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Mark E. Limes

^{129}Xe Relaxation and Rabi Oscillations

A dissertation submitted to the faculty of The University of Utah in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics

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Foreword

The year 2014 marks the 20th Anniversary of the publication (appearing in *Nature* and co-authored by me and several others) that first reported the magnetic resonance imaging of a hyperpolarized noble gas in a biological sample—^{129}Xe in the lungs of a mouse. The study of optical pumping, spin-exchange, and angular-momentum-transfer in atomic systems rather suddenly had a quite visible, interesting, and viable application that had potential clinical relevance. MRI with hyperpolarized noble gases is being pursued now by many groups worldwide and has continued to develop, if a bit methodically, toward clinical relevance. All the while a smaller group of scientists, mostly physicists and a few chemists, have continued to pursue the basic physics of spin-exchange optical pumping, which has its roots in the early work of Kastler and co-workers in Paris in the late 1940s and is absolutely crucial to the success of the various applications. I have worked both in the MRI application and on the basic physics, and while the former often pays the bills, the latter (as exemplified by a portion of this thesis) is probably a bit closer to my heart. My group has worked on longitudinal nuclear spin relaxation of ^{129}Xe in frozen hyperpola-rized xenon for some time, since it relates to how one generates and stores large quantities of hyperpolarized ^{129}Xe for various applications, such as lung MRI.

With this work, Dr. Limes has made the only truly reproducible T_1 measurements of solid ^{129}Xe near 77 K, the temperature at which hyperpolarized ^{129}Xe is usually cryogenically accumulated. His experiments have demonstrated differences in relaxation dependent upon how the solid is condensed (polycrystalline "snow" or "ice" that passes through the liquid phase prior to freezing), and he has also shown why previous results by our own and other groups were less consistent and reproducible. To do all this, Dr. Limes used a glass-dewar/NMR probe that can condense hyperpolarized ^{129}Xe gas as a polycrystalline snow, but can also manipulate the sample through the liquid phase and back to the solid state. The NMR spectrum is used to determine the amount of each phase in the sample. Mark also worked to thoroughly understand the Raman-phonon scattering relaxation theory for a spin-1/2 lattice (developed by Happer from earlier work by van Kranendonk) and its potential limitations. He has proposed modifications that may explain both the longer T_1 values that he now consistently observes compared to the published theory, as well as an observed linear component to the T_1 temperature dependence that would not be predicted by the

Raman mechanism alone. At once, one sees in this work Dr. Limes' ability to conduct elegant experiments, provide the needed theoretical background, and to pursue doggedly a difficult measurement problem that has previously produced inconsistent or inexplicable results.

Another significant portion of this thesis came out of collaborative work of our group with that of Christoph Boehme, under the aegis of the Utah Materials Research Science and Engineering Center (MRSEC), awarded by the U.S. National Science Foundation in 2011. Prof. Boehme had been trying for more than a year to get a student to do computational modeling of the nature of the Rabi nutation spectrum for two coupled spins (as with electron-hole charge carriers in a semiconductor) in different regimes of dipolar-coupling and exchange-coupling strengths. Dr. Limes' was able to properly implement a Liouville-superoperator formalism to solve the problem numerically and to generate the complicated two-spin spectra across the multi-dimensional parameter space; the work was done in a matter of a couple of months. These computational results have been validated by others from both an analytical perspective and through experimental work. The ongoing work of this particular collaborative group within the Utah MRSEC is to understand spin-dependent carrier transport in organic semiconducting devices, such as organic LEDs. Although use of the spin degree of freedom in these materials is an emerging field, the promise of cheap, easily synthesized organic semiconductors has already been realized in modern portable electronics (cell phones, tablets, *etc*.) The problem Dr. Limes' addresses here is relevant precisely because weak spin-orbit coupling in these materials provides for weak, coulombically bound electron-hole pairs (polaron pairs—precursors to exciton pairs), for which the spin-permutation symmetry is both non-trivial and alterable with microwave fields.

Finally, the third major portion of this thesis addresses a problem in nuclear magnetic resonance (NMR) that has potential far-reaching implications for the broad study of two-level systems. Dr. Limes led the experimental effort to validate the theoretical predictions having to do with beats in the Rabi precession pattern in the presence of a small longitudinal modulation field (added on top of the main applied Zeeman field). The predictions stem from the analysis of a weakly driven two-level system *with* such modulation, which can be mapped onto a strongly driven system *without* such modulation, and suggest that different regimes of spin dynamics, previously known for a strongly driven system (i.e., multi-photon resonances) can be realized under easily accessible (conventional NMR) conditions with proper choice of modulation frequency and amplitude. The theoretical work was done by Prof. Mikhail Raikh in our department (also as a collaborative MRSEC effort), along with his graduate student, Rachel Glenn. Mark brought Dr. Glenn into the laboratory and had her help with the design and execution of these experiments. This work has stimulated ongoing experiments in our laboratory, first to convert this experiment to one in which the radiofrequency field is modulated instead of the applied magnetic field, and ultimately to employ these techniques to perform useful NMR spin manipulations in solid materials.

I believe it is relatively rare for a graduate student to work so closely and productively with three different faculty members on three separate but related projects in

pursuit of a Ph.D. It speaks to Dr. Limes breadth and versatility as a physicist that he was able to generate and validate important results in each of the three main areas of his thesis.

University of Utah
Department of Physics and Astronomy
14 October 2014

Prof. Brian Saam, Ph.D.

Abstract

Several studies in magnetic resonance experiment and theory are presented. The longitudinal relaxation of solid ^{129}Xe is shown to have an unexpected structural dependence through experiments that provide previously unattainable reproducibility; also, groundwork is laid for theories that describe the observed data. A history of the field is given, including a theory of nuclear spin relaxation due to the coupling of the spins to the phonon bath, as well as the description of an extension of this theory. Theoretical work is also presented that involves nontraditional methods of magnetic resonance detection, such as optically and electrically detected magnetic resonance in semiconducting material. This work confirms, using computational and theoretical methods, the presence of dipolar coupling between two paramagnetic spin-half states to account for observed behavior in Rabi oscillations resulting in an increase of the Rabi frequency by a factor of $\sqrt{2}$; however, it is also shown that a strong presence of exchange coupling is required. Additional Rabi oscillation studies are given that involve experimental NMR water data, which confirm predictions of Rabi oscillation beat envelopes in three different regimes of longitudinal field modulation during a magnetic resonance experiment. Ancillary material include results from: a theoretical study of Rb atomic transition strengths, transverse relaxation in dilute-spin solid ^{129}Xe, and longitudinal relaxation of gaseous ^{129}Xe with regards to practical hyperpolarized ^{129}Xe storage.

Introductory quote

An idea is more important than its creator.
—George Fredrick Limes, Jr., (1951–2009)

Acknowledgments

Through the course of the work of this thesis and my graduate career, I have many people to thank. The order in which I'll thank them is work, friends, family.

To be cliché, I'd first like to thank Prof. Brian Saam for letting me in his group as it was an admittedly risky venture on his part. His guidance has been invaluable, from the initial time he spent with me on electronics, right up to the present day with writing papers and teaching me basic English again (though I'll not stop trying to reintroduce "vicinitude" into the language). A true Tigers fan (though also a Michigan Man), he leads by example, and I'll never be able to repay him for the various jams he's gotten me out of over my graduate career; situations that prove he's not only a great advisor, but a great human being—for that I thank him. Needless to say I've had those situations go completely the other way in the past, so it makes me appreciate all the more what he's done for me over these last 4 years. It's safe to say that a person's success in their career can be traced back to but a handful of people, and for me he is one of those people. If I had the choice to do it all over again, in his group, I would in a heartbeat—he's just that good of a boss to work for, and I'm happy to call him a friend as well.

One of the situations Brian fixed for me was that of funding, when he asked if I would be interested in working for Prof. Christoph Boehme, the second person I'd like to thank. Christoph also took a chance on me when he really didn't have to, and introduced me to the world of organic semiconductors. Seeing Christoph in action is quite remarkable, working for him and writing with him has been a pleasure and very valuable career experience. I'd also like to thank the rest of my committee, as I was lucky enough to interact with them outside of simply showing up and signing things for me. Prof. Mikail Raikh and Dr. Rachel Glenn were gracious enough to let me in on their project, and I think the end product was quality. In short, I'm lucky to have received all the opportunities that I've gotten at the University of Utah's Department of Physics and Astronomy, working with good people makes it hard to leave, and it'll be hard to top this experience. In this vein, I'd also like to thank the Swigart Scholarship Fund for support, especially for the finishing of my dissertation and writing up the solid xenon work, as our NSF funding had been lost for that project.

Now on to the friends, of which I've made many through the years here in Utah. First and foremost concerning this work is the patience and wisdom expressed by my

old lab mates in Brian's group, Dr. Eric Sorte and Dr. Zayd Ma. Eric taught me the importance and effectiveness of raw determination, and that at some point it doesn't make sense to keep talking about an experiment, just set it up in a day and go—quite a novel thought for me at the time. Zayd was also very self-motivated, and that kind of work ethic is infectious for me—he also always had just the right question that would feed my insomnia and curiosity in just the right way. (I don't send "World's Best Labmate" plaques to just anyone, you know?) I'll always remember our late nights rendezvous quite fondly, and I can honestly say I'd never be a Reverend of the Church of the Latter-day Dude if not for knowing him. Zayd always took me out of my element, in a very good and productive way, and I think our professional relationship is perfectly summed up by an analogy of him and his wonderful now-wife, Dr. Monica Allen, selecting me to preside over their wedding. I wasn't necessarily comfortable doing it, but Zayd got me through it kicking and screaming; I enjoyed every minute of it, and the end result was pretty good, if I do say so myself.

I also had the pleasure of working with a plethora of undergrads and a high school student in Brian's group that had the patience enough to listen to my convoluted ramblings; in no particular order: Elliot Nielsen, Haliegh Emerson, Laurel Hales, Oliver Jeong, Touchdown Tommy, Erik Houghtby, Matt Hunsaker, and Tom Paskvan. I'll single out Tom Paskvan (and his wife Dr. Meg) for being awesome friends and neighbors outside of work, even though we didn't have all that much time to get to know each other. Lastly in the group but certainly not least, I had the privilege of teaching the new guy, Eddie Thennel, some physics things... but he schooled me on most every other topic that was culture related. I hope a majority of these group interactions were positive for the other people too, and I've been lucky to have good people like Eddie around me.

I keep using the word "lucky," but I don't use it lightly, it simply fits perfectly. I was lucky to get in the graduate class I did, at the time I did, because I've made some really good, what I consider life-long friends in the process of being in graduate school. When Dr. Aaron Ballard and I first worked on some homework together, and when Dr. Nick Borys and I first introduced each other in our TA training program, I had no idea we'd still be talking to this day, let alone be good friends. Apart from the vestiges of our music recording and begging the question of "Dogecoin," Aaron and I still meet on a weekly basis to watch shows or movies, and will undoubtedly get rich with each other someday. Nick and his great wife, Stefanie, are always open to having us visit and stay with them, wherever they live, and I can only dream and patiently wait until the day we open that dive bar in the country. In the same vein of good friends, Dr. Dustin Winslow and his fiance, Dr. Michelle Hui, let me live with them when I moved back to Salt Lake City, and they were both incredibly awesome to hang out with and know in general. Michelle was, in my opinion, probably the most intelligent out of anyone in our class even though she never let on, and I still enjoy her eccentric e-mails to this day. Dustin and I came from similar backgrounds, education-and life-wise, which is probably why we hit it off quickly and remain good friends—his slowly meandering stories with no point will never be quieted, no matter how many times he asks me to stop them. Dr. Kipp van Schooten and his awesome wife, Tea, are also an extreme pleasure to know and hang out with, especially for

Sunday breakfasts. Kipp has become very important in my professional life as well, and we've worked on many projects together, whether just bouncing off crazy ideas in private (Iroc-Z's and Winnebago's) or writing papers—he's an invaluable resource for all things scientific (but Python schilling, really?). It's the same situation for all of these people in our entry class, they were awesome to work with, but they're even funner to hang out with in an unprofessional setting.

That notion extends to other students and post-docs I've worked with in the department, too. The first I'd like to mention on that list is Dr. Will Baker, because without him I'd have given up on this theoretical problem in Christoph's group, but he convinced me to continue and it wound up to be my first first-author paper, and Chap. 3 of this dissertation. Alex Theissen has also been generally awesome, with the highlights for me probably being a yurt excursion for Zayd's bachelor party (see above: kicking and screaming) and the Artsy Partsy's birthday bashes with Dr. Philippe Klemm. Dr. Hans Malissa knows the finer points of good beer (as well as spin techniques) and was a pleasure to get to know, ditto for Dr. Dane McCamey. There are many more people I'm leaving out for the sake of space, but I'll echo the sentiment—they were awesome to work with, but they're even funner to hang out with in an unprofessional setting.

Speaking of an unprofessional setting, I have to thank all of my Ohio friends that I grew up with and helped me along the way. I came from a relatively small, rural high school, but again I was lucky to have the class that I did, because we ended up with a few doctors, many professionals, and a few alcholics. Speaking of alcoholics, I'll mention Adam Hock. (That joke was the thanks for everybody at Otsego High School.) The Mauk's were, and are, good friends, but we don't really know why. Pat Ryan, Brad Babcock, Sam Wright, Jay Rider, Tim Joseph, and Bob Brandeberry all had the displeasure to listen to me sing, and are all now doing well, presumably as a result of not having to see me on a regular basis. My cousin, Josh, always said I was smarter than him, but he makes more money than I'll ever make, so who's the smart one?

More influential on what I've been doing lately, are Adam Sears, Ty Brott, and Kurt Gerken. I've known Adam for what I can only describe as feeling like an eternity, and we've essentially been holding self-deprecation contests ever since. Ty, his supercool wife, Jenn, and their families I was all lucky enough to meet through Adam, and they have been awesome to hang out with, through good times and sad pants. Kurt completes the wrecking crew we had assembled for awhile, and I only hope that someday we'll get the band back together.

I'd like to give the most, moster, and moistest thanks to my lovely wife, Heidi, who has been the most patient and understanding person I could have ever imagined through this whole process (by process, I mean me living life). I'm really glad that she came out to Utah to live with me, pretty much on a whim, and she's been ultra-supportive the entire way. In addition to amassing an insurmountable debt of "cuddle dollars," whatever those are, I'll truly never be able to repay her for keeping my sanity (mostly) and having someone awesome and motivating to always hang out with. I could literally write a Tolstoy-length treatise of thanks for her, and it wouldn't do the situation justice, so she'll have to settle for... thanks babe. We'll always have

Man-Man in Buffalo, and I'm looking forward to you showing me the ropes of New York. In return, I'll show you how to get a higher credit score, and teach you about compounded interest and calculus. Love you, Heidikins!

Finally, I'd like to thank my family, as probably the hardest part of being out in Utah was being away from them. My grandparents were great, with the Weaver side always playing card games and puzzles, and the Limes side giving me candy and laughs. I'm lucky to have the supportive and great extended family that I do, and it's always a pleasure getting together with anyone and everyone. My brother Chip taught me algebra at a very young age, and my brother Matt taught me how to drink. They both have beautiful families now, and I always look forward to coming back for Christmas. My mom has been putting up with me for all of my life, and the absolute hardest part of doing this was being away from her. She is the best mom anybody could ask for, teaching me the hard, quality lessons that you can only get from good parents. Lessons such as: nothing is free, and you get what you pay for. My dad is the one who convinced me to come back out to finish my degree, and it's what he would have wanted out of me, so I dedicate this work to him. An electrician by trade, I truly think he'd have gotten a kick out of the experimental end of physics (and would have been pretty good at it), and I think about him every day in the lab, and in my life in general. He was an awesome guy.

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