\chi_{\beta\beta\leftarrow\alpha\alpha} \\
 \langle S_{\alpha\beta} \rangle^{xzxz} &= b_1\chi_{\alpha\alpha\leftarrow\alpha\alpha} + b_2\chi_{\beta\beta\leftarrow\beta\alpha} + b_3 (\chi_{gg\leftarrow\alpha\alpha} - \chi_{\beta\beta\leftarrow\alpha\alpha} - 1) \\
 \langle S_{\beta\alpha} \rangle^{zzzz} &= a_{10} (\chi_{gg\leftarrow\beta\beta} - \chi_{\alpha\alpha\leftarrow\beta\beta} - 1) + a_{11}\chi_{\alpha\beta\leftarrow\alpha\beta} + a_{12}\chi_{\beta\beta\leftarrow\beta\beta} \\
 \langle S_{\beta\beta} \rangle^{zzzz} &= a_7\chi_{\alpha\alpha\leftarrow\beta\beta} + a_8\chi_{\beta\beta\leftarrow\alpha\beta} + a_9 (\chi_{gg\leftarrow\beta\beta} - \chi_{\beta\beta\leftarrow\beta\beta} - 1) \\
 \langle S_{\alpha\alpha} \rangle^{zzzz} &= a_4 (\chi_{gg\leftarrow\alpha\alpha} - \chi_{\alpha\alpha\leftarrow\alpha\alpha} - 1) + a_5\chi_{\alpha\beta\leftarrow\beta\alpha} + a_6\chi_{\beta\beta\leftarrow\alpha\alpha} \\
 \langle S_{\alpha\beta} \rangle^{zzzz} &= a_1\chi_{\alpha\alpha\leftarrow\alpha\alpha} + a_2\chi_{\beta\beta\leftarrow\beta\alpha} + a_3 (\chi_{gg\leftarrow\alpha\alpha} - \chi_{\beta\beta\leftarrow\alpha\alpha} - 1)
 \end{aligned}$$

Which can in principle be solved... but we can make it easier to do so still

7.2.5 SIMPLIFICATIONS

The Quantum Process Matrix has a few mathematical bounds it has to follow. Namely:

$$\sum_a \chi_{aa\leftarrow cd} = \delta_{cd}$$

which together are essentially just conservation of probability. For our case, this constraint gives us three equations:

$$\chi_{gg\leftarrow gg} + \chi_{\alpha\alpha\leftarrow gg} + \chi_{\beta\beta\leftarrow gg} = 1$$

$$\chi_{gg\leftarrow\alpha\alpha} + \chi_{\alpha\alpha\leftarrow\alpha\alpha} + \chi_{\beta\beta\leftarrow\alpha\alpha} = 1$$

$$\chi_{gg\leftarrow\beta\beta} + \chi_{\alpha\alpha\leftarrow\beta\beta} + \chi_{\beta\beta\leftarrow\beta\beta} = 1$$

Which we will use to get rid of the terms dumping amplitude into the ground state. In general, though, we assume that no process will evolve the system from the ground state during free evolution and thus that the first equation in the group above will simply be $1 = 1$.

$$\chi_{gg\leftarrow\alpha\alpha} = 1 - \chi_{\alpha\alpha\leftarrow\alpha\alpha} - \chi_{\beta\beta\leftarrow\alpha\alpha}$$

$$\chi_{gg\leftarrow\beta\beta} = 1 - \chi_{\alpha\alpha\leftarrow\beta\beta} - \chi_{\beta\beta\leftarrow\beta\beta}$$

Which then changes the system of equations to be this:

$$\langle S_{\beta\alpha} \rangle^{xzxz} = b_{10} (-\chi_{\alpha\alpha\leftarrow\beta\beta} - \chi_{\beta\beta\leftarrow\beta\beta} - \chi_{\alpha\alpha\leftarrow\beta\beta}) + b_{11}\chi_{\alpha\beta\leftarrow\alpha\beta} + b_{12}\chi_{\beta\beta\leftarrow\beta\beta}$$

$$\langle S_{\beta\beta} \rangle^{xzxz} = b_7\chi_{\alpha\alpha\leftarrow\beta\beta} - b_8\chi_{\beta\beta\leftarrow\alpha\beta} + b_9 (-\chi_{\alpha\alpha\leftarrow\beta\beta} - \chi_{\beta\beta\leftarrow\beta\beta} - \chi_{\beta\beta\leftarrow\beta\beta})$$

$$\langle S_{\alpha\alpha} \rangle^{xzxz} = b_4 (-\chi_{\alpha\alpha\leftarrow\alpha\alpha} - \chi_{\beta\beta\leftarrow\alpha\alpha} - \chi_{\alpha\alpha\leftarrow\alpha\alpha}) + b_5\chi_{\alpha\beta\leftarrow\beta\alpha} + b_6\chi_{\beta\beta\leftarrow\alpha\alpha}$$

$$\langle S_{\alpha\beta} \rangle^{xzxz} = b_1\chi_{\alpha\alpha\leftarrow\alpha\alpha} + b_2\chi_{\beta\beta\leftarrow\beta\alpha} + b_3 (-\chi_{\alpha\alpha\leftarrow\alpha\alpha} - \chi_{\beta\beta\leftarrow\alpha\alpha} - \chi_{\beta\beta\leftarrow\alpha\alpha})$$

$$\langle S_{\beta\alpha} \rangle^{zzzz} = a_{10} (-\chi_{\alpha\alpha\leftarrow\beta\beta} - \chi_{\beta\beta\leftarrow\beta\beta} - \chi_{\alpha\alpha\leftarrow\beta\beta}) + a_{11}\chi_{\alpha\beta\leftarrow\alpha\beta} + a_{12}\chi_{\beta\beta\leftarrow\beta\beta}$$

$$\langle S_{\beta\beta} \rangle^{zzzz} = a_7\chi_{\alpha\alpha\leftarrow\beta\beta} + a_8\chi_{\beta\beta\leftarrow\alpha\beta} + a_9 (-\chi_{\alpha\alpha\leftarrow\beta\beta} - \chi_{\beta\beta\leftarrow\beta\beta} - \chi_{\beta\beta\leftarrow\beta\beta})$$

$$\langle S_{\alpha\alpha} \rangle^{zzzz} = a_4 (-\chi_{\alpha\alpha\leftarrow\alpha\alpha} - \chi_{\beta\beta\leftarrow\alpha\alpha} - \chi_{\alpha\alpha\leftarrow\alpha\alpha}) + a_5\chi_{\alpha\beta\leftarrow\beta\alpha} + a_6\chi_{\beta\beta\leftarrow\alpha\alpha}$$

$$\langle S_{\alpha\beta} \rangle^{zzzz} = a_1\chi_{\alpha\alpha\leftarrow\alpha\alpha} + a_2\chi_{\beta\beta\leftarrow\beta\alpha} + a_3 (-\chi_{\alpha\alpha\leftarrow\alpha\alpha} - \chi_{\beta\beta\leftarrow\alpha\alpha} - \chi_{\beta\beta\leftarrow\alpha\alpha})$$

which becomes this upon simplification:

$$\begin{aligned}
 \langle S_{\beta\alpha} \rangle^{xzxz} &= -2b_{10}\chi_{\alpha\alpha\leftarrow\beta\beta} + b_{11}\chi_{\alpha\beta\leftarrow\alpha\beta} + (b_{12} - b_{10})\chi_{\beta\beta\leftarrow\beta\beta} \\
 \langle S_{\beta\beta} \rangle^{xzxz} &= (b_7 - b_9)\chi_{\alpha\alpha\leftarrow\beta\beta} - b_8\chi_{\beta\alpha\leftarrow\alpha\beta} - 2b_9\chi_{\beta\beta\leftarrow\beta\beta} \\
 \langle S_{\alpha\alpha} \rangle^{xzxz} &= -2b_4\chi_{\alpha\alpha\leftarrow\alpha\alpha} + b_5\chi_{\alpha\beta\leftarrow\beta\alpha} + (b_6 - b_4)\chi_{\beta\beta\leftarrow\alpha\alpha} \\
 \langle S_{\alpha\beta} \rangle^{xzxz} &= (b_1 - b_3)\chi_{\alpha\alpha\leftarrow\alpha\alpha} + b_2\chi_{\beta\alpha\leftarrow\beta\alpha} - 2b_3\chi_{\beta\beta\leftarrow\alpha\alpha} \\
 \langle S_{\beta\alpha} \rangle^{zzzz} &= -2a_{10}\chi_{\alpha\alpha\leftarrow\beta\beta} + a_{11}\chi_{\alpha\beta\leftarrow\alpha\beta} + (a_{12} - a_{10})\chi_{\beta\beta\leftarrow\beta\beta} \\
 \langle S_{\beta\beta} \rangle^{zzzz} &= (a_7 - a_9)\chi_{\alpha\alpha\leftarrow\beta\beta} - a_8\chi_{\beta\alpha\leftarrow\alpha\beta} - 2a_9\chi_{\beta\beta\leftarrow\beta\beta} \\
 \langle S_{\alpha\alpha} \rangle^{zzzz} &= -2a_4\chi_{\alpha\alpha\leftarrow\alpha\alpha} + a_5\chi_{\alpha\beta\leftarrow\beta\alpha} + (a_6 - a_4)\chi_{\beta\beta\leftarrow\alpha\alpha} \\
 \langle S_{\alpha\beta} \rangle^{zzzz} &= (a_1 - a_3)\chi_{\alpha\alpha\leftarrow\alpha\alpha} + a_2\chi_{\beta\alpha\leftarrow\beta\alpha} - 2a_3\chi_{\beta\beta\leftarrow\alpha\alpha}
 \end{aligned}$$

But we are not done: density matrices must remain hermitian and thus, we have another constraint on our quantum process matrix:

$$\chi_{ab\leftarrow cd} = \chi_{ba\leftarrow dc}^*$$

Which means that all of the population-to-anything and anything-population terms are real and that

$$\chi_{\beta\alpha\leftarrow\beta\alpha} = \chi_{\alpha\beta\leftarrow\alpha\beta}^*$$

$$\chi_{\beta\alpha\leftarrow\alpha\beta} = \chi_{\alpha\beta\leftarrow\beta\alpha}^*$$

Getting rid of an additional two terms in our system of equations:

$$\begin{aligned}
 \langle S_{\beta\alpha} \rangle^{xzxz} &= -2b_{10}\chi_{\alpha\alpha\leftarrow\beta\beta} + b_{11}\chi_{\alpha\beta\leftarrow\alpha\beta} + (b_{12} - b_{10})\chi_{\beta\beta\leftarrow\beta\beta} \\
 \langle S_{\beta\beta} \rangle^{xzxz} &= (b_7 - b_9)\chi_{\alpha\alpha\leftarrow\beta\beta} - b_8\chi_{\alpha\beta\leftarrow\beta\alpha}^* - 2b_9\chi_{\beta\beta\leftarrow\beta\beta} \\
 \langle S_{\alpha\alpha} \rangle^{xzxz} &= -2b_4\chi_{\alpha\alpha\leftarrow\alpha\alpha} + b_5\chi_{\alpha\beta\leftarrow\beta\alpha} + (b_6 - b_4)\chi_{\beta\beta\leftarrow\alpha\alpha} \\
 \langle S_{\alpha\beta} \rangle^{xzxz} &= (b_1 - b_3)\chi_{\alpha\alpha\leftarrow\alpha\alpha} + b_2\chi_{\alpha\beta\leftarrow\alpha\beta}^* - 2b_3\chi_{\beta\beta\leftarrow\alpha\alpha} \\
 \langle S_{\beta\alpha} \rangle^{zzzz} &= -2a_{10}\chi_{\alpha\alpha\leftarrow\beta\beta} + a_{11}\chi_{\alpha\beta\leftarrow\alpha\beta} + (a_{12} - a_{10})\chi_{\beta\beta\leftarrow\beta\beta} \\
 \langle S_{\beta\beta} \rangle^{zzzz} &= (a_7 - a_9)\chi_{\alpha\alpha\leftarrow\beta\beta} - a_8\chi_{\alpha\beta\leftarrow\beta\alpha}^* - 2a_9\chi_{\beta\beta\leftarrow\beta\beta} \\
 \langle S_{\alpha\alpha} \rangle^{zzzz} &= -2a_4\chi_{\alpha\alpha\leftarrow\alpha\alpha} + a_5\chi_{\alpha\beta\leftarrow\beta\alpha} + (a_6 - a_4)\chi_{\beta\beta\leftarrow\alpha\alpha} \\
 \langle S_{\alpha\beta} \rangle^{zzzz} &= (a_1 - a_3)\chi_{\alpha\alpha\leftarrow\alpha\alpha} + a_2\chi_{\alpha\beta\leftarrow\alpha\beta}^* - 2a_3\chi_{\beta\beta\leftarrow\alpha\alpha}
 \end{aligned}$$

Also now that we know more about the real and imaginary structure of the problem, this necessitates splitting the problem in two:

$$\begin{aligned}
 \mathbf{Re} [\langle S_{\beta\alpha} \rangle^{xzxz}] &= \\
 -2\mathbf{Re} [b_{10}] \chi_{\alpha\alpha\leftarrow\beta\beta} &+ \mathbf{Re} [b_{11}] \mathbf{Re} [\chi_{\alpha\beta\leftarrow\alpha\beta}] - \mathbf{Im} [b_{11}] \mathbf{Im} [\chi_{\alpha\beta\leftarrow\alpha\beta}] + \mathbf{Re} [(b_{12} - b_{10})] \chi_{\beta\beta\leftarrow\beta\beta}
 \end{aligned}$$

$$\begin{aligned}
 \mathbf{Im} [\langle S_{\beta\alpha} \rangle^{xzxz}] &= \\
 -2\mathbf{Im} [b_{10}] \chi_{\alpha\alpha\leftarrow\beta\beta} &+ \mathbf{Im} [b_{11}] \mathbf{Re} [\chi_{\alpha\beta\leftarrow\alpha\beta}] + \mathbf{Re} [b_{11}] \mathbf{Im} [\chi_{\alpha\beta\leftarrow\alpha\beta}] + \mathbf{Im} [(b_{12} - b_{10})] \chi_{\beta\beta\leftarrow\beta\beta}
 \end{aligned}$$

$$\mathbf{Re} [\langle S_{\beta\beta} \rangle^{xzxz}] =$$

$$\mathbf{Re} [(b_7 - b_9)] \chi_{\alpha\alpha\leftarrow\beta\beta} - \mathbf{Re} [b_8] \mathbf{Re} [\chi_{\alpha\beta\leftarrow\beta\alpha}] - \mathbf{Im} [b_8] \mathbf{Im} [\chi_{\alpha\beta\leftarrow\beta\alpha}] - 2\mathbf{Re} [b_9] \chi_{\beta\beta\leftarrow\beta\beta}$$

$$\mathbf{Im} [\langle S_{\beta\beta} \rangle^{xzxz}] =$$

$$\mathbf{Im} [(b_7 - b_9)] \chi_{\alpha\alpha\leftarrow\beta\beta} - \mathbf{Im} [b_8] \mathbf{Re} [\chi_{\alpha\beta\leftarrow\beta\alpha}] + \mathbf{Re} [b_8] \mathbf{Im} [\chi_{\alpha\beta\leftarrow\beta\alpha}] - 2\mathbf{Im} [b_9] \chi_{\beta\beta\leftarrow\beta\beta}$$

$$\mathbf{Re} [\langle S_{\alpha\alpha} \rangle^{xzxz}] =$$

$$- 2\mathbf{Re} [b_4] \chi_{\alpha\alpha\leftarrow\alpha\alpha} + \mathbf{Re} [b_5] \mathbf{Re} [\chi_{\alpha\beta\leftarrow\beta\alpha}] - \mathbf{Im} [b_5] \mathbf{Im} [\chi_{\alpha\beta\leftarrow\beta\alpha}] + \mathbf{Re} [(b_6 - b_4)] \chi_{\beta\beta\leftarrow\alpha\alpha}$$

$$\mathbf{Im} [\langle S_{\alpha\alpha} \rangle^{xzxz}] =$$

$$- 2\mathbf{Im} [b_4] \chi_{\alpha\alpha\leftarrow\alpha\alpha} + \mathbf{Im} [b_5] \mathbf{Re} [\chi_{\alpha\beta\leftarrow\beta\alpha}] + \mathbf{Re} [b_5] \mathbf{Im} [\chi_{\alpha\beta\leftarrow\beta\alpha}] + \mathbf{Im} [(b_6 - b_4)] \chi_{\beta\beta\leftarrow\alpha\alpha}$$

$$\mathbf{Re} [\langle S_{\alpha\beta} \rangle^{xzxz}] =$$

$$\mathbf{Re} [(b_1 - b_3)] \chi_{\alpha\alpha\leftarrow\alpha\alpha} + \mathbf{Re} [b_2] \mathbf{Re} [\chi_{\alpha\beta\leftarrow\alpha\beta}] + \mathbf{Im} [b_2] \mathbf{Im} [\chi_{\alpha\beta\leftarrow\alpha\beta}] - 2\mathbf{Re} [b_3] \chi_{\beta\beta\leftarrow\alpha\alpha}$$

$$\mathbf{Im} [\langle S_{\alpha\beta} \rangle^{xzxz}] =$$

$$\mathbf{Im} [(b_1 - b_3)] \chi_{\alpha\alpha\leftarrow\alpha\alpha} + \mathbf{Im} [b_2] \mathbf{Re} [\chi_{\alpha\beta\leftarrow\alpha\beta}] - \mathbf{Re} [b_2] \mathbf{Im} [\chi_{\alpha\beta\leftarrow\alpha\beta}] - 2\mathbf{Im} [b_3] \chi_{\beta\beta\leftarrow\alpha\alpha}$$

$$\begin{aligned} \mathbf{Re} [\langle S_{\beta\alpha} \rangle^{zzzz}] = \\ -2\mathbf{Re} [a_{10}] \chi_{\alpha\alpha\leftarrow\beta\beta} + \mathbf{Re} [a_{11}] \mathbf{Re} [\chi_{\alpha\beta\leftarrow\alpha\beta}] - \mathbf{Im} [a_{11}] \mathbf{Im} [\chi_{\alpha\beta\leftarrow\alpha\beta}] + \mathbf{Re} [(a_{12} - a_{10})] \chi_{\beta\beta\leftarrow\beta\beta} \end{aligned}$$

$$\begin{aligned} \mathbf{Im} [\langle S_{\beta\alpha} \rangle^{zzzz}] = \\ -2\mathbf{Im} [a_{10}] \chi_{\alpha\alpha\leftarrow\beta\beta} + \mathbf{Im} [a_{11}] \mathbf{Re} [\chi_{\alpha\beta\leftarrow\alpha\beta}] + \mathbf{Re} [a_{11}] \mathbf{Im} [\chi_{\alpha\beta\leftarrow\alpha\beta}] + \mathbf{Im} [(a_{12} - a_{10})] \chi_{\beta\beta\leftarrow\beta\beta} \end{aligned}$$

$$\begin{aligned} \mathbf{Re} [\langle S_{\beta\beta} \rangle^{zzzz}] = \\ \mathbf{Re} [(a_7 - a_9)] \chi_{\alpha\alpha\leftarrow\beta\beta} - \mathbf{Re} [a_8] \mathbf{Re} [\chi_{\alpha\beta\leftarrow\beta\alpha}] - \mathbf{Im} [a_8] \mathbf{Im} [\chi_{\alpha\beta\leftarrow\beta\alpha}] - 2\mathbf{Re} [a_9] \chi_{\beta\beta\leftarrow\beta\beta} \end{aligned}$$

$$\begin{aligned} \mathbf{Im} [\langle S_{\beta\beta} \rangle^{zzzz}] = \\ \mathbf{Im} [(a_7 - a_9)] \chi_{\alpha\alpha\leftarrow\beta\beta} - \mathbf{Im} [a_8] \mathbf{Re} [\chi_{\alpha\beta\leftarrow\beta\alpha}] + \mathbf{Re} [a_8] \mathbf{Im} [\chi_{\alpha\beta\leftarrow\beta\alpha}] - 2\mathbf{Im} [a_9] \chi_{\beta\beta\leftarrow\beta\beta} \end{aligned}$$

$$\begin{aligned} \mathbf{Re} [\langle S_{\alpha\alpha} \rangle^{zzzz}] = \\ -2\mathbf{Re} [a_4] \chi_{\alpha\alpha\leftarrow\alpha\alpha} + \mathbf{Re} [a_5] \mathbf{Re} [\chi_{\alpha\beta\leftarrow\beta\alpha}] - \mathbf{Im} [a_5] \mathbf{Im} [\chi_{\alpha\beta\leftarrow\beta\alpha}] + \mathbf{Re} [(a_6 - a_4)] \chi_{\beta\beta\leftarrow\alpha\alpha} \end{aligned}$$

$$\begin{aligned} \mathbf{Im} [\langle S_{\alpha\alpha} \rangle^{zzzz}] = \\ -2\mathbf{Im} [a_4] \chi_{\alpha\alpha\leftarrow\alpha\alpha} + \mathbf{Im} [a_5] \mathbf{Re} [\chi_{\alpha\beta\leftarrow\beta\alpha}] + \mathbf{Re} [a_5] \mathbf{Im} [\chi_{\alpha\beta\leftarrow\beta\alpha}] + \mathbf{Im} [(a_6 - a_4)] \chi_{\beta\beta\leftarrow\alpha\alpha} \end{aligned}$$

$$\mathbf{Re} [\langle S_{\alpha\beta} \rangle^{zzzz}] =$$

$$\mathbf{Re} [(a_1 - a_3)] \chi_{\alpha\alpha\leftarrow\alpha\alpha} + \mathbf{Re} [a_2] \mathbf{Re} [\chi_{\alpha\beta\leftarrow\alpha\beta}] + \mathbf{Im} [a_2] \mathbf{Im} [\chi_{\alpha\beta\leftarrow\alpha\beta}] - 2\mathbf{Re} [a_3] \chi_{\beta\beta\leftarrow\alpha\alpha}$$

$$\mathbf{Im} [\langle S_{\alpha\beta} \rangle^{zzzz}] =$$

$$\mathbf{Im} [(a_1 - a_3)] \chi_{\alpha\alpha\leftarrow\alpha\alpha} + \mathbf{Im} [a_2] \mathbf{Re} [\chi_{\alpha\beta\leftarrow\alpha\beta}] - \mathbf{Re} [a_2] \mathbf{Im} [\chi_{\alpha\beta\leftarrow\alpha\beta}] - 2\mathbf{Im} [a_3] \chi_{\beta\beta\leftarrow\alpha\alpha}$$

From which we can define an over-defined matrix equation

$$\vec{S}(T) = \mathbf{M}\vec{\chi}(T) \tag{7.2.8}$$

which must be positive and semi-definite like all quantum process matrices. Thus it follows this relationship.

$$\sum_{i,j,q,p} z_{iq}^* \chi_{ij\leftarrow qp} z_{jp} \geq 0 \tag{7.2.9}$$

For **any** matrix z . We use the numerical package `cvxopt` to ensure that our optimization routine outputs a semi-definite map even in the presence of noise. Then, we solve for each time step of the problem, in principle. See there are many problems here. First is that we probably won't know the precise amplitudes of the system at any given time. We can solve that though because we know the initial conditions.

7.2.6 INITIAL CONDITIONS

The aforementioned initial condition is:

$$\chi_{cd \leftarrow ab}(0) = \delta_{ca} \delta_{db} \quad (7.2.10)$$

which intuitively tells us that at time $T = 0$, no state can have changed from its initial state yet (since there has been non time to evolve) such that only terms looking like $\chi_{ij \leftarrow ij}$ are 1 and everything else is zero. For us, this gives us the terms:

$$\chi_{\alpha\alpha \leftarrow \alpha\alpha}(0) = 1$$

$$\chi_{\beta\beta \leftarrow \beta\beta}(0) = 1$$

$$\mathbf{Re} [\chi_{\alpha\beta \leftarrow \alpha\beta}(0)] = 1$$

$$\mathbf{Re} [\chi_{\beta\alpha \leftarrow \beta\alpha}(0)] = 1$$

Which we can then plug in to the matrix equation to get a sanity check on the experimental signal

$$\mathbf{Re} [\langle S_{\beta\alpha}(T=0) \rangle^{xzxz}] = \mathbf{Re} [b_{12} - b_{10} + b_{11}]$$

$$\mathbf{Im} [\langle S_{\beta\alpha}(T=0) \rangle^{xzxz}] = \mathbf{Im} [b_{12} - b_{10} + b_{11}]$$

$$\mathbf{Re} [\langle S_{\beta\beta}(T=0) \rangle^{xzxz}] = 2\mathbf{Re} [b_9]$$

$$\mathbf{Im} [\langle S_{\beta\beta}(T=0) \rangle^{xzxz}] = 2\mathbf{Im} [b_9]$$

$$\mathbf{Re} [\langle S_{\alpha\alpha}(T=0) \rangle^{xzxz}] = -2\mathbf{Re} [b_4]$$

$$\mathbf{Im} [\langle S_{\alpha\alpha}(T=0) \rangle^{xzxz}] = -2\mathbf{Im} [b_4]$$

$$\mathbf{Re} [\langle S_{\alpha\beta}(T=0) \rangle^{xzxz}] = \mathbf{Re} [b_1 - b_3 + b_2]$$

$$\mathbf{Im} [\langle S_{\alpha\beta}(T=0) \rangle^{xzxz}] = \mathbf{Im} [b_1 - b_3 + b_2]$$

$$\mathbf{Re} [\langle S_{\beta\alpha}(T=0) \rangle^{zzzz}] = \mathbf{Re} [a_{12} - a_{10} + a_{11}]$$

$$\mathbf{Im} [\langle S_{\beta\alpha}(T=0) \rangle^{zzzz}] = \mathbf{Im} [a_{12} - a_{10} + a_{11}]$$

$$\mathbf{Re} [\langle S_{\beta\beta}(T=0) \rangle^{zzzz}] = 2\mathbf{Re} [a_9]$$

$$\mathbf{Im} [\langle S_{\beta\beta}(T=0) \rangle^{zzzz}] = 2\mathbf{Im} [a_9]$$

$$\mathbf{Re} [\langle S_{\alpha\alpha}(T=0) \rangle^{zzzz}] = -2\mathbf{Re} [a_4]$$

$$\mathbf{Im} [\langle S_{\alpha\alpha}(T=0) \rangle^{zzzz}] = -2\mathbf{Im} [a_4]$$

$$\mathbf{Re} [\langle S_{\alpha\beta}(T=0) \rangle^{zzzz}] = \mathbf{Re} [a_1 - a_3 + a_2]$$

$$\mathbf{Im} [\langle S_{\alpha\beta}(T=0) \rangle^{zzzz}] = \mathbf{Im} [a_1 - a_3 + a_2]$$

And it's clear here that we can get some algebraic brevity easily by combining real and imaginary:

$$\langle S_{\beta\alpha}(0) \rangle^{xzxz} = b_{11} + b_{12} - b_{10}$$

$$\langle S_{\beta\beta}(0) \rangle^{xzxz} = -2b_9$$

$$\langle S_{\alpha\alpha}(0) \rangle^{xzxz} = -2b_4$$

$$\langle S_{\alpha\beta}(0) \rangle^{xzxz} = b_1 - b_3 + b_2$$

$$\langle S_{\beta\alpha}(0) \rangle^{zzzz} = a_{11} + a_{12} - a_{10}$$

$$\langle S_{\beta\beta}(0) \rangle^{zzzz} = -2a_9$$

$$\langle S_{\alpha\alpha}(0) \rangle^{zzzz} = -2a_4$$

$$\langle S_{\alpha\beta}(0) \rangle^{zzzz} = a_1 - a_3 + a_2$$

Now let's put in their actual values for a_i and b_j :

$$\langle S_{\beta\alpha} \rangle^{xzxz} = -\frac{1}{10} C_{\beta\alpha\beta}^{xzxz} \mu_{\alpha g}^2 \mu_{\beta g}^2 + \frac{1}{15} C_{\beta\beta\alpha}^{xzxz} \mu_{\beta g}^4 + \frac{1}{30} C_{\beta\beta\alpha}^{xzxz} \mu_{\alpha g}^2 \mu_{\beta g}^2$$

$$\langle S_{\beta\beta} \rangle^{xzxz} = -\frac{2}{15} C_{\beta\beta\beta}^{xzxz} \mu_{\beta g}^4$$

$$\langle S_{\alpha\alpha} \rangle^{xzxz} = -\frac{2}{15} C_{\alpha\alpha\alpha}^{xzxz} \mu_{\alpha g}^4$$

$$\langle S_{\alpha\beta} \rangle^{xzxz} = \frac{1}{15} C_{\alpha\alpha\beta}^{xzxz} \mu_{\alpha g}^4 + \frac{1}{30} C_{\alpha\alpha\beta}^{xzxz} \mu_{\alpha g}^2 \mu_{\beta g}^2 - \frac{1}{10} C_{\alpha\beta\alpha}^{xzxz} \mu_{\alpha g}^2 \mu_{\beta g}^2$$

$$\langle S_{\beta\alpha} \rangle^{zzzz} = -\frac{2}{15} C_{\beta\alpha\beta}^{zzzz} \mu_{\alpha g}^2 \mu_{\beta g}^2 + \frac{1}{5} C_{\beta\beta\alpha}^{zzzz} \mu_{\beta g}^4 - \frac{1}{15} C_{\beta\beta\alpha}^{zzzz} \mu_{\alpha g}^2 \mu_{\beta g}^2$$

$$\langle S_{\beta\beta} \rangle^{zzzz} = -\frac{2}{5} C_{\beta\beta\beta}^{zzzz} \mu_{\beta g}^4$$

$$\langle S_{\alpha\alpha} \rangle^{zzzz} = -\frac{2}{5} C_{\alpha\alpha\alpha}^{zzzz} \mu_{\alpha g}^4$$

$$\langle S_{\alpha\beta} \rangle^{zzzz} = \frac{1}{5} C_{\alpha\alpha\beta}^{zzzz} \mu_{\alpha g}^4 - \frac{1}{15} C_{\alpha\alpha\beta}^{zzzz} \mu_{\alpha g}^2 \mu_{\beta g}^2 - \frac{2}{15} C_{\alpha\beta\alpha}^{zzzz} \mu_{\alpha g}^2 \mu_{\beta g}^2$$

Now we want to use these 16 different equations to set the constants that all of the a and b constants are in terms of: namely C_{ijk} .

Starting with the C constants we have a lot of options open to us depending on how comfortable we are with various possible approximations:

$$C_{\alpha\alpha\alpha}^{zzz} = f_0 = A_1A_2A_3 = x_0 = B$$

$$C_{\alpha\alpha\beta}^{zzz} = f_1 = A_1A_2B_3 = x_1 = B$$

$$C_{\alpha\beta\alpha}^{zzz} = f_2 = A_1B_2A_3 = x_1 = B$$

$$C_{\beta\alpha\alpha}^{zzz} = f_3 = B_1A_2A_3 = x_1 = B$$

$$C_{\beta\beta\alpha}^{zzz} = f_4 = B_1B_2A_3 = x_2 = B$$

$$C_{\beta\alpha\beta}^{zzz} = f_5 = B_1A_2B_3 = x_2 = B$$

$$C_{\beta\beta\beta}^{zzz} = f_6 = B_1B_2B_3 = x_3 = B$$

$$C_{\alpha\alpha\alpha}^{xzx} = l_0 = a_1a_2a_3 = y_0 = A$$

$$C_{\alpha\alpha\beta}^{xzx} = l_1 = a_1a_2b_3 = y_1 = A$$

$$C_{\alpha\beta\alpha}^{xzx} = l_2 = a_1b_2a_3 = y_1 = A$$

$$C_{\beta\alpha\alpha}^{xzx} = l_3 = b_1a_2a_3 = y_1 = A$$

$$C_{\beta\beta\alpha}^{xzx} = l_4 = b_1b_2a_3 = y_2 = A$$

$$C_{\beta\alpha\beta}^{xzx} = l_5 = b_1a_2b_3 = y_2 = A$$

$$C_{\beta\beta\beta}^{xzx} = l_6 = b_1b_2b_3 = y_3 = A$$

The first column is the safest assumption: that each different combinations will, for whatever unpredictable oddities, be different. The next approximation assumes that the amplitude of the n th pulse is consistent across the different constants—which this author expects is the appropriate level

of approximation since the pulses shouldn't change. The next column reflects that it's likely, given that in the theory or other non-idealities that each pulse that in each pulse, the α and the β amplitude will be the same (the subscript is the number of times β appears). The last, least safe, approximation is that all the beams are the same which would be semi-justified if the overlap of the laser spectrum with the α peak of the absorption spectrum was about the same as the overlap with the β peak.

Only 6 of the 8 f or l constants show up in the initial conditions and assuming that all beams are exactly the same gives an unsolvable set of equations. So, for now, we will assume that each beam is the same but with different amplitudes for α and for β and that we know the transition dipoles. To make notation simpler, we assign $a = \mu_{\alpha g}^2$ and $b = \mu_{\beta g}^2$.

$$\begin{aligned}\langle S_{\beta\alpha} \rangle^{xzxz} &= x_2 \frac{1}{15} (b^2 - ab) \\ \langle S_{\beta\beta} \rangle^{xzxz} &= -\frac{2}{15} x_3 b^2 \\ \langle S_{\alpha\alpha} \rangle^{xzxz} &= -\frac{2}{15} x_0 a^2 \\ \langle S_{\alpha\beta} \rangle^{xzxz} &= x_1 \frac{1}{15} (a^2 - ab)\end{aligned}$$

We are now ready to apply these equations to data obtained from Professor Greg Engel. He gave us $zzzz$ and $xzxz$ polarized 2D-Electronic Spectroscopy data on Light-Harvesting Complex 2 (LH2). A typical time slice looked like Figure 7.1. By feeding this into the algorithm we developed, we can get the elements of the QPT matrix. First up is Figure 7.2 which rather non-controversially shows the excited populations decaying. Showing the populations decay another way is Figure 7.3 which instead shows the proportion which has gone to the ground state. We see slightly faster decay fro the higher energy β state.

Then for Coherences there are the decay terms in Figure 7.4 showing a trend towards zero as

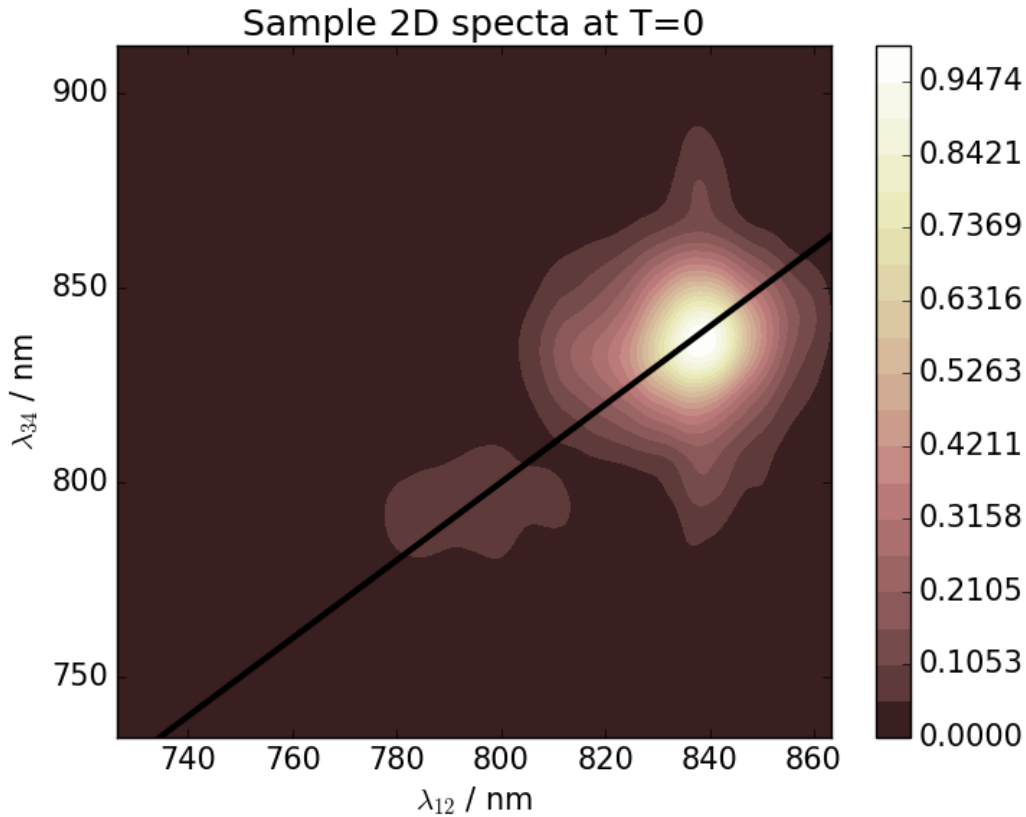


Figure 7.1: This is data obtained from the Engel group for LH2. Specifically this is the xzxx polarization setting at $T = 0$.

would be expected with decoherence from interactions with the thermal bath. In Figure 7.5, there are real and imaginary parts of the coherence transfer element; they simply show the sloshing back and forth of the coherence term between the two possible density matrix elements.

Then lastly we have what turned out to be the problem element: the population transfer terms in Figure 7.6. This figure indicates that there is a small, but insignificant uphill energy transfer. Now this would be really cool if it were true as it would indicate that the bath imparted some useful energy to the light-harvesting apparatus of LH2. But extraordinary claims require extraordinary evidence, so we need to revisit how we got here. to develop these Quantum Process Matrices, we had to assume that all three laser excitation pulses have the same power amplitude at both the α

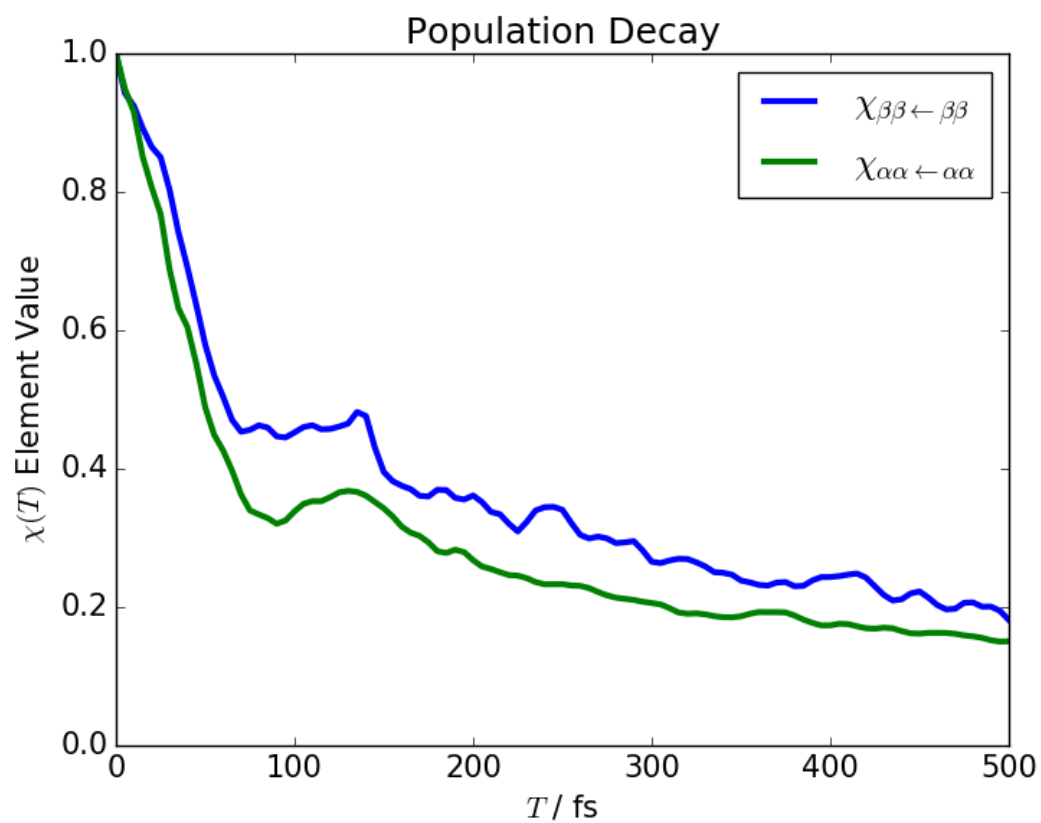


Figure 7.2: These are the two elements of the calculated Process Matrix which determine what proportion of the singly excited populations stay in the same state

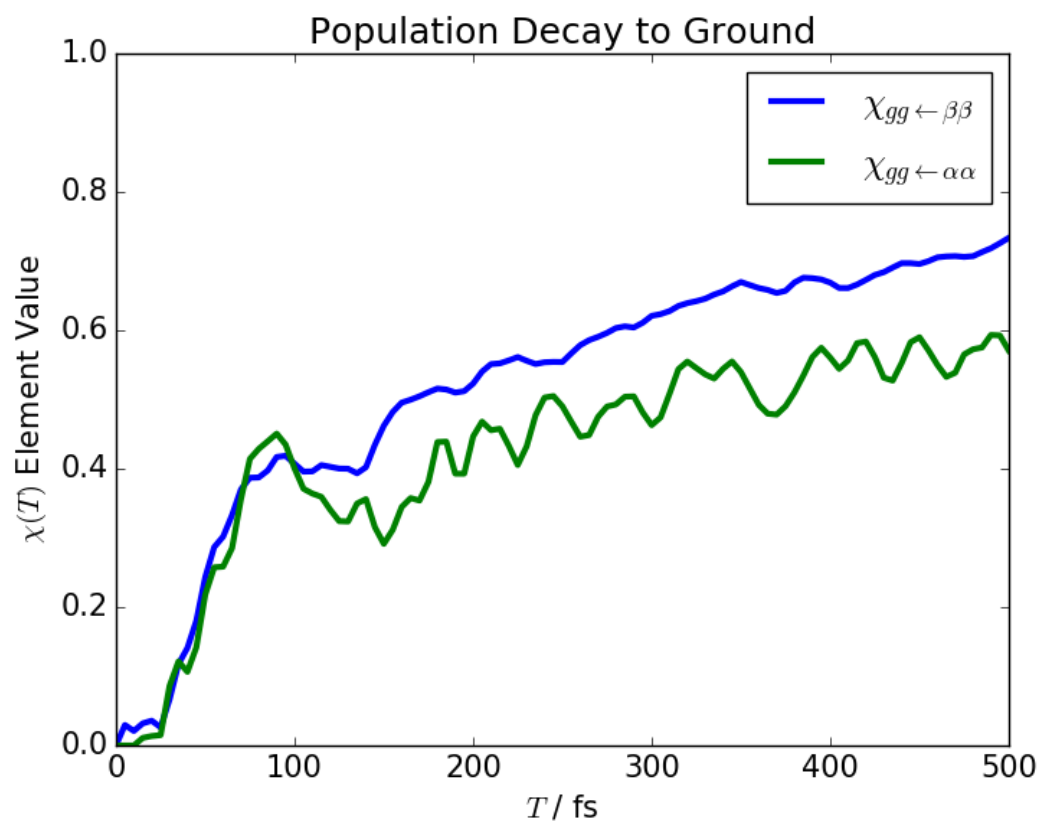


Figure 7.3: These are the two elements of the calculated Process Matrix which determine the decay of the singly excited populations to the ground state population

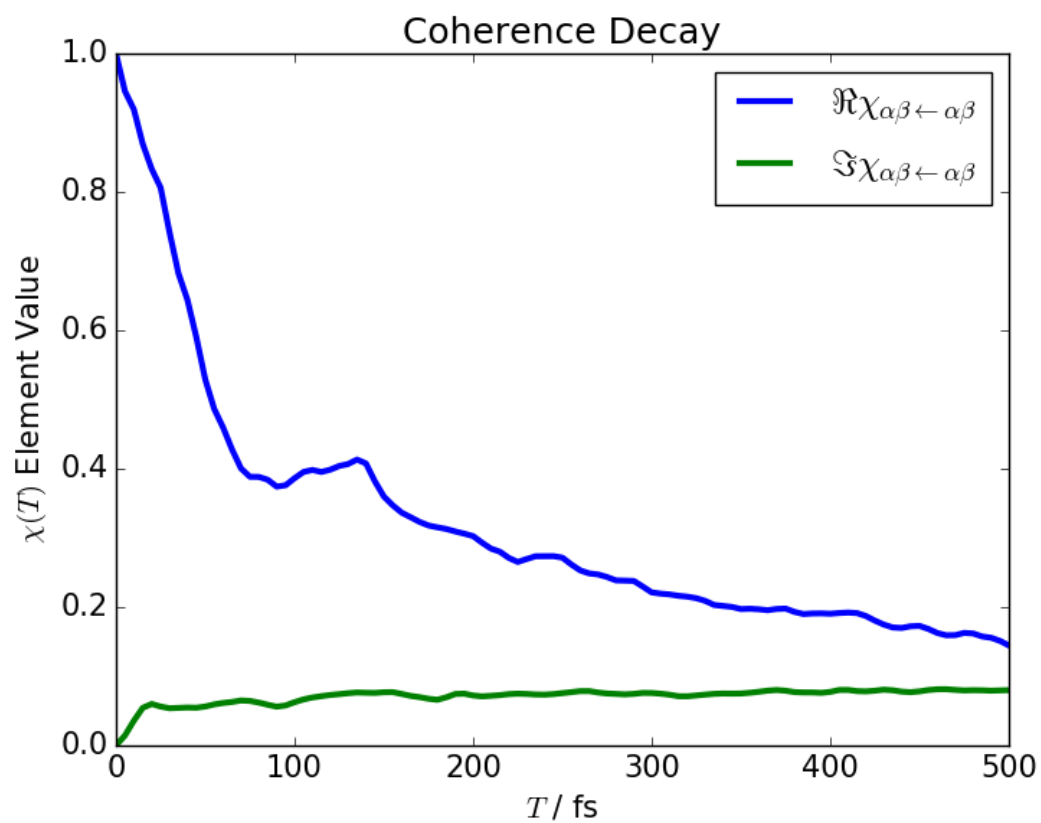


Figure 7.4: These are the two elements of the calculated Process Matrix which show what proportion of the singly excited coherences stay in the same coherent state

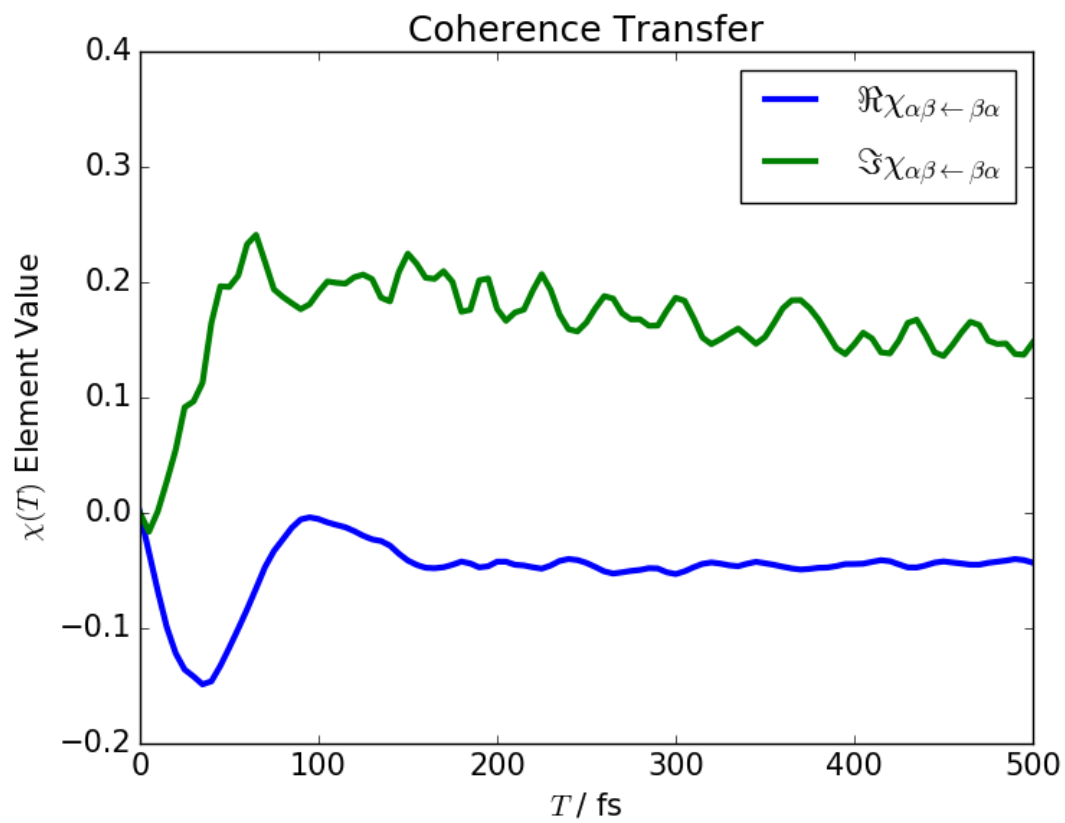


Figure 7.5: These are the two elements of the calculated Process Matrix which determine what proportion of the singly excited coherences flop to the other coherence.

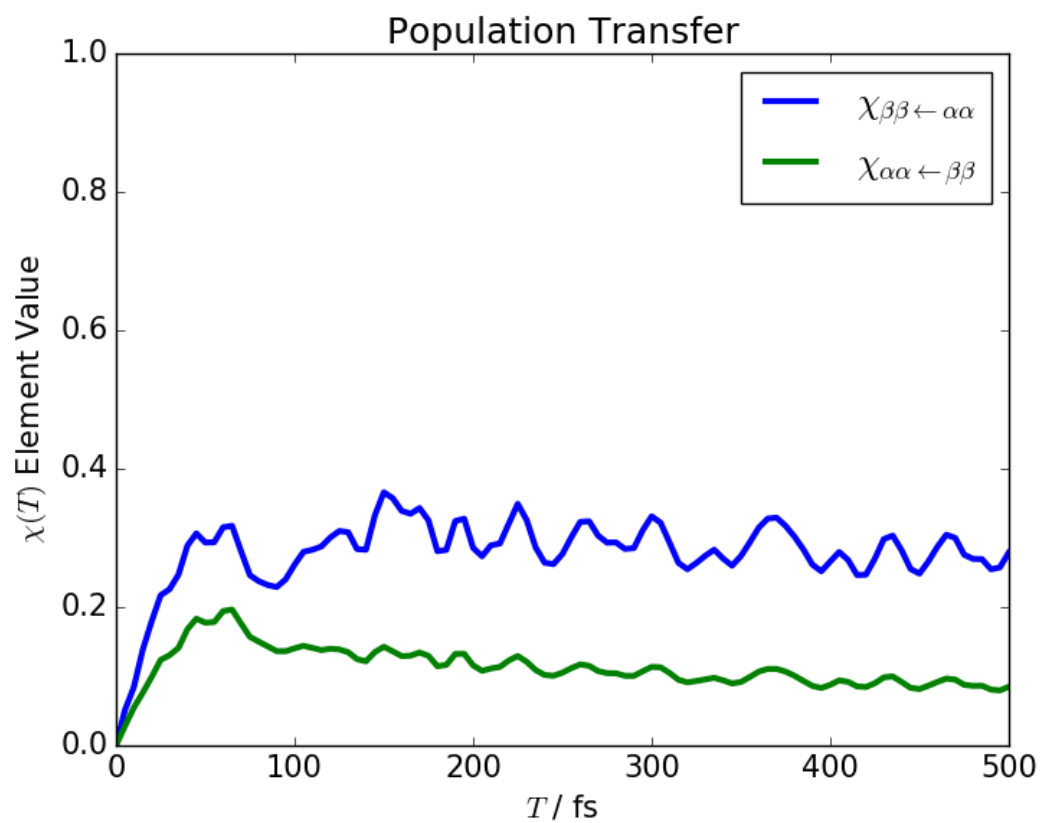


Figure 7.6: These are the two elements of the calculated Process Matrix which determine the transfer of the singly excited populations to the other singly excited population. This is where we ran into problems. The $\beta\beta$ population is higher in energy than the $\alpha\alpha$ population so if this graph was correct, there would be uphill energy transfer.

and β transitions and at both polarizations. This should not quite be true, and this assumption could very easily affect the expected probabilities of transfer into and out of α and β states. So we go back and see if we can correct this loose assumption.

7.2.7 MORE CORRECT FORMS FOR LASER AMPLITUDE

Knowing that we need to be more ignorant about the pulses, we recognize that for the $xzxz$ experiments, it is not reasonable to assume that all the beams are the same because they have different polarizations, we have to stop and go back a level of approximation. We now assume that the x pulse amplitudes are the same and the z pulse amplitudes are the same

$$\begin{aligned}\langle S_{\beta\alpha} \rangle^{xzxz} &= -\frac{1}{10}B_1A_2B_1ab + \frac{1}{15}B_1B_2A_1b^2 + \frac{1}{30}B_1B_2A_1ab \\ \langle S_{\beta\beta} \rangle^{xzxz} &= -\frac{2}{15}B_1B_2B_1b^2 \\ \langle S_{\alpha\alpha} \rangle^{xzxz} &= -\frac{2}{15}A_1A_2A_1a^2 \\ \langle S_{\alpha\beta} \rangle^{xzxz} &= \frac{1}{15}A_1A_2B_1a^2 + \frac{1}{30}A_1A_2B_1ab - \frac{1}{10}A_1B_2A_1ab\end{aligned}$$

and let's move things around to simplify them:

$$\begin{aligned}\langle S_{\beta\alpha} \rangle^{xzxz} &= B_1A_2B_1 \left(-\frac{1}{10}ab \right) + B_1B_2A_1 \left(\frac{1}{15}b^2 + \frac{1}{30}ab \right) \\ \langle S_{\beta\beta} \rangle^{xzxz} &= B_1B_2B_1 \left(-\frac{2}{15}b^2 \right) \\ \langle S_{\alpha\alpha} \rangle^{xzxz} &= A_1A_2A_1 \left(-\frac{2}{15}a^2 \right) \\ \langle S_{\alpha\beta} \rangle^{xzxz} &= A_1A_2B_1 \left(\frac{1}{15}a^2 + \frac{1}{30}ab \right) + A_1B_2A_1 \left(-\frac{1}{10}ab \right)\end{aligned}$$

Which should, in principle, be soluble with 8 equations and 8 unknowns. For the 4 $zzzz$ equations, the solution is trivial. When we put the four for $xzxz$ into Mathematica, both

numerically and symbolically, it gives the null set. What do we do?

7.2.8 ANCILLA

We find that turning the equation into a quadratic with ancilla variables allows Mathematica to solve. First some definitions

$$\langle S_{\beta\alpha} \rangle^{xzxz} = B_1^2 A_2 \left(-\frac{1}{10} ab \right) + A_1 B_1 B_2 \left(\frac{1}{15} b^2 + \frac{1}{30} ab \right)$$

$$\langle S_{\beta\beta} \rangle^{xzxz} = B_1^2 B_2 \left(-\frac{2}{15} b^2 \right)$$

$$\langle S_{\alpha\alpha} \rangle^{xzxz} = A_1^2 A_2 \left(-\frac{2}{15} a^2 \right)$$

$$\langle S_{\alpha\beta} \rangle^{xzxz} = A_1 A_2 B_1 \left(\frac{1}{15} a^2 + \frac{1}{30} ab \right) + A_1^2 B_2 \left(-\frac{1}{10} ab \right)$$

$$c_1 = -\frac{ab}{10} \tag{7.2.11}$$

$$c_2 = \frac{b^2}{15} + \frac{ab}{30} \tag{7.2.12}$$

$$c_3 = \frac{-2b^2}{15} \tag{7.2.13}$$

$$c_4 = \frac{-2a^2}{15} \tag{7.2.14}$$

$$c_5 = \frac{a^2}{15} + \frac{ab}{30} \tag{7.2.15}$$

$$c_6 = \frac{-ab}{10} \tag{7.2.16}$$

now our ancilla variables:

$$q_1 = B_1^2 \quad (7.2.17)$$

$$q_2 = B_1 B_2 \quad (7.2.18)$$

$$q_3 = A_1^2 \quad (7.2.19)$$

$$q_4 = A_1 A_2 \quad (7.2.20)$$

$$(7.2.21)$$

which turns the original system into:

$$\langle S_{\beta\alpha} \rangle^{xzxz} = c_1 q_1 A_2 + c_2 q_2 A_1$$

$$\langle S_{\beta\beta} \rangle^{xzxz} = c_3 q_1 B_2$$

$$\langle S_{\alpha\alpha} \rangle^{xzxz} = c_4 q_3 A_2$$

$$\langle S_{\alpha\beta} \rangle^{xzxz} = c_5 q_4 B_1 + c_6 q_3 B_2$$

for Matlab fsolve, we need to turn into an equation which equals 0:

$$B_1^2 - q_1 \tag{7.2.22}$$

$$B_1 B_2 - q_2 \tag{7.2.23}$$

$$A_1^2 - q_3 \tag{7.2.24}$$

$$A_1 A_2 - q_4 \tag{7.2.25}$$

$$c_1 q_1 A_2 + c_2 q_2 A_1 - S_{ba} \tag{7.2.26}$$

$$c_3 q_1 B_2 - S_{bb} \tag{7.2.27}$$

$$c_4 q_3 A_2 - S_{aa} \tag{7.2.28}$$

$$c_5 q_4 B_1 + c_6 q_3 B_2 - S_{ab} \tag{7.2.29}$$

we also need to split into real and imaginary equations

$$\begin{aligned}
 & \mathbf{Re}[B_1]^2 - \mathbf{Im}[B_1]^2 - \mathbf{Re}[q_1] \\
 & 2\mathbf{Re}[B_1]\mathbf{Im}[B_1] - \mathbf{Im}[q_1] \\
 & \mathbf{Re}[B_1]\mathbf{Re}[B_2] - \mathbf{Im}[B_1]\mathbf{Im}[B_2] - \mathbf{Re}[q_2] \\
 & \mathbf{Re}[B_1]\mathbf{Im}[B_2] + \mathbf{Im}[B_1]\mathbf{Re}[B_2] - \mathbf{Im}[q_2] \\
 & \mathbf{Re}[A_1]^2 - \mathbf{Im}[A_1]^2 - \mathbf{Re}[q_3] \\
 & 2\mathbf{Re}[A_1]\mathbf{Im}[A_1] - \mathbf{Im}[q_3] \\
 & \mathbf{Re}[A_1]\mathbf{Re}[A_2] - \mathbf{Im}[A_1]\mathbf{Im}[A_2] - \mathbf{Re}[q_4] \\
 & \mathbf{Re}[A_1]\mathbf{Im}[A_2] + \mathbf{Im}[A_1]\mathbf{Re}[A_2] - \mathbf{Im}[q_4] \\
 & c_1(\mathbf{Re}[q_1]\mathbf{Re}[A_2] - \mathbf{Im}[q_1]\mathbf{Im}[A_2]) + c_2(\mathbf{Re}[q_2]\mathbf{Re}[A_1] - \mathbf{Im}[q_2]\mathbf{Im}[A_1] - \mathbf{Re}[S_{ba}]) \\
 & c_1(\mathbf{Re}[q_1]\mathbf{Im}[A_2] + \mathbf{Im}[q_1]\mathbf{Re}[A_2]) + c_2(\mathbf{Re}[q_2]\mathbf{Im}[A_1] + \mathbf{Im}[q_2]\mathbf{Re}[A_1] - \mathbf{Im}[S_{ba}]) \\
 & c_3(\mathbf{Re}[q_1]\mathbf{Re}[B_2] - \mathbf{Im}[q_1]\mathbf{Im}[B_2]) - \mathbf{Re}[S_{bb}] \\
 & c_3(\mathbf{Re}[q_1]\mathbf{Im}[B_2] + \mathbf{Im}[q_1]\mathbf{Re}[B_2]) - \mathbf{Im}[S_{bb}] \\
 & c_4(\mathbf{Re}[q_3]\mathbf{Re}[A_2] - \mathbf{Im}[q_3]\mathbf{Im}[A_2]) - \mathbf{Re}[S_{aa}] \\
 & c_4(\mathbf{Re}[q_3]\mathbf{Im}[A_2] + \mathbf{Im}[q_3]\mathbf{Re}[A_2]) - \mathbf{Im}[S_{aa}] \\
 & c_5(\mathbf{Re}[q_4]\mathbf{Re}[B_1] - \mathbf{Im}[q_4]\mathbf{Im}[B_1]) + c_6(\mathbf{Re}[q_3]\mathbf{Re}[B_2] - \mathbf{Im}[q_3]\mathbf{Im}[B_2] - \mathbf{Re}[S_{ab}]) \\
 & c_5(\mathbf{Re}[q_4]\mathbf{Im}[B_1] + \mathbf{Im}[q_4]\mathbf{Re}[B_1]) + c_6(\mathbf{Re}[q_3]\mathbf{Im}[B_2] + \mathbf{Im}[q_3]\mathbf{Re}[B_2] - \mathbf{Im}[S_{ab}])
 \end{aligned}$$

but this strategy does not yield answers in fsolve.

7.2.9 EXPERIMENTAL CONSIDERATIONS

Perhaps by considering the experimental setup, we can eliminate variables and make the equations solvable. The Engel group tells us they generate an x polarization by putting a half waveplate in front of the beam. They use a different waveplate for the first and third pulse, unfortunately, but for now we are going to assume they both impart a perfect, identical phase-shift and contemplate how this additional information changes the equations.

Half waveplates are designed to impart a π phase-shift. The amplitude effect of this is $e^{i\pi} = -1$. This means that $A_1 = -A_2$ and the same for B . We turns these constants into just A and B.

$$\begin{aligned}\langle S_{\beta\alpha} \rangle^{xzxz} &= -\frac{1}{10}B^2(-A)ab + \frac{1}{15}B(-B)Ab^2 + \frac{1}{30}B(-B)Aab \\ \langle S_{\beta\beta} \rangle^{xzxz} &= -\frac{2}{15}B(-B)Bb^2 \\ \langle S_{\alpha\alpha} \rangle^{xzxz} &= -\frac{2}{15}A(-A)Aa^2 \\ \langle S_{\alpha\beta} \rangle^{xzxz} &= \frac{1}{15}A(-A)Ba^2 + \frac{1}{30}A(-A)Bab - \frac{1}{10}A(-B)Aab\end{aligned}$$

which simplifies to

$$\begin{aligned}\langle S_{\beta\alpha} \rangle^{xzxz} &= \frac{1}{10}B^2Aab - \frac{1}{15}B^2Ab^2 - \frac{1}{30}B^2Aab \\ \langle S_{\beta\beta} \rangle^{xzxz} &= \frac{2}{15}B^3b^2 \\ \langle S_{\alpha\alpha} \rangle^{xzxz} &= \frac{2}{15}A^3a^2 \\ \langle S_{\alpha\beta} \rangle^{xzxz} &= -\frac{1}{15}A^2Ba^2 - \frac{1}{30}A^2Bab + \frac{1}{10}A^2Bab\end{aligned}$$

and further simplifies to

$$\begin{aligned}\langle S_{\beta\alpha} \rangle^{xzxz} &= B^2 A \left(\frac{1}{10} ab - \frac{1}{15} b^2 - \frac{1}{30} ab \right) \\ \langle S_{\beta\beta} \rangle^{xzxz} &= \frac{2}{15} B^3 b^2 \\ \langle S_{\alpha\alpha} \rangle^{xzxz} &= \frac{2}{15} A^3 a^2 \\ \langle S_{\alpha\beta} \rangle^{xzxz} &= A^2 B \left(-\frac{1}{15} a^2 - \frac{1}{30} ab + \frac{1}{10} ab \right)\end{aligned}$$

and again to

$$\begin{aligned}\langle S_{\beta\alpha} \rangle^{xzxz} &= B^2 A \left(\frac{1}{15} ab - \frac{1}{15} b^2 \right) \\ \langle S_{\beta\beta} \rangle^{xzxz} &= \frac{2}{15} B^3 b^2 \\ \langle S_{\alpha\alpha} \rangle^{xzxz} &= \frac{2}{15} A^3 a^2 \\ \langle S_{\alpha\beta} \rangle^{xzxz} &= A^2 B \left(\frac{1}{15} ab - \frac{1}{15} a^2 \right)\end{aligned}$$

and again to

$$\begin{aligned}\langle S_{\beta\alpha} \rangle^{xzxz} &= B^2 A \frac{1}{15} (ab - b^2) \\ \langle S_{\beta\beta} \rangle^{xzxz} &= \frac{2}{15} B^3 b^2 \\ \langle S_{\alpha\alpha} \rangle^{xzxz} &= \frac{2}{15} A^3 a^2 \\ \langle S_{\alpha\beta} \rangle^{xzxz} &= A^2 B \frac{1}{15} (ab - a^2)\end{aligned}$$

But this method did not yield a solution either.

7.2.10 CONCLUSION

While we thought that we could get out a process matrix for data given to us by the Engel group, and we did get one that had some radical claims in it with equally dubious assumptions behind them, we found no way to de-dubify the assumptions and thus we left it at this.

7.3 INVESTIGATING CONICAL INTERSECTIONS USING PULSE-WIDTH DEPENDENT DYNAMICS

A very simple molecular Hamiltonian looks like this:

$$\hat{H} = \frac{1}{2\mu} \nabla_R^2 + \frac{1}{2m_e} \nabla_r^2 + \frac{Z_1 Z_2}{R^2} + \frac{Z_1}{r_1^2} + \frac{Z_2}{r_2^2}$$

Which we can separate into a nuclear kinetic, an electronic kinetic, a nuclear potential and an electron-nuclear potential:

$$\hat{H} = T_n + T_e + V_n(R) + V_e(R) + V_{en}(R, r)$$

If we assume we can separate the components which solve the wavefunction into an electronic and a nuclear part:

$$\Psi(R, r) = \psi(R)\phi(r)$$

which is the heart of the Born-Oppenheimer approximation. But it's not terribly physical. This approximation, effectively, says that even if you compress the bond in, say, a hydrogen molecule, to some fraction of the equilibrium length, the electronic configuration would be the same. Which is clearly not true. As the nuclei move, you would of course expect the oppositely charged

electrons to “follow” them around.

So the next level of approximation down is to say that the nuclei will still probably not see the electrons moving around, the electrons will definitely see the nuclei if they change positions and because the electrons move around much faster, than the nuclei, it would make sense that we would see them react to a change in position of the nuclei. So we change the prototype wavefunction to have a nuclear part and an electronic part, conditioned on the nuclear coordinates:

$$\Psi(R, r) = \psi(R)\phi(r; R)$$

You can imagine this will complicate things but still allow us more simplicity and tractability than would be had through not separating things at all. For example, this gives us the ability to solve the electronic part of the equation for every possible nuclear configuration R to come up with an electronic energy landscape:

$$\hat{H}_e\phi(r; R) = (T_e + V_e(R) + V_{en}(R, r))\phi(r; R) = E(R)\phi(r; R)$$

where it’s important here to recognize we are able to solve for the full electronic spectrum

$$\hat{H}_e\phi(r; R) = \hat{H}_e \sum_n a_n \phi_n(r; R) = \phi(r; R) = \sum_n E_n(R) a_n \phi_n(r; R)$$

But that’s not the whole equation is it? We can take this solution to the electronic equation and put it back into the full equation:

$$\begin{aligned} \hat{H}[\psi(R)\phi(r; R)] &= (T_n + T_e + V_n(R) + V_e(R) + V_{en}(R, r))[\psi(R)\phi(r; R)] \\ &= (T_e + V_e(R) + V_{en}(R, r))[\psi(R)\phi(r; R)] + (T_n + V_n(R))[\psi(R)\phi(r; R)] \end{aligned}$$

none of the operators in the front will change the nuclear part of the wavefunction in any manner so that we can just substitute in the solution to the electronic problem: $E(R)$. It seems a natural pairing to go with $V_N(R)$ so we do that

$$\hat{H}[\psi(R)\phi(r;R)] = (E(R) + V_n(R))[\psi(R)\phi(r;R)] + T_n[\psi(R)\phi(r;R)]$$

and are left with one term. Which is going to cause some problems. This is because it will introduce new terms as the nuclear kinetic operator acts on the electronic wavefunction also,

$$\begin{aligned} T_n\Psi(R,r) &= \frac{1}{2\mu}\nabla_R^2\psi(R)\phi(r;R) \\ &= \frac{1}{2\mu}\nabla_R\cdot(\psi(R)\nabla_R\phi(r;R) + \nabla_R\psi(R)\phi(r;R)) \\ &= \frac{1}{2\mu}(\psi(R)\nabla_R^2\phi(r;R) + \nabla_R\psi(R)\cdot\nabla_R\phi(r;R) + \nabla_R^2\psi(R)\phi(r;R) + \nabla_R\psi(R)\cdot\nabla_R\phi(r;R)) \\ &= \frac{1}{2\mu}(\psi(R)\nabla_R^2\phi(r;R) + 2\nabla_R\psi(R)\cdot\nabla_R\phi(r;R)) + \frac{1}{2\mu}\nabla_R^2\psi(R)\phi(r;R) \end{aligned}$$

The third term is the boring old nuclear kinetic energy we know about from the Born-Oppenheimer approximation wavefunction, but the first two terms complicate things and they are the heart of why we are talking here. If we decide to ignore then:

$$\begin{aligned} \hat{H}[\psi(R)\phi(r;R)] &= (E(R) + V_n(R))[\psi(R)\phi(r;R)] + \phi(r;R)T_n\psi(R) \\ &= \phi(r;R)(E(R) + V_n(R) + T_n)\psi(R) \\ \hat{H}\psi(R) &= (E(R) + V_n(R) + T_n)\psi(R) \end{aligned}$$

we can basically prescribe that you go solve the electronic problem $E(R)$ and then come back to solve the nuclear problem. The solutions to this problem are called the “**Adiabatic Representation**” and represent the solutions which preserve ordering of the energy levels so for

the energy eigenstates of the problem, $\Psi_i(R, r) = \psi_i(R)\phi_i(r; R)$ the set of E_i 's form a ladder of energies, going up from 0 to infinity.

Now let's look at what happens when we put those exact adiabatic solutions into the full Hamiltonian:

$$\hat{H}\Psi_i(R, r) = \phi_i(r; R) (E(R) + V_n(R) + T_n) \psi_i(R) + \frac{1}{2\mu} (\psi_i(R) \nabla_R^2 \phi_i(r; R) + 2\nabla_R \psi_i(R) \cdot \nabla_R \phi_i(r; R)) \quad (7.3.1)$$

and let's average away the electronic degrees of freedom by coming in with $\phi_j(r; R)$ and integrating out the electronic degrees of freedom:

$$\int dr \phi_j(r; R) \hat{H}\Psi_i(R, r) = H_{ij}(R) \psi_i(R) = \int dr \psi_j(R) \phi_j(r; R) \phi_i(r; R) (E(R) + V_n(R) + T_n) \psi_i(R) \quad (7.3.2)$$

$$+ \int dr \phi_j(r; R) \frac{1}{2\mu} (\psi_i(R) \nabla_R^2 \phi_i(r; R) + 2\nabla_R \psi_i(R) \cdot \nabla_R \phi_i(r; R)) \quad (7.3.3)$$

$$= \delta_{ij} (E(R) + V_n(R) + T_n) \psi_i(R) \quad (7.3.4)$$

$$+ \frac{1}{2\mu} \left[\int dr \phi_j(r; R) \nabla_R^2 \phi_i(r; R) \right] \psi_i(R) \quad (7.3.5)$$

$$+ \frac{1}{\mu} \left[\int dr \phi_j(r; R) \nabla_R \phi_i(r; R) \right] \cdot \nabla_R \psi_i(R) \quad (7.3.6)$$

So we have additional quantities to calculate from the electronic states:

$$\vec{T}_{ij}^{(1)}(R) = \frac{1}{\mu} \left[\int dr \phi_j(r; R) \nabla_R \phi_i(r; R) \right] \quad (7.3.7)$$

$$T_{ij}^{(2)}(R) = \frac{1}{2\mu} \left[\int dr \phi_j(r; R) \nabla_R^2 \phi_i(r; R) \right] \quad (7.3.8)$$

Which when all is said and done, we are left with a final answer of:

$$H_{ij}(R)\psi_i(R) = \delta_{ij}(E(R) + V_n(R) + T_n)\psi_i(R) + T_{ij}^{(2)}(R)\psi_i(R) + \vec{T}_{ij}^{(1)}(R) \cdot \nabla_R \psi_i(R) \quad (7.3.9)$$

$$= \left[\delta_{ij}(E(R) + V_n(R) + T_n) + \vec{T}_{ij}^{(1)}(R) \cdot \nabla_R + T_{ij}^{(2)}(R) \right] \psi_i(R) \quad (7.3.10)$$

We can prove that

$$\text{Re}[\vec{T}_{ij}^{(1)}(R)] = 0 \quad (7.3.11)$$

$$\vec{T}_{aa}^{(1)}(R) = 0 \quad (7.3.12)$$

7.3.1 ADIABATIC REPRESENTATION

Say we don't care about energy ordering, and we only care about the electronic character of the wavefunctions staying the same. We can instead pick some arbitrary geometry—let's call it R_0 —and then solve the full Hamiltonian for each of those geometries:

$$\Psi(R, r) = \sum_i \phi_i(r; R_0) \psi_i^{(0)}(R) \quad (7.3.13)$$

And now let's do what we did last time and act the Hamiltonian on the electronic part of the wavefunction:

$$\begin{aligned} \hat{H} \phi_i(r; R_0) &= (T_n + T_e + V_n(R) + V_e(r) + V_{en}(R, r)) \phi_i(r; R_0) \\ &= (T_e + V(r, R_0)) \phi_i(r; R_0) = E_i(R_0) \phi_i(r; R_0) \end{aligned}$$

and that will be the equation we solve to get the electronic states. We can then put the whole thing with the vibrational part back in

$$\begin{aligned}
 \hat{H}\phi_i(r;R_0)\psi_i^{(0)}(R) &= (T_n + T_e + V_n(R) + V_e(r) + V_{en}(R,r))\phi_i(r;R_0)\psi_i^{(0)}(R) \\
 &= (T_e + V(R,r) + T_n)\phi_i(r;R_0)\psi_i^{(0)}(R) \\
 &= (T_e + V(R,r) + V(R_0,r) - V(R_0,r) + T_n)\phi_i(r;R_0)\psi_i^{(0)}(R) \\
 &= (T_e + V(R_0,r))\phi_i(r;R_0)\psi_i^{(0)}(R) + (T_n + V(R,r) - V(R_0,r))\phi_i(r;R_0)\psi_i^{(0)}(R) \\
 &= E_i(R_0)\phi_i(r;R_0)\psi_i^{(0)}(R) + (T_n + V(R,r) - V(R_0,r))\phi_i(r;R_0)\psi_i^{(0)}(R)
 \end{aligned}$$

Now we come in with the j th basis function and integrate out over the electronic degrees of freedom

$$\begin{aligned}
 \hat{H}_{ij}\psi_i^{(0)}(R) &= \int dr\phi_j(r;R_0)E_i(R_0)\phi_i(r;R_0)\psi_i^{(0)}(R) \\
 &\quad + \int dr\phi_j(r;R_0)(T_n + V(R,r) - V(R_0,r))\phi_i(r;R_0)\psi_i^{(0)}(R) \\
 &= \delta_{ij}E_i(R_0)\psi_i^{(0)}(R) + \delta_{ij}T_n\psi_i^{(0)}(R) + \int dr\phi_j(r;R_0)(V(R,r) - V(R_0,r))\phi_i(r;R_0)\psi_i^{(0)}(R) \\
 &= \delta_{ij}[E_i(R_0) + T_n]\psi_i^{(0)}(R) + U_{ji}(R)\psi_i^{(0)}(R) \\
 U_{ji}(R) &= \int dr\phi_j(r;R_0)(V(R,r) - V(R_0,r))\phi_i(r;R_0)
 \end{aligned}$$

7.3.2 DETECTING A CONICAL INTERSECTION

Looking at the diabatic energy corrections, one finds a term in the Hamiltonian which looks like this:

$$2\nabla_R\psi(R) \cdot \nabla_R\phi(r;R) \tag{7.3.14}$$

the second part of which can be integrated out to find a vector-like coupling between two different electronic states and the first part of which is clearly the nuclear momentum. This ends up giving a term in the Hamiltonian proportional to:

$$\vec{p}_r \cdot \vec{J}_{i,j} \tag{7.3.15}$$

So why not manipulate the momentum of the wavefunction to manipulate the dynamics and thus create a way of detecting a electronic vector coupling $\vec{J}_{i,j}$. Preliminary work on this proved not to be fruitful. I wasn't, however, entirely sure what I was looking for and would return to this hypothesis again if I ever think that I have found something that might actually be different. By including this in my thesis, even though no one will read it, I hope to possibly inspire someone to continue this work.

8

Computational Methods Used

I put a lot of blood sweat and tears into making my code work. It is available on my github page: github.com/jgoodknight. I made heavy use of the numpy and scipy libraries^{26,55} There are some details I wish to point out, however, in my thesis and this seems the appropriate place to do so.

8.1 WORKING WITH NATURAL UNITS: OR, WHY MESS WITH SI?

While an experimentalist needs a systems of units he or she can measure, we theorists prefer to have a system of units which is easy to write down, so we can worry less about dropping factors here and there. Take for example the hydrogen atom Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r}$$

That is a lot of constants. Wouldn't it be better if we could just write this out:

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r}$$

This easy-to-not-mess-up Hamiltonian can be yours with a little algebra and a bit of thought.

8.1.1 SETTING CONSTANTS EQUAL TO 1

The astute observer will note that one can get the miraculous Hamiltonian Transformation by making the following algebraic declarations:

$$\begin{aligned}\hbar &= 1 \\ e &= 1 \\ m_e &= 1 \\ \frac{1}{4\pi\epsilon_0} &= k_e = 1\end{aligned}$$

You may now be wondering how they can be 1. You've probably had many professors talk to you for many hours about the painstaking effort that went into determining the exact values of these constants throughout the history of physics, and here I go, willy-nilly just setting them to one: doesn't this throw off all of physics into non-physical nonsense? Yes and no.

There is, unsurprisingly, a limit to the number of units you can set to being 1. This limit is imposed by the fine-structure constant α :

$$\alpha = \frac{k_e e^2}{\hbar c}$$

Which, unless you listen to some theoretical cosmologists, is completely constant in our universe and has a value of $\sim 1/137$. So in our system of units we have set all but one of these constants which make up the fine-structure constant to be unity (the absolute limit), so we must get out that $c = \frac{1}{\alpha}$ to keep our system of units from describing a universe other than our own.

8.1.2 SETTING UNITS EQUAL TO 1 OR: FINDING THE “NATURAL” UNITS

The only reason we are able to set these units to be one is because we now measure things like energy, distance and time in units which MAKE the constants one. \hbar for example is not really just 1; it's 1 atomic-energy-unit-atomic-time-unit or $1E_a \cdot t_a$. To figure out exactly what these atomic units are, we do this for each constant noting that energy will be $E_a = m_a l_a^2 / t_a^2$:

$$\hbar = 1E_a \cdot t_a = m_a \frac{l_a^2}{t_a}$$

$$k_e = 1 \frac{E_n \cdot l_a}{q_a^2}$$

We've already defined our charge units to be e and our mass units to be m_e (although that can easily change).

$$\frac{\hbar}{m_e} = \frac{l_a^2}{t_a}$$

$$k_e e^2 = m_e \frac{l_a^2}{t_a^2} \cdot l_a$$

Now with two equations and two unknowns, we begin to solve

$$\frac{\hbar}{m_e} = \frac{l_a^2}{t_a}$$

$$t_a = \frac{l_a^2 m_e}{\hbar}$$

$$t_a^2 = \frac{l_a^3 m_e}{k_e e^2}$$

$$\frac{l_a^4 m_e^2}{\hbar^2} = \frac{l_a^3 m_e}{k_e e^2}$$

$$l_a = \frac{\hbar^2}{m_e k_e e^2}$$

Which the astute observer will note has an α hidden in there... somewhere:

$$l_a = \frac{\hbar}{m_e \alpha c}$$

And the even more astute observer will notice that it is the Bohr radius. This quickly emits the time and then energy units:

$$1l_a = \frac{\hbar}{m_e \alpha c} = a_0 \approx 5.29 \times 10^{-11} \text{ m}$$

$$1t_a = \frac{\hbar}{m_e \alpha^2 c^2} \approx 2.419 \times 10^{-17} \text{ s}$$

$$1E_a = m_e \alpha^2 c^2 \approx 4.3597 \times 10^{-18} \text{ J}$$

wavenumbers come up a lot on spectroscopy so let's figure out what the atomic wavenumber unit is:

$$1\omega_a = \frac{1E_a}{hc} = 219474.6 \text{ cm}^{-1} = \frac{1}{1l_a}$$

$$hc = 2\pi\hbar c = \frac{2\pi}{\alpha} = 861.022576 E_a \cdot l_a$$

So to convert a wavenumber ω into an atomic energy unit:

$$\begin{aligned} E_a(\omega) &= \frac{\omega}{1\omega_a} \frac{2\pi}{\alpha} \\ &= \omega \left(0.00392310807 \frac{E_a}{\text{cm}^{-1}} \right) \end{aligned}$$

8.1.3 SETTING OTHER THINGS EQUAL TO 1

Now let's say you are reading a paper which quotes all of its energy units in wavenumbers, all of its position units in square-root-centimeters and time units in femtoseconds. How do you make

sense of this?

Let's say this particular paper is talking about harmonic oscillators, the Hamiltonian of which looks like so:

$$\hat{H} = \frac{\hbar^2 p^2}{2m} + \frac{1}{2} m \omega^2 (x - x_0)^2$$

In the paper, however, the author quotes the Hamiltonian as being thus:

$$\hat{H} = \frac{p^2}{2} + \frac{1}{2} \omega^2 (x - x_0)^2$$

and all energy units are given in terms of wavenumbers. All-together, these implies 3 unitary unit relationships:

$$\hbar = 1$$

$$hc = 1$$

$$m = 1$$

Luckily, we don't care about coulomb relations so we can just set $c = 2\pi$ and let the electron charge and Coulomb constant float to strange numbers. Anyway, as we know from earlier, these really do have units associated with them so we add them in, calling them j units.

$$\hbar = 1E_j \cdot t_j$$

$$m = 1m_j$$

The author has chosen wavenumbers as the units of choice for energy: specifically 100

wavenumbers.

$$1E_j \sim 100.0 \text{ cm}^{-1}$$

$$1E_j = hc(100.0 \text{ cm}^{-1}) = 1.986 \times 10^{-21} \text{ J}$$

which also gives us the natural units for time:

$$1t_j = \frac{\hbar}{1E_j} = 5.308837 \times 10^{-12} \text{ s} = 5.3 \text{ ps}$$

8.1.4 CONCLUSION ON UNITS

I have shown you the basic derivation for how to get the system of natural units (units with a bunch of constants equal to one) known as atomic units. Hopefully you can follow my logic to create any easy-to-derive-with system of units that you desire. Up for a challenge? Let the mass and charge float, set $c = 1$ and then figure out how to set Boltzmann's constant and the universal gravitational constant equal to 1 also. These are known as the Planck units and are cool because they set all the fundamental constants of the forces to 1, instead of any property of an object

8.2 DISCRETE FOURIER TRANSFORM

Let's say you want a computer to do the following integral

$$\tilde{f}(\omega) = \int e^{i\omega t} f(t) dt \tag{8.2.1}$$

And your t values stretch from $0 \rightarrow n\delta t$. We could then do the integral like a Riemann Sum:

$$\tilde{f}(\omega) = \delta t \sum_{j=0}^n e^{i\omega j\delta t} f(j\delta t) \tag{8.2.2}$$

but how to discretize ω ? I'm going to skip over why but say that Numpy's Fast Fourier Transform algorithm takes a list of function values $\{f_m\}$ and returns:

$$\tilde{f}_k = \sum_{m=0}^{n-1} e^{-2\pi i \frac{mk}{n}} f_m \quad (8.2.3)$$

which implies we get $d\omega = \frac{2\pi}{n\delta t}$ with $-\frac{n-1}{2} < k < \frac{n-1}{2}$. But we defined our Fourier transforms in terms of the positive exponent. We're in luck, however, because numpy's inverse FFT algorithm looks like this:

$$f_m = \frac{1}{n} \sum_{k=0}^{n-1} e^{2\pi i \frac{mk}{n}} \tilde{f}_k \quad (8.2.4)$$

8.3 CHOOSING THE PARAMETERS OF SPACE

In the course of simulation, we have to figure out a proper value for the box we put our wavefunctions in that doesn't affect the observables. So we need something big enough in position space and big enough in momentum space (small enough Δx . Let's look at a ladder of harmonic oscillators:

$$H_i = \frac{1}{2m_i} \hat{p}^2 + \frac{1}{2} m_i \omega_i^2 (x - \bar{x}_i)^2 \quad (8.3.1)$$

for the sake of simplicity, we'll say that all the oscillators are accessible to each other via transition dipole moments and that oscillator 0 is the leftmost. The ground state we will say has

non-negligible amplitude from $x_0 \pm n\sigma_0$ where $\sigma_0 = \sqrt{\frac{\hbar}{m\omega_i}}$.

When the ground state (or any initial state but we're being simple here) from the 0th state ends up in the oscillator j whose center is furthest away from its center, the center's have distance $\Delta x_{\max} = \Delta x_{0j} = (x_j - x_0)$. Because of the magic of Gaussian wavepackets in harmonic potentials,

the wavepacket will distort and swing to the other side of the potential energy surface and settle at the classical turning point intact. That wavepacket will now have approximate extent of $x_0 + 2\Delta x_{\max} + n\sigma_0$. Which, is the furthest out the wavepacket can ever get. So If we're only **simulating a one-interaction experiment,**

$$x_{\min} = x_0 - n\sigma_0 \quad (8.3.2)$$

$$x_{\max} = x_0 + 2\Delta x_{\max} + n\sigma_0 \quad (8.3.3)$$

$$x_{\max} - x_{\min} = 2\Delta x_{\max} + 2n\sigma_0 \quad (8.3.4)$$

If, however, we are interacting more than once, things get slightly more complicated. We have to assume that at some point, the wavepacket centered about $x = x_0 + 2\Delta x_{\max}$ will once again end up in the 0th oscillator. Which means that it will swing all the way over to center around $x = x_0 - 2\Delta x_{\max}$ and thus for more than two interactions:

$$x_{\min} = x_0 - 2\Delta x_{\max} - n\sigma_0 \quad (8.3.5)$$

$$x_{\max} = x_0 + 2\Delta x_{\max} + n\sigma_0 \quad (8.3.6)$$

$$x_{\max} - x_{\min} = 4\Delta x_{\max} + 2n\sigma_0 \quad (8.3.7)$$

8.3.1 MOMENTUM-SPACE CONSIDERATIONS

Alas, if only computers did not require us to simulate things discretely, we would not have to worry about momentum space but they do and thus we do. We must chose N points to simulate the system on. When you discrete Fourier transform a function in x , you get values of k ranging from roughly $-\frac{\pi}{dx}$ to $\frac{\pi}{dx}$ which means we must chose a dx which is small enough to study the largest momentum the problem will end up seeing.

8.3.2 ONE-INTERACTION

How do we do this? Well, consider that our rightmost amplitude is at $x = x_0 + 2\Delta x_{\max} + n\sigma_0$. For one interaction, the highest momentum we will see is when it gets to the center of the j th well. Thinking classically, that rightmost piece of amplitude will be motionless at the top and then be potential energy-less at the center so we can say:

$$\frac{p_{\max}^2}{2m_j} = V_j(x_0 + 2\Delta x_{\max} + n\sigma_0) \quad (8.3.8)$$

Since $p = \hbar k$ and we already know the form of the potential energy surface:

$$\frac{(\hbar k_{\max})^2}{2m_j} = \frac{1}{2}m_j\omega_j^2(x_0 + 2\Delta x_{\max} + n\sigma_0 - x_j)^2 \quad (8.3.9)$$

$$k_{\max} = \frac{1}{\hbar}m_j\omega_j(\Delta x_{\max} + n\sigma_0) = \frac{\pi}{dx} \quad (8.3.10)$$

$$dx = \frac{\pi\hbar}{m_j\omega_j(\Delta x_{\max} + n\sigma_0)} = \frac{x_{\max} - x_{\min}}{N} \quad (8.3.11)$$

$$\frac{\pi\hbar}{m_j\omega_j(\Delta x_{\max} + n\sigma_0)} = \frac{2\Delta x_{\max} + 2n\sigma_0}{N} \quad (8.3.12)$$

$$N = \frac{2m_j\omega_j(\Delta x_{\max} + n\sigma_0)^2}{\pi\hbar} \quad (8.3.13)$$

8.3.3 TWO-INTERACTIONS

But what if that wavepacket at it's absolute rightmost position is then suddenly plummeted down to the leftmost 0th potential energy well? Then there will be a non-trivially larger maximum

momentum as it will have much further to travel to get to the center of the potential energy well.

$$\frac{(\hbar k_{\max})^2}{2m_0} = V_0(x_0 + 2\Delta x_{\max} + n\sigma_0) \quad (8.3.14)$$

$$k_{\max} = \frac{1}{\hbar} m_0 \omega_0 (x_0 + 2\Delta x_{\max} + n\sigma_0 - x_0) = \frac{\pi}{dx} \quad (8.3.15)$$

$$dx = \frac{\pi \hbar}{m_0 \omega_0 (2\Delta x_{\max} + n\sigma_0)} = \frac{x_{\max} - x_{\min}}{N} \quad (8.3.16)$$

$$\frac{\hbar \pi}{m_0 \omega_0 (2\Delta x_{\max} + n\sigma_0)} = \frac{4\Delta x_{\max} + 2n\sigma_0}{N} \quad (8.3.17)$$

$$N = \frac{2m_0 \omega_0 (2\Delta x_{\max} + n\sigma_0)^2}{\pi \hbar} \quad (8.3.18)$$

8.3.4 SUMMARIZE

8.3.4.1 ONE-INTERACTION

$$x_{\min} = x_0 - n\sigma_0 \quad (8.3.19)$$

$$x_{\max} = x_0 + 2\Delta x_{\max} + n\sigma_0 \quad (8.3.20)$$

$$N = \frac{2\pi m_j \omega_j (\Delta x_{\max} + n\sigma_0)^2}{\hbar} \quad (8.3.21)$$

$$dx = \frac{\hbar}{\pi m_j \omega_j (\Delta x_{\max} + n\sigma_0)} \quad (8.3.22)$$

8.3.4.2 TWO-INTERACTIONS

$$x_{\min} = x_0 - 2\Delta x_{\max} - n\sigma_0 \quad (8.3.23)$$

$$x_{\max} = x_0 + 2\Delta x_{\max} + n\sigma_0 \quad (8.3.24)$$

$$N = \frac{2\pi m_0 \omega_0 (2\Delta x_{\max} + n\sigma_0)^2}{\hbar} \quad (8.3.25)$$

$$dx = \frac{\hbar}{\pi m_0 \omega_0 (2\Delta x_{\max} + n\sigma_0)} \quad (8.3.26)$$

8.3.4.3 MORE-THAN-TWO-INTERACTIONS

With a third interaction, one must consider the scenario where the wavepacket at its leftmost is promoted to the rightmost potential energy well where it can again go out to the rightmost edge of the j th potential energy well giving us a different maximum distance needed and different maximum potential needed.

8.4 APPLYING $U(t)$ NUMERICALLY: THE SPLIT OPERATOR METHOD

Let's say you want to apply an exponential operator to something:

$$U = e^{-it\mathcal{H}/\hbar}$$

This does not appear to be terribly difficult at first sight if you know how to take the exponential of whatever \mathcal{H} is. Let's just make life difficult and call \mathcal{H} the Hamiltonian of a quantum system which would make U the time-evolution operator:

$$U = e^{-it/\hbar\mathcal{H}(p,x)} = e^{-it/\hbar(\mathcal{T}(p)+\mathcal{V}(x))}$$

So now it appears to be rather difficult as the potential energy is best expressed in the position basis whereas the kinetic energy is best expressed in the momentum basis. We might consider doing this (to make our lives easier, define $\lambda = \frac{-it}{\hbar}$) to make things simpler:

$$U = e^{\lambda(\mathcal{T}+\mathcal{V})} = e^{\lambda\mathcal{T}} e^{\lambda\mathcal{V}}$$

Then we could apply the first bit, Fourier transform, apply the second bit and then inverse Fourier transform back to the original basis. Is this, correct, though? Let's look at the Taylor Series for the

two. First the “correct” operator:

$$\begin{aligned}
 U &= e^{\lambda(\mathcal{T}+\mathcal{V})} \\
 &= \sum_{k=0}^{\infty} \frac{\lambda^k}{k!} (\mathcal{T} + \mathcal{V})^k \\
 &= 1 + \lambda(\mathcal{T} + \mathcal{V}) + \frac{\lambda^2}{2} (\mathcal{T}^2 + \mathcal{V}^2 + \mathcal{T}\mathcal{V} + \mathcal{V}\mathcal{T}) \\
 &\quad + \frac{\lambda^3}{6} (\mathcal{T}^3 + \mathcal{V}^3 + \mathcal{T}\mathcal{V}^2 + \mathcal{T}^2\mathcal{V} + \mathcal{T}\mathcal{V}\mathcal{T} + \mathcal{V}\mathcal{T}^2 + \mathcal{V}\mathcal{T}\mathcal{V} + \mathcal{V}^2\mathcal{T}) + O(\lambda^4)
 \end{aligned}$$

Now the proposed correction:

$$\begin{aligned}
 U &= e^{\lambda\mathcal{T}} e^{\lambda\mathcal{V}} \\
 &= \sum_{k=0}^{\infty} \frac{\lambda^k}{k!} \mathcal{T}^k \sum_{l=0}^{\infty} \frac{\lambda^l}{l!} \mathcal{V}^l \\
 &= 1 + \lambda(\mathcal{T} + \mathcal{V}) + \frac{\lambda^2}{2} (\mathcal{T}^2 + \mathcal{V}^2 + 2\mathcal{T}\mathcal{V}) + \frac{\lambda^3}{6} (\mathcal{T}^3 + \mathcal{V}^3 + 3\mathcal{T}\mathcal{V}^2 + 3\mathcal{T}^2\mathcal{V}) + O(\lambda^4)
 \end{aligned}$$

So because normally you have commutivity $xy = yx$, because the kinetic and potential operators don't necessarily commute, there is an error term here:

$$\begin{aligned}
 E &= e^{\lambda(\mathcal{T}+\mathcal{V})} - e^{\lambda\mathcal{T}} e^{\lambda\mathcal{V}} \\
 &= \frac{\lambda^2}{2} (\mathcal{T}\mathcal{V} - \mathcal{V}\mathcal{T}) + O(\lambda^3) \\
 &= \frac{\lambda^2}{2} [\mathcal{T}, \mathcal{V}] + O(\lambda^3)
 \end{aligned}$$

So our approximation is good, so long as λ is small enough to keep λ^2 sufficiently small. This can be accomplished by letting $t = N\Delta t$ and applying the operator for Δt , N times.

You can get even better accuracy at the cost of more Fourier transforms using certain schemes as

shown below. (I will spare you the proofs of these)

$$\begin{aligned}
 U &\approx e^{\lambda T/2} e^{\lambda V} e^{\lambda T/2} + O(\lambda^3) \\
 U &\approx \left(e^{\gamma \lambda T/2} e^{\gamma \lambda V} e^{\gamma \lambda T/2} \right) \left(e^{(1-2\gamma)\lambda T/2} e^{(1-2\gamma)\lambda V} e^{(1-2\gamma)\lambda T/2} \right) \left(e^{\gamma \lambda T/2} e^{\gamma \lambda V} e^{\gamma \lambda T/2} \right) + O(\lambda^4) \\
 &= e^{\gamma \lambda T/2} e^{\gamma \lambda V} e^{(1-\gamma)\lambda T/2} e^{(1-2\gamma)\lambda V} e^{(1-\gamma)\lambda T/2} e^{\gamma \lambda V} e^{\gamma \lambda T/2} + O(\lambda^4) \\
 \gamma &= \frac{1}{2 - \sqrt[3]{2}}
 \end{aligned}$$

You can, in principle, get a splitting method for an arbitrary level of accuracy, but it will involve more computational time.*

8.5 TRAPEZOIDAL INTEGRATION FOR PERTURBATION THEORY CALCULATIONS WITH SMALLER TIME DISCRETIZATION

The integral one performs to do one “interaction” with a perturbative Hamiltonian $H'(t)$ with a time-independent Hamiltonian H_0 is:

$$|\Psi'(t)\rangle = -\frac{i}{\hbar} \int_{-\infty}^t e^{-\frac{i}{\hbar} H_0(t-\tau)} H'(\tau) |\Psi(\tau)\rangle d\tau$$

Where $|\Psi(\tau)\rangle$ is the underlying wavefunction being interacted with, τ represents the different times that the interaction can happen at and $e^{-\frac{i}{\hbar} H_0(t-\tau)} = U_0(t, \tau)$ is the non-perturbative time-evolution operator. This integral phenomenologically represents some field represented by H' having being able to interact at many different points in time—all where the field is nonzero. At each of these points in time (represented by τ), one must interact the field with the underlying wavefunction and then propagate that wavefunction out to the time-point of interest. Then, for every τ before t there is a contribution to the interacted wavefunction at time t that is averaged over by the integral.

*Referenced <http://www.pci.uni-heidelberg.de/tc/usr/andreasm/academic/handouthtml/node13.html> for part of this derivation

Now it is not hard to imagine that a naive implementation of this integral would be numerically very expensive. Indeed, if you turn my above paragraph into an algorithm directly, if the perturbation is “on” for N time steps, you are storing $O(N^2)$ wavefunctions which gets hairy very quickly.

We can do better, though and we will: to start with, we will assume that our perturbation can be “turned on” at a time $t_0 > -\infty$ without affecting the calculation at all, the integral reduces to this.

$$|\Psi'(t)\rangle = -\frac{i}{\hbar} \int_{t_0}^t U_0(t, \tau) H'(\tau) |\Psi(\tau)\rangle d\tau$$

now we shall discretize time: $t_i = t_0 + i\delta t$ and $\tau_j = t_0 + j\delta t$. t and τ have the same initial value because τ is never lower than t . Later on we will exploit this to simplify the expression but for now, I shall keep τ separate to make it abundantly clear that it is the variable which represents the point at which the perturbation acts on the system.

We decide to perform the integral with a simple Riemann sum:

$$\int_{t_0}^{t_f} f(t) dt = \delta t \sum_n f(t_n) + O(\delta t^2)$$

which gives us:

$$|\Psi'(t_i)\rangle = -\frac{i}{\hbar} \delta t \sum_{j=0}^{j=i} U_0(t_i, \tau_j) H'(\tau_j) |\Psi(\tau_j)\rangle$$

now at this point, we decide to try mathematical induction for the heck of it and we calculate

$$\begin{aligned} |\Psi'(t_{i+1})\rangle &= -\frac{i}{\hbar} \delta t \sum_{j=0}^{j=i+1} U_0(t_{i+1}, \tau_j) H'(\tau_j) |\Psi(\tau_j)\rangle \\ &= -\frac{i}{\hbar} \delta t \left[\sum_{j=0}^{j=i} U_0(\delta t) U_0(t_i, \tau_j) H'(\tau_j) |\Psi(\tau_j)\rangle + U_0(t_{i+1}, \tau_{i+1}) H'(\tau_{i+1}) |\Psi(\tau_{i+1})\rangle \right] \end{aligned}$$

which, since $t_n = \tau_n$ we can say

$$|\Psi'(t_{i+1})\rangle = U_0(\delta t) |\Psi'(t_i)\rangle - \frac{i}{\hbar} \delta t H'(\tau_{i+1}) |\Psi(\tau_{i+1})\rangle$$

which has a really interesting interpretation. At each time step, we merely take the previous time step's perturbation and propagate it forward one step in time. Then, we take the perturbation and interact it with the current step of the wavefunction and add it to the propagated step and that is the current step's perturbed wavefunction. This is a phenomenal savings in space and time of calculation over an naive implementation of the integral.

This is not without it's problems, however. The error in this integration is of the order δt^2 whereas the error for most split-operator propagation methods (if one is being smart) is of the order δt^3 . This is entirely a failing of the Riemann sum algorithm. Remembering back to High school calculus, though, one might recall another method called trapezoidal rule for integration.

$$\int_{t_0}^{t_f} f(t) dt = \frac{\delta t}{2} \left[f(t_0) + f(t_f) + 2 \sum_{n=1}^{n=f-1} f(t_n) \right] + O(\delta t^3)$$

which we make use of to get an even lower error

$$|\Psi'(t_{i+1})\rangle = U_0(\delta t) |\Psi'(t_i)\rangle - \frac{i}{\hbar} \frac{\delta t}{2} U_0(\delta t) H'(\tau_i) |\Psi(\tau_i)\rangle - \frac{i}{\hbar} \frac{\delta t}{2} H'(\tau_{i+1}) |\Psi(\tau_{i+1})\rangle$$

8.6 CALCULATION METHOD FOR HEATING CALCULATIONS

To look at molecular heating, we would care most about the average vibrational quantum number

$$\bar{n}(t) = \sum_n n |\langle g | \langle n_\gamma | \Psi(t) \rangle|^2$$

But then what does the time-dependent wavefunction look like? We're interested in the exact picture. The interaction Hamiltonian is

$$\hat{H}'(t) = E(t) (|g\rangle\langle e| + |e\rangle\langle g|) \mu(x)$$

and the time-independent Hamiltonian is as above:

$$H_0 = \sum_n \hbar\omega_\gamma \left(n + \frac{1}{2} \right) |n_\gamma\rangle\langle n_\gamma| \tag{8.6.1}$$

$$+ \sum_m \left(\hbar\omega_\epsilon \left(m + \frac{1}{2} \right) + \omega_e \right) |m_\epsilon\rangle\langle m_\epsilon| \tag{8.6.2}$$

If we turn the electronic degrees of freedom, putting it into Matrix form, we then have:

$$\hat{H}(t) = \begin{bmatrix} H_\gamma(x) & E(t)\mu(x) \\ E(t)\mu(x) & H_\epsilon(x) \end{bmatrix}$$

no that won't work since the coefficients of the Pauli matrices won't commute...

Let's try a blast form undergrad and calculate the time-dependent coefficients! We assume the following form of the time-varying wavefunction:

$$|\Psi(t)\rangle = \sum_a G_a(t) |a_\gamma\rangle |g\rangle + \sum_b E_b(t) |b_\epsilon\rangle |e\rangle$$

where we know the initial conditions are $G_0(0) = 1, G_{a \neq 0}(0) = 0, E_b(0) = 0$. We now take the full time-dependent Schrodinger equation:

$$\frac{d}{dt} |\Psi(t)\rangle = -\frac{i}{\hbar} \hat{H}(t) |\Psi(t)\rangle$$

starting with the left and simplest side:

$$\frac{d}{dt} |\Psi(t)\rangle = \sum_a \frac{dG_a(t)}{dt} |a_\gamma\rangle |g\rangle + \sum_b \frac{dE_b(t)}{dt} |b_\epsilon\rangle |e\rangle$$

Then the right side can be split in twain:

$$-\frac{i}{\hbar} (\hat{H}_0 + \hat{H}'(t)) |\Psi(t)\rangle$$

the easiest part of that being:

$$\begin{aligned} \hat{H}_0 |\Psi(t)\rangle &= \sum_a G_a(t) \left[E_g + E_\gamma \left(a + \frac{1}{2} \right) \right] |a_\gamma\rangle |g\rangle \\ &+ \sum_b E_b(t) \left[E_e + E_\epsilon \left(b + \frac{1}{2} \right) \right] |b_\epsilon\rangle |e\rangle \\ &= \sum_a G_a(t) \Omega_{(a)} |a_\gamma\rangle |g\rangle \\ &+ \sum_b E_b(t) \Omega^{(b)} |b_\epsilon\rangle |e\rangle \end{aligned}$$

and now for the interaction term:

$$\frac{\hat{H}'(t)}{E(t)} |\Psi(t)\rangle = \sum_a G_a(t) \mu(x) |a_\gamma\rangle |e\rangle + \sum_b E_b(t) \mu(x) |b_\epsilon\rangle |g\rangle$$

we may find it useful to diagonalize the vibrational eigenstates into the same manifold as the

electronic state using the identities: $\sum_q |q_\gamma\rangle \langle q_\gamma|$ and $\sum_j |j_\epsilon\rangle \langle j_\epsilon|$. We also define $\mu_a^b = \langle a_\gamma | \mu(x) | b_\epsilon \rangle$:

$$\frac{\hat{H}'(t)}{E(t)} |\Psi(t)\rangle = \sum_{a,q} G_a(t) \mu_a^q |q_\epsilon\rangle |e\rangle + \sum_{b,r} E_b(t) \mu_r^b |r_\gamma\rangle |g\rangle$$

Now we put everything together:

$$\begin{aligned} \left(\frac{d}{dt} + \frac{i}{\hbar} \hat{H}_0 \right) |\Psi(t)\rangle &= -\frac{i}{\hbar} \hat{H}''(t) |\Psi(t)\rangle \\ \sum_a \left(\frac{dG_a(t)}{dt} + \frac{i}{\hbar} \Omega_{(a)} \right) |a_\gamma\rangle |g\rangle + \sum_b \left(\frac{dE_b(t)}{dt} + \frac{i}{\hbar} \Omega^{(b)} \right) |b_\epsilon\rangle |e\rangle \\ &= -E(t) \frac{i}{\hbar} \left[\sum_{a,q} G_a(t) \mu_a^q |q_\epsilon\rangle |e\rangle + \sum_{b,r} E_b(t) \mu_r^b |r_\gamma\rangle |g\rangle \right] \end{aligned}$$

Now we can pick out specific terms by ket-ing in with $|g\rangle |a_\gamma\rangle$ and $|b\rangle |b_\epsilon\rangle$.

$$\left(\frac{dG_a(t)}{dt} + \frac{i}{\hbar} \Omega_{(a)} \right) = -E(t) \frac{i}{\hbar} \sum_b E_b(t) \mu_a^b$$

and then:

$$\left(\frac{dE_b(t)}{dt} + \frac{i}{\hbar} \Omega^{(b)} \right) = -E(t) \frac{i}{\hbar} \sum_a G_a(t) \mu_a^b$$

This can be re-cast as a matrix problem,

$$\frac{d}{dt} \begin{bmatrix} G_a(t) \\ E_b(t) \end{bmatrix} = -\frac{i}{\hbar} \begin{bmatrix} \Omega_{(a)} & E(t) \mu_a^b \\ E(t) \mu_a^b & \Omega^b \end{bmatrix} \cdot \begin{bmatrix} G_a(t) \\ E_b(t) \end{bmatrix}$$

Then this is put into a numeric first order differential equation solver. At every point I make sure there is not too much amplitude in the highest vibrational state and then re-start the calculation if so, ensuring no nonphysical results from truncation of the Hilbert Space.

8.7 NOTORIOUS RWA: THE ROTATING WAVE APPROXIMATION

There's another trick we can use to save a lot of computational time called the rotating wave approximation. Let's take a look at some laser excitation operator:

$$\hat{H}'_+(t) = E_0 e^{-i\omega_c \tau} e^{\frac{\tau^2}{2\sigma^2}} |e\rangle \langle g|$$

if we assume the ground state has zero energy and the excited state has energy/frequency (because $\hbar = 1$ here) Ω then we expect the zero and first order perturbation to look like:

$$\begin{aligned} |\psi_0(t)\rangle &= |g\rangle \\ |\psi_+(t)\rangle &= -\frac{i}{\hbar} \int_{-\infty}^t U(t, \tau) \hat{H}'_+(\tau) |g\rangle d\tau \\ &= -\frac{iE_0}{\hbar} \int_{-\infty}^t U(t, \tau) e^{-i\omega_c \tau} e^{\frac{\tau^2}{2\sigma^2}} |e\rangle d\tau \\ &= -\frac{iE_0}{\hbar} \int_{-\infty}^t e^{-i\Omega(t-\tau)} e^{-i\omega_c \tau} e^{\frac{\tau^2}{2\sigma^2}} |e\rangle d\tau \\ &= -\frac{iE_0}{\hbar} e^{-i\Omega t} |e\rangle \int_{-\infty}^t e^{-i(\omega_c - \Omega)\tau} e^{\frac{\tau^2}{2\sigma^2}} d\tau \end{aligned}$$

so we see that after the excitation perturbation only depends on $\omega_c - \Omega$ or the difference between the central frequency of the pulse and the laser. Which means that we can wrap those two things together and say that the energy of the excited state is zero and that the laser oscillates at a frequency of $\omega_c - \Omega$ instead.

$$\begin{aligned} |\psi_0(t)\rangle &= |g\rangle \\ |\psi_+(t)\rangle &= -\frac{iE_0}{\hbar} |e\rangle \int_{-\infty}^t e^{-i\delta\omega\tau} e^{\frac{\tau^2}{2\sigma^2}} d\tau \end{aligned}$$

What does that give us computationally? It means, primarily, that we can use a smaller time step and have the same accuracy, which will greatly speed up the calculation. One must be careful, though. It only works for diagonal Hamiltonians. Once one has a diagonal (or block diagonal) Hamiltonian, one can use this trick to consider the possible transitions between the diagonal states.

Part III

Conclusion

This page intentionally left blank.

9

Conclusion

The Work contained in this thesis hopefully makes it painfully clear that the Condon Approximation, must be tested against for all proposed protocols and it should be included in all molecular models going forward. Molecules have non-trivial transition dipoles which can and do affect not just their electronic spectroscopy, but their electron-transfer rates³³ and their Raman Spectra²⁰. It's just a matter of time before more effects are found.

Bibliography

- [1] D. H. Arias, K. W. Stone, S. M. Vlaming, B. J. Walker, M. G. Bawendi, R. J. Silbey, V. Bulović, and K. A. Nelson. Thermally-limited exciton delocalization in superradiant molecular aggregates. *The journal of physical chemistry. B*, **117**, 4553 (2013).
- [2] D. J. Berkeland, J. D. Miller, J. C. Bergquist, W. M. Itano, and D. J. Wineland. Minimization of ion micromotion in a Paul trap. *J. Appl. Phys.* (1998).
- [3] M. D. Bowdrey, D. K. Oi, A. Short, K. Banaszek, and J. Jones. Fidelity of single qubit maps. 2002.
- [4] J. J. Burdett, A. M. Müller, D. Gosztola, and C. J. Bardeen. Excited state dynamics in solid and monomeric tetracene: The roles of superradiance and exciton fission. *J. Chem. Phys.*, **133**, 144506 (2010).
- [5] J. Bylisma, P. Dey, J. Paul, S. Hoogland, E. H. Sargent, J. M. Luther, M. C. Beard, and D. Karaickaj. Quantum beats due to excitonic ground-state splitting in colloidal quantum dots. *Phys. Rev. B*, **86**, 125322 (2012).
- [6] W.-L. Chan, J. R. Tritsch, and X.-Y. Zhu. Harvesting singlet fission for solar energy conversion: One- versus two-electron transfer from the quantum mechanical superposition. *J. Am. Chem. Soc.*, **134**, 18295 (2012).
- [7] A. Chenu, N. Christensson, H. F. Kauffmann, and T. Mančal. Enhancement of vibronic and ground-state vibrational coherences in 2d spectra of photosynthetic complexes. *Scientific Reports*, **3**, 2029 (2013).
- [8] E. Collini, C. Y. Wong, K. E. Wilk, P. M. G. Curmi, P. Brumer, and G. D. Scholes. Coherently wired light-harvesting in photosynthetic marine algae at ambient temperature. *Nature*, **463**, 644 (2010).
- [9] E. Condon. Nuclear Motions Associated with Electron Transitions in Diatomic Molecules. *Phys. Rev.*, **32**, 858 (1928).
- [10] E. U. Condon. The Franck-Condon Principle and Related Topics. *Am. J. Phys.*, **15**, 365 (1947).
- [11] C. Creatore, M. A. Parker, S. Emmott, and A. W. Chin. Efficient Biologically Inspired Photocell Enhanced by Delocalized Quantum States. *Phys. Rev. Lett.*, **111**, 253601 (2013).
- [12] G. S. Engel, T. R. Calhoun, E. L. Read, T.-K. Ahn, T. Mancal, Y.-C. Cheng, R. E. Blankenship, and G. R. Fleming. Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems. *Nature*, **446**, 782 (2007).
- [13] A. F. Fidler, V. P. Singh, P. D. Long, P. D. Dahlberg, and G. S. Engel. Timescales of Coherent Dynamics in the Light Harvesting Complex 2 (LH2) of Rhodobacter sphaeroides. *The journal of physical chemistry letters*, **4**, 1404 (2013).

-
- [14] P. A. Fraser. A method of determining the electronic transition moment for diatomic molecules. *Can. J. Phys.*, **32**, 515 (1954).
- [15] D. J. Griffiths. *Introduction to Electrodynamics*. Pearson, 2012.
- [16] H. HAFFNER, C. ROOS, and R. BLATT. Quantum computing with trapped ions. *Phys. Rep.*, **469**, 155 (2008).
- [17] A. Halpin, J. J. M., R. Tempelaar, R. S. Murphy, J. Knoester, J. L. C., and M. J. Dwayne. Two-dimensional spectroscopy of a molecular dimer unveils the effects of vibronic coupling on exciton coherences. *Nat Chem*, **6**, 196 (2014).
- [18] E. Harel, A. F. Fidler, and G. S. Engel. Single-Shot Gradient-Assisted Photon Echo Electronic Spectroscopy. *J. Phys. Chem.A*, **115**, 3787 (2011).
- [19] D. Hayes, J. Wen, G. Panitchayangkoon, R. E. Blankenship, and G. S. Engel. Robustness of electronic coherence in the Fenna-Matthews-Olson complex to vibronic and structural modifications. *Faraday Discuss.*, **150**, 459 (2011).
- [20] E. J. Heller, Y. Yang, L. Kocia, W. Chen, S. Fang, M. Borunda, and E. Kaxiras. Theory of graphene raman scattering. *ACS Nano*, **10**, 2803 (2016).
- [21] P. Hockett, C. Z. Bisgaard, O. J. Clarkin, and A. Stolow. Time-resolved imaging of purely valence-electron dynamics during a chemical reaction. *Nat Phys*, **7**, 612 (2011).
- [22] J. Huh, S. K. Saikin, J. C. Brookes, S. Valleau, T. Fujita, and A. Aspuru-Guzik. Atomistic study of energy funneling in the light-harvesting complex of green sulfur bacteria. *J. Am. Chem. Soc.*, **136**, 2048 (2014).
- [23] A. S. Johnson, J. Yuen-Zhou, A. Aspuru-Guzik, and J. J. Krich. Practical witness for electronic coherences. *J. Chem. Phys.*, 141 (2014).
- [24] K. G. Johnson, J. D. Wong-Campos, A. Restelli, K. A. Landsman, B. Neyenhuis, J. Mizrahi, and C. Monroe. Active stabilization of ion trap radiofrequency potentials. *Rev. Sci. Instrum.*, **87**, 053110 (2016).
- [25] D. M. Jonas, S. E. Bradforth, S. A. Passino, and G. R. Fleming. Femtosecond Wavepacket Spectroscopy: Influence of Temperature, Wavelength, and Pulse Duration. *J. Phys. Chem.*, **99**, 2594 (1995).
- [26] E. Jones, T. Oliphant, P. Peterson, et al. SciPy: Open source scientific tools for Python, 2001–.
- [27] J. K. Joseph Goodknight and A. Aspuru-Guzik. Detecting the Variation of Electronic Transition Dipole Moments in Absorption Spectra. (*In Preparation*) (2017).
- [28] J. K. Joseph Goodknight, Peter Rose and A. Aspuru-Guzik. Problems with Detection of Electronic Coherences in Systems with Coordinate-Varying Transition Dipole. (*In Preparation*) (2017).

- [29] C. Kreisbeck and T. Kramer. Long-Lived Electronic Coherence in Dissipative Exciton Dynamics of Light-Harvesting Complexes. *J. Phys. Chem. Letters*, **3**, 2828 (2012).
- [30] C. Kreisbeck, T. Kramer, and A. Aspuru-Guzik. Disentangling electronic and vibronic coherences in two-dimensional echo spectra. *The journal of physical chemistry. B*, **117**, 9380 (2013).
- [31] N. Lambert, Y.-N. Chen, Y.-C. Cheng, C.-M. Li, G.-Y. Chen, and F. Nori. Quantum biology. *Nat Phys*, **9**, 10 (2013).
- [32] M. Khalil, N. Demirdöven, and A. Tokmakoff. Coherent 2D IR Spectroscopy: Molecular Structure and Dynamics in Solution. *J. Phys. Chem. A* (2003).
- [33] M. G. Mavros, D. Hait, and T. Van Voorhis. Condensed phase electron transfer beyond the condon approximation. *J. Chem. Phys.*, 145 (2016).
- [34] D. M. Meekhof, C. Monroe, B. E. King, W. M. Itano, and D. J. Wineland. Generation of Nonclassical Motional States of a Trapped Atom. *Phys. Rev. Lett.*, **76**, 1796 (1996).
- [35] M. Mohseni, P. Rebentrost, S. Lloyd, and A. Aspuru-Guzik. Environment-assisted quantum walks in photosynthetic energy transfer. *Journal of chemical physics*, **129**, 174106 (2008).
- [36] C. Monroe, C. A. Sackett, D. Kielpinski, B. E. King, C. Langer, V. Meyer, C. J. Myatt, M. Rowe, Q. A. Turchette, W. M. Itano, and D. J. Wineland. Experimental entanglement of four particles. *Nature*, **404**, 256 (2000).
- [37] S. Mukamel. *Principles of Nonlinear Optical Spectroscopy*. Oxford University Press, New York, NY, 1995.
- [38] S. Mukamel. Multidimensional femtosecond correlation spectroscopies of electronic and vibrational excitations. *Annual review of physical chemistry*, **51**, 691 (2000).
- [39] A. B. Myers. 'time-dependent' resonance raman theory. *J. Raman Spectrosc.*, **28**, 389 (1997).
- [40] T. Nakagawa, T. Suzuki, M. König, D. M. Guldi, and Y. Matsuo. Synthesis, photophysical properties, and excited state dynamics of a platinum complex of tetracene imide disulfide. *Chem. Commun.*, **49**, 10394 (2013).
- [41] I. Nielsen, Michael; Chuang. *Quantum Computation and Quantum Information*. Cambridge University Press, 2005.
- [42] L. A. Pachon and P. Brumer. Physical Basis for Long-Lived Electronic Coherence in Photosynthetic Light-Harvesting Systems. *J. Phys. Chem. Letters*, **2**, 2728 (2011).
- [43] G. Panitchayangkoon, D. V. Voronine, D. Abramavicius, J. R. Caram, N. H. C. Lewis, S. Mukamel, and G. S. Engel. Direct evidence of quantum transport in photosynthetic light-harvesting complexes. *Proc. Natl. Acad. Sci. U. S. A.*, **108**, 20908 (2011).

- [44] T. Renger, A. Klingner, F. Steinecker, M. Schmidt am Busch, J. Numata, and F. Mueh. Normal mode analysis of the spectral density of the fenna-matthews-olson light-harvesting protein: How the protein dissipates the excess energy of excitons. *J. Phys. Chem.B*, **116**, 14565 (2012).
- [45] G. D. Scholes, G. R. Fleming, L. X. Chen, A. Aspuru-Guzik, A. Buchleitner, D. F. Coker, G. S. Engel, R. van Grondelle, A. Ishizaki, D. M. Jonas, J. S. Lundeen, J. K. McCusker, S. Mukamel, J. P. Ogilvie, A. Olaya-Castro, M. A. Ratner, F. C. Spano, K. B. Whaley, and X. Zhu. Using coherence to enhance function in chemical and biophysical systems. *Nature*, **543**, 647 (2017).
- [46] B. W. Shore and P. L. Knight. The Jaynes-Cummings Model. *J. Mod. Opt.*, **40**, 1195 (1993).
- [47] A. Sørensen and K. Mølmer. Quantum Computation with Ions in Thermal Motion. *Phys. Rev. Lett.*, **82**, 1971 (1999).
- [48] A. P. Spencer, W. O. Hutson, and E. Harel. Quantum coherence selective 2D Raman- δ 2D electronic spectroscopy. *Nature Commun.*, **8**, 14732 (2017).
- [49] G. Stock and W. Domcke. Model studies on the time-resolved measurement of excited-state vibrational dynamics and vibronic coupling. *Chem. Phys.*, **124**, 227 (1988).
- [50] G. Stock and W. Domcke. Detection of ultrafast molecular-excited-state dynamics with time- and frequency-resolved pump-probe spectroscopy. *Phys. Rev. A*, **45**, 3032 (1992).
- [51] D. J. Tannor. *Introduction to Quantum Mechanics: A Time Dependent Perspective*. University Science Books, Sausalito, California, 2007.
- [52] V. Tiwari, W. K. Peters, and D. M. Jonas. Electronic resonance with anticorrelated pigment vibrations drives photosynthetic energy transfer outside the adiabatic framework. *Proc. Natl. Acad. Sci. U. S. A.*, **110**, 1203 (2013).
- [53] Q. A. Turchette, Kielpinski, B. E. King, D. Leibfried, D. M. Meekhof, C. J. Myatt, M. A. Rowe, C. A. Sackett, C. S. Wood, W. M. Itano, C. Monroe, and D. J. Wineland. Heating of trapped ions from the quantum ground state. *Phys. Rev. A*, **61**, 063418 (2000).
- [54] D. B. Turner, K. W. Stone, K. Gundogdu, and K. A. Nelson. Invited article: The coherent optical laser beam recombination technique (COLBERT) spectrometer: coherent multidimensional spectroscopy made easier. *The Review of scientific instruments*, **82**, 081301 (2011).
- [55] S. van der Walt, S. C. Colbert, and G. Varoquaux. The numpy array: A structure for efficient numerical computation. *Computing in Science & Engineering*, **13**, 22 (2011).
- [56] D. J. Wineland, C. J. Myatt, B. E. King, Q. A. Turchette, C. A. Sackett, D. Kielpinski, W. M. Itano, and C. Monroe. Decoherence of quantum superpositions through coupling to engineered reservoirs. *Nature*, **403**, 269 (2000).
- [57] W. H. Wollaston. A Method of Examining Refractive and Dispersive Powers, by Prismatic Reflection. *Philos. Trans. R. Soc. London*, **92**, 365 (1802).

- [58] J. M. Womick, B. A. West, N. F. Scherer, and A. M. Moran. Vibronic effects in the spectroscopy and dynamics of c -phycoyanin. *J. Phys. B Physics*, **45**, 154016 (2012).
- [59] J. Yuen-Zhou and A. Aspuru-Guzik. Quantum process tomography of excitonic dimers from two-dimensional electronic spectroscopy. I. General theory and application to homodimers. *Journal of chemical physics*, **134**, 134505 (2011).
- [60] J. Yuen-Zhou, J. J. Krich, and A. Aspuru-Guzik. A witness for coherent electronic vs vibronic-only oscillations in ultrafast spectroscopy. *J. Chem. Phys.*, **136**, 234501 (2012).
- [61] J. Yuen-Zhou, J. J. Krich, I. Kassal, A. S. Johnson, and A. Aspuru-Guzik. *Ultrafast Spectroscopy*. 2053-2563. IOP Publishing, 2014.
- [62] J. Yuen-Zhou, J. J. Krich, M. Mohseni, and A. Aspuru-Guzik. Quantum state and process tomography of energy transfer systems via ultrafast spectroscopy. *Proc. Natl. Acad. Sci. U. S. A.*, **108**, 17615 (2011).
- [63] A. H. Zewail. Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond. *J. Phys. Chem.A* (2000).
- [64] H. Zhou, Q. Chen, G. Li, S. Luo, T.-b. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu, and Y. Yang. Interface engineering of highly efficient perovskite solar cells. *Science*, 345 (2014).