

Ultrafast spectroscopy and control of correlated quantum materials

By

Bryan T. Fichera

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Authored by: Bryan T. Fichera
Department of Physics
May?, 2024

Certified by: Nuh Gedik
Donner Professor of Physics, Thesis supervisor

Accepted by: ?
? Professor of ?
? Chair of ?

Abstract

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Acknowledgements

Preface

The physics of solids is, to me, one of the most important and fundamental fields of modern science. This might seem, to some, a bit of a hot take. After all, by studying condensed matter physics, one learns next to nothing about, say, the formation of the stars and planets, or the origin of the universe. Nor does one learn about life, death, consciousness, disease, ethics, God, or any other question that perhaps puzzled humanity prior to about five hundred years ago. Certainly no one would argue that condensed matter physics is quite *useless*, given that nearly every device we interact with in modern life required some condensed matter physicist somewhere along the way to make one brilliant discovery or another – yet when the human mind starts to wander, and our thoughts turn to the metaphysical, we tend to look up, not down.

In my work I have taken a quite different view. Condensed matter physics, to me, is ultimately the study of how *truly boring* objects, when brought together in large quantities, *become* interesting, seemingly in spite of themselves. When electrons are put together in a lattice and allowed to interact slightly with the massive nuclei, at low enough temperatures they pair, the low-energy excitations become gapped, and current can flow for infinite times and with absolutely zero energy loss. Those same electrons, with some other set of interactions, may instead ionize (the opposite of pairing!) to create an electrically insulating state, whose low-energy excitation spectrum is nevertheless gapless and consisting of charge-neutral spin- $1/2$ particles. In all such cases, these systems exist in otherwise ordinary-looking rocks, fit in the palm of a hand¹, and are more or less indistinguishable from something you might find sticking into the bottom of your shoe.

While such systems may not tell us a lot² about the early universe, considering these and related problems lets us ask deep, fundamental questions about the world we live in – like, why is this thing a metal, but this thing is an insulator? What do those terms even mean? – that I don't think we would try to ask otherwise. To me, focusing our attention on

¹Hopefully, gloved.

² This discussion is obviously intentionally reductive. In truth there is still quite a bit one can learn about, e.g. the early universe by studying condensed matter physics, see the review by Kibble *et al.*, Ref. ?.

these problems, despite their obviously terrestrial nature, is not a waste of time; rather, I think they remind us that even the most mundane aspects of the human experience involve a level of complexity far beyond what we are capable of understanding absent the pursuit of science.

Throughout the seven years of my Ph.D., I hope to have made a few contributions to this pursuit. As the title of this work implies, I have mainly focused on the application of ultrafast techniques to the study of correlated quantum materials, which I loosely define as those materials in which the interaction between particles is large enough so as to compete with the kinetic energy of those particles. It is in these materials that I think lies the true frontier of condensed matter physics; here, much of our basic intuition about non- or weakly-interacting theory fails, and more complicated notions of phase competition, phase separation, disorder, pairing, coherence, etc. are needed to properly describe the relevant physics.

In my own view, and in the view of many scientists in this field [?], the main question for strongly correlated physics amounts to: “Given a correlated system with some defined combination of different interaction strengths, is there a general theory which allows us to predict the phase diagram of this system *a priori*?” Related of course are questions about the origins of high- T_c superconductivity, strange metallicity, quantum spin liquids, and other exotic phases that we find emerging from strongly interacting systems. Since such a theory does not currently exist, at least with the level of predictive power that I think most would find satisfactory, new advances in this field typically come directly from experiment. Ultrafast optics plays a special role in this regard, for reasons that I will explain in chapter 1.

Progress thus happens in this field somewhat unsystematically, with small pieces of the puzzle added at random, but not infrequent, intervals. Usually it is either new techniques or new materials that are the driving force here. To this end, I have tried to pursue both directions in my Ph.D. Appearing also in chapter 1 is thus a description of the materials I studied the most during my thesis, two of them, CuBr_2 and CaMn_2Bi_2 I consider criminally understudied. On the technique side, almost all of the work presented in this thesis was done using time resolved second harmonic generation (tr-SHG), a relatively new, nonlinear optical technique which, at the most basic level, probes the point group assumed by the charge distribution function $\rho(\mathbf{x})$ at any given point in time. Sec-

ond harmonic generation (SHG) and tr-SHG are tricky techniques, with many pitfalls both practically and theoretically; chapter 2 and ?? are thus devoted to what I hope is a useful, if not fully comprehensive, description of the technique. My hope is that these sections are useful not only for the new student trying to build their own setup or analyze their own SHG data, but also for people for whom SHG is not a focus but nevertheless want to learn about it in slightly more detail than one would get from a typical paper or review article. Some aspects of ?? are devoted to work that we did developing a new way to control the polarization of the light in a tr-SHG experiment using stepper motors.

What follows, then, is a description of the three main research works I contributed during my Ph.D.. The first, which I describe in ??, involves work that I did during my second and third years on 1-TTaS_2 , a very interesting charge density wave (CDW) material that, among other things, undergoes a mirror symmetry breaking CDW transition at 350 K that shows up in the SHG as a sudden distortion of the flower pattern at that temperature. Since this transition breaks mirror symmetry, two energetically degenerate domains should be present, corresponding to two opposite planar chiralities; in this work, we showed that SHG could differentiate between these two domains (i.e. the flower pattern in either domain looks different).

The second and third works, which I describe in ????, in contrast to the 1-TTaS_2 work, both involve taking the system out of equilibrium to study the dynamics. In CaMn_2Bi_2 (?), we discovered that photoexcitation causes the antiferromagnetic (AFM) order in that compound to reorient (relative to equilibrium) to a metastable state which is impossible to reach from the equilibrium state thermodynamically. Light is thus used to *control* the magnetic order in this material.

In CuBr_2 (?), light is not used to control the order parameter like in CaMn_2Bi_2 , but it does excite coherent oscillations of the collective modes of the multiferroic order (electromagnons), whose frequency, amplitude, damping, etc. may be probed in tr-SHG as a function of temperature – a methodology referred to as ultrafast *spectroscopy*. In doing so, we found that one of these collective modes is actually quite special, as it is in fact the analogue of the Higgs mode of particle physics in the context of a multiferroic material.

I conclude with various remarks in ??, as well as an appendix, in which I enumerate briefly all of the null-result experiments I performed

during my Ph.D., in the hopes that future scientists don't have to waste time on what we already know are fruitless pursuits. If you have any questions about this or any other section of this thesis, please do not hesitate to reach out via email.

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Ultrafast optics in correlated electron systems

Chapter Two

Second harmonic generation: theory

2.1 Space groups and point groups

The utility of SHG in studying condensed matter systems is derived from the following simple statement, attributed to Franz Neumann [?] and later Pierre Curie [?]:

Theorem 2.1.1 (Neumann’s principle) *Let P_G be the symmetry group of a crystal structure and P_H the symmetry group of some physical property of that crystal. Then, G is a subgroup of H .*

There are a few things to digest here. Let us start by understanding the meaning of the phrase “symmetry group”. For any given crystal, there exists some infinitely large set of operations G under which the crystal structure is symmetric. Each of these operations may be decomposed into two parts: a “point-preserving operation” R , corresponding to either the identity, rotation, inversion, mirror, or the product of mirror and rotation, followed by a translation by some vector τ :

$$G = \{(R|\tau)\} \quad (2.1)$$

where $(R|\tau)$ means “Perform R , then translate by τ ”. Clearly, the set G forms a group, since if both g_1 and $g_2 \in G$ leave the crystal structure invariant, so does the product g_1g_2 , and so $g_1g_2 \in G$. Thus, G is called

the *space group* of the crystal. In three dimensions, there are 230 crystallographic space groups, which are tabulated in a number of places, most usefully Wikipedia [?].

For 73 of these groups, the translation parts of the τ s in eq. (2.1) are only ever linear combinations of integer multiples of the lattice vectors \mathbf{a} , \mathbf{b} , and \mathbf{c} ; these are called *symmorphic* space groups. The remaining 157 groups involve translations that are not integer multiples of the lattice vectors; these are one's screw axes and glide planes, and so these groups are called *asymmorphic*.

Importantly, the “physical properties” of theorem 2.1.1 refer to the truly macroscopic properties of the crystal, like it's conductivity, dielectric, or pyroelectric tensors. Consider, for example, that in SHG, we are typically studying the sample at optical wavelengths, where the wavelength of light is three or four orders of magnitude larger than the lattice spacing. Clearly, then, these properties do not care whether the correct symmetry is $(R|\tau)$ or $(R|\tau + \mathbf{a}/2)$. A more useful group, then, is the *point group* of the crystal

$$P_G = \{R \text{ s.t. } \exists \tau \text{ s.t. } (R|\tau) \in G\} \quad (2.2)$$

i.e., the point group is the set of point-preserving operations R for which R appears in G , regardless of whether you need to perform a translation with it. One can show that P_G is also a group, and thus it is P_G which is involved in Neumann's principle for all intents and purposes¹.

The last ingredient that we need to understand theorem 2.1.1 is the concept of what is meant by “physical property”. The idea is that the response of the crystal $J_{i_1 i_2 \dots i_n}$ (i.e., the current J_i , or the quadrupole moment Q_{ij}) is proportional to some field $F_{i'_1 i'_2 \dots i'_m}$ via some tensor χ :

$$J_{i_1 i_2 \dots i_n} = \chi_{i_1 i_2 \dots i_n i'_1 i'_2 \dots i'_m} F_{i'_1 i'_2 \dots i'_m}. \quad (2.3)$$

For example, the conductivity σ_{ij} relates a current density J_i to an applied electric field E_j :

$$J_i = \sigma_{ij} E_j. \quad (2.4)$$

Likewise, the polarization P_i due to the pyroelectric effect is related to the a temperature difference ΔT by a tensor p_i :

$$P_i = p_i \Delta T. \quad (2.5)$$

¹Of course this breaks down when the wavelength of light is comparable to the lattice spacing; in that case you need to consider the full space group.

The tensors σ_{ij} , p_i , and generally, $\chi_{i_1 i_2 \dots i_n i'_1 i'_2 \dots i'_m}$ are commonly referred to as *matter tensors* [?], to emphasize the fact that they are the only part of the response equations that depend on the material.

We are now ready to restate theorem 2.1.1.

Chapter Three

Second harmonic generation: practical

Chapter Four

Second harmonic generation as a probe of broken mirror symmetry in $1T\text{-TaS}_2$

Chapter Five

Light-induced reorientation transition in the antiferromagnetic semiconductor CaMn_2Bi_2

Chapter Six

Amplitude-mode electromagnon in the XXZ chain CuBr_2

Chapter Seven

Concluding remarks

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