Ultrafast spectroscopy and control of correlated quantum materials

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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 quantites, *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 hand[1], 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 lot[2] 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

[1] Hopefully, 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 Kibble and Pickett [2].

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 property describe the relevant physics.

In my own view, and in the view of many scientists in this field[1], 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 infrequenct, 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 $\rho(\boldsymbol{x})$ at any given point in time. Second harmonic

generation (SHG) and tr-SHG are tricky techniques, with many pitfalls both practically and theoretically; **????** are thus devoted to what I hope is a useful, if not fully compehensive, description of the technique. **??** is 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. My hope is that these chapters 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.

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*T*-TaS_2, a very interesting charge density wave (CDW) material that, among other things, undergoes a mirror symmetry breaking CDW transition at $350\ \mathrm{K}$ 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*T*-TaS_2work, 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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Chapter One

Ultrafast optics in correlated electron systems

Interactions between electrons in solids can be treated broadly in two different ways, depending on the strength of the interaction. Let us start with the case where the interactions are weak compared to their kinetic energy. In this case, interactions may be treated as a perturbation

$$V = \sum_{\boldsymbol{p}\boldsymbol{p}'\boldsymbol{q},\sigma\sigma'} V(\boldsymbol{q}) c^\dagger_{\boldsymbol{p}+\boldsymbol{q},\sigma} c^\dagger_{\boldsymbol{p}'-q,\sigma'} c_{\boldsymbol{p}',\sigma'} c_{\boldsymbol{p},\sigma} \tag{1.1}$$

on top of the usual hamiltonian

$$H_0 = \epsilon_{\boldsymbol{p}} c^\dagger_{\boldsymbol{p},\sigma} c_{\boldsymbol{p},\sigma} \tag{1.2}$$

for the noninteracting electrons. The key insight, due conceptually to **?**] and later formalized by **?**], is that, as long as the interactions are sufficiently weak, this problem can be adiabatically connected to a similar problem with non-interacting quasiparticles. Since these quasiparticles are fermions, they obey the Pauli exclusion principle, and the phase space available for scattering low-energy excitations is thus goes to zero at small energies. By Fermi's golden rule, the lifetime of such particles thus approaches infinity as we get closer and closer to the Fermi surface; i.e., there are still well-defined quasiparticles there, even though we started with an interacting Hamiltonian. Such a system is hence referred as a "Fermi liquid," to signify the fact that we have made only a slight departure from the nominal model of a Fermi gas where the particles are treated as noninteracting.

Fermi liquid theory is almost unreasonably successful in describing the ground state of a large number of correlated electron systems. Truly *most* metals can be very adequately described as a simple Fermi gas with renormalized effective mass, specific heat, etc.; while these modifications may be large (e.g. $m^*/m \approx 10^3$ in $CeAl_3$), they otherwise look like normal metals. Nevertheless, we can discuss circumstances in which the theory fails. Clearly various electronic instabilities may gap out the Fermi surface, resulting in an insulator; this happens for arbitrarily weak interactions in quasi-1D systems due to the Peierls mechanism, and in higher dimensions due to, e.g., Fermi surface nesting. Whether the interaction is attractive or repulsive determines whether the instability occurs in the charge or the spin channel. In the other limit, where the kinetic energy hamiltonian 1.2 is treated as a perturbation to the interaction term 1.1, the Fermi liquid state gives way to an (Mott) insulating state where the electrons become localized so as to minimize the coulomb repulsion U.

Studying such departures from Fermi liquid theory has become one of the most important fields in condensed matter physics. It is usually referred to as "strongly correlated electron physics", but many of the instabilities mentioned above are present even in the limit of weak interactions. Much of this interest was spurred by the discovery in 1986 by **?**] of high-T_c superconductivity in $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$, although the field has grown to include many other phenomena which occur in the strongly interacting limit that may or may not be related to superconductivity. Despite nearly four decades of research, however, there still exists no universal theory for strongly correlated electron systems, in the sense that, if someone hands you a random strongly correlated material, it is impossible from the outset to *predict* what will be the ground state, what are its low-energy excitations, etc. In fact, it is not even clear such a theory ought to exist[1].

The *field* of strongly correlated physics is thus, in some sense, still very much in its infancy, although that's not to say there haven't been huge advances, both theoretically and experimentally, especially since the discovery by **?**]. A lot of the effort experimentally has been focused on cataloguing the huge number of different exotic ordered phases—charge density wave, spin density wave, superconducting, strange metals, spin liquids, pseudogap, etc.—that are realized in these systems. Usually this is done by mapping out a phase diagram for a given material, which indicates which phases are present at various values of external parameters like magnetic field, pressure, strain, etc. Ultrafast optics has played an

important role in this respect, as it allows one (heuristically) to add a *nonequilibrium* axis to such phase diagrams. Such experiments, for example, have not only helped illustrate the extent to which different phases compete with one another in the cuprate phase diagram, but also the extent to which the action of the light pulse in strongly correlated materials can be used to tune the properties of those materials for practical purposes. This is paradigm is referred to as "ultrafast control," and I will discuss it in more detail in **??**.

A parallel effort in the field of ultrafast optics is to use the pump not to control the state of the material, but rather to excite coherent oscillations of the low-energy collective modes and study these oscillations in the time domain in a pump-probe scheme. This approach is advantageous for two reasons. For one, the frequencies accessible with this technique are bounded from below only by the length of one's delay stage, in contrast to conventional spectrometer-based methods which involve finite-frequency filters, gratings, etc. Second of all, the ability to select both the excitation mechanism (the pump) and the measurement apparatus (the probe) allows one to design experiments that target specific degrees of freedom of interest. Thus, for example, in multiferroics, one can use SHG to selecitively probe the collective modes which modulate the macroscopic polarization. This direction is referred to as "ultrafast spectroscopy," which I will explain in detail in section 1.1.

This chapter may thus be regarded as an introduction to strongly correlated electron systems, with a special emphasis on ultrafast experiments (of the two types explained above). A complete review of this material is beyond the scope of this thesis; instead, I will focus on a few seminal works that I think tell this story most pedagogically. We will also need a bit of machinery to understand **??????**, which focus on CDW, AFM, and multiferroic materials, respectively; hence I will primarily focus on these types of ground states, although of course this obviously misses e.g. strange metal phases, unconventional superconductivity, quantum spin liquids, etc. When appropriate, I point to pedagogical references that may be more useful than this thesis for these and other concepts.

1.1 Spectroscopy

1.1.1 Collective modes

The low-energy excitations of any many-body system are typically *collective*, in the sense that they involve motion of all of the particles in the system rather than just one. Let us consider, for example, the classical model consisting of two identical coupled harmonic oscillators

$$H = \sum_{i=1}^{2} \left(\frac{p_i^2}{2m} + \frac{m\omega_0^2}{2} x_i^2 \right) + g x_1 x_2, \tag{1.3}$$

with mass m, natural frequency ω_0, and coupling constant g. When $g = 0$, the normal modes of this system are simply the independent oscillation modes of the two oscillators. However, for any nonzero g, the normal modes involve either symmetric or antisymmetric linear combinations of the two oscillator coordinates; that is, they involve collective motion of the two oscillators. The extension to an ensemble of harmonic oscillators is straightforward; there, too, the normal modes of the Hamiltonian involve collective motion of all of the coordinates at once.

Of course the solids that we are interested in are more complicated than a simple ensemble of harmonic oscillators. Usually, though, more complicated systems can be broken down into a small number of *subsystems* which may, as a first approximation, be treated separately. Thus, for example, it makes sense to refer to the phonon subsytem independently from the electronic subsystem, with different and independent collective mode spectra in the limit where the inter-subsystem coupling goes to zero.

When this coupling is finite, however, many interesting phenomena may occur. For example, spin-orbit coupling coupling—which implies a coupling between spin and orbital degrees of freedom of the electron—can, in the right circumstances, cause the statically ordered state of the spin subsystem to also induce a ferroelectric distortion of the electron orbitals. The normal modes of the system in the presence of this coupling are no longer pure magnon or orbital modes, but rather collective modes of the spin and orbital degrees of freedom together. Let us look at this phenomenon from a different perspective. Suppose we didn't know the ground state of the system, but we did know that the relevant low-energy

excitations involved both spin and orbital degrees of freedom (for example, we might see a response in both the time-resolved kerr rotation as well as the tr-SHG). This is good evidence that the ground state of the system involves this coupling to some extent. Thus, we have learned something quite important about our system without doing anything but look at the low-energy collective excitations.

1.1.2 Coherent oscillations

Clearly understanding the low-energy excitations corresponding to a given ground state is a useful way to understand its properties. So far, however, we have made no mention of how to *probe* these excitations in pump-probe spectroscopy. Let us consider the following Hamiltonian consisting of electrons $c_{\boldsymbol{k}\sigma}$ (with dispersion $\epsilon_{\boldsymbol{k}\sigma}$) and bosons $b_{\boldsymbol{q}}$ (with dispersion $\omega_{\boldsymbol{q}}$) interacting via some potential $V^{\sigma}_{\boldsymbol{kq}}$

$$H = \sum_{\boldsymbol{k}\sigma} \epsilon_{\boldsymbol{k}\sigma} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + \sum_{\boldsymbol{q}} \hbar\omega_{\boldsymbol{q}} b^{\dagger}_{\boldsymbol{q}} b_{\boldsymbol{q}} + \sum_{\sigma \boldsymbol{kq}} V^{\sigma}_{\boldsymbol{kq}} \left(b_{\boldsymbol{q}} + b^{\dagger}_{-\boldsymbol{q}} \right) c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}+\boldsymbol{q}\sigma}. \tag{1.4}$$

The average lattice displacement is given by

$$\langle u(\boldsymbol{r}) \rangle \propto \sum_{\boldsymbol{q}} \left(\langle b_{\boldsymbol{q}} \rangle \, e^{i\boldsymbol{q}\cdot\boldsymbol{r}} + \left\langle b^{\dagger}_{\boldsymbol{q}} \right\rangle e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \right). \tag{1.5}$$

Clearly, in order for us to have a macroscopic lattice displacement, we need to have a finite value for $\langle b_{\boldsymbol{q}} \rangle$ and $\left\langle b^{\dagger}_{\boldsymbol{q}} \right\rangle$, which is impossible if there are a definite number of phonons in the mode $\boldsymbol{q}$ (since $\langle n| \, b_{\boldsymbol{q}} \, |m\rangle = 0$ for $n = m$). In contrast, if the wavefunction of the system consists of a coherent superposition of different phonon numbers, $\langle u(\boldsymbol{r}) \rangle$ may acquire a finite value. One thematic example of such a wavefunction is the so-called "coherent state" of the quantum harmonic oscillator

$$|\alpha_{\boldsymbol{q}}\rangle = \sum_{n} \frac{\alpha^n e^{-z^2/2}}{n!} (b^{\dagger}_{\boldsymbol{q}})^n \, |0\rangle \,, \tag{1.6}$$

although the real wavefunction need not be fully coherent to have a nonzero average lattice displacement.

One can show (see **?**]) that the equation of motion for the operator $D_{\boldsymbol{q}} \equiv \langle b_{\boldsymbol{q}} \rangle + \langle b^\dagger_{-\boldsymbol{q}} \rangle$ due to Eq. 1.4 is

$$\frac{\partial^2}{\partial t^2} D_{\boldsymbol{q}} + \omega_{\boldsymbol{q}}^2 D_{\boldsymbol{q}} = -2\omega_{\boldsymbol{q}} \sum_{\boldsymbol{k}\sigma} V^\sigma_{\boldsymbol{k}\boldsymbol{q}} \left\langle c^\dagger_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}+\boldsymbol{q}\sigma} \right\rangle , \tag{1.7}$$

i.e., $D_{\boldsymbol{q}}$ obeys a *wave equation* with an inhomogenous part related (in this case) to the electronic subsystem.[1] Thus, if we manage to initialize a wavefunction with a finite $D_{\boldsymbol{q}}$, the frequency with which $D_{\boldsymbol{q}}$ oscillates in time is the frequency $\omega_{\boldsymbol{q}}$ of the boson $b_{\boldsymbol{q}}$.

The central idea in ultrafast spectroscopy is therefore to excite coherent modes like Eq. 1.6, and then measure the frequency, damping, etc. of these modes by measuring $D_{\boldsymbol{q}}$. This is in contrast to equilibrium spectroscopies, which measure, for example, the transfer of energy from the light field to states with a definite number of bosons (i.e., $|n\rangle \to |n+1\rangle$). In theory, of course, the information obtained is the same—the frequency and damping coefficient of the collective modes in question may readily be optained in the equilibrium spectroscopies as well as in the pump-probe scheme. However, as I argued at the start of this chapter, the pump-probe techniques offer a number of advantages, most notably (i) the ability to design the pump and the probe to specify exactly which excitations we would like to measure, and (ii) the ability to measure much lower frequencies than in conventional spectroscopy due to the energy being measured in the time domain, rather than the frequency domain.

1.1.3 Excitation mechanisms

The next question is how we typically excite these coherent collective oscillations in real materials. The truth is there are many such mechanisms; however, we can start by placing them into two generic categories. *Impulsive* mechanisms involve using the light pulse to apply an effective force to the relevant degrees of freedom in the material, which lasts for the duration of the light pulse; i.e., it is a delta function in time. *Displacive* mechanisms are, in contrast, typically a step function; i.e., the equilibrium position of the oscillator is different before and after the light pulse. One important experimental difference is that impulsive excitation results

[1] There will also be a damping term, which may be added phenomenologically but is otherwise not considered in this treatment.

in a coordinate $D_{\boldsymbol{q}}(t) \propto \sin(\omega t)$, whereas displacive excitation results in $D_{\boldsymbol{q}}(t) \propto \cos(\omega t)$; this can be seen simply by solving

$$\frac{\partial^2}{\partial t^2} D_{\boldsymbol{q}} + \omega_{\boldsymbol{q}}^2 D_{\boldsymbol{q}} = f(t) \tag{1.8}$$

for $f(t) \propto \delta(t)$ or $f(t) \propto \theta(t)$, respectively.

In absorption

Let us consider the Hamiltonian in Eq. 1.4. We saw that this Hamiltonian resulted in an equation of motion given by Eq. 1.7, which is a wave equation for $D_{\boldsymbol{q}}$ with a force term

$$f(t) = -2\omega_{\boldsymbol{q}} \sum_{\boldsymbol{k}\sigma} V_{\boldsymbol{k}\boldsymbol{q}}^{\sigma} \left\langle c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}+\boldsymbol{q}\sigma} \right\rangle , \tag{1.9}$$

where the time-dependence of the right hand side is complicated but may be phonemnologically modeled. For example, let us suppose that we are in a semiconductor and that photon energy of our pump pulse is greater than the band gap of the material. Thus, the action of the pump is to excite electrons from the valence band into the conduction band. On a very fast timescale (0.1–$10\,\mathrm{fs}$) these electrons thermalize with themselves via electron-electron scattering, resulting in a quasi-equilibrium carrier distribution in which electrons and holes have settled at the bottom of the conduction band and the top of the valence band, respectively. Since further decay of these excitations is gapped, the relaxation of this state back to equilibrium may be quite long, especially if the gap is indirect; thus, together with the assumption that the lattice dynamics happen on much longer timescales than the electron thermalization time, it is appropriate to model the force term in Eq. 1.9 as a step function in time

$$f(t) \propto \begin{cases} 0 & t < 0 \\ 1 & t \geq 0 \end{cases} . \tag{1.10}$$

Thus we have the generic result that above-gap excitation typically excites coherent oscillations *displacively*. In the case that the bosons of Eq. 1.4 are phonons, this is known as displacive excitation of coherent phonons (DECP), and was studied by many authors, notably Zeiger et al.

[5]. An important insight which follows from Eq. 1.9 is that, in the limit where the quasi-equilibrium electron distribution doesn't break any symmetries of the original hamiltonian, the applied force also does not break any symmetries. Thus only totally-symmetric phonons may be excited via DECP.

In transparency

While the DECP-like mechanisms tend to dominate when the photon energy is above the band gap, they are forbidden in transparency. In this case, the dominant excitation mechanism is actually impulsive. Let us consider the case of a collective mode with energy $\hbar\omega_0$ which we wish to excite coherently with an ultrafast laser pulse, below the band gap. If the central frequency of the light pulse is resonant with the collective mode (i.e., we have $\nu_{\text{photon}} = \hbar\omega_0$), then we may drive the coherent oscillation directly; i.e., the mode coordinate Q simply follows the electric field. This is of course only possible if the mode carries a finite dipole moment (i.e. it is odd under parity). Alternatively, we will see that, under the right conditions, we can also excite coherent oscillation of low-energy collective modes even if the photon energy is far away from any direct resonance.

To see this, recall that ultrafast laser pulses always have a nonzero bandwidth, proportional to the inverse of the pulse width. In a nonlinear optical effect known as difference frequency generation (DFG), pairs of these frequencies may *interfere* to produce electric field components at the difference frequency between the two members of the pair. Thus, as long as the collective mode in question has a frequency less than approximately the bandwidth $\delta\nu_{\text{photon}}$ of the incident light pulse, there will exist pairs of frequencies (ω_1, ω_2) in that light pulse such that $|\omega_1 - \omega_2| \approx \omega_0$. This electric field will last for the duration of the light pulse, which may be treated as a delta function in time. This phenomenon is referred to as impulsive stimulated raman scattering (ISRS).

Since the force is a delta function in time, the result indeed is an impulsive excitation where the coordinate $D_{\boldsymbol{q}}(t) \sim \sin(\omega_0 t)$. Unlike the direct excitation mechanism mentioned above, ISRS requires two photons and the force is thus even under parity; i.e., we can only excite even-parity bosons.

It is instructive at this point to consider ISRS in a phenomenological Ginzburg-Landau (GL) model. We start by writing down an effective free

energy[**?**]

$$F = -\chi_{ij} E_i(t) E_j(t) Q \tag{1.11}$$

where $\boldsymbol{E}(t)$ is the incident electric field, Q the mode coordinate,[2] and χ_{ij} is some tensor of coefficients (see **??**). The effective force f due to Eq. 1.11 is

$$f = -\frac{\partial F}{\partial Q} \tag{1.12}$$

$$= \chi_{ij} E_i(t) E_j(t) \tag{1.13}$$

which appears on the right hand side of Eq. 1.8. Clearly, if the $\boldsymbol{E}(t)$ has Fourier components ω_1 and ω_2 such that $|\omega_1 - \omega_2| \approx \omega_0$, then the force will be *resonant* with the oscillator frequency.

Some interesting insights may be made in light of **??**. Let us consider for example the limit where the "mode" Q is a static magnetization M_k. The free energy reads[**?**]

$$F = -\chi_{ijk} E_i(t) E_j(t) M_k, \tag{1.14}$$

where we have expanded χ_{ij} to linear order in $\boldsymbol{M}$. Then, there is an *effective magnetic field*

$$H_k^{\text{eff}} = \frac{\partial F}{\partial M_k} \tag{1.15}$$

$$= \chi_{ijk} E_i(t) E_j(t) \tag{1.16}$$

which exists for the duration of the pump pulse. This is the inverse Faraday effect (IFE), which may thus be thought of as a particular limit of ISRS.[3] A similar effect (known as the inverse Cotton-Mouton effect (ICME)) is also present; expanding χ_{ij} to second order in $\boldsymbol{M}$, we have

$$F = -\chi_{ijkl} E_i(t) E_j(t) M_k M_l \tag{1.17}$$

and

$$H_l^{\text{eff}} = \frac{\partial F}{\partial M_l} \tag{1.18}$$

$$= \chi_{ijkl} E_i(t) E_j(t) M_k, \tag{1.19}$$

[2] Here we treat the mode Q as nondegenerate, although the generalization to the degenerate case is straightforward.

[3] Despite the similarities presented here, the two effects are actually quite different. For example, the spectral content of the pump pulse in the IFE does not change before and after interacting with the sample[**?**].

which, in contrast to the IFE, may occur when the pump is linearly polarized. The ICME is also available in AFMs; writing

$$F = -\chi_{ijkl} E_i(t) E_j(t) L_k L_l, \tag{1.20}$$

where $\boldsymbol{L}$ is the Néel vector (defined as the different in sublattice magnetizations), we have

$$H_l^{\text{eff}} = \frac{\partial F}{\partial L_l} \tag{1.21}$$

$$= \chi_{ijkl} E_i(t) E_j(t) L_k. \tag{1.22}$$

A full treatment of these and related effects is beyond the scope of this work;[4] the point is just to make a connection between the many different impulsive excitation mechanisms.

1.1.4 Collective modes in correlated materials

Phase transitions and Goldstone's theorem

In this section we illustrate one way we can understand the low-energy collective modes of a given material system without knowing precisely the form of the interaction Hamiltonian in Eq. 1.1. The important insight is that we can simply write down all of the *symmetry-allowed* terms in the Hamiltonian (or, at nonzero temperature, the free energy), and examine fluctuations near a phase transition where some order parameter takes on a nonzero value. In doing so, we find quite generally Goldstone's result that there is a gapless collective mode at the Γ point for each spontaneously broken symmetry. We also see that, in addition to the gapless Goldstone bosons, we also get a gapped *amplitude* mode which may be measurable in certain circumstances. The goal of this section is not to give a rigorous proof of Goldstone's theorem, but to illustrate how it comes about in a very simple model.

Let us consider the GL free energy density in the case of superfluidity, which is a functional of the coarse-grained order parameter $\Psi(\boldsymbol{x}) \equiv \psi(\boldsymbol{x}) e^{i\theta(\boldsymbol{x})}$ and whose lowest-order terms are

$$f[\Psi(\boldsymbol{x})] = -\frac{t}{2}|\Psi(\boldsymbol{x})|^2 + \frac{u}{4}|\Psi(\boldsymbol{x})|^4 + \frac{K}{2}|\nabla\Psi(\boldsymbol{x})|^2, \tag{1.23}$$

[4] See Kirilyuk et al. [4] for a comprehensive review.

where $u, K > 0$ and $t = (T_c - T)/T_c$. Clearly at all temperatures the minimum of Eq. 1.23 is spatially uniform, but for $T < T_c$ it occurs at a finite value of $\psi(\boldsymbol{x})$ (see **??**)

$$\Psi(\boldsymbol{x}) = \overline{\psi} \equiv \sqrt{\frac{t}{u}}, \tag{1.24}$$

where we have (without loss of generality) set $\overline{\theta} = 0$. Now consider fluctuations $\delta\theta(\boldsymbol{x})$ in the phase of the order parameter Ψ. We have

$$f[\overline{\psi}e^{i\delta\theta}] = f[\overline{\psi}] + \frac{K\overline{\psi}^2}{2}|\nabla\delta\theta(\boldsymbol{x})|^2, \tag{1.25}$$

where we have used that $-t + u\overline{\psi}^2 = 0$. Let us write the fluctuation $\delta\theta(\boldsymbol{x})$ in terms of its Fourier transform

$$\delta\theta(\boldsymbol{x}) = \sum_{\boldsymbol{q}} e^{i\boldsymbol{q}\cdot\boldsymbol{x}}\delta\theta_{\boldsymbol{q}}. \tag{1.26}$$

Then we have

$$F[\overline{\psi}e^{i\delta\theta(\boldsymbol{x})}] \equiv \int f[\overline{\psi}e^{i\delta\theta(\boldsymbol{x})}]\, d^3\boldsymbol{x} = F[\overline{\psi}] + \frac{KV\overline{\psi}^2}{2}\sum_{\boldsymbol{q}} q^2|\delta\theta_{\boldsymbol{q}}|^2. \tag{1.27}$$

Thus, uniform ($\boldsymbol{q} = 0$) fluctuations in the phase of Ψ cost zero energy, and long-wavelength ($\boldsymbol{q} \approx 0$) fluctuations in the phase of Ψ cost very little energy. The collective modes corresponding to these long-wavelength fluctuations are exactly our Goldstone modes.

Let us also examine the energy cost of fluctuations in the amplitude of Ψ, i.e. $\delta\psi(\boldsymbol{x}) \equiv \psi(\boldsymbol{x}) - \overline{\psi}$. To order $\delta\psi^2$, we have

$$f[\overline{\psi} + \delta\psi(\boldsymbol{x})] = f[\overline{\psi}] - \frac{t}{2}\delta\psi(\boldsymbol{x})^2 + \frac{3u}{2}\overline{\psi}^2\delta\psi(\boldsymbol{x})^2 + \frac{K}{2}(\nabla\delta\psi(\boldsymbol{x}))^2, \tag{1.28}$$

and, inserting $\overline{\psi} = \sqrt{\frac{t}{u}}$,

$$f[\overline{\psi} + \delta\psi(\boldsymbol{x})] = f[\overline{\psi}] + \frac{t}{2}\delta\psi(\boldsymbol{x})^2 + \frac{K}{2}(\nabla\delta\psi(\boldsymbol{x}))^2, \tag{1.29}$$

so that (for $T < T_c$), even *uniform* fluctuations in the amplitude of Ψ cost nonzero energy. The collective mode associated with such uniform fluctuations is the so-called "amplitude" or "Higgs" mode of our ordered

superfluid, with the important result that the energy of this mode approaches zero for $T \to T_c$.

Observing the amplitude mode in real systems is challenging because its decay into the lower-energy Goldstone modes is not typically forbidden, and so its lifetime is usually too low to observe it as a true quasiparticle[**?**]. Nevertheless, amplitude modes have been observed in a number of different circumstances; mainly, of course, in superconductors, where the amplitude mode may appear as a Raman peak in the A_{1g} channel[**?**], but also in charge density wave[**?**] and magnetic[**? ?**] systems (see **?**] for a good review).

Example: electromagnons in multiferroics

In the above we have described how coherent oscillations of collective modes in solids may be excited with an ultrafast laser, and we have explored how we can understand what those modes are without having to solve the full many-body Hamiltonian. Let us start to apply this machinery to a relevant physical system. A full accounting of the different collective modes in correlated systems is beyond the scope of this work; instead. let us focus on a particular class of physical system—multiferroics—which encompasses a lot of the physics of correlated materials and may also be described well in terms of the GL theory we outlined above. **??** is concerned with one member of this class ($CuBr_2$); in this material, we believe we are seeing the amplitude mode of the magnetic Hamiltonian imprinted on the charge degree of freedom in the form of an electromagnon. The understanding developed in this chapter will thus be quite helpful when we encounter that chapter.

Multiferroics are materials in which magnetic order exists in the same phase as ferroelectric order. They may typically be classified into two types. In the so-called type-II multiferroics, the transition to the ferroelectric state appears at the same temperature as a concomitant magnetic transition. This is because the ferroelectricity is *due to* some inversion symmetry breaking of the magnetic order, for instance by a helical spin density wave.[5] The microscopic mechanism will be discussed shortly, but let us contrast this with the case of type-I multiferroics—in type-I multiferroics, the magnetic and ferroelectric transition temperatures are

[5]The ferroelectricity is thus considered of the "improper" type.

different, and neither is "due" to the other; they just happen to exist in the same material. Intuitively this may happen when magnetic ions exist alongside different ions which participate in the ferroelectricity; this is the case in $BiFeO_3$[?]. Here we will focus on type-II multiferroics, not only because they tend to be more interesting but also because they usually have larger magnetoelectric effects (since the ferroelectric order is due to the magnetic order) and have thus been the central focus of the modern research on multiferroics.

The central question is then: can we describe (microscopically) how ferroelectricity may appear as a *result* of long-range magnetic order? A critical insight due to **?**] is that type-II multiferroicity can happen in quasi-1D Mott insulators when spin-orbit coupling is strong and the spins are ordered in a *magnetic spiral*. **?**] consider a 3-site 1D cluster model in which two transition metal ions with local spin-orbit coupled d electron orbitals interact via superexchange across an intermediate ligand atom (with an associated set of p orbitals). The tendency towards magnetic ordering is put in by hand, by placing a local spin at each transition metal site j in the direction $\hat{e}_j = (\cos\phi_j \sin\theta_j, \sin\phi_j \sin\theta_j, \cos\theta_j)$, and letting the d spins $\boldsymbol{S}_j$ interact with these local spins via a Hamiltonian $H_U = -U \sum_j \hat{e}_j \cdot \boldsymbol{S}_j$. They find quite generally the following geometrical relation between the spin directions $\hat{e}_j$ and an *induced* polarization $\boldsymbol{P}$:

$$\boldsymbol{P} \propto \hat{e}_{12} \times (\hat{e}_1 \times \hat{e}_2) \tag{1.30}$$

where $\hat{e}_{12}$ is the unit vector parallel to the bond connecting the two transition metal sites.

Clearly if $\hat{e}_1$ and $\hat{e}_2$ are either parallel or anti-parallel to one another, there is no induced polarization. However, if the magnetic order is *non-colinear*, and the spin plane is not perpendicular the chain direction, an induced polarization appears via Eq. 1.30. This explains very generally the multiferroicity of many noncollinear magnets. The multiferroic state thus described is also clearly "type-II", since the polarization is zero absent the magnetic ordering. Heuristically, such a spiral magnetic order may occur due to competition between a ferromagnetic nearest neighbor exchange interaction J_1 and an antiferromagnetic next-nearest neighbor interaction J_2 in a 1D spin chain; for $|J_2/J_1| < 4$ one can show that the ground state is such a noncollinear spiral.

Let us now consider the low-energy excitations of such a 1D chain.

The Hamiltonian may be written as

$$H = H_1 + H_2 + H_3 + H_4, \tag{1.31}$$

where

$$H_1 = \sum_i J_1 \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+1} + J_2 \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+2}, \tag{1.32}$$

$$H_2 = -\lambda \sum_i \boldsymbol{u}_i \cdot [\hat{x} \times (\boldsymbol{S}_i \times \boldsymbol{S}_{i+1})], \tag{1.33}$$

$$H_3 = \sum_i \frac{\kappa}{2} \boldsymbol{u}_i^2 + \frac{1}{2m} \boldsymbol{P}_i^2, \tag{1.34}$$

and

$$H_4 = \sum_i D(S_i^z)^2. \tag{1.35}$$

This Hamiltonian describes a 1D spin chain along $\hat{x}$ interacting with a charge coordinate u_i (with conjugate momentrum P_i) via Eq. 1.30. The anisotropy $D > 0$ pins the magnetic order to the xy plane. As discussed above, for $|J_2/J_1| < 4$ the ground state is a noncollinear spin spiral with spins lying in the xy plane, and the relative angle between adjacent spins is defined by some quantity $\phi \neq 0, \pi$ which is related to $|J_2/J_1|$.

?] discuss the low-lying excitations of this ground state in light of Eq. 1.31. First of all, clearly uniform rotations of all of the spins in the chain cost zero energy; this is the *Goldstone mode* of Eq. 1.31, and is in direct analogy with the Goldstone mode of the superfluid discussed in section 1.1.4.

If we temporarily set $D \to 0^+$ in Eq. 1.35, we may also observe that, in this limit, uniform rotations of the spin spiral *about the chain axis* also cost zero energy. This mode is also a Goldstone mode, although in this case it is due to the spontaneous breaking of the $\hat{x}$ rotational symmetry rather than the $\hat{z}$ rotational symmetry. For nonzero D, this mode of course acquires a finite energy; it is thus referred to as the *pseudo*-Goldstone mode, to highlight the fact that the symmetry is explicitly broken by the Hamiltonian rather than spontaneously broken.

The pseudo-Goldstone mode, however, is still quite interesting—note that, due to Eq. 1.33 and Eq. 1.30, a rotation of the spins about the chain axis *also* rotates the induced polarization about that axis. This mode is thus our first encounter with an electromagnon, which is any spin boson

that acquires a finite electric dipole moment due to coupling to the charge degrees of freedom.

Electromagnons are in fact an intrinsic feature of multiferroics, and what we have discussed above is by no means the only mechanism by which such modes may be achieved.[6] While a complete description of electromagnons and multiferroics is beyond the scope of this work (see **?**] and **?**] for review), I hope to have nevertheless motivated the idea that elementary excitations in correlated systems may still be understood in the context of broken symmetries and the GL paradigm—a notion that we will encounter frequently in the course of this thesis.

1.2 Control

From a technological perspective, ultrafast spectroscopy is useful because it helps us understand the physics of materials in equilibrium and how those materials might function in practical applications. Ultrafast control is different in the sense that it seeks to understand the different ways we can *manipulate* materials, with the idea that the knowledge thus gained may be used as a control scheme in some future technology, whether that involves using light or some other stimulus. The material of study is thus of a different kind of importance in ultrafast control—we are more interested in the phenomenology of the light-matter interaction rather than the phenomenology of the material itself. Usually the phenomenology of interest is, for example, being able to control the *state* of the material (like the direction of a magnetization, or the presence of a charge density wave) using light.

In my view, the dynamics relevant for ultrafast control fall into two categories. In one case, the dynamics following the light pulse are *coherent*; that is, the light field, for instance, excites coherent oscillations (see section 1.1.2), and those coherent oscillations drive the system to a new state.[7] In contrast, *incoherent* dynamics do not involve coherent oscillations of

[6] For example, in cases where magnetoelastic coupling is strong, a multi-particle excitation in which a spin boson couples to a phonon, and a phonon then couples to the electric polarization, is possible and common[**?**].

[7] Here I take the view that simply exciting coherent oscillations (i.e. without a dynamical phase transition) is *not* coherent control, but some may disagree with this point perspective, especially when the amplitude of such oscillations are large.

any degrees of freedom; instead, the light is used to, for example, heat the material, or excite quasiparticles away from the Fermi surface. This can also drive the material into a different (nonequilibrium) state, for example by quenching some long-range order (LRO) of the electrons near the Fermi surface, but the mechanism is qualitatively different from the coherent case. We will discuss both cases below.

1.2.1 Incoherent

Heating across a phase transition

The most basic level of ultrafast control is to use the light pulse simply to heat the material; if the initial and final temperatures lie below and above an equilibrium phase transition, then ultrafast control has been achieved. This is a somewhat trivial mechanism, but it played an important part in early research on ultrafast control, especially in materials where dynamical phase control *not* based on heating was rare or difficult (such as antiferromagnetis[3]). In addition, interactions between the sample area melted by the pump pulse and the surrounding unpumped area may cause interesting effects, such as magnetization reversal in ferromagnetic thin films due to the stray field of the unpumped sample volume[**?**]. We are more interested, however, in *nonthermal* ultrafast phenomena—that is, dynamical phenomena which cannot be replicated quasi-adiabatically.

Ultrafast quench

One example of such a phonemonon is the ultrafast quench (or "nonthermal melting") of some equilibrium order parameter via photoexcitation of electrons by the pump pulse. Let us consider, for example, the case discussed briefly in the beginning of this chapter of a quasi-1D Fermi liquid which becomes gapped by a periodic lattice distortion (i.e. via the Peierls mechanism). The basis for this mechanism is that quasiparticles near the Fermi vector in the undistorted Fermi liquid decrease their energy when the gap is opened via hybridization of folded bands, which happens at the expense of some energy gain associated with distorting the lattice away from its equilibrium configuration. When light is incident on this system in the distorted phase,[8] quasiparticles are excited *away* from the valence

[8] Let us say that the pump photon energy is above the Peierls gap.

band top, and the energy savings we gained by distorting the lattice disappears. The system thus relaxes back to its previous configuration and we lose our periodic lattice distortion—the light pulse destroyed the LRO.

Note that this is referred to as a *nonthermal* effect, even though for typical metals the quasiparticles experience an effective temperature change in this picture on the order of 10^3 K[**?**]. Nevertheless, the dynamical phase transition we just described proceeds, by construction, via the creation of a *nonequilibrium* distribution of photoexcited electrons, and in this sense it is nonthermal. There is often difficulty encountered in *proving* that the action of the pump is truly nonthermal. Indeed, the existence of an ordered phase implies some finite temperature T_c where that order is destroyed by equilibrium thermal fluctuations—it is the job of the experimenter to show that the laser pulse is not simply heating the material above this critical temperature. This is obvious if the phenomenology following the quench (see the next section) is in any case not reproduced in equilibrium, but may also be shown (heuristically) by dividing the energy absorbed by the material from the pulse by the heat capacity.

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