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Robust Platforms for Superconductivity

Disorder Robustness and Topological Density of States Peaks

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Abstract

Löthman, T. 2021. Robust Platforms for Superconductivity. Disorder Robustness and Topological Density of States Peaks. *Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology* 2030. 91 pp. Uppsala: Acta Universitatis Upsaliensis. ISBN 978-91-513-1183-8.

We explore the connection between robust material platforms for superconductivity and the modern condensed matter physics paradigms of two-dimensional materials, topological states of matter, and odd-frequency superconductivity. Specifically, the recent discoveries of gapless topological matter and truly two-dimensional materials with graphene have greatly expanded the class of materials for which topology produces large, robust, even singular, density of states (DOS) peaks in the electronic structure that in turn are highly susceptible to new ordered states of matter, including superconductivity.

In this thesis, we address the crucial question of superconductivity and competing orders near such DOS peaks, in addition to the stability of unconventional superconducting orders towards disorder. We show that DOS peaks are not only highly conducive to ordered states, but also that they are particularly favorable for superconductivity. We show that superconducting domes are especially likely to appear near DOS peaks. The result is fundamental, and stems from an inherent difference between the ordering susceptibilities towards superconductivity and all competing orders, providing a distinctive advantage for superconductivity. The result has relevance for several concrete material platforms that we consider further, including graphene doped to the van Hove singularity, magic angle twisted bilayer graphene, and rhombohedral graphite with its topological protected flat bands surface states.

In both single layer and in magic angle twisted bilayer graphene, the symmetry of the lattice promotes unconventional d-wave superconductivity with either a time-reversal-breaking d+id chiral or a nematic symmetry. In the single graphene sheet, the chiral state is ubiquitously favored, while as we show, using full-scale atomistic modeling capturing the long-ranged moiré patterns, a nematic ordering is unexpectedly dominant in twisted bilayer graphene. Furthermore, we show that that d+id-wave state in graphene close to the van Hove doping is remarkably disorder robust, despite the unconventional pairing, with a robustness that is comparable to a conventional superconducting state. Likewise, we show that a proximity induced odd-frequency p-wave pairing in a normal-superconducting junction is not only robust to disorder, but is in fact generated by such disorder, demonstrating again an unexpected interplay between order symmetry and robustness. Alongside with method development for finite time-correlations in superconductors, our results points towards new and unconventional platforms for realizing robust superconductivity.

Keywords: Superconductivity, Odd-Frequency Superconductivity, Nematic superconductivity, Topological Phases of Matter, Flat bands, Van Hove Singularity, Graphene, Twisted Bilayer Graphene, Rhombohedral graphite

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One must imagine Sisyphus happy.
Albert Camus

List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I **Defects in the d+id-wave superconducting state in heavily doped graphene**
Tomas Löthman and Annica M. Black-Schaffer
*Physical Review B **90**, 224504 (2014)*

II **Universal phase diagrams with superconducting domes for electronic flat bands**
Tomas Löthman and Annica M. Black-Schaffer
*Physical Review B **96**, 064505 (2017)*

III **Efficient numerical method for evaluating normal and anomalous time-dependent equilibrium Green's functions in inhomogeneous systems**
Tomas Löthman, Christopher Triola, Jorge Cayao, Annica M. Black-Schaffer
Manuscript (2020), arXiv:2004.10783 (Accepted in Phys. Rev. B)

IV **Disorder-robust p-wave pairing with odd frequency dependence in normal metal-conventional superconductor junctions**
Tomas Löthman, Christopher Triola, Jorge Cayao, Annica M. Black-Schaffer
Manuscript (2020), arXiv:2004.01456 (submitted to Phys. Rev. B)

V **Nematic superconductivity in magic-angle twisted bilayer graphene from atomistic modeling**
Tomas Löthman, Johann Schmidt, Fariborz Parhizgar, Annica M. Black-Schaffer
Manuscript (2021), arXiv:2101.11555 (submitted to Commun. Phys.)

Author's contributions

I I made the derivations, wrote the code, and performed the numerical calculations. I also prepared the data and figures. Both authors contributed equally to the interpretation of the data and results, the design of the work, and the writing of the manuscript.

II I performed the derivations and initially noted the universality of the critical temperature results and its implications for the phase diagrams of flat band systems. I also performed the numerical calculations and produced the figures. Both authors contributed equally to the interpretation of the results and the writing of the manuscript.

III I derived all results and wrote the initial manuscript. All authors contributed to the interpretation and writing of the manuscript.

IV I developed the computational framework, performed the numerical calculations, and produced the figures. JC wrote the initial manuscript. All authors contributed to the planing, interpretation, and writing of the manuscript.

V I developed the computational framework, performed the numerical calculations, and produced the figures with the help of JS and FP. All authors contributed to the planing, interpretation, and writing of the manuscript.

Contents

Summary in English

Superconductivity is the phenomena in which a material is able to conduct electricity without any power losses or heat generation, which is in sharp contrast to normal metals where electrical heating occurs due to a finite electrical resistance. While superconductivity is not uncommon, it generally only occurs at very low temperatures, requiring the use of specialized cooling equipment. In fact, superconductivity was only first discovered little over a century ago by the research group of Kamerlingh Onnes, after their earlier pioneering work on cooling techniques that also made them the first to liquidize helium. Upon cooling, the onset of superconductivity occurs in a sharp transition at a given critical temperature, marking a phase transition. The transition is analogous in character to the familiar transition of when water freezes to ice. But whereas the liquid to solid phase transition of water signals the ordering of the water molecules, from a disordered state with freely moving molecules to an ordered state with the molecules arranged in a regular pattern, the superconducting phase transition instead signals a reordering of the electrons within a material. A similar type of ordering is also responsible for certain types of magnets. Schematically, a common feature of phase transitions in both water and in superconductors alike, is that the ordering occurs from a balance between the interactions and the thermal fluctuations. At the critical temperature the balance is tipped and an ordered state that is better able to align with the interactions of the system emerges.

Given the highly desirable and unusual properties of superconductors, a long standing quest within the field of condensed matter physics has been to find new forms of superconductivity and in new materials, preferably with high critical temperatures. In particular, if superconductivity could be achieved at room temperature (and atmospheric pressure) it would have far reaching technological implications, not just limited to dissipation less power distribution. While several new classes of superconductors have already been discovered, some with critical temperatures above the boiling point of nitrogen, the quest still stands along with the desire to better understand, predict, and control this unusual phase of matter. In this thesis, we theoretically consider new material platforms for superconductivity, analyze possible superconducting orders, and examine the disorder robustness of unconventional superconducting orders.

A natural heuristic for realizing robust platforms for superconductivity is to identify electronic states for which the development of a superconducting order will result in particularly large energy gains that are in turn able to balance a strong thermal disorder. The total energy gain does however depend on many

factors, including the interactions, electronic properties, and effects of disorder. The electronic interactions are generally challenging to treat theoretically and difficult to engineer. This is especially true of the particular interactions that give rise to superconductivity. Given any interaction however, the energy gain of a system will be large if many electronic states are gathered near the same energy. Thus, a large peak in the density of states (DOS) will in general make a system more susceptible to ordering, so that even relatively weak interactions can drive a transition at relatively high temperatures. The recent high impact discoveries of both two-dimensional materials with graphene and certain classes of topological matter have greatly expanded the class of materials with robust, large, even singular, DOS peaks. These classes of matter are therefore one of the main focuses of this thesis.

The discovery and classification of topological phases of matter has recently transformed much of condensed matter physics. In a topological phase the electronic structure is characterized by having certain features that can not be undone without significantly altering the entire electronic structure. The certain features are therefore robust to small changes of the system, such as disorder. Topology enters as the mathematical tool used to specify the immutable features and sort out the difficult task of classifying which electronic structures can be smoothly transformed from one to another without abrupt changes. A related but striking implication of topological phases is therefore that such abrupt changes will have to occur at the interface (possibly to vacuum) between materials of different topology. On the boundaries of topological non-trivial matter are therefore particular electronic states that can not be removed without first changing the topology of the host material. The states are therefore exceptionally robust. Importantly for our purposes, certain topological classes of matter have topologically protected boundary states that necessarily have the same energy. The states are said to have a low or even flat energy dispersion. In these materials, including some topological semi-metals, the topology therefore produces a very large DOS peak on the boundary that in turn are consequently highly susceptible to ordering, inducing superconductivity. An example of a material with flat dispersion boundary states is offered by a restacked version of ordinary pencil lead called rhombohedral graphite, which has recently been predicted to readily become superconducting even at high temperatures.

A second important material class are two-dimensional materials. The isolation and characterization of graphene, a single layer of graphite, in the 21th century, demonstrated both the realization of a truly two-dimensional material and the advances in fabrication and characterization on the nanoscale that made it possible. Graphene has become on of the most researched materials and has been followed by many other two-dimensional materials. For our purposes, all two-dimensional materials have a special property; the electronic structure of an regular atomic lattice in two-dimensions must contain locally flat energy dispersions and must therefore also have a very large DOS peak. Such features

are called van Hove singularities and are also expected to be highly susceptible to ordering, further enlarging the class of materials containing DOS peaks.

While both two-dimensional materials and certain topological phases of matter produce robust and large DOS peaks that are highly susceptible to ordering, a long-standing objection have been whether a flat dispersion could support a transport phenomena like superconductivity. Recent work has however shown that even states with a flat dispersion can in fact support the required superconducting currents, due to previously unrecognized geometric contributions that are always finite for systems with a non-trivial topology. Consequently, superconductivity is therefore a realistic possible even within systems that have flat dispersions. Nonetheless, the increased susceptibility at DOS peaks enhances not only superconducting orders but also competing states, e.g magnetic orders. In our work, we therefore consider the important question of competing orders near large DOS peaks. We show that while a peak in the DOS increases the susceptibility of all orders equally, the increased susceptibility for superconducting orders extends over a much larger energy range then for non-superconducting orders. Superconducting orders are therefore more resilient to a shift away from the DOS peak by e.g electric gating or chemical doping. Consequently, even when a superconducting order is initially weaker than a non-superconducting competing order, the superconducting order is still highly likely to appear on the flanks of the DOS peak. Generally therefore a large DOS peak, of e.g. topological boundary states or van Hove singularities, will readily give rise to high critical temperatures but also give an additional distinct advantage to superconducting orders. Such materials are therefore very likely to be favorable for realizing exotic high-temperature superconductivity.

For instance, a highly unconventional chiral d+id-wave superconducting state has been predicted to emerge in doped graphene, being particularly likely when doped close to one of its van Hove singularities. Thus, while a pristine graphene sheet is a semi-metal with a vanishingly small DOS, and consequently unlikely to undergo any electronic phase transition, the situation is changed if the number of electrons in the graphene sheet is changed by doping, and there are many predictions of superconductivity in doped graphene. In particular, the symmetry of the lattice favors the formation of the chiral d+id-wave superconducting state that close to one of the van Hove singularities in graphene shows exceptionally large critical temperatures even for relatively weak interactions. The very large amount of doping required to reach one of the singularities is however also likely to introduce a significant amount of disorder and defects to the graphene sheet. As a part of this thesis, we show that despite its exotic and unconventional nature, the d+id-wave state is nearly as robust against defects as a disorder robust conventional superconducting order. The unconventional d+id-wave state therefore remains as a highly likely order in doped graphene.

Alternatively, low-energy van Hove singularities are produced in bilayers of graphene with a relative twist angle between the two layers. On closing the twist angle, the van Hove singularities are brought closer to the charge neutral point and can therefore be easily accessed in experiments. Ever since the discovery of both correlated insulating phases and superconductivity within these states in 2018 there as been an immense research activity devoted to understanding these new phases. As a highlight, we further show using full scale atomistic modeling that a rotationally symmetry breaking nematic superconducting order is favored in twisted bilayer graphene close to the magic angle, which is in contrast to graphene where a chiral superconducting state is favored. The nematic state is realized for experimentally observed critical temperatures and realistic interaction strengths together with resulting unusual features and experimental signatures that we report.

Recent developments have also demonstrated the importance of finite time superconducting correlations. The extension of the correlations in time simultaneously gives rise to an extended set of possible symmetries that the correlations can have, including odd-frequency superconductivity where the correlations are only finite for finite time differences. Such odd-frequency correlations have been found to appear ubiquitously, especially in systems with reduced symmetry, such as heterostructures, where they produce unusual experimental signatures. Spatially anisotropic superconducting correlations have however generally been assumed to be sensitive to disorder and often ignored. In our work, we however find the very surprising result that the exotic odd-frequency anisotropic p-wave correlations of a disordered normal metal-conventional superconductor junction are not only robust to disorder but are even generated by disorder. To obtain the result for the finite time correlations, we have also adapted an efficient quantum time-evolution method from quantum chemistry, providing a generalization to treat the statistics of many-electron systems found in condensed matter physics. The robustness of odd-frequency p-wave correlations challenges existing views within the field, opening up for new research directions.

In conclusion, we examine in this thesis large new classes of matter that, as we corroborate, are robust platforms for superconductivity. In general, our results point towards new avenues for realizing exotic unconventional forms of superconductivity with large critical temperatures and with implications for both experimental realizations and further research directions.

Sammanfattning på svenska

Supraledning är framförallt ett fenomen där ett material kan leda elektricitet utan värmeförluster, vilket är i skarp kontrast med vanliga metaller där värmeförluster uppstår på grund av ett ändligt elektriskt motstånd. Även om supraledning inte är ovanligt förekommande så sker det i allmänhet bara vid mycket låga temperaturer som kräver specialiserad kylutrustning. I själva verket upptäcktes supraledning för första gången av Kamerlingh Onnes forskargrupp för drygt hundra år sedan. Detta efter deras tidigare banbrytande arbete med kyltekniker som också gjorde dem till de första att likviderade helium. Vid kylning sker supraledningen plötsligt i en skarp övergång vid en specifik kritisk temperatur som markerar en fasövergång. Övergången är analog med den välbekanta övergången mellan vatten och is. Men medan övergången mellan vätska och fast fas hos vatten påvisar att vattenmolekylerna ordnas, från ett tillstånd med fritt rörliga molekyler till ett ordnat tillstånd där molekylerna har ett regelbundet mönster, så påvisar den supraledande fasövergången istället en omordning av elektronerna i materialet. En liknande typ av ordning sker också för vissa typer av magneter. Schematiskt sett så delar både fasövergångarna i vatten och i supraledare inslaget att ordningen sker utifrån en balans mellan interaktioner och värmefluktuationer. Vid den kritiska temperaturen skiftar balansen och ett ordnat tillstånd som bättre kan anpassa sig till systemets interaktioner framkommer.

Med tanke på de önskvärda och ovanliga egenskaperna som supraledare har, så har en långvarig strävan inom området för kondenserade materiens fysik varit att hitta nya former av supraledning och i nya material, med fördel vid höga kritiska temperaturer. I synnerhet, om supraledning kan uppnås vid rumstemperatur (och atmosfäriskt tryck) så skulle det ha långtgående tekniska konsekvenser som inte vore begränsade till energiförsörjning. Medan flera nya typer av supraledare redan har upptäckts, vissa med kritiska temperaturer över kokpunkten för kväve, så kvar står den långvariga strävan tillsammans med önskan att bättre förstå, förutsäga och kontrollera denna ovanliga fas hos material. I denna avhandling betraktar vi teoretiskt nya materialplattformer för supraledning, analyserar möjliga supraledande ordningar och undersöker robustheten hos okonventionella supraledande tillstånd mot orenheter.

En naturlig heuristik för att förverkliga robusta plattformar för supraledning är att identifiera elektroniska strukturer i vilka ett supraledande tillstånd skulle resultera i särskilt stora energivinster, som i sin tur kan balansera stora värmefluktuationer. Den totala energivinsten beror dock på många faktorer, så som vilka interaktioner som finns, elektroniska egenskaper, och effekter av

orenheter. De elektroniska interaktionerna är generellt svåra att behandla teoretiskt och svåra att experimentellt konstruera. Detta gäller särskilt de unika interaktioner som ger upphov till supraledning. Däremot, med givna interaktioner sker stora energivinster om ett system har ett stort antal energinivåer samlade vid samma energi. Således kommer en stor topp i tillståndstätheten (DOS av eng. density of states) i allmänhet göra att ett system blir betydligt mera instabilt mot ordnade tillstånd, så att även relativt svaga interaktioner kan driva en fasövergång vid relativt höga temperaturer. Upptäckterna av både tvådimensionella material i och med grafen och vissa klasser av topologisk materia har nyligen kraftigt utökat antalet material som har robusta, stora, till och med singulära DOS-toppar. Dessa kategorier av material tillhör därför ett av huvudområdena av denna avhandling.

Upptäckten och klassificeringen av topologiska faser av material har nyligen haft stora konsekvenser inom kondenserade materiens fysik. En topologisk fas kännetecknas av att den elektroniska strukturen har egenskaper som inte kan tas bort utan att markant förändra hela den elektroniska strukturen. Egenskaperna är därför särskilt robusta mot små förändringar i systemet, såsom orenheter. Topologi är det matematiska verktyget som används för att kvantifiera dessa robusta egenskaper, men också för att klassificera vilka elektroniska strukturer som kontinuerligt kan omvandlas från en till annan. En relaterad men slående konsekvens av de topologiska faserna är att det vid ett gränssnitt (eventuellt mot vakuum) mellan två material med olika topologi måste finnas särskilda energinivåer. På ytor av topologisk icke-trivial materia finns därför särskilda elektroniska tillstånd som inte kan tas bort utan att först helt ändra materialets topologi. Tillstånden är därför exceptionellt robusta. Det viktiga för våra ändamål är att vissa topologiska klasser av materia har topologiskt skyddade yttillstånd som alla nödvändigtvis har samma energi. De sägs därför ha en liten eller till och med en platt energidispersion. I dessa material producerar topologin därför en mycket stor DOS-topp på ytorna, som i sin tur följaktligen är mycket instabila mot nya ordnade tillstånd som också inkluderar supraledning. Ett exempel på ett material med sådana tillstånd är en variant av grafit i viket de enskilda kollagren har en annan ordningsföljd. Det har nyligen förutspåtts att tillstånden i denna variant av kol lätt kan bli supraledande även vid höga temperaturer.

Ytterligare en viktig kategori av material är tvådimensionella material. Isoleringen och karakteriseringen av grafen, som är ett enda lager av grafit, på 2000-talet, förverkligade inte bara tvådimensionella material utan visade också på de framstegen inom tillverkning och karakterisering på nanoskalan som gjorde detta möjligt. Grafen har sedan dess varit fokus av mycket forskning och upptäckten har också följts av många andra tvådimensionella material. För våra ändamål, så har alla tvådimensionella material en speciell egenskap; den elektroniska strukturen hos atomgitter i två dimensioner måste innehålla energidispersioner som är delvis platta och därför också ha mycket stora DOS-toppar. Sådana toppar kallas för van Hove singulariteter och förväntas också

vara mycket instabila mot ordnade tillstånd. Tvådimensionella material utökar därför antalet material med stora DOS-toppar ytterligare.

Medan både tvådimensionella material och vissa topologiska faser av materia ger robusta och stora DOS-toppar, har en långvarig invändning varit huruvida platta energidispersioner kan ge upphov till ett transportfenomen så som supraledning. Nyare resultat har dock visat att även platta energidispersioner inte är ett hinder mot supraledning, eftersom det har upptäckts att den supraledande strömmen kan ha tidigare okända geometriska bidrag som inte kräver någon energidispersion men som alltid bidrar i system med en icketrivial topologi. Supraledning är därför möjligt även för platta energidispersioner. DOS-toppar är däremot inte bara fördelaktiga för supraledning utan också för konkurrerande, t.ex. magnetiska, tillstånd. I vårt arbete betraktar vi därför den viktiga frågan angående sådana konkurrerande ordningar i närhet av stora DOS-toppar. Vi visar att medan DOS-toppar är lika fördelaktiga för alla vanliga typer av ordnade tillstånd, så förstärker DOS-toppar alla supraledande ordningar över ett mycket större energiområde än vad de gör icke-supraledande ordningar. Som en följd av detta är supraledning mer motståndskraftigt mot avvikelser från DOS-toppen som kan introduceras genom t.ex. spänningsfält eller kemisk dopning. Av denna anledning kan ett initialt svagare supraledande tillstånd framkomma på flankerna av DOS-toppen, där de är mer stabila än icke-supraledande konkurrerande ordningar. Generellt kommer därför en stor DOS-topp, t.ex. från topologiska yttillstånd eller van Hove singulariteter, lätt kunna ge upphov till höga kritiska temperaturer men också ge en ytterligare fördel till de supraledande tillstånden. Sådana material är därför mycket gynnsamma för att realisera exotiska former av supraledning vid höga temperaturer.

Till exempel har ett mycket okonventionellt kiralt d+id-supraledande tillstånd förutspåtts i dopat grafen, som också är särskilt sannolikt vid dopning i närhet av en av grafens van Hove singulariteter. Medan ett rent grafenlager är en metall med ett försvinnande liten DOS, och följaktligen osannolikt att genomgå en elektronisk fasövergång, så ändras situationen markant om antalet elektroner i grafenarket ändras med hjälp av dopning, och flera fall av supraledning har förutspåtts. I synnerhet bidrar symmetrin hos grafen gittret till bildandet av det kirala d+id-våg supraledande tillståndet som också tros ha exceptionellt höga kritiska temperaturer i närhet av van Hove singulariteterna. Samtidigt krävs en mycket stor mängd dopning för att nå en av singulariteterna, och det är därför mycket sannolikt att alla försök att dopa grafenarket kommer medföra en stor mängd defekter. Som en del av denna avhandling visar vi emellertid att trots dess exotiska och okonventionella natur är d+id-tillståndet nästan lika robust mot defekter som en stabil konventionell supraledande ordning. Det okonventionella d+id-tillståndet förblir därför som en mycket sannolik ordning i dopat grafen.

Som ett alternativ har det också visats att van Hove singulariteter uppkommer vid låga energier när två lager av grafen placeras på varandra med en relativ vridningsvinkel mellan de två skikten. När vridningsvinkeln minskas för-

flyttas van Hove singulariteterna närmare den laddningsneutrala punkten och singulariteterna kan därför lätt nås i experiment. Sedan upptäckten 2018 av både isolerande och supraledande faser i vridna grafenlager så har mycket stor forskningsaktivitet ägnats åt att förstå dessa nya faser. Med hjälp av en fullskalig atomistisk modellering visar vi bland annat att ett nematisk supraledande tillstånd är mest fördelaktigt i vridna grafen lager, vilket står i kontrast till det kirala tillstånd som ä mest gynnsamt i ett ensamt grafenlager. Det nematiska tillståndet uppkommer vid det experimentellt observerade kritiska temperaturerna och för realistiska interaktionsstyrkor, som vi rapporterar tillsammans med ytterligare ovanliga egenskaper och unika experimentella signaturer.

Den senaste tidens utveckling har också visat att supraledande korrelationer mellan olika tidpunkter kan ha stor betydelse. Utökningen av att betrakta korrelationerna mellan olika tidspunkter ger samtidigt också upphov till en utvidgning av de möjliga uppsättningar symmetrier som korrelationerna kan anta. En möjlighet är udda frekvens supraledning för vilken korrelationerna endast förkommer vid ändliga tidsförskjutningar. Sådana udda frekvenskorrelationer har visat sig vara vanligt förkommande särskilt i system som har en nedsatt symmetri såsom i heterostrukturer, där korrelationerna också producerar ovanliga experimentella signaturer. Samtidigt så har anisotropa supraledande korrelationer i allmänhet antagits vara mycket känsliga mot orenheter och därför också ofta försummats. I vårt arbete finner vi däremot det mycket överraskande resultatet att de exotiska udda frekventa anisotropa p-vågskorrelationerna vid övergången mellan en supraledare och en oren metall är inte bara robusta mot orenheterna utan kan till och med bildas med hjälp av orenheterna. För att beräkna de ändliga tidskorrelationerna har vi anpassat en effektiv tidsutvecklingsmetod från kvantkemi genom en generalisering av metoden till de mångelektronsystem som betraktas inom den kondenserade materiens fysik. De robusta udda frekvens p-vågkorrelationer utmanar tidigare antaganden inom området och öppnar upp för nya forskningsriktningar.

Sammanfattningsvis så undersöker vi i denna avhandling stora nya klasser av materia som vi bidrar med att visa också är robusta plattformar för supraledning. I allmänhet pekar våra resultat mot nya vägar för att förverkliga exotiska och okonventionella former av supraledning med stora kritiska temperaturer som har konsekvenser både för experimentella förverkliganden och för ytterligare forskningsinriktningar.

1. Introduction

The main concern of this thesis is superconductivity. Foremost, superconductivity is one of many possible ordered states of matter. The superconducting order is however characterized by the astonishing ability to carry a dissipationless electrical current as well as by unusual interactions with the electromagnetic field. While the superconducting state is rather common, it generally only appears at low temperatures, far below room temperature. A long standing quest within the field of condensed matter physics has therefore been the desire to realize a stable superconducting phase at higher temperatures but also to develop further theoretical understanding of the superconducting state. Without overstatement, if a room temperature superconducting state was realized it would constitute a transformative breakthrough discovery with far reaching technological applications. Just the prospect of long distance dissipationless power transmission would transform much of how the world goes about meeting its energy demands. Even existing superconductors have found important application as high power magnets, enabling medical imaging [1], particle accelerators [2], and magnetically levitating trains [3], just to name a few, and they also form the basis of highly sensitive measurement devices [4, 5]. With emerging application of superconductors to information technology, including quantum computing by e.g superconducting qubits [6, 7], these examples give just a hint of the highly desirable properties that the superconducting phase has to offer.

While the superconducting state has proven somewhat elusive since its century old discovery, new discoveries and predictions of new forms of superconductivity and material platforms regularly stir the field. Previous milestones include the discovery of the high-temperature superconductors in the late 20th century [8] and the realization of critical temperatures above the 77 K boiling point of liquid nitrogen, a far more achievable temperature. New discoveries continue to push boundaries. Following the very recent discovery of superconductivity in hydrogen sulfide at 203 K under extremely high pressures [9], even higher critical temperatures have been observed in related hydrogen-rich materials under similar extreme pressures [10, 11], even above room temperature [12]. While the pressures involved for these very recent superconductors still precludes direct applications and are only achieved in a lab setting using a diamond anvil, the discoveries demonstrate in principle the feasibility of even room temperature superconductivity and the activity surrounding superconductivity research.

In this thesis, we theoretically explore robust platforms for superconductivity in connection with three radically new paradigms in condensed matter

physics that only came to maturity within the 21th century: two-dimensional materials and graphene, topological phases of matter, and odd-frequency superconductivity. The experimental discovery of graphene [13–15], a single monolayer of graphite, demonstrated the existence of truly two-dimensional materials and at the same time the strides in both fabrication and characterization techniques that made it possible. The unexpected discovery together with the exotic electronic properties of graphene, has turned it into one of the most researched materials [14, 16, 17]. While systems of low dimensionality are generally inhospitable to ordered states due to increased fluctuations [18, 19], two-dimensional materials must at the same time have non-analytical points in the electronic structure, called van Hove singularities, that give rise to very large density of states (DOS) at certain energies [20–22]. In turn, such DOS peaks are very susceptible to ordering and new phases of matter, including exotic superconducting phases. The simple underlying reason is that the system can greatly reduce its energy by reordering the large number of electronic states. Systems with large DOS peaks, including two-dimensional materials, are therefore highly interesting venues for realizing superconductivity and are one of the main focuses of this thesis.

The ability to host large DOS peaks is also found in certain classes of topological states of matter [23, 24], which simultaneously is only a small aspect of the recent discovery and theoretical classification of several large classes of topologically non-trivial states of matter [23–25]. In a topological phase, the electronic structure is characterized by one or more global properties that are immutable with respect to small perturbations. Likewise, it is impossible to smoothly transform the electronic structure between two different topological phases without an abrupt change or symmetry breaking. A striking implication is the bulk-boundary correspondence, dictating that special topologically protected states have to appear when crossing a boundary between two different topological phases. Topological phases of matter are therefore associated with extraordinary robust electronic states appearing on their boundaries. One possibility of certain classes of topological matter is that the topology forces the states to have the same energy, thus creating a DOS peak. The two-dimensional materials and topological materials have greatly expanded the class of materials with large, or even singular, DOS peaks in the electronic structure, and therefore also possible hosts of superconductivity.

In Paper II we considered the important question of competing orders near large DOS peaks, and showed that DOS peaks not only favors the emergence of new phases of matter, but that superconductivity is particularly favored close to such DOS peaks. The underlying reason is that the ordering susceptibility towards any superconducting order is enhanced by any DOS peak over a much wider range of energies compared to any non-superconducting order. Our results therefore show that systems with a large DOS peak are particular interesting platforms for realizing possibly high-temperature superconductivity. In Paper II, we consider two such systems. First is the topological

semi-metal rhombohedral graphite which has been shown to host topologically protected surface flat bands that are prone to superconductivity [25–31]. Second is graphene doped close to the van Hove filling, which has been proposed to develop an exotic unconventional chiral d+id-wave superconducting order [32–35]. In Paper I, we further showed that the unconventional chiral d+id-wave superconducting state in graphene is surprisingly robust against disorder and impurities that are likely to accompany any attempts to reach the van Hove filling. Additionally, low-energy van Hove singularities are also produced in twisted bilayer graphene (TBG), as seen in spectroscopy [36–38]. Recent highly impactful experimental results on TBG have also found a rich phase diagram of competing phases, including correlated insulators and superconductivity [39–42]. In Paper V, we rigorously showed using full-scale atomistic modeling that a large inhomogeneous nematic ordering is favored in TBG.

The third development to impact this thesis is the growing realization of the importance of finite time dynamical electronic correlations in superconductors [43–45]. Central is how the extension in time intertwines with the possible symmetries of superconducting correlations, leading to the possibility of odd-frequency superconductivity. While the first proposals of odd-frequency superconductivity extend back into the 20th century [46], there has recently been a growing recognition that odd-frequency states appear ubiquitously in many superconductors, especially in symmetry breaking structures such as interfaces, disordered states, or heterostructures, where the odd-frequency correlations have been associated with unusual experimental signatures [43, 47–52]. While odd-frequency superconductivity allows for pair correlations with exotic symmetries, spatially anisotropic superconducting correlations have at the same time generally been assumed to be sensitive to disorder and therefore also often ignored. In Paper IV we however found that exotic odd-frequency anisotropic p-wave correlations of a disordered normal metal-conventional superconductor junction are not only robust to disorder but are even generated by disorder. We establish these findings based on fully quantum mechanical calculations of a large scale model, where we further used a linear scaling method we developed in Paper III to obtain the superconducting pair correlations.

This thesis is a comprehensive summary of the accompanying original articles, Papers I to V, that are included at the end of this thesis. Our goal is therefore not to reproduce the main results outline above, but to make these results more accessible and highlight the relevant connections. We focus on providing the conceptual background and methods used to derive the results of the original articles.

We therefore first introduce the central concept of phases within condensed matter physics in Sec. 2, and in particular how symmetry is used to classify phases of matter and their properties, while also leading to the concept of symmetry breaking phase transitions. For electronic phase transitions, a key ingredient is interactions. Section 2.2 therefore outlines how to account for interac-

tions and how they can favor certain symmetry broken ordered states, including superconductivity which is considered thereafter in Sec. 2.3. As we point out in Sec. 2.4 the ordering susceptibilities crucially depends on the number of available states around the Fermi energy, directly suggesting how a DOS peak in the electronic structure is conducive to ordering. Motivated by the fact that topology can produce flat bands and large DOS peaks, the topological phases of matter are introduced in Sec. 2.5, before we in Sec. 3 review how singular DOS scenarios can give rise to higher superconducting critical temperatures due to increased susceptibility and sensitivity to interactions. In particular, Secs. 3.1 and 3.2 focus on the implications of van Hove singularities of two-dimensional materials and of the flat band states that have been shown to occur in topological semi-metals. We then go on to consider the concrete examples of graphene, twisted bilayer graphene, and ABC-stacked rhombohedral graphite in further detail.

Starting with Sec. 4, the second part is devoted to our main theoretical and computational tools. First we derive a completely general mean-field theory that corresponds to the best possible non-interacting description of an interacting quantum system. In particular, the mean-fields are shown to satisfy self-consistency equations that can spontaneously break the symmetry of the system and give rise to new ordered states. The following Secs. 5 and 6 are therefore devoted to a derivation of the onset of ordering, which can be derived within the framework of linear response theory to produce the linearized self-consistency equations, also know as linear-T_c equations, given that the critical temperature of symmetry breaking orders are implicit in these equations. As a microscopic theory of superconductivity, the general mean-field theory of Sec. 4 is equivalent to the original description of the superconducting state by Bardeen, Cooper and Schrieffer (BCS) [53], but involves particle non-conserving terms in the Hamiltonian. We review their treatment within the Bogoliubov de Gennes (BdG) formalism in Sec. 7. In connection to the microscopic theory of superconductivity, we focus on the possible pairing symmetries in Sec. 7.1 and in particular the possibility of odd-frequency superconductivity of Sec. 7.2. Since solving the mean-field self-consistency equations or computing Green's functions and superconducting correlations for very large systems is numerically challenging, we review the concept of linear scaling electronic structure methods in Sec. 8. In the last part, we give a detailed summary of the results of the accompanying original papers and give conclusions and outlook.

2. Condensed matter phases

A fundamental paradigm in condensed matter physics is the existence of distinct phases of matter, in which the same constituent particles are in distinct arrangements. Different physical properties emerge from the unique arrangements and serve to define the different phases [54]. Concretely, both diamond and graphite are made from carbon atoms but are in two different phases with very distinct properties. Diamond is transparent, hard, and does not conduct electricity well, but with one of the largest known heat conductivities. Graphite, in contrast, absorbs visible light, is soft, and is an electrical conductor [55]. Thus, the prediction of phases of matter is at the heart of understanding, predicting, and designing material properties.

The phase concept applies not only to the atomic positions of a material but also to the electronic arrangements within for instance a crystalline phase. Thus without necessitating a structural transition, passing above the Curie temperature, a magnet will lose its net magnetic moment in a phase transition [55]. For just like water freezes to ice when cooled, changes in phase with temperature is the rule rather than the exception. Such phase transitions originates from the competition between thermal disorder and the minimization of the internal energy E of the system at equilibrium through the minimization of the free energy $F = E - TS$, where T is the temperature, and S the entropy [56]. At a higher temperature a more disordered phase with a larger entropy S is preferred, even when accompanied by an additional energy cost. A phase transition therefore depends on the delicate balance between the entropy of the available microscopic arrangements and their energy. Phase transitions are therefore generally hard to accurately predict; especially since there are usually several candidate phases that the material could transition to. To sort out the complexity, symmetry is often used to characterize the different phases as well as their properties.

2.1 Symmetry

A central tool in condensed matter physics is the classification of phases of matter by their symmetry [56–58]. In general, at low temperatures, where the minimization of the free energy is heavily biased towards a minimization of the total internal energy over the entropy, the interaction of a system may prefer a distinct alignment with a lower energy, resulting in a higher degree of

order. The degree of order can be quantified by all the symmetry transformations that leave the state invariant, together forming a mathematical symmetry group. For example, at a very low temperature, all the magnetic moments of a ferromagnet are aligned along an arbitrary but specific axis, as this configuration minimizes the total energy. In this phase, only the transformations that leave the magnetic axis invariant are symmetry transformations. In contrast, at a high temperature, all moments are randomly oriented and therefore any rotation will leave the system invariant. At a critical temperature, a spontaneously symmetry breaking phase transition separates the high and the low temperature phase. At the transition, even when starting from isotropic interactions, a preferred direction emerges, defined by the axis of the net magnetic moment. Quantities like the magnetic moment, which are non-vanishing only in the ordered state, are called order parameters. The symmetry breaking process can generally be understood in terms of an effective field theory for the order parameters, as in Landau theory [56, 58, 59]. Assuming that the free energy is smooth analytic function around the transition, the free energy can be series expanded in powers of symmetry invariant combinations of the order parameters. Despite the symmetric free energy functional, the free energy minima may still be at a finite order parameter and therefore not symmetry invariant but symmetry breaking. The theory demonstrates the symmetry breaking process regardless of whether the free energy function is derived microscopically or assumed on the basis of symmetry and phenomenology [60]. In general, the symmetries of a given phase of matter are further intimately connected to the excitations and the properties of the phase, which gives further characterization.

2.1.1 Quasiparticles

For most of condensed matter physics the symmetry of a phase are intimately connected to the properties of that phase. The reason is that in most systems, the symmetries determine the quantum numbers that label the available low energy excitations and the quantum mechanical many-body states. For instance, translational symmetry ensures that momentum is a good quantum number [61]. Thus, each phase usually admits a robust description of its excitations based on the symmetry of that phase. In most systems and even in the presents of interactions, it is therefore possible to identify independence low-lying excitations or quasiparticles labels by such quantum numbers. The underlying assumption, and the idea embodied in the Landau-Fermi-liquid theory, is that the excitations of an interacting system are smoothly (adiabatically) connected to those of a non-interacting system with the same quantum numbers [58]. During this imagined slow evolution from the non-interacting to the possibly strongly interacting system, the quantitative properties of the excitations may change, but retain their identity as independent particles labeled by the

same quantum numbers. In particular, in fermionic systems the Pauli exclusion principle leads to reduced scattering by interactions close to the Fermi surface, because the particles have limited phase space for scattering to occur [62]. The reduced scattering ensures that the low energy excitations have a long enough life time so as to allow them to be identified as distinctive quasiparticles with definite energies and quantum numbers. A notable exception to this are one-dimensional systems that naturally lack an extended Fermi surface which leads to non-Fermi liquid behavior [60, 63]. While the adiabatic assumption breaks down were it to encounter a phase transition along the way, the Landau-Fermi-liquid theory ensures that a good approximate starting point for many electronic condensed matter system is a non-interacting model describing the quasiparticles of the system that is based on symmetries of the system.

A staple of condensed matter physics is the crystalline phase where the constituent atoms are arranged in regular periodic lattices. Assume that there is no additional spontaneous symmetry breaking besides the underlying crystal lattice, the lattice periodicity in the crystalline phase implies that the system is invariant under any number of translations by the lattice vectors along which the motif is repeated. According to Bloch's theorem, the non-interacting quasiparticles in a periodic lattice can therefore be labeled by the crystal momentum k, defined on the reciprocal lattice, that correspond to the different irreducible representations of the translation symmetry group [55]. Since the reciprocal lattice is periodic, too, the quasiparticle energies $\epsilon_n(k)$ form regular bands. Collectively the energy bands are referred to as the electronic band structure. Using the formalism of second quantization [64], the electronic structure is therefore described by $H = \sum_{k,n} \epsilon_n(k) c^\dagger_{kn} c_{kn} + \text{H.c.}$, where n are the band indices that labels additional, such as spin or orbital, degrees of freedom.

2.2 Interactions and the Hubbard Model

Even if the non-interacting Bloch states are a good starting point, residual interactions typically remain, and are specially important when the adiabatic assumption breaks down close to a phase transition. While the bare Coulomb interaction between charge particle has a long power law tail, in most condensed matter systems and especially metals the interactions are typically much more localized in space due to collective screening [65]. Since the interactions are local in space they are non-local in momentum space. It is therefore desirable to transition to a real space description where the states are localized. This can be done by the introduction of Wannier orbitals, $c^\dagger_{rn} = N^{-1/2} \sum_k e^{-ir\cdot k} c^\dagger_{kn}$ that are localized around the lattice site r, where N is the size of the lattice [66, 67]. In the Wannier basis, the non-interacting Hamiltonian has the general form, $H = \sum_{r,r',n,m} T_{rr'nm} c^\dagger_{rn} c_{rn} + \text{H.c.}$, describing quasiparticles hopping

between lattice sites with the amplitudes $T_{rr'nm}$. Within the Wannier basis, an arbitrary two-body interaction is easily introduced as,

$$H_{\text{int}} = \sum_{\substack{ijkl \\ r_1 r_2 r_3 r_4}} U_{ijkl}(r_1, r_2, r_3, r_4) c^\dagger_{r_1 i} c^\dagger_{r_2 j} c_{r_3 k} c_{r_4 l}, \tag{2.1}$$

where the expectation is that the series can be terminated after a few terms, because of the localization of the Wannier orbitals.

Remarkably, retaining only the nearest-neighbor hopping terms of a single band model together with the on-site interaction term still results in a highly non-trivial but important model, the Hubbard model [68–70], that has been broadly applied within condensed matter physics, including the areas of metal-insulator transitions [71, 72] and high-temperature superconductivity [73–75].

The Hamiltonian of the Hubbard model,

$$\hat{H}_{\text{Hubbard}} = \mu \sum_i \hat{n}_i - t \sum_{\langle i,j \rangle} c^\dagger_i c_j + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}, \tag{2.2}$$

only depends on the the ratio of the hopping amplitude t between nearest-neighbors $\langle i, j \rangle$ and the on-site interaction strength, U/t, in addition to the dimensionless temperature T/t and the filling factor that is controlled through the chemical potential μ/t. The model does not have any known general solution, except in one dimension [76]. For weak coupling $U/t \ll 1$, the system described by the Hubbard model remains a metal, except at very low temperatures, while at stronger coupling the outcome is less certain, but theorized to including both (Mott) insulating and superconducting behavior [74, 75]. Any doubly occupied site has an interaction energy cost of U. At half-filling and strong coupling, the model is expect to describe an Mott insulating state where each site is singly occupied without hopping. With doping the Mott insulator is widely theorized to include a transition to a superconducting state [73, 74].

In the Hubbard model at half filling and in the strong coupling limit $1 \ll U/t$, the interaction energy is minimized if each site is singly occupied. The subspace of the singly occupied states is however highly degenerate with respect to the interaction terms, since the interaction does not depend on the spin orientation. If the hopping term is included perturbatively, then the degeneracy is expected to be lifted. The reason has to do with the Pauli exclusion principle. A particle can only hop to a neighboring site, and thereby also lower the overall kinetic energy, if the two neighboring sites initially have the opposite spin orientation. If instead the two sites initially have the same spin orientation, then the hopping term would place two particles of same spin on the same site, i.e. the same quantum state, which is forbidden for fermions by the Pauli exclusion principle. The combination of the repulsive on-site interaction and the hopping term therefore gives rise to a superexchange mechanism that favors an anti-ferromagnetic alignment of the spins.

Formally, the superexchange mechanism can be derived by expanding the Hubbard Hamiltonian to second order in perturbation in U/t using the Schrieffer-Wolff transformation [65], resulting in a effective an effective Hamiltonian,

$$H_{\text{eff}} = \hat{P}_S \Bigg[-t \sum_{\langle i,j \rangle} c_i^\dagger c_j + \frac{t^2}{U} \sum_{i,\xi_1,\xi_2,\sigma} \left(c^\dagger_{i+\xi_1\bar{\sigma}} c^\dagger_{i\sigma} c_{i\bar{\sigma}} c_{i+\xi_2\sigma} - c^\dagger_{i+\xi_1\sigma} c^\dagger_{i\bar{\sigma}} c_{i\bar{\sigma}} c_{i+\xi_2\sigma} \right) \Bigg] \hat{P}_S + \mathcal{O}(t^3/U^2)\,, \tag{2.3}$$

where $\hat{P}_S$ is the projection operator on to the subspace without double occupancies and the ξ_j are nearest-neighbor vectors. The terms with $\xi_1 \neq \xi_2$ involve three different sites. Since the end state has to be without double occupancies to be non-zero after the projection, these terms are only non-zero if the end site was initially unoccupied. Close to half-filling, the three site terms are therefore assumed to only have a small contribution when compared to the terms with $\xi_1 = \xi_2$, because of the low concentration of holes. It is the terms with $\xi_1 = \xi_2$ that give rise to the superexchange, which can be seen explicitly when these terms are expressed in the spin basis $\hat{S} = 1/2 \sum_{\sigma,\sigma'} c^\dagger_\sigma S_{\sigma\sigma'} c_{\sigma'}$ from the vector of Pauli matrices $S = \left(\sigma_x, \sigma_y, \sigma_z\right)$,

$$\frac{t^2}{U} \sum_{\langle i,j \rangle,\sigma} \hat{P}_S \left[c^\dagger_{i\bar{\sigma}} c^\dagger_{j\sigma} c_{i\bar{\sigma}} c_{j\sigma} - c^\dagger_{i\sigma} c^\dagger_{i\bar{\sigma}} c_{i\bar{\sigma}} c_{i\sigma} \right] \hat{P}_S = J \sum_{\langle i,j \rangle} \left[\hat{S}_i \cdot \hat{S}_j - \frac{\hat{n}_i \hat{n}_j}{4} \right], \tag{2.4}$$

where the exchange coupling is $J = 4t^2/U$. Exactly at half-filling, this is the only term that survives the projection and the Hubbard model in the strong coupling limit at half filling therefore reduces to an anti-ferromagnetic Heisenberg model for the spins on each lattice. More generally, restoring the projection operators, the strong coupling limit of the Hubbard model is the t-J-model,

$$\hat{H}_{t-J} = -t \sum_{\langle i,j \rangle} \hat{P}_S c_i^\dagger c_j \hat{P}_S + J \sum_{\langle i,j \rangle} \left[\hat{S}_i \cdot \hat{S}_j - \frac{\hat{n}_i \hat{n}_j}{4} \right]. \tag{2.5}$$

The t-J-model has been extensively studied in the context of high-temperature superconductivity, demonstrating both the possibility of superconducting and insulating orders [74, 77]. The superconducting phase however requires some further explanation that we turn to in the next section.

2.3 Superconductivity

A particularly striking phase of matter was discovered in 1911 by the experimental group of Kamerlingh Onnes during experiments on the electrical conductivity of metals at very low temperatures [78]. These experiments where

made possible by their earlier pioneering cooling techniques of gases, which also made them the first to liquidize helium. Thus, they surprisingly found that the electrical resistance of solid mercury abruptly vanished at a critical temperature of 4.2K, marking the phase transition to a superconducting phase, as it became known. Rather than being an anomaly of mercury, most metals have a superconducting transition [55]. However, it was not until 1957 with the work of Bardeen, Cooper, and Schrieffer (BCS) that superconductivity received a widely predictive microscopic explanation [53].

Underpinning the advance in theory, was the earlier observation that the superconducting critical temperature was dependent on the mass of the atoms, through isotope replacement [79, 80]. Coupling between the electronic degrees of freedom and the vibrations of the lattice was therefore concluded to be involved in the transition. The interaction between the electrons and the lattice vibrations, was captured in a Hamiltonian by Fröhlich, describing the absorption and emission of quantized lattice vibrations (phonons) by the electrons [81]. Notably, the electron-phonon coupling could, for a certain energy ranges close to the Fermi surface, result in an effective attractive interaction. Crucially, as Cooper showed, the electrons near the Fermi surface are unstable towards any arbitrary weak attractive interaction, leading to bound pairs of electrons and suggesting a mechanism for the phase transition [82]. By incorporating this insight to a simplified model together with a variational trial wave function, Bardeen, Cooper, and Schrieffer put forward a theory that accurately described the then known superconductors [53]. In particular, the theory made definite predictions of spectral and thermodynamical and temperature dependences [53].

The electronic pairing described by the BCS theory is a very general concept that captures the condensation of bound fermions into a symmetry breaking state in presence of an effective attractive interactions. As a description of the superconducting state, the theory is therefore more general than the particular origin of the attractive interaction. From this point of view, the central aspect of the BCS theory is that the superconducting phase develops a macroscopic phase coherence that breaks the global $U(1)$ gauge symmetry. The long range phase coherence is captured by a superconducting order parameter with a definite $U(1)$ phase, akin to a macroscopic wave function. Given the order parameter symmetry, the main macroscopic properties of superconductors are captured by an effective, Ginzburg-Landau, field theory. These diverse phenomena include flux quantization and the Josephson effects [83]. Additionally, the $U(1)$ gauge field minimally couples to the electromagnetic field and gives rise to the unusual and characteristic electromagnetic properties of superconductors. Notably, through the Higgs-Anderson mechanism, an applied magnetic field below a critical strength is entirely repelled from the interior of a superconductor with the creation of screening supercurrents in the Meissner effect [84–86].

With the experimental discovery of the high-temperature cuprate superconductors in 1986 by Bednorz and Müller [8], it became clear that superconductivity could also arise from mechanisms other then the electron-phonon coupling that could not account for the observed transitions, which is also true of the later iron-based [87] and heavy fermion superconductors [88]. While still highly debated, superconductivity in these materials are instead believed to arise from correlation effects and strong electron interactions. Conceptually, this raises the question how an effective attraction can arise from purely repulsive forces. Part of the answer, is that an effective interaction need only develop in one symmetry channel, e.g. a fixed angular moment channel as shown by Landau and Pitaevskii [62], for condensation to occur. To the point, Khon and Luttinger showed early on that the screened Coulomb interaction always produces an effective attractive interaction, at least in an isotropic system and for large enough odd angular momenta [89, 90]. The origin of the attraction is the over screening of the interactions, due to the sharp cut-off of the Fermi surface, which in real space produces long-ranged Friedel oscillations that are in part attractive at large distances [90, 91]. While the Kohn-Luttinger mechanism only produces very low critical temperatures in their proposal and by itself is unlikely to account for observed superconducting transitions [90], it conceptually shows that attraction can arise from purely repulsive interactions. It also shows how the superconducting pairing channel can intertwine with the breaking of additional symmetries, such as rotational symmetry. When accompanied by additional symmetry breaking, the superconducting state is called unconventional [92]. For instance, the superconducting order parameter of the cuprate superconductors has been shown to break the rotational symmetry of the lattice point group with a resulting d-wave symmetry [93]. While theoretical understanding of the superconducting glue is yet to be complet, viable pairing mechanisms based on electronic interactions may result from coupling to spin or charge-fluctuation and in the doped Mott insulator scenario [73–75, 94, 95].

As shown by Zhang and Rice, the copper oxide planes of the cuprate superconductors can be mapped to a strongly coupled single-band effective Hubbard model on the square lattice [96]. The t-J limit therefore suggest an insulating anti-ferromagnetic state at half-filling. But as pointed out by Anderson [97], there is an alternative variational ground state of the Heisenberg model consisting of a superposition of all configurations where singlet pairs of electrons occupy the bonds and that is favored by quantum fluctuations in low dimensions and for small spins. This singlet configuration is reminiscent of the resonating valence bonds (RVB) used by Pauling in relationship to aromatic molecules and the fluctuating single and double bonds of a benzene rings [97, 98], and the configuration is therefore called the RVB state. Strikingly, Anderson showed that doping the RVB state naturally gives rise to superconductivity [99, 100]. In fact, the RVB state is identical to the BCS wave function with any double occupancies projected out, the so called Gutzwiller projection, for fixed par-

ticle number [100]. While the argument is variational and does not prove a superconducting ground state, superconductivity from an RVB state is corroborated by variational Monte Carlo with a d-wave superconducting state as a likely ground state of the t-J model [101]. The RVB state is therefore a highly competitive state, thereby presenting a viable mechanism fro superconducting correlations from repulsive interactions.

In practice, the Gutzwiller projection found in the t-J model that prohibits double occupancy, is difficult to treat. Methods of enforcing the no-double-occupancy conduction have been developed, including the slave-boson method where auxiliary-boson fields are introduced to remove the double occupancies [99, 102]. Equivalently, in the Gutzwiller approximation, the expectation values in the projected subspace are approximated by a renormalization of the expectation values with respect to the full Hilbert space using filling dependent statistical weighting factors, $\langle \hat{P}_S \hat{O} \hat{P}_S \rangle \approx g_O \langle \hat{O} \rangle$ [74, 102–107]. As a consequence the t-J model in the projected Hilbert space can be replaced by a renormalized Hamiltonian $H_{\text{eff}} = -g_t t \sum_{\langle ij \rangle \sigma} c^\dagger_{i\sigma} c_{i\sigma} + g_J J \sum_{\langle i,j \rangle} \left[\hat{S}_i \cdot \hat{S}_j - \frac{\hat{n}_i \hat{n}_j}{4} \right]$, in the Gutzwiller approximation scheme. In many ways returning to Pauling's treatment of organic molecules [108], an effective t-J model has also been proposed as a model Hamiltonian of graphene, capable of driving a superconducting transition [32].

2.4 Susceptibilities and Instabilities

The t-J model illustrates how interactions in a material can favor a particular symmetry breaking ground state, such as an anti-ferromagnetic or superconducting order. Whether ordering is energetically favorable, depends on the interplay between both the interactions and the properties of the electronic system. From a physical point of view, the quasiparticles become correlated in the presences of interactions and develop a collective response to an external perturbation but also to any intrinsic fluctuation that arises. Through such a collective response, the susceptibility in the thermodynamic limit may diverge, causing an instability and an order transition. Importantly, in fermionic systems, it is the quasiparticles near the Fermi surface that have the greatest susceptibility and therefore contribute the most to any given response, all else being equal. This feature is due to the low excitation energy of the states near the Fermi energy as well as the availability of both occupied and unoccupied states necessary for scattering. Generally therefore, a large number of quasiparticles near the Fermi energy will result in a larger response and a system that is more prone to ordering.

As an example, consider the case of magnetic ordering arising from the competition between the kinetic energy and Coulomb exchange interaction I, then the ordering occurs at a finite temperature if Stoner's criterion, $I\rho(\epsilon_F) > 1$

is satisfied, where $\rho(\epsilon_F)$ is the density of states (DOS) at the Fermi energy. When the criterion is satisfied, a ferromagnetic ordering is achieved by aligning the spins at an increased kinetic energy cost [109, 110]. Consequently, either a strong Coulomb interaction or a large DOS gives rise to spontaneous ferromagnetism. Qualitatively, the criterion explains why iron and nickel are ferromagnetic and while copper is not [55]. While magnetic ordering involves the spontaneous breaking of spin rotational symmetry, a similar interplay between interactions and DOS also holds for other symmetry breaking orders, including spin-density-waves, charge-density-waves, and superconductivity. Thus, as suggested by Stoner's criterion and the quasiparticle susceptibilities, one way of finding quantum systems with high critical temperatures and robust ordering is to look for electronic system with a large DOS. In this respect, the two recent discoveries of two-dimensional materials with graphene and gapless topological materials have demonstrated that the topology of the electronic structure is able to produces both robust and large, or even singular DOS peaks. Given the central role of topology to these findings, we review its development within condensed matter physics in the next section.

2.5 Topological Phases of Matter

The late 20th century brought about several important examples of the application of topology to condensed matter physics. A hallmark was the discovery of the quantum Hall effect in two-dimensional electron gases at high magnetic fields which was revealed to be a topological state characterized by a quantized Hall conductance. Computing the conductance from the Kubo conductivity formula showed that the Hall conductivity was related to a topological invariant, the first Chern number, known as the Thouless-Kohmoto-Nightingale-Nijs (TKNN) invariant [111–114]. The discovery demonstrated the important and dramatic role that topology can have in condensed matter systems.

The prediction and experimental discovery of the topological insulators in the early 21th century brought about an unprecedented development with the classification, prediction, and discovery of many topological materials [23, 24, 115]. In particular, the time-reversal invariant gapped topological quantum spin Hall phase demonstrated the existence of additional topological phases with gapless edge states in materials with strong spin-orbit coupling [115–117], which were shortly observed thereafter in mercury telluride quantum wells [115, 118]. The quantum spin Hall phase was then generalized to three-dimensional topological insulators [119, 120] and observed in bismuth-antimony compounds [121]. In both two and three dimensions these materials are time-reversal invariant band insulators that cannot be transformed into a trivial state without closing the band gap, and by the bulk-boundary correspondence these materials host gapless Dirac fermion metallic edge states [23, 24].

The general concepts underpinning the topological phases of matter, of course stem from topology, a branch of mathematics concerned with the study and classification of topological spaces [122]. In these spaces there is a notion of locality, or what it means for points to be close by to each other. A continuous map is one that preserves the topological structure, which means that points that are close remain close to each other in the image of the map. Two topological spaces can be regarded as topological equivalent, if there is an invertible continuous map between them. Since this definition is manifestly an equivalence relationship, it partitions all the topological spaces into equivalence classes of topologically identical spaces. A natural question in topology is therefore which surfaces in a given dimension can be continuously deformed into one and another, where for example the sphere in two dimensions cannot be transformed into the torus, since the hole of the tours cannot be removed during a continuous deformation. A standard technique in topology for classifying topological spaces is to define easy-to-compute objects that nonetheless are invariant under a continuous mapping. When such a topological invariant attains different values for two different topological spaces it shows that the two are inequivalent.

When applying topology to the study of condensed matter systems, a similar fundamental question can be asked; whether two systems can be adiabatically connected; that is, if the two Hamiltonians of the systems can be continuously connected to each other. Without further restrictions on the allowed transformations, the non-interacting Hamiltonians of condensed matter systems are not topologically distinct. Thus, to achieve a more detailed classification, the set of allowed transformations needs to be further restricted by taking symmetry in to account. That is by only allowing the subset of continuous transformations that also preserve a set of symmetries. The restriction necessary leads to a finer topological distinction between systems.

If two systems belong to different topological classes, then it follows by definition that it is impossible to transition smoothly from one to the other without a discontinuous and abrupt change in the electronic properties. It therefore follows even from these general considerations that the surfaces and interfaces of topological matter will have special properties. This is the so called bulk-boundary correspondence of topological matter; that the bulk of the material dictates distinctive features of the surfaces and interfaces [23, 24].

A complete classification of all non-interacting gapped fermionic systems with respect to the Altland and Zirnbauer symmetry classes [123] was completed shortly after the discovery of the topological insulators [124–126]. The ten Altland and Zirnbauer symmetry classes are obtained from the possible combinations of the non-local symmetries: time-reversal symmetry, particle-hole symmetry, and chiral symmetry. The classification gives the number of distinct topological phases of gapped Hamiltonians that exist within each symmetry class and dimension of space. Specifically, the classification gives the number of distinct topological phases that can not be adiabatically connected

while preserving the imposed symmetries. The number of topological phases depends in the spatial dimension and follows the Bott periodicity [124]. Within each spatial dimension there are five topologically non-trivial classes of insulators or superconductors [124–126]. These topological phases are characterized by topological invariants that are either an integer $\mathcal{Z}$ Chern number or a $\mathcal{Z}_2$ number. By the bulk-boundary correspondence these topological phases support either gapless Dirac or Majorana edge states. By imposing the conservation of additional symmetries, such as local crystal-lattice symmetries, additional topological classes can be distinguished [126–130].

2.5.1 Gapless Topological Matter

Besides the gapped topological phases of matter, recently there has also been a growing recognition of the gapless topological states of matter, such as the topological (semi-)metals and the nodal topological superconductors [26–29]. These states of matter are characterized by a non-trivial topology in momentum space and of the Fermi surface [26, 27], that are the analogues to the real-space topological defects such as magnetic skyrmions and hedgehogs, and superconducting vortices [131]. In these phases the non-trivial topology is identical with the stability of the Fermi surface (Fermi surfaces, Fermi points, or Fermi nodal lines) to perturbations [132, 133].

An example of a gapless topological state is given by the Weyl semimetals, possessing band structure Weyl nodes in momentum space [134–136]. The Weyl nodes are the momentum space analogs of the magnetic hedgehog and carry a topological charge or chirality. By the Nielsen and Ninomiya theorem [137] such nodes always come in pairs, but they can be separated in momentum space. Since the nodes can only be removed by merging two nodes of opposite chirality, they are very robust. By the bulk-boundary correspondence, the Weyl semimetals have topologically protected edge states, especially the projection of the bulk nodes on the surface momentum space are connected by one-dimensional Fermi arcs. Likewise, in the related Weyl superconductor the edge state are Majorana arcs [138, 139]. A Weyl semimetal, tantalum arsenide (TaAs), was predicted in [140, 141] and experimentally discovered [142].

The gapless topological phases and stable Fermi surfaces are likewise classified with respect to the ten symmetry classes of Altland and Zirnbauer [123]. Across the symmetry classes, there are five distinct topologically non-trivial classes for each Fermi surface dimension (e.g. line or point) with a codimension larger or equal to one in two-dimensional and three-dimensional materials. By the bulk-boundary correspondence, the gapless topological classes have zero-energy edge states. The edge states are either dispersionless or they have a linear dispersion. If they are dispersionless, then they either form two-dimensional flat bands that are flat over a finite region of momentum space or they form a one-dimensional zero energy arc. Since the dispersion inside a

zero energy loop is restricted by the fixed loop, these states are called drumhead states from their appearance in the band structure [143–145].

Some examples of known gapless topological states of matter include graphene, nodal d-wave superconductors, and rhombohedral graphite [26]. In the d-wave superconductors the topology of the nodal dispersion gives rise to flat bands on the $\{110\}$ edge, as shown in [27, 28, 146], and experimentally observed in spectroscopic measurements [147, 148]. Similarly the nodal Dirac cones of graphene causes the zigzag edges of graphene ribbons to have flat bands that connect the two Dirac points in momentum space and are localized to the edge [149], as shown by ab-initio calculations [150], tight-binding calculations [151], and observed in scanning tunneling microscope experiments [152–154]. In graphene, the topology is however dependent on the chiral sublattice symmetry, and therefore breaking this symmetry can open a gap [155].

3. Singular Density of States Scenarios

In BCS theory, regardless of the origin of the attractive interaction, a natural dimensionless coupling parameter is set by $\lambda = V\rho(\epsilon_F)$ which combines the DOS at Fermi energy $\rho(\epsilon_F)$ and the pairing interaction V. In the standard BCS theory of an isotropic metal, the superconducting critical temperature is given by $k_B T_c = 1.14\hbar\omega \exp(-1/V\rho(\epsilon_F))$, where T_D is the Debye phonon temperature and V the strength of the effective phonon mediated electronic attraction [53]. The expression assumes a metal with an approximately constant DOS near around the Fermi energy.

The relationship implies that a larger critical temperature for a larger DOS near the Fermi energy. Importantly, a departure from the constant DOS assumption has even more striking consequences for the superconducting order transition. One such departure is produced by non-interacting quasiparticles in any two dimensional periodic lattice that always have a logarithmic divergent van Hove singularity in the DOS, arising from saddle points in band structure [20]. As a consequence, the dependence of the standard BCS critical temperature on the coupling λ is replace by $\sqrt{\lambda}$, which for weakly coupled systems, results in an significant increase in the critical temperature [21]. This enhancement due to the divergent DOS, is know as the van Hove scenario [22], and seems to offer a direct way to increases critical temperatures of superconductors. Importantly, the guaranteed existence of van Hove singularities in periodic two dimensional materials is due to topology.

The discovery of topological phases of matter and their recent classification has further proved that topology can even produce completely dispersionless topologically protect states. In such a flat band scenarios, the critical temperature has been shown to be directly proportional to the coupling strength V, suggesting an even more striking enhancement over the van Hove scenario. But both the flat band and van Hove scenarios critically asks if a dispersionless spectrum is capable of supporting a transport phenomena like superconductivity. Recent results show that this is so, which is again made possible by non-trivial topology and geometry of the band structure [156, 157]. But first, in the next section, we review the van Hove scenario and its challenges.

3.1 van Hove Scenario

As pointed out by L. van Hove on the basis of the topological results of M. Morse [20, 158], the topology of a crystal lattice in two dimensions always leads to the

existence of saddle points in the electronic dispersion which is defined on the periodic reciprocal lattice. Further in two dimensions, the saddle points give rise logarithmic divergent peaks in the electronic DOS, known as van Hove singularities (VHS). As alluded to in Sec. 2.4, the divergent DOS causes an increased susceptibility to ordering instabilities [159–162].

The possibility of a VHS enhanced order, or the so called van Hove scenario [22], received a lot of attention after the discovery of the high-temperature superconductors [8], since both theoretical models and photoemission studies showed that the Fermi energy is close to a VHS in most of the high-Tc cuprates [22, 73]. In these materials the VHS appears because the cuprates have a layered crystal structure where the electrons are largely confined to the quasi-two-dimensional copper oxide CuO_2 planes. As shown by Zhang and Rice, the copper oxide planes can be mapped to a single-band effective Hubbard model on the square lattice, where the non-interacting part exhibit VHSs around half-filling [96].

The enhancement of the critical temperature in quasi-two-dimensional layered materials due to a logarithmic VHS near the Fermi energy was pointed out for a charge-density-wave order in Ref. [163] and for a superconducting transition in Ref. [21]. It was also shown that Cooper pairing is enhanced near a VHS [164], where for an attractive potential V, the Cooper binding energy was found to be $2\hbar\omega_D \exp(-\sqrt{2/V})$, which is a strong enhancement over the normal metal result of $2\hbar\omega_D \exp(-1/V)$ [82], especially for weaker interactions. Consistently, the change in the binding energy is also seen in the BCS theory when the VHS close to the Fermi energy is account for, in which case, $\rho(\epsilon) = n \ln(D/\epsilon)$, and the critical temperature was found to be $k_B T_c = 1.13D \exp(-1/\sqrt{\lambda})$, where D is the width of the VHS [165]. The enhancement is also seen for anisotropic pairing [166]. Treating the singular behavior of the VHS of the two-dimensional Hubbard model with scaling theory shows that a antiferromagnetic phase transition occurs at half-filling with and that for small doping away from half-filling spin-fluctuations leads to the development of a d-wave superconducting phase transition [167].

While an increase in the DOS appears to be a straightforward way to increase the superconducting temperature, through an enhancement of the coupling parameter $\lambda = \rho(\epsilon_F)V$, it assumes that the DOS can be adjusted independently of the strength of the pairing interactions. In the case of phonon-driven superconductors V is largely determined by the lattice, suggesting a weak dependence on the DOS or the band width. When accounting for the present of the Coulomb repulsion in addition to the phonon-coupling, the overall coupling parameter λ is reduced [168]. Even when accounting for the Coulomb repulsion in the van Hove scenario, an enhancement is seen for phonon-driven superconductors [169], but since the reduction in the coupling is larger for narrow bands the enhancement is reduced.

3.2 Flat Band Scenario

The VHS seen in two dimensions arises from a locally flat saddle point in the band structure, which raises the question if even more pronounced singularities are possible. The well-known Landau levels that appear in an electron gas placed in a magnetic field [170] demonstrate that possibility of completely flat, yet non-trivial, bands that are dispersionless within a finite region of momentum space. Flat bands have also been known to occur in certain types of lattices, including the Lieb lattice [171] and the kagome lattice [172]. Recent developments in creating and manipulating optical lattices with cold atoms [173, 174] have allowed the creation, and the manipulation, of lattices with flat bands [175] including both the kagome lattice [176, 177], and Lieb lattice [178–180].

Another distinctive mechanism of producing flat bands was found in models of graphene nano-ribbons in 1996 [150, 151]. Specifically, the zigzag edge of graphene nano-ribbons exhibit special edge states that, depending on the width of the nano-ribbon, are almost flat and located near the Fermi energy at half filling. Due to the corresponding sharp peak in the DOS, the dispersionless edge states where also shown to readily order magnetically [151]. As long as the chiral symmetry in maintained, the edge states were shown to have topological origin with a corresponding topological number [27, 181]. Experimentally, the edge states were observed in scanning tunneling microscopy and spectroscopy [154, 182, 183]. The same general topological mechanism also produces flat bands states on the $\{110\}$ edge of two-dimensional d-wave superconductors [27, 146, 147]. Ways of generalizing the flat bands of graphene nano-ribbons to other lattices have been proposed in [184]. The central ingredient is a bipartite lattice structure, and a general construction method for topological semimetals with flat band edge states has been given in [185]. For instance, both the diamond and the würtzite lattice structures can be shown to host, in the same way as graphene, flat topological surface bands [186, 187]. Similarly, a class of two-dimensional tight-binding models have been shown to host topological flat bands [188]. Periodic strain of materials with a Dirac spectrum have also been shown to produce flat bands [189], including graphene [189, 190] and of the surface topological Dirac spectrum of topological crystalline insulators [191]. Similarly, the surface Dirac spectrum of topological insulators have been shown to become flat in an applied Zeeman field [192] that are large enough to be seen at room temperature in experiments [193].

The singular DOS and the associated quenched kinetic energy in flat bands amplify the effects of many-body phenomena and increases the susceptibility towards exotic correlated phases of matter, including ferromagnetism [171, 194], Wigner crystallization [195], and superconductivity [30, 31, 196]. For instance, the topologically protected flat bands on the zigzag edge of graphene nano-ribbons have been shown to develop a robust magnetic order in ab-initio calculations [197, 198], mean-field models [151, 199, 200], and quantum Monte

Carlo calculations [201, 202]. Consistent with this, recent experiments also show a room temperature magnetic ordering on the zigzag edge of graphene nano-ribbons [183].

With respect to superconductivity, it was recently shown that the presence of a flat band modifies the BCS transition temperature result so that the transition temperature T_c is proportional to the pairing interaction strength V and the d-dimensional volume of the flat band Ω_{FB}, as $T_C \propto \Omega_{FB}V$, instead of the exponential suppression, $T_c \propto \exp(-1/\rho(\epsilon_F)V)$, found for conventional pairing in normal metals [30, 31, 203, 204]. That is, for the same strength of the pairing interactions, the transition temperature is much larger in the presence of a flat band, especially for weak interactions. Thus, flat bands open up for realizing exotic phases of high-temperature superconductivity. Where a candidate system for flat band superconductivity is the topological semi-metal rhombohedral graphite [30, 31].

3.3 Superfluid weight

As we have seen in the previous two sections, the superconducting critical temperatures near a singular DOS are enhanced, even a taking on a linear dependence on the coupling strength in the case of flat band. While the critical temperature signals the development of a finite order parameter of bound Cooper pairs, the criteria for a true superconducting state is instead that the system has a finite superfluid weight [205]. The reason is that the superfluid weight relates directly to the ability of the material to carry a dissipationless current and to the Meissner effect [156]. Given that the Fermi velocity vanishes at van Hove singularities and for flat bands, a crucial question is therefore if such flat dispersions are compatible with a finite superfluid weight. In fact, for a single-band normal metal the superfluid weight is proportional to the Fermi velocity, which therefore vanishes for a flat dispersion, and therefore seems to suggest the incompatibility of superconductivity with flat dispersions [156].

A very significant result was therefore provided when it was shown that a conventional superconducting state in the flat band surface of ABC-graphite has a finite superfluid weight [206]. The result was generalized in Refs. [156, 207, 208], where it was shown that in addition to the conventional dispersion dependent contribution to the superfluid weight there is in multiband superconductor also the possibility of a geometric contribution to the superfluid weight. The geometric contribution to the superfluid weight can in contrast be finite even for a flat band dispersion. In fact, as shown in Refs. [156], the geometric contributions are bounded below by the Chern number, representing the total integrated Berry curvature of the quantum metric. The geometric contribution is therefore non-zero for topologically nontrivial bands with a finite Chern number.

A true superconducting state is therefore possible even in electronic band with a flat dispersion, as long as the geometric contribution are finite. Generally, the superfluid weight is related to the energy cost of a phase gradient in the superconducting order parameter and therefore also to the stability of the superconducting phase. In particular, for a uniform phase twist $\Delta(\mathbf{r}) = |\Delta|e^{2i\mathbf{q}\cdot\mathbf{r}}$ the superfluid weight tensor is directly related to the curvature of the free energy F [156],

$$[D_{\mathrm{s}}]_{\mathrm{i,j}} = \frac{1}{V\hbar^2}\frac{\partial^2 F}{\partial q_{\mathrm{i}}\partial q_{\mathrm{j}}}\bigg|_{\mu,\Delta,\mathbf{q}=0}. \tag{3.1}$$

Fluctuations generally prohibits true long-range orders in systems with low dimensionality [18, 209]. In two-dimensional systems however, there is the possibility of developing a superconducting state with a quasi-long-range order via a Berezinskii-Kosterlitz-Thouless (BKT) phase transition of bound vortex pairs [210–212]. The superfluid weight, as it relates to the phase stiffness, is directly related to the superconducting BKT transition temperature as $k_B T_{\mathrm{BKT}} = \frac{\pi}{8}\sqrt{\det\left[D^s\left(T_{\mathrm{BKT}}\right)\right]}$ [212, 213], which has been shown to give finite transition temperatures in systems with flat dispersions, including strained and twisted bilayer graphene [214–217], partly due to finite geometric contributions to the superfluid weight. In conclusion, the recently recognized possibility of having geometric contributions to the superfluid weight in multiband systems also makes it possible to realize a true superconducting state that does not depend on a finite band dispersion, even in two-dimensions.

3.4 Graphene

First isolated in 2004 [13–15], graphene is a two-dimensional material of carbon atoms with a hexagonal honeycomb lattice [16]. The electronic structure of pristine graphene can accurately be described by a tight-binding model among states corresponding to the out-of-plane p_z orbitals on each carbon atom,

$$H = -t\sum_{\langle i,j\rangle,\sigma} a^\dagger_{i\sigma} b_{j\sigma} + \mathrm{H.c.},$$

where $t \approx 3\mathrm{eV}$ is the hopping amplitude between nearest-neighbors, the operators $a^\dagger_{il\sigma}$ ($b^\dagger_{il\sigma}$) creates a quasi-particle in the orbital on the A (B) sublattice, in unit cell i, with spin σ. In this model the electronic structure is dominated by two features: at a doping of the size of the hopping parameter $\mu = \pm t$, the DOS has a logarithmically divergent van Hove singularity. At the undoped level, however, the dispersion is linear around the two high symmetry points K and K' in momentum space. Around these points the energy bands form two Dirac cones with a Fermi velocity v_F, and the density of states is linearly vanishing. Thus, a low energy effective theory of graphene takes the form of massless chiral Dirac fermions. This and the accompanying linear dispersion

have important implications for the electronic properties of graphene [14, 16, 17].

3.4.1 Interactions and Instabilities in Graphene

The vanishing DOS of the Dirac cones at the undoped level suppresses all phase instabilities of short-range interactions [218]. The effects of interactions are therefore mainly to renormalize the quasi-particle dispersion [219], and a critical coupling is needed to achieve a phase instability for a magnetic semimetal-insulator transition [220–224], and superconductivity [33, 34, 225, 226]. Mean-field or random phase approximation calculations on the Hubbard model give a critical Hubbard $U/t = 2.23$ for the semimetal-insulator transition [220], and quantum Monte Carlo, large-N limit, and Dynamical mean-field theory calculations all increase this estimate by about a factor of two [220, 222, 223]. Ab-initio estimates of the Coulomb interaction parameters ($U/t \sim 3$) nonetheless show that they are close to the critical coupling [227]. The vanishing of the DOS does however also lead to a reduced screening of the Coulomb interactions, and nonlocal Coulomb terms are therefore important, but can readily be modified by choice of substrate [34, 227–229]. Away from half-filling graphene acquires a finite DOS and the situation, therefore, changes drastically and graphene show instabilities towards superconducting [32, 33, 35, 225, 226, 230–233], charge-density-wave, and spin-density-wave orders [33, 34, 225, 234].

Because of the sixfold symmetry of the honeycomb lattice, superconducting orders with d-wave symmetry are automatically two-fold degenerate. This leads to a breaking of time-reversal symmetry and a very exotic unconventional superconducting chiral $d_{x^2-y^2} \pm \mathrm{i} d_{xy}$-wave state below the transition temperature [32–35]. This chiral state is fully gapped and topological, and therefore it supports edge modes at interfaces. Notably, it has been shown to emerge from repulsive short-ranged electron-electron interactions at all finite doping levels both at the mean-field level [33, 234], in quantum Monte Carlo simulations [230] [231], and in renormalization group calculations for weak repulsive interactions [35]. A mechanism by which a superconducting transition can occur from repulsive electronic interactions is the Kohn-Luttinger mechanism [89], which has also been explored for graphene [235, 236]. While plausible close to the half-filling and for weak couplings, the Kohn-Luttinger mechanism has been shown to be inadequate close to the VHS where the critical temperatures are enhanced above the estimates of this mechanism [237].

The DOS increases monotonically from half filling to a 1/4-doping where it has a logarithmic van Hove divergence, as shown by both theory and recent experiments on highly doped graphene achieved through both chemical doping and electrolytic gating [238, 239], or from electrostatically doped multilayer graphene [240]. The divergent DOS significantly enhances the instability to-

wards many different electronically ordered states such as spin-density-wave, charge-density-waves, and pairing instabilities [232, 237, 241–244]. At the van Hove doping the Fermi surface is a perfect hexagon with three different nesting vectors which favors the formation of a spin-density-wave. In particular a uniaxial spin density has been identified [245]. Renormalization group calculations of the susceptibilities of the instabilities, nonetheless indicate a close competition between the two most relevant instabilities a spin-density-wave and the chiral d+id-wave order at the van Hove doping [35], but where a d+id-wave order is dominant away from the van Hove doping [34, 232, 233]. A significant instability towards a f-wave pairing is however also possible depending on the range of the interactions [34, 232, 237].

3.5 Twisted Bilayer Graphene

The VHSs in graphene are however quite far away from half-filling. They are therefore very difficult to reach through by using standard techniques, including gating and chemical doping. An alternative is to look systems where the topologically dictated VHS are closer positioned in energy so as to be closer to half-filling and therefore far easier to reach with gating and doping techniques. Such low-energy Van Hove singularities are produced in twisted bilayer graphene and seen in spectroscopy experiments [36–38]. By adjusting the twist angle, the Van Hove singularities can be brought arbitrarily close to the charge natural point. In particular, the electronic structure of TBG exhibits magical angles where the Fermi velocity completely vanishes resulting in a flat band dispersion [246–248]. Recent highly impactful experimental results on TBG have found a rich phase diagram of competing phases, including correlated insulators and superconductivity [39–42], with intriguing similarities to the high-temperature superconductors [74, 75]. While the superconducting critical temperatures experimentally observed in TBG are relatively small in absolute terms, around a few Kelvin, when compared to the very small total carrier density of the involved states the observed critical temperatures are large [40], suggesting a strong-coupling. Together with the high experimental control achieved by gating, applied pressure, and tuning of the twist angle [41, 249–251], TBG has become hot test bed of superconductivity both theoretically and experimentally.

3.6 ABC graphite

Graphite is made from stacked layers of graphene [252]. The layers can however be stacked in multiple ways. The energetically relevant positions have one sublattice placed above the center of the hexagon with the other sublattice place above one of the sublattices of the previous layer. Together with the

direct placement there are three positions for the graphene layers, referred to as A, B, and C. Graphite commonly has a repeating (AB) sequence (Bernal stacking), but it can, as shown by experiments, also have a repeating (ABC) sequence which makes rhombohedral graphite [253–256].

In rhombohedral graphite, the electronic dispersion on a surface perpendicular to the stacking direction have been shown to have a power-law dependence on the $\epsilon(k) \propto |k|^N$ number of layers with N layers [257]. Thus, in the limit of a large number of layers, the surface dispersion becomes flat over a finite region. The interlayer hybridization in ABC-graphite morphs the Dirac cones of graphene into Fermi spirals in momentum space that carry a non-trivial topological invariant [258]. Because of the non-trivial topological structure of the Fermi spiral, a zero-energy dispersionless surface band is formed inside of the projection of the spiral onto the surface Brillouin zone. Thus, on the surface, the flat band gives rise to a large DOS peak at the zero-energy that are seen in both scanning tunneling spectroscopy and angle-resolved photoemission spectroscopy experiments [255]. Moreover, because of the topological protection the surface flat bands are robust to disorder [26] and they appear at interfaces with topologically trivial materials, as demonstrated by ab-initio calculations [259]. Thus, an interesting consequence of the topology is the appearance of flat bands at interfaces between a ABC-stacked and a AB-stacked sequence in a graphite sample [259, 260]. Because of the large DOS at these interfaces, even a weak pairing interaction would, as noted above, trigger a high-temperature superconducting transition at these interfaces. This has been shown by large scale tight-binding Bogoliubov–de Gennes calculations that show that the superconducting pairing is enhanced at ABC-AB interfaces, which through the proximity effect can support high-temperature superconductivity throughout the bulk [261]. Such a mechanism has also been invoked to explained experimental signatures of a superconducting transition above room temperature in natural graphite crystals [262, 263]. Along with the enhanced superconducting transition temperature [31], the surface flat bands of ABC-stacked graphite can also readily order to a strong ferrimagnetic state, as shown by ab-initio calculations [264–267], and by mean-field analysis [265]. Thus, as with in the VHS of graphene, the singular DOS makes for a fierce order competition close to the flat band.

4. Mean-field theory

The Hamiltonian of a non-interacting system is quadratic and therefore all the information of the system can be attained by diagonalization of the Hamiltonian matrix. In contrast, the Hamiltonian of an interacting system has at least one term that involve two or more particles and can therefore not be solved by direct diagonalization due to electronic correlations. Closed solutions of interacting problems are therefore, in general, hard to come by, and it is often necessary to proceed by approximations. The mean-field approximation technique replaces the interacting problem with a non-interacting problem, where the particles interact with a static potential that represents the average distribution of all the other particles.

To motivate the mean-field approximation method, we note that a single particle operator, $c_i^\dagger c_j$, can be expanded around its static expectation value, $c_i^\dagger c_j = (c_i^\dagger c_j - \langle c_i^\dagger c_j\rangle) + \langle c_i^\dagger c_j\rangle$. Thus, expanding the operators in a general two-body interaction term, $V_{ijkl}c_i^\dagger c_j^\dagger c_k c_l$, around the static values,

$$\sum_{ijkl} V_{ijkl}c_i^\dagger c_j^\dagger c_k c_l = \sum_{ijkl} 2n_{ij}c_i^\dagger c_j + \text{H.c.} - V_{ijkl}\langle c_j^\dagger c_k\rangle\langle c_i^\dagger c_l\rangle + V_{ijkl}[c_j^\dagger c_k - \langle c_j^\dagger c_k\rangle][c_i^\dagger c_l - \langle c_i^\dagger c_l\rangle], \tag{4.1}$$

where we have used the fermionic symmetry of the interaction $V_{ijkl} = -V_{jikl} = -V_{ijlk}$. The first term corresponds to a single particle interacting with the expectation value of the other particles through the mean-field potential, $n_{ij} = \sum_{jk} V_{i\alpha\beta j}\langle c_\alpha^\dagger c_\beta\rangle$. The second term is a constant energy shift from the interactions of the static distribution. The last term represents an interaction between the fluctuations away from the static averages. Assuming that these deviations are small, the last term can be omitted, and the result is a quadratic mean-field Hamiltonian H_{MF}.

The expectation values that enter the mean-field Hamiltonian H_{MF} can be determined by two equivalent methods; the equivalence between these two methods is shown below. In the first method, we ask that the expected values evaluated with respect to the equilibrium distribution of H_{MF} be self-consistent. In the second method we regard the expectation values as variational parameters with the objective of minimizing the free energy. The stationary condition arrived at by the second method is the self-consistent condition, which is the basis of the equivalence between these two methods.

Despite the relative simplicity of the mean-field approximation, a great virtue is that the method is able to describe the symmetry breaking process of phase

transitions. Analogous to the Landau theory, at low temperatures the mean-fields that minimize the free energy have the possibility of reducing the symmetry of the system and establishing a new phase. Conveniently, the mean-fields themselves form the order parameters that also corresponds to expectation values of the system, making it easy to identify the phase. By solving for the first onset of non-zero mean-field order parameters, it is also possible within mean-field theory to solve for the critical temperatures of the phase transitions.

As is often the case with phase transitions, the free energy landscape may develop more than one minima, or equivalently have several critical temperatures for different competing orders within the system. Mean-field theory makes it possible to compare the critical temperatures and the free energies of the competing orders, and the theory is therefore also able to make predictions on when certain orders are favored. However, to capture all the interactions and all possible conventional symmetry breaking orders, the motivating expansion around the static expectation values has to be generalized so as to include all possible mean-fields. In particular, to capture superconducting phases of matter terms with anomalous expectation values $\langle c_i^\dagger c_j^\dagger \rangle$, breaking the gauge invariance, has to be included. To attain the suitable generalization, we show in the next section how the fully generalized mean-field approximation is obtained as a variational principle.

4.1 Generalized Mean-Field Theory

To proceed we will make use of the Bogoliubov-Peierls variational theorem of the free energy [268, 269], which states that for any Hamiltonian $H = H_0 + V$,

$$F \leq F_0 + \langle V \rangle_0 \tag{4.2}$$

where

$$F = -\frac{1}{\beta} \ln [Z] = -\frac{1}{\beta} \ln \left[\mathrm{Tr} \left(e^{-\beta H} \right) \right]. \tag{4.3}$$

is the free energy of the full Hamiltonian and F_0 is the free energy of the unperturbed Hamiltonian H_0. The expectation value $\langle V \rangle_0 = \mathrm{Tr}\,(\rho_0 V)$ is with respect to the equilibrium distribution $\rho_0 = e^{-\beta H_0}/Z_0$ of the unperturbed Hamiltonian H_0. This theorem can easy be proven in the case that H_0 and V commute. For if we let $H = H_0 + \lambda V$, where λ is a free parameter and if both H_0 and V commute, then

$$\frac{dF}{d\lambda} = \langle V \rangle \quad \text{and} \quad \frac{d^2F}{d\lambda^2} = -\beta \langle (V - \langle V \rangle)^2 \rangle. \tag{4.4}$$

Because $\langle (V - \langle V \rangle)^2 \rangle \geq 0$, we immediately have that $\frac{d^2F}{d\lambda^2} \leq 0$ for all λ. Thus, the free energy is a concave function of λ, and therefore,

$$F(\lambda) \leq F(0) + \lambda \left. \frac{dF}{d\lambda} \right|_{\lambda=0}, \tag{4.5}$$

and by identifying the terms and setting $\lambda = 1$, we arrive at the Bogoliubov-Peierls variational theorem, $F \leq F_0 + \langle V \rangle_0$. The proof for the general case when H_0 and V do not commute is given in the footnote on page 48 or in [268]. If we regard this inequality as a variational statement for the density matrix ρ_0, then the free energy of the Hamiltonian H is minimized for the equilibrium distribution of H. But more importantly, the generalized mean-field equation will be derived by restricting the variational space to all density matrices of equilibrium distributions of quadratic Hamiltonians. The importance of restricting the variational space to the space of quadratic Hamiltonians is that their spectrum can be found by diagonalization and that the expectation values of an arbitrary number of particle operators can be evaluated using Wick's theorem [270]. This variational procedure results in the complete Hartree-Fock-Bogoliubov decomposition of the interactions, which through the variational definition is the best possible quadratic approximation to the full interacting system $H = H_0 + V$ [271]. Moreover, this procedure was used in [272] to derive the generalized thermal Hartree-Fock equation without the Bogoliubov terms. Here we offer a simplified derivation of this result by deriving the stationary condition for a quadratic Hamiltonian, for a complete solution we refer to [271]. Thus, let $H = \sum_{ij} T_{ij} c_i^\dagger c_j + \text{H.c.} + \sum_{ijkl} V_{ijkl} c_i^\dagger c_j^\dagger c_k c_l$ be the full Hamiltonian, and let $H_0 = \sum_{ij} h_{ij} c_i^\dagger c_j + \Delta_{ij} c_i^\dagger c_j^\dagger + \text{H.c.}$ be a completely general quadratic Hamiltonian that includes anomalous particle non-conserving expectation values through the Δ_{ij} terms. From the Bogoliubov-Peierls variational theorem, $F \leq F_0 + \langle H - H_0 \rangle_0$, where we now can evaluate $\langle H - H_0 \rangle_0$ using Wick's theorem,

$$\langle c_i^\dagger c_j^\dagger c_k c_l \rangle_0 = \langle c_i^\dagger c_j^\dagger \rangle_0 \langle c_k c_l \rangle_0 + \langle c_j^\dagger c_k \rangle_0 \langle c_i^\dagger c_l \rangle_0 - \langle c_i^\dagger c_k \rangle_0 \langle c_j^\dagger c_l \rangle_0. \tag{4.6}$$

Thus from the fermionic symmetry of V_{ijkl},

$$\begin{aligned} \langle H - H_0 \rangle_0 = \sum_{ij} \left[T_{ij} + 2 \sum_{\alpha\beta} V_{i\alpha\beta j} \langle c_\alpha^\dagger c_\beta \rangle_0 - h_{ij} \right] \langle c_i^\dagger c_j \rangle_0 \\ + \sum_{ijkl} V_{ijkl} \langle c_i^\dagger c_j^\dagger \rangle_0 \langle c_k c_l \rangle_0 - \Delta_{ij} \langle c_i^\dagger c_j^\dagger \rangle_0 - \Delta_{ij}^* \langle c_i^\dagger c_j^\dagger \rangle_0 \end{aligned} \tag{4.7}$$

Thus the stationary condition is,

$$\frac{d}{dX_{rs}} \left(F_0 + \langle H - H_0 \rangle_0 \right) = 0, \tag{4.8}$$

where X_{rs} is one of the parameters of H_0, i.e. h_{rs} or Δ_{rs}. After evaluating the derivatives, the stationary condition becomes

$$\sum_{ij}\left[T_{ij}+4\sum_{\alpha\beta}V_{i\alpha\beta j}\langle c_\alpha^\dagger c_\beta\rangle_0-h_{ij}\right]\frac{d\langle c_i^\dagger c_j\rangle_0}{dX_{rs}}$$
$$+\sum_{ij}\left[\sum_{kl}V_{ijkl}\langle c_k c_l\rangle_0-\Delta_{ij}\right]\frac{d\langle c_i^\dagger c_j^\dagger\rangle_0}{dX_{rs}}$$
$$+\sum_{kl}\left[\sum_{ij}V_{ijkl}^*\langle c_i^\dagger c_j^\dagger\rangle_0-\Delta_{ij}^*\right]\frac{d\langle c_k c_l\rangle_0}{dX_{rs}}=0. \tag{4.9}$$

A sufficient condition for a stationary variation is that all the coefficients independently vanish, which is true if the the matrix elements of the variational quadratic Hamiltonian H_0 satisfies,

$$h_{ij}=T_{ij}+4\sum_{\alpha\beta}V_{i\alpha\beta j}\langle c_\alpha^\dagger c_\beta\rangle_0=T_{ij}+4n_{ij} \tag{4.10}$$

$$\Delta_{ij}=\sum_{kl}V_{ijkl}\langle c_k c_l\rangle_0 \tag{4.11}$$

with n_{ij} and Δ_{ij} are resulting mean-fields. Since the expectation values in the above expressions are with respect to the equilibrium distribution of H_0 they depend on the matrix elements h_{ij} and Δ_{ij}. These equations therefore represent a set of non-linear equations that have to be solved self-consistently. Thus, to any interacting Hamiltonian H, we have the associated mean-field model H_0 that depends on unknown parameters n_{ij} and Δ_{ij},

$$H_0=\sum_{ij}\left(T_{ij}+n_{ij}\right)c_i^\dagger c_j+\Delta_{ij}c_i^\dagger c_j^\dagger+\text{H.c.}, \tag{4.12}$$

with the self-consistent free energy,

$$\begin{aligned}F_{MF}&=F_0+\langle H-H_0\rangle_0\\&=F_0-\sum_{ijkl}\left[2V_{ijkl}\langle c_i^\dagger c_l\rangle_0\langle c_j^\dagger c_k\rangle_0+V_{ijkl}\langle c_i^\dagger c_j^\dagger\rangle_0\langle c_k c_l\rangle_0\right],\end{aligned} \tag{4.13}$$

where F_{MF} is the minimum over all density matrices of a quadratic Hamiltonian.

The above demonstrates that the mean-field theory is the best possible quadratic approximation to the free energy of the interacting system. Since measurable quantities are calculated from the free energy (e.g. susceptibilities, particle densities, but also fluctuations through second order derivatives), this strongly indicates that the mean-field theory is a tractable method for calculating the properties of condensed matter systems.

5. Linear Response Theory

A possibility introduced by the mean-field parameters is that the self-consistent solutions need not have the same symmetry as the original Hamiltonian. This occurs through a process of spontaneous symmetry breaking as mentioned in Sec. 2. In this process, expectation values, that would be prohibited from developing a non-zero values on the basis of symmetry, can after a spontaneous symmetry breaking at some critical temperature acquire a none-zero value. Close to the critical temperature of a second-order phase transition the parameters of a symmetry breaking order are by definition vanishingly small. Thus, close to the critical temperature the formation of symmetry breaking orders can be treated using linear response theory, which we show in the next section.

5.1 Isothermal Linear Response

The thermal equilibrium distribution of a Hamiltonian H is $\rho = \mathrm{e}^{-\beta H}/Z$. The unnormalized distribution $\tilde{\rho} = \mathrm{e}^{-\beta H}$ therefore satisfies the Bloch equation $\partial_\beta \tilde{\rho} = -H\tilde{\rho}$, with the boundary condition $\lim_{\beta\to 0} \tilde{\rho}(\beta) = I$. Let the Hamiltonian H_0 be perturbed by an operator B, so that the full Hamiltonian is $H = H_0 + B$. If B is small, then the density matrix, ρ, of H, will be close to the unperturbed density matrix ρ_0. Therefore it should be possible to expand the matrix quotient $\tilde{\rho}_0^{-1}\tilde{\rho} = \mathrm{e}^{\beta H_0}\tilde{\rho}$ in powers of the perturbation B around the identify matrix. From the Block equation for $\tilde{\rho}$,

$$\partial_\beta \left(\mathrm{e}^{\beta H_0}\tilde{\rho}\right) = -\mathrm{e}^{-\beta H_0}(H - H_0)\tilde{\rho} = -\mathrm{e}^{-\beta H_0} B\tilde{\rho}. \tag{5.1}$$

Integration gives,

$$\begin{aligned}\tilde{\rho}(\beta) &= \tilde{\rho}_0(\beta)\left[1 - \int_0^\beta \tilde{\rho}_0^{-1}(\beta')B\tilde{\rho}(\beta')\mathrm{d}\beta'\right] \\ &\approx \tilde{\rho}_0(\beta)\left[1 - \int_0^\beta \tilde{\rho}_0^{-1}(\beta')B\tilde{\rho}_0(\beta')\mathrm{d}\beta'\right],\end{aligned} \tag{5.2}$$

where the last expression shows the first order expansion in the perturbation B. The redistribution due to the perturbation is therefore,

$$\delta\tilde{\rho} = -\tilde{\rho}_0(\beta)\int_0^\beta \tilde{\rho}_0^{-1}(\beta')B\tilde{\rho}_0(\beta')\mathrm{d}\beta'. \tag{5.3}$$

Because of the redistribution, the expectation values of observables will change. The change $\delta\langle A\rangle$ in the expectation value of an observable A is,

$$\begin{aligned}\delta\langle A\rangle &= \frac{\mathrm{Tr}\left([\tilde{\rho}_0(\beta)+\delta\tilde{\rho}]A\right)}{\mathrm{Tr}\left(\tilde{\rho}_0(\beta)+\delta\tilde{\rho}\right)} - \langle A\rangle_0 \\ &= -\int_0^\beta \langle\tilde{\rho}_0^{-1}(\beta')B\tilde{\rho}_0(\beta')A\rangle_0 \mathrm{d}\beta' + \beta\langle A\rangle_0\langle B\rangle_0, \end{aligned} \tag{5.4}$$

where the last term comes from the expansion of the normalization factor, and the cyclic property of the trace.

5.2 Time Dependent Linear Response

Because the time evolution operator, $U(t,t_0) = \mathrm{e}^{iH(t-t_0)}$, and the equilibrium non-normalized density matrix, $\exp(-\beta H)$, have an near identical form, there is a deep connection between the time evolution and the equilibrium statistics. Indeed, the response to a time-dependent perturbation follows a similar derivation to the isothermal perturbation [111].

By definition, the Hamiltonian is the infinitesimal time evolution operator, and the states of the system evolve according to $|n(t)\rangle = U(t,t_0)\,|n(t_0)\rangle$ where,

$$i\partial_t U(t,t_0) = HU(t,t_0)\,, \tag{5.5}$$

with the boundary condition $\lim_{t\to t_0}(t,t_0) = I$. For a time independent Hamiltonian the unitary evolution operator has the closed from $U(t,t_0) = \mathrm{e}^{-iH(t-t_0)}$.

If the system H_0, is subject to a time dependent perturbation $f(t)B$, so that the full Hamiltonian is $H = H_0 + f(t)B$, then if the perturbation is small the evolution operator will be close to the unperturbed evolution operator $\mathrm{e}^{-iH_0(t-t_0)}$. Thus, the matrix quotient satisfies,

$$i\partial_t\left(\mathrm{e}^{+iH_0(t-t_0)}U(t,t_0)\right) = \mathrm{e}^{+iH_0(t-t_0)}f(t)BU(t,t_0)\,. \tag{5.6}$$

Integrating the above equation and solving it to first order in the perturbation gives,

$$\begin{aligned}U(t,t_0) &= U_0(t,t_0)\left[1 - i\int_{t_0}^t U_0(t_0,t')\,f(t')BU_0(t',t_0)\,\mathrm{d}t'\right] \\ &= U_0(t,t_0)\left[1 - i\int_{t_0}^t f(t')B(t')\mathrm{d}t'\right]\end{aligned} \tag{5.7}$$

where $B(t') = U_0(t_0,t')\,BU_0(t',t_0)$ is expressed in the Heisenberg picture.

The time evolution changes the equilibrium distribution. The density matrix at a later time is,

$$\rho(t) = \sum_n p_n |n\rangle\langle n| = U\left(t_0, t\right) \rho(t_0) U\left(t, t_0\right), \tag{5.8}$$

which to first order is,

$$\begin{aligned}\rho(t) &= U\left(t_0, t\right) \rho(t_0) U\left(t, t_0\right) \\ &= U_0\left(t, t_0\right) \left[\rho(t_0) + i \int_{t_0}^{t} [\rho(t_0), f(t')B(t')]\mathrm{d}t'\right] U_0\left(t_0, t\right) + \mathcal{O}(B^2).\end{aligned} \tag{5.9}$$

This redistribution from the equilibrium distribution, implies that the expectation value of an operator A will change by an amount $\delta\langle A(t)\rangle$ with time according to,

$$\begin{aligned}\delta\langle A(t)\rangle &= \mathrm{Tr}\left(\rho(t)A\right) - \langle A\rangle_0 = i \int_{t_0}^{t} \mathrm{Tr}\left([\rho(t_0), f(t')B(t')]A(t)\right) \mathrm{d}t' \\ &= -\int_{t_0}^{t} i\langle[A(t), B(t')]\rangle_0 f(t')\mathrm{d}t' = \int_{t_0}^{t} \chi_{AB}(t-t')f(t')\mathrm{d}t',\end{aligned} \tag{5.10}$$

where in the last step $\chi_{AB}(\tau) = -i\theta(\tau)\langle i[A(\tau), B]\rangle_0$ is the susceptibility of A to B at a later time displacement τ. For a time invariant unperturbed system the frequency response is diagonal, $\delta\langle A(\omega)\rangle = \chi_{AB}(\omega)f(\omega)$.

5.3 Energy representation

To see the difference between the isothermal and the time-dependent response we write both responses in an eigenstates representation (Lehmann representation). In this representation the density matrix is diagonal, and the probability of an eigenstate with energy E_n is $p_n = \exp\left(-\beta E_n\right)/Z$, where E_n are the energies of the eigenstates of the unperturbed system H_0. Because of this, both the integral and the expectation value in the thermal response can be evaluated. Thus, with $\omega_{nm} = E_n - E_m$,

$$\langle\tilde{\rho}_0^{-1}(\beta')B\tilde{\rho}_0(\beta')A\rangle_0 = \int_0^{\beta} p_n \mathrm{e}^{\beta'\omega_{nm}} B_{nm}A_{mn}\mathrm{d}\beta', \tag{5.11}$$

where $A_{mn} = \langle m|A|n\rangle$ and $B_{nm} = \langle n|B|m\rangle$ are the operator matrix elements in the eigenvalue basis. After evaluating the integral, the response in A is,

$$\delta\langle A\rangle = \sum_{nm}\left(\frac{p_n - p_m}{\omega_{nm}} - p_n\beta\delta_{nm}\right) B_{nm}A_{mn} + \beta\langle A\rangle_0\langle B\rangle_0, \tag{5.12}$$

which shows that the response decays with the inverse of ω_{nm}. This form of the perturbation is also the starting point for the proof the Bogoliubov-Peierls inequality [1]

Similarly, the expectation value in the time-dependent response can also be evaluated in the Lehmann representation,

$$\langle [A(\tau), B] \rangle_0 = \sum_{nm} (p_n - p_m) \mathrm{e}^{i\omega_{nm}\tau} A_{nm} B_{mn}. \tag{5.13}$$

Therefore, the frequency response becomes,

$$\chi_{AB}(\omega) = -\sum_{nm} \frac{(p_n - p_m)}{\omega - \omega_{nm} + i\eta} A_{nm} B_{mn}. \tag{5.14}$$

In the adiabatic limit, $\omega \to 0$, this term becomes identical with the first term of the isothermal response [273]. Thus, if we denote the isothermal response of A to a perturbation B by χ^T_{AB}, then the difference between the isothermal response and the adiabatic response is,

$$\chi^T_{AB} - \lim_{\omega\to 0} \chi_{AB}(\omega) = -\beta \left(\sum_n B_{nn} A_{nn} - \langle A \rangle_0 \langle B \rangle_0 \right). \tag{5.15}$$

The two responses need therefore not be the same. This is because the time-evolution can have conserved quantities, as is evidenced by the commutator in the time-dependent response, whereas the isothermal has no such restrictions. If we however, consider the perturbation B to be the initial formation of a symmetry breaking order, then both $\langle B \rangle_0$ and B_{nn} are identically zero, and the two responses are identical. We conclude that, when considering the initial formation of a symmetry breaking order, we can think of the process both as an isothermal process and as an adiabatic evolution in time. Specifically, we will see that the condition for the development is that the response of the system can amplify an initial small formation of the symmetry breaking order.

[1] Starting from $H = H_0 + \lambda V$ and the free energy $F = -\ln(\mathrm{Tr}\, \mathrm{e}^{-\beta H})/\beta$, it holds true that $\partial_\lambda F = \langle V \rangle$ even when H_0 and V do not commute because of the cyclic property of the trace. The second derivative of the free energy is therefore given by $\partial^2_\lambda F = \delta \langle V \rangle_\lambda$. Using the Lehmann representation of the first order perturbation we have that $\partial^2_\lambda F = \sum_{nm} (p_n - p_m)|V_{nm}|^2/\omega_{nm} - \beta \sum_n p_n |V_{nn}|^2 + \beta \langle V \rangle^2_\lambda$. We also have that $0 \leq \sum_n p_n (V_{nn} - \langle V \rangle_\lambda)^2 = \sum_n p_n |V_{nn}|^2 - \langle V \rangle^2_\lambda$. Applying this inequality to the last two terms in previous expression for $\partial^2_\lambda F$, we have that $\partial^2_\lambda F \leq \sum_{nm} (p_n - p_m)|V_{nm}|^2/\omega_{nm} \leq 0$, since the quotient $(p_n - p_m)/\omega_{nm} = (p_n - p_m)/(E_n - E_m)$ is always negative because larger energies have smaller probabilities. Thus, even for the general case when H_0 and V do not commute we find that the free energy is a concave function for all λ and the proof of the Bogoliubov-Peierls inequality follows in the same ways as for the commuting case.

6. Mean-Field Critical Temperature

In this section we evaluate the self-consistency equations Eq. (7.1) of mean-field theory for symmetry breaking orders using the linear isothermal response of Eq. (5.4). The resulting equations give the critical temperatures for second-order phase transition of symmetry breaking orders. We start from a completely general translationally invariant Hamiltonian H with a quadratic part H_0 and a general two-body interaction term V in H_{int}:

$$\begin{aligned} H &= H_0 + H_{\text{int}} \\ &= \sum_{k\sigma\alpha} \xi_\alpha(k)\, c^\dagger_{k\sigma\alpha} c_{k\sigma\alpha} + \sum_{\substack{kpq \\ \alpha\beta\gamma\delta \\ 1234}} V^{1234}_{\alpha\beta\gamma\delta}(k,p,q)\, c^\dagger_{k1\alpha} c^\dagger_{p2\beta} c_{p+q3\gamma} c_{k-q4\delta}, \end{aligned} \tag{6.1}$$

where H_0 is assumed to be both spin and particle number conserving with energy bands $\xi_\alpha(k)$, where Greek indices are bands indices, numbers label spins, and k, p, and q label crystal momenta vectors. From section 4, the associated mean-field Hamiltonian is,

$$\begin{aligned} H_{\text{MF}} = &\sum_{kp\alpha\beta 12} \left[d_{\alpha\beta}(k,p)\cdot\chi\right]_{12} c^\dagger_{k1\alpha} c^\dagger_{p2\beta} + \text{H.c.} \\ &+ 4 \sum_{kq\alpha\delta 14} \left[g_{\alpha\delta}(k,q)\cdot\sigma\right]_{14} c^\dagger_{k1\alpha} c_{k-q4\delta}, \end{aligned} \tag{6.2}$$

with the mean-field parameters,

$$\begin{aligned} d^\mu_{\alpha\beta}(k,p) &= \frac{1}{2} \sum_{q\gamma\delta 1234} [\chi^\mu]^\dagger_{21} V^{1234}_{\alpha\beta\gamma\delta}(k,p,q) \left\langle c_{p+q3\gamma} c_{k-q4\delta}\right\rangle \\ g^\mu_{\alpha\delta}(k,q) &= \frac{1}{2} \sum_{p\beta\gamma 1234} [\sigma^\mu]_{14} V^{1234}_{\alpha\beta\gamma\delta}(k,p,q) \left\langle c^\dagger_{p2\beta} c_{p+q3\gamma}\right\rangle. \end{aligned} \tag{6.3}$$

Here, σ^μ are the Pauli matrices including the identity and $\chi^\mu = \sigma^\mu(i\sigma^y)$. $g_{\alpha\delta}(k,q)$ are the order parameters for the normal particle-hole (PH) channel, and $d_{\alpha\beta}(k,p)$ are the anomalous particle-particle (PP) order parameters. In this form, the first components of both d^μ and g^μ behave as scalars under spin rotations and the last three components transform as vectors.

Using the linear isothermal response Eq. (5.4) of the previous section, the linearized mean-field self-consistency equation of Eq. (7.1),

$$\begin{aligned} d^{\mu}_{\alpha\beta}(k,p) &= 4 \sum_{q\gamma\delta 1234} \beta V^{1234}_{\alpha\beta\gamma\delta}(k,p,q) \left[\chi^{\mu}\right]^{\dagger}_{12} \times \\ & W^{+}\Big(\beta\xi_{\delta}(k-q)\,, \beta\xi_{\gamma}(p+q)\Big) \left[d_{\delta\gamma}(k-q,p+q)\cdot\chi\right]_{43} \\ g^{\mu}_{\alpha\delta}(k,q) &= -8 \sum_{p\beta\gamma 1234} \beta V^{1234}_{\alpha\beta\gamma\delta}(k,p,q) \left[\sigma^{\mu}\right]_{41} \times \\ & W^{-}\Big(\beta\xi_{\gamma}(p+q)\,, \beta\xi_{\beta}(p)\Big) \left[g_{\gamma\beta}(p+q,q)\cdot\sigma\right]_{32}. \end{aligned} \tag{6.4}$$

If we gather the order parameters in vectors $D^{\pm}$ with $+(-)$ superscript for the PP(PH) channel, these self-consistency equations have a manifest linear form,

$$D^{\pm} = \beta \mathbb{V}^{\pm} \mathbb{W}^{\pm} D^{\pm}, \tag{6.5}$$

where the matrix $\mathbb{V}^{\pm}$ contains all interactions terms and $\mathbb{W}^{\pm}$ is a diagonal polarizability matrix and its matrix elements,

$$W^{\pm}(\beta\xi_1, \beta\xi_2) = \frac{\tanh\left(\frac{\beta\xi_1}{2}\right) \pm \tanh\left(\frac{\beta\xi_2}{2}\right)}{\beta(\xi_1 \pm \xi_2)/2}, \tag{6.6}$$

depends on both the temperature through $\beta = 1/T$ and the quasiparticle energies ξ_1 and ξ_2. The linear self-consistency equations have the same symmetry as H_0, and the two types of order parameters, g^{μ} and d^{μ}, do therefore not mix.

The matrices $\beta\mathbb{V}^{\pm}\mathbb{W}^{\pm}$ give the response of the order parameters to their own perturbation. The eigenvectors of these matrices correspond to stable orders that do not mix and they are therefore only rescaled in the response by their eigenvalues. An eigenvalue that is larger than 1 corresponds to an order that is self-amplifying. Such an order is therefore an instability of the system and therefore also a viable phase transition. An eigenvalue that is smaller than 1, on the other hand, corresponds to an unsustainable and decaying order. As the temperature is reduced, the response tends to increase in strength, as is evidenced by the explicit β-factor. If at some point the largest eigenvalue of the response matrix grows to 1, then the corresponding order is self-consistent and the first instability of the system. This order therefore appears through a phase transition at that critical temperature.

7. Microscopic Theory of Superconductivity

In the previous section, we derived the critical temperatures of conventional orders within the mean-field theory. Below the critical temperature, the mean-field of a symmetry breaking order takes on a finite value. The finite value also imply that the full non-linear self-consistency equations have to be solved for the mean-field. If the order is superconducting, then the mean-field couples to particle non-conserving terms in the Hamiltonian that scatter between particle and hole states. The eigenstates of the Hamiltonian with a superconducting order will therefore be a superposition of both particles and holes. The situation therefore requires some care, but can be generally treated within the Bogoliubov de Gennes (BdG) formalism [274].

To simplify the discussion, we do not consider all possible pair density waves, but focus instead on the more common case of pairing between opposite momenta. Otherwise the discussion is completely general. For this case, a general BCS pairing model Hamiltonian has the following form,

$$\hat{H} = \sum_{\substack{k\alpha\beta \\ \sigma\sigma'}} \xi_{\alpha\beta}^{\sigma\sigma'}(k)\, c_{k\sigma\alpha}^{\dagger} c_{k\sigma'\beta} + \sum_{\substack{kk' \\ \alpha\beta\gamma\delta \\ \sigma_1\sigma_2\sigma_3\sigma_4}} V_{\alpha\beta\gamma\delta}^{\sigma_1\sigma_2\sigma_3\sigma_4}\left(k,k'\right) c_{-k\sigma_1\alpha}^{\dagger} c_{k\sigma_2\beta}^{\dagger} c_{-k'\sigma_3\gamma} c_{k'\sigma_4\delta}. \tag{7.1}$$

The model describes the scattering of opposite momenta k quasiparticle pairs via the potential V among the possibly spin polarized orbital degrees of freedom with the energy dispersion $\xi_{\alpha\beta}^{\sigma\sigma'}(k)$, where α and β label orbitals. As such the model is a direct generalization of the original BCS Hamiltonian [53].

In the mean-field approximation for the pairing-channels, the resulting quadratic Hamiltonian (with a constant energy shift C)

$$\hat{H}_{\text{MF}} = \sum_{\substack{k\alpha\beta \\ \sigma\sigma'}} \xi_{\alpha\beta}^{\sigma\sigma'}(k)\, c_{k\sigma'}^{\dagger} c_{k\sigma'} + \sum_{k\alpha\beta\sigma\sigma'} \Delta_{\alpha\beta}^{\sigma\sigma'}(k)\, c_{-k\sigma_1\alpha}^{\dagger} c_{k\sigma_2\beta}^{\dagger} + C, \tag{7.2}$$

depends on the pair potentials defined by

$$\Delta_{\alpha\beta}^{\sigma\sigma'}(k) = \sum_{\substack{k'\gamma\delta \\ \sigma_3\sigma_4}} V_{\alpha\beta\gamma\delta}^{\sigma\sigma'\sigma_3\sigma_4}\left(k,k'\right) \left\langle c_{-k'\sigma_3\gamma} c_{k'\sigma_4\delta} \right\rangle. \tag{7.3}$$

The pair potentials are defined in terms of the anomalous particle non-conserving expectations values that break the gauge symmetry. To minimize the free energy of the mean-field model the pair-potential should be self-consistent,

meaning that both sides of Eq. (7.3) are equal when the expectation values are evaluated for the pair potentials on the left-hand side. Despite the finite anomalous expectation values, it is possible to diagonalize the mean-field Hamiltonian using the canonical transformations introduced by Bogoliubov and Valatin [275, 276]. For this purpose, we introduce the block Nambu-spinor

$$X_k = (\{c_{k,\uparrow}\}, \{c_{k,\downarrow}\}, \{c^\dagger_{-k,\uparrow}\}, \{c^\dagger_{-k,\downarrow}\})^T, \tag{7.4}$$

containing particle and hole degrees of freedom. Using the Nambu basis, the mean-field Hamiltonian has a BdG bilinear form

$$\begin{aligned} \hat{H}_{\text{BdG}} &= \sum_k X_k^\dagger \begin{pmatrix} \xi(k) & \Delta(k) \\ \Delta^\dagger(k) & -\xi_N^T(-k) \end{pmatrix} X_k + C \\ &= X_k^\dagger H_{\text{BdG}}(k) X_k + C\,, \end{aligned} \tag{7.5}$$

where all the particle non-conserving terms enter in the off-diagonal blocks $\Delta(k)$. While it at first appears as though the total number of degrees of freedom have been doubled in the transition to the Nambu basis, the fact is that the BdG matrix necessarily has a particle-hole symmetry where each eigenstate has a partner state with the opposite energy. Explicitly, the bilinear form is diagonalized by a unitary transformation of the following block structure

$$U(k) = \begin{pmatrix} u(k) & v(k) \\ v^*(-k) & u^*(-k) \end{pmatrix}. \tag{7.6}$$

In the resulting diagonal representation the eigenstates are partitioned in to two blocks of opposite energy $\pm E$.

$$U(k)^\dagger H_{\text{BdG}}(k) U(k) = \mathcal{E}(k) = \text{diag}(\{E(k)\}, \{-E(-k)\}). \tag{7.7}$$

As a result, there is no contradiction in the total number of degrees of freedom within the Nambu basis. The benefit of the Nambu basis is that the model can directly diagonalized since accompanying the diagonalization is a canonical transformation

$$Y_k = (\{\gamma_{k,\uparrow},\}\{\gamma_{k,\downarrow},\}\{\gamma^\dagger_{-k,\uparrow}\}\{\gamma^\dagger_{-k,\downarrow}\})^T \qquad X_k = U(k) Y_k, \tag{7.8}$$

that defines the fermionic Bolgoliubov quasiparticles. Since the Bolgoliubov quasiparticles are arrived at via a canonical transformation, the Bolgoliubov quasiparticles obey the standard Fermi-Dirac statistics of fermions, such that only the diagonal expectation values are non-zero and given by the Fermi-Dirac distribution function $\langle \gamma^\dagger_{k\alpha\sigma} \gamma_{k\alpha\sigma} \rangle = F_\beta(E_{k\alpha\sigma})$ for any inverse temperature β. Consequently, any expectation value of the mean-field Hamiltonian can be evaluated by using the inverse transformation to express the desired expectation value as a linear combination of the occupation numbers of the Bolgoliubov quasiparticles. In particular, this is also true of the mean-field expectation

values $\langle c_{-k'\sigma_3\gamma} c_{k'\sigma_4\delta} \rangle$ that enter the self-consistency equation, Eq. (7.3). The self-consistency equation can therefore be expressed for the unknown pair potentials. The resulting equation is non-linear and is generally difficult to solve beyond simple models. In practice, the self-consistency equation therefore often has to be solved numerically by iterating the equation after starting from an initial guess of the pair potentials until a self-consistent fixed point is found.

To connect back to the previous section and the critical temperatures, it is instructive to derive the critical temperatures of the general BCS model of Eq. (7.1) for the rather simple case of a single band metal with a symmetric dispersion $\xi(k) = \xi(-k)$. In this case the general expression of the critical temperature T_c in Eq. (6.5) becomes

$$\Delta^{\sigma\sigma'}(k) = \sum_{k\tau\tau'} V^{\sigma\sigma'\tau\tau'}(k,k') \frac{\tanh(\beta_c \xi_{k'}/2)}{2\xi_{k'}} \Delta_{k'}^{\tau\tau'}, \tag{7.9}$$

up to a conventional numerical factor that can be absorbed in the definition of the interaction V. By taking the continuum limit, the sum over the crystal momenta are replace by a corresponding integral. The integration over the momenta can in turn be expressed as an integral over the constant energy surfaces in reciprocal space of the band dispersion $\xi(k)$ and the energy. After these two steps, the linear gap equation becomes,

$$\Delta_k^{\sigma\sigma'} = \sum_{\tau\tau'} \int \mathrm{d}\xi \int_{S(\xi)} \frac{\mathrm{d}S}{v_F(k')} V^{\sigma\sigma'\tau\tau'}(k,k') \frac{\tanh(\beta_c \xi/2)}{2\xi} \Delta_{k'}^{\alpha\beta}, \tag{7.10}$$

where $\mathrm{d}S$ is the surface element on the constant energy surface $S(\xi)$, which is weighted by the density of states that is inversely related to the Fermi velocity perpendicular to the surface $v_F(k) = \nabla \xi_k \cdot \hat{k}$. In standard BCS theory, the potential V is assumed to be attractive within a narrow range of energies of the Fermi energy, consistent with an electron-phonon coupling. With this assumption, the energy integral is restricted to $|\xi_k| \leq \hbar\omega_c$, where the small cut-off energy ω_c defines the attractive region. Assuming that ω_c is small and that v_F is both finite and smooth, then both v_F and V can be also taken as radially constant. With these assumptions, the energy integral can be factored in the linearized self-consistency equation with the value, $\int_{-\hbar\omega_c}^{\hbar\omega_c} \tanh(\beta_c\xi/2)\,\mathrm{d}\xi/(2\xi) \approx \ln(1.14\beta_c\hbar\omega_c)$, for $1 \ll \beta_c\hbar\omega_c$. After the factorization the self-consistency equation

$$\Delta_{\hat{k}}^{\sigma\sigma'} = \ln(1.14\beta_c\hbar\omega_c) \sum_{\alpha,\beta} \int_{\mathrm{FS}} \frac{\mathrm{d}S}{v_F(\hat{k}')} V^{\sigma\sigma'\tau\tau'}(\hat{k},\hat{k}') \Delta_{\hat{k}'}^{\alpha\beta} \tag{7.11}$$

is clearly an eigenvalue problem. If λ is the largest eigenvalue of the kernel containing the interactions, then the critical temperature will satisfy $k_B T_c = 1.14\hbar\omega_c \mathrm{e}^{-1/\lambda}$. The original BCS result with $\lambda = \rho(\epsilon_F)V$ is then obtained by

also assuming a constant density of states $\rho(\epsilon_F)$ around the Fermi energy and that the interaction V only enters one spin channel [53]. At the same time, the Fermi velocity $v_F(\hat{k})$ enters the denominator in Eq. (7.11). It is therefore clear that the above standard BCS result for the critical temperature is invalid when encountering a flat band or a van Hove singularity where the Fermi velocity vanishes, which instead leads to the alternative expressions for the critical temperature detailed in Sec. 3.

7.1 Pairing Symmetry

The superconducting state is distinguished by a broken $U(1)$ gauge symmetry and by the associated existence of anomalous Green's functions with of non-zero finite values, where the time-ordered anomalous expectation values,

$$F_{\alpha\beta}^{\sigma_1\sigma_2}(r_1, t_1, r_2, t_2) = \langle \mathcal{T} c_{r_1\sigma_1\alpha}(t_1) c_{r_2\sigma_2\beta}(t_2) \rangle, \tag{7.12}$$

describe the bound Cooper pairs within the superconductor and is called the pair amplitude. The quantum statistics of Fermions places a restriction on the possible pairing symmetries. For at equal times $t_1 = t_2 = t$, the two fermionic operators anti-commute, $\{c_{r_1\sigma_1\alpha}(t), c_{r_2\sigma_2\beta}(t)\} = 0$. A simultaneous interchange of all the indices of the anomalous Green's function has therefore to result in an overall sign change,

$$F_{\alpha\beta}^{\sigma_1\sigma_2}(r_1, t, r_2, t) = -F_{\beta\alpha}^{\sigma_2\sigma_1}(r_2, t, r_1, t). \tag{7.13}$$

It is therefore evident that a finite pair amplitude can not have all indices equal, which is just a restatement of the Pauli principle that no two Fermions are allowed to occupy the same quantum state. This is also the reason why Eq. (7.13) places a limitation on the possible non-vanishing pair-amplitudes. By introducing the separate permutation operators for each set of indices, then the condition imposed by the Fermi statistic can be written succinctly as an operator identity $SPO = -1$, where the operator S interchanges the spin indices, P the position indices, and O the orbital indices.

The act of interchanging any pair of indices twice, necessarily brings the pair amplitude back to its starting value, and therefore the permutations are idempotent, $S^2 = P^2 = O^2 = 1$. Consequently, the eigenvalues of each permutation are restricted to ± 1. In addition, because the three permutation operators act on different non-overlapping sets of indices, the permutation operators commute, as the order in which any two permutations are applied does not matter. The permutations can therefore be simultaneously diagonalized. As a result, the superconducting pair-amplitudes can be resolved according to their signature with respect to the permutation operators. Enumerating the possibilities, it is clear from the requirement $SPO = -1$ that either one or all three permutations must result in a sign change. There are therefore four distinct possibilities. The

nomenclature for the classification is spin singlet/triplet, odd/even parity, and orbital singlet/triplet.

An important fact is that the classification with respect to the permutation operators intertwines with the additional symmetries of the non-interacting system further characterizing the possible states. We first note that, as stated in Sec. 6, the linearized self-consistency equation Eq. (6.5) has the same symmetry as the non-interacting part of the Hamiltonian H_0, i.e is left invariant under a group of symmetry transformations $\mathcal{G}$. The symmetry operations of H_0, $g \in \mathcal{G}$, therefore also have a representation on the space of the order parameters. Consequently, the linear self-consistency equation is block diagonal in the irreducible representations (irrep) of the symmetry group $\mathcal{G}$. All eigenvalues therefore belong to a definite irrep. Necessarily, any superconducting order breaks the $U(1)$ gauge symmetry since the pair potentials are not invariant under a global gauge transformation. If however the superconducting order breaks any additional symmetry beyond the $U(1)$ gauge symmetry, i.e. transforms as a higher order irrep of $\mathcal{G}$, then it is called unconventional [92].

To see how the symmetries of the system affects the symmetry classification of the pair amplitudes, we consider the concrete case of a simple single-band metal that is additionally both spin and spatially isotropic. The relevant symmetry group in this case is therefore comprised of the gauge symmetry $U(1)$, the spatial rotations in the group $SO(3)$ (assuming three dimensions), and the spin-rotations in $SU(2)$ which in total gives $\mathcal{G} = U(1) \times SO(3) \times SU(2)$. Because the superconducting order parameter is comprised out of two spin-$1/2$ particles, the action of the spin-rotations has two irreps, the one-dimensional singlet irrep and the three-dimensional spin-triplet irrep, both arising from the direct product of the two spin-$1/2$ representations. The irreps of spatial rotations in $SO(3)$ are labeled by their total angular momentum $l = 0, 1, 2 \ldots$ each with a $(2l + 1)$ dimensional basis. For historical reasons, the $SO(3)$ irreps are also referred to as $s, p, d, f, g, \ldots$-wave, starting from the lowest angular momentum representation. Because all even-l (odd-l) irreps have an even (odd) parity, it follows that a superconducting order parameter with an even l-wave symmetry must necessarily have a spin-component that is singlet (odd under spin index) to satisfy the statistics condition $SP = -1$, since $O = 1$ for a single band. The possible superconducting orders therefore include spin-singlet s-wave and spin-triplet p-wave, but for instance not triplet s-wave.

For crystals that instead have a discreet number of rotational symmetries, a similar enumeration of the possible pairing symmetries can be made with respect to the irreps of the relevant crystal point group [92]. Typically, even in this case the orders are still referred to within the $s, p, d, \ldots$-wave nomenclature where the relevant angular momentum label is inferred from the symmetry of the basis functions of the respective irrep to which the order belongs. An important distinction is that below the critical temperature the self-consistency equation Eq. (7.3) is no-longer linear, due to the already finite order parameters entering the Hamiltonian. Because of the non-linearity as well as the re-

duced symmetry due to the finite order parameters, the symmetry degeneracy found at the critical temperature can be lifted so that different irreps may mix. Another possibility is that a further symmetry breaking occurs below the critical temperature. In such cases, multi-component orders may emerge, e.g. an (s+d)-wave, or that some preferred linear combination, e.g. a time-reversal breaking (d+id)-wave, emerges.

7.2 Odd-Frequency Superconductivity

The standard BCS theory is formulated in terms of the equal time anomalous expectation values. On the other hand, the pair correlations generally expressed by the pair amplitudes by Eq. (7.12) extend beyond equal times to finite time differences. While the fermionic anti-commutation relation strictly holds only at equal times, the properties of the time-ordering however implies that the pair amplitudes of Eq. (7.12) can be shown to also satisfy $SPOT = -1$, where in addition to the previously introduced operators the operator T interchanges the time-coordinates of the anomalous Green's function. A direct consequence of including T is that the resulting classification of the superconducting pair amplitudes is immediately doubled in size, to a total of 8 possibilities. The additional possibilities correspond to pairing amplitudes that are odd in the time coordinates. Historically, the two possible signatures with respect to the operators T are referred to as odd- and even-frequency (odd-ω and even-ω) superconductivity, and the idea of odd-ω superconductivity was originally introduced by Berezinskii [46]. At equal times, the distinction introduced by T does not matter, because any odd-ω components necessarily vanishes at equal times, but the distinction matters for finite time correlations. In particular, the possibility of odd parity with respect to the operator T is able to absorb a sign change in the $SPOT$ signature, thus allowing the remaining permutations to take on different signatures than at equal time. As an example, a triplet s-wave pairing state is possible but only if it is also odd in time.

The fact that the odd-ω pair amplitudes can only be non-zero at finite time-differences, does however make odd-ω superconductivity somewhat elusive, since correlations do not by themselves directly contribute to static measurements. In particular, while Berezinskii proposed odd-ω superconductivity as an intrinsic order [46], the restriction of all pairing to non-equal times challenges attempts to define a corresponding order parameter, entering the free energy, and producing an intrinsic thermodynamically stable superconducting phase [277, 278]. Investigations into intrinsic bulk odd-ω states are however still ongoing [278]. Still, yet another possibility in which odd-ω can appear is instead by the scattering of Cooper pairs originating from an already existing superconducting order with a traditional even-ω order parameter. The a necessary condition for such pair scattering is the existence of at least some hy-

bridization between states of different indices, e.g. spin or band index, which in general introduces many possibilities for odd-ω pairing to occur.

In fact, there is a growing realization that odd-ω components are regularly generated whenever a symmetry braking structure, such as an interface or heterostructure, also involves a superconductor. The underlying generative process in such cases is that an odd-ω component is generated by a simultaneous flip of two entries in the $SPOT$ signature so that the total sign change remains invariant. For instance, at the interface of a normal metal conventional superconductor junction, the isotropic s-wave even-ω pairs of the parent superconductor are able to scatter in to anisotropic p-wave odd-ω pairs due to the broken translational invariance at the interface [279–282], in which case the spatial and the time parity both undergo a compensating flip. Similarly, odd-ω pairing was also shown to be induced for spin-triplet parent superconductors with a resulting unusual Meissner effect and appearance of zero energy states [283–286]. Instead replacing the normal metal, odd-ω pairings was likewise shown to appear in superconductor-topological insulators heterostructures with accompanying predicted signatures of the pairing in the density of states [287, 288].

Even without a symmetry breaking structure, it was shown that odd-ω pairing is always present in multiband superconductors as long as there is a finite band hybridization among at least two non-equivalent bands [289, 290]. Multiband superconductors therefore present an instance where odd-ω pairing appears homogeneously throughout the bulk of a material [45]. Examples of odd-ω pairing in multiband systems include MgB_2 when placed in an magnetic field [291] and Sr_2RuO_4 for which it is is predicted that a finite Kerr effect correspond to a finite odd-ω pairing [48]. The general condition for odd-ω pairing to appear in multiband systems is that $\xi(k)\Delta(k) - \Delta(k)[\xi(-k)]^* \neq 0$, where $\xi(k)$ and $\Delta(k)$ are the diagonal and off-diagonal blocks of the BdG matrix [45]. At the same time, the quantity is one of the recently introduced superconducting fitness parameters that has however been shown to reduce the superconducting critical temperature [45, 292, 293]. Odd-ω pairing is therefore deleterious to the superconducting order, but given the stringent condition for the fitness parameters to be zero also means that odd-ω pairing is nonetheless expected to be an ubiquitous feature of multiband systems.

More in line with chronology, the importance of proximity induced odd-ω pairing was however drastically demonstrated by the prediction of a long-ranged proximity effect in conventional superconductor-ferromagnet hybrid structures [294–296]. At the interface, the spin-isotropy of the superconductor is broken by the inhomogeneous exchange field of the magnet, resulting in proximity induced s-wave pairs of both spin-singlet and odd-ω spin-triplet symmetry. Well inside ferromagnet the singlet pairs are adversely affected by the exchange field, but not the triplet pairs which instead are long ranged [294]. The existence of such proximity induced odd-ω pairs is experimentally corroborated by spectroscopy [52, 297], as well as response of an associated charac-

teristic paramagnetic Meissner response [47, 51, 52]. Strong evidence for long ranged spin-triplet pairs is provided in ferromagnetic Josephson junctions, especially through particular dependence on the magnetic interface layers [298, 299]. Further replacing the ferrromagnet with a half-metal precludes the proximity induced spin-singlet pairs leaving only the odd-ω spin-triplet pairs [50, 300], providing a basis for inferring spin triplet supercurrents observed in a Josephson junction of the half-metal CrO_2 [301].

The preceding mentioned examples shows that odd-ω pairing appears ubiquitously in many systems together with unusual experimental signatures including optical response [290], the density of states [52, 287, 288, 297], supercurrents [50, 298–301], and a paramagnetic Meissner response [47, 51, 52]. While odd-ω pairing opens up for exotic pairing symmetries, how such exotic pair symmetries fare in the presents of disorder is less certain. Famously, in what has become known as Anderson's theorem, Anderson argued that the electron pairing of BCS theory between opposite momenta would generalize in the presents of strong scattering between pairing between time reverse states [302]. The implication is that isotropic conventional superconductors are expected to be very robust against disorder that does not break time-reversal symmetry, so that even charge impurities scattering that is large compared to the energy gap does not significantly suppress the superconducting critical temperature or destroy the superconducting energy gap, which is also seen in full scale BdG numerical analysis [303]. Unconventional pair symmetries are however not protected in a similar way by Anderson's theorem and are therefore generally expected to be incompatible with strong disorder. Whether similar conclusions holds for the exotic non-equal time odd-ω pairing is a less resolved question. For instance, the odd-ω spin-singlet p-wave pair correlations that appear in normal metal-conventional superconductor junctions have largely been ignored because of the spatial anisotropy of the pair correlations and the assumption that disorder will lead to isotropization [279, 304–306]. In Paper IV, we however show that the odd-ω p-wave pair correlations are not only robust against disorder, but that the ratio between the odd-ω p-wave and the isotropic even-ω s-wave pair correlations actually increases for stronger impurity scattering in the normal region. In fact, odd-ω p-wave pair correlations can as we show even be generated by disorder.

8. Linear Scaling Electronic Structure Methods

In this section we consider numerical methods that are need to treat large quantum mechanical systems and the general underpinning that enables such methods. In particular, the focus is on methods that achieve a so called linear scaling by carefully targeting required quantities and using beneficial properties of the systems involved. Such methods are also the basis for our work presented in Papers IV and V for which we have further adapted and developed such methods.

To start, we consider challenges that comes with a quantum mechanical description of condensed matter systems from a numerical point of view. First, the Hamiltonian always gives a complete description of any condensed matter system. This is because by definition the Hamiltonian is the time-evolution operator, describing the motion of all particles of the system via the fundamental Schrodinger equation. Condensed matter systems are however comprised of an macroscopic number of interacting particles. Their fundamental quantum mechanical description is therefore situated within an exponentially large Hilbert space spanned by all the product Fock states of the system. The dimensionality of the resulting problem therefore scales as $N \sim L^{dM}$ for a system with linear dimension L, in d dimensions, and with a macroscopic number of particles M. Consequently, a complete quantum mechanical description of any condensed matter systems is therefore infeasible. Alternatively, non-interacting theories keep the problem manageable, while at the same time often offering a good approximate description, even of interacting systems, which is in large part due to the Fermi-liquid paradigm presented in Sec. 2.1.1, even if there are many important exceptions where strong correlations are very important. Given the independent motions of the quasiparticles in an non-interacting system, there is a significant simplification in that the system can be treated as a single particle problem, requiring only that the quantum statistics is included as an additional step. I particular, mean-field theory, as presented in Sec. 4, demonstrates the versatility of the independent particle pictures, extending even to the superconducting state as in Sec. 7.

In any non-interacting theory, the Hamiltonian is quadratic in the field operators, and the problem dimension has the same scaling as single quantum particle with a total scaling as $N \sim L^D$. Given the linear unitary evolution in quantum mechanics, the problem is captured by a Hamiltonian matrix that proportional in size to the system dimensionality. However, the size of the

problem is typically further reduced by symmetries that immediately block diagonalizes the Hamiltonian matrix. For instance, in the crystallize phase, characterized by translational invariance, the non-interacting problem is block diagonal in the Bloch wave basis. Thus, with a full set of symmetries, non-interacting condensed matter problems are often analytically solvable. While interactions, defects, and heterostructures that reduce the symmetry of the system can be treated perturbatively using analytical methods [307, 308], the challenges quickly become intractable and numerical approaches become necessary. Numerically, the independent particle problem is completely solved by eigenvalue diagonalization of the Hamiltonian matrix, since it is equivalent to identifying all the solution of the time-independent Schrodinger equation. From the eigenvalues and eigenfunction that are obtained in diagonalization, any expectation values and correlation functions may be evaluated. While modern diagonalization algorithms are very efficient and available in most numerical libraries, the computation cost, time complexity, of diagonalization scales as $O(N^3)$ with an $O(N^2)$ memory footprint.

The time complexity of diagonalization therefore becomes significant for large problems. Consequently, for systems that naturally lack translation invariance from the presents of junctions, interfaces, edges, or disorder, even eigenvalue diagonalization may become completely unrealistic. Additionally, advances in fabrication as well as experimental measurement techniques, e.g. Scanning tunneling microscopy (STM) and spectroscopy, make atomistic resolution increasingly relevant. Likewise, a growing number of condensed matter systems of high interest go beyond a homogenous bulk description in the thermodynamic limit where symmetries dominate. This is for instance exemplified by topological phases of matter, where some of the most interesting phenomena occurs at the bulk to surface boundary which are therefore crucial to capture [119, 127]. Further examples are also offered by systems such as twisted bilayer graphene or buckled graphene where an exotic electronic structure results from twist or strain engineering but also creates large scale patterns that reduce the translation symmetry [248, 309]. Similarly, heterostructures and careful device geometries are proving decisive in creating extraordinary material properties.

For these types of systems the large growth in the number of unrelated degrees of freedom make diagonalization very costly. Two aspects limiting aspects of diagonalization also suggest how to proceed to achieve a more favorable scaling. First, diagonalization simply ask for too much information, namely all the eigenvalues together with eigenvectors. In most applications however only a handful of expectation values are required. A general way to achieve a better scaling is therefore to directly targeting only the required quantities instead of a complete description. Secondly, standard diagonalization algorithms are general purpose and do not exploit advantages properties of the system in question. When combining both there two aspects, it is pos-

sible to find methods that achieve a linear scaling with respect to the system size [310].

Underpinning linear-scaling methods is the physical intuition that a local change even to a quantum system should not be felt sufficiently far away from the disturbance. In other words, even quantum systems should possess some degree of locality or nearsightedness [311], which in turn implies that when expanding an already large system the time complexity should only increase by the added degrees of freedom. Connected to such nearsightedness is the fact that the interactions and hybridization of most condensed matter systems are typically short ranged in part due to screening. It therefore often possible to construct a description that short-ranged. Popular methods for their construction include the constructed of localized Wannier orbitals on the basis ab initio methods as well as by semi-empirical modeling of atomic orbitals [67, 312–315]. Mathematically, the advantageous property of such models is that the Hamiltonian matrix in such a description has a high degree of sparseness and that the one-particle density matrix decays rapidly as a function of separation between degrees of freedom [310, 311].

8.1 Fermi Operator Expansion Method

We do not thoroughly review the field of linear scaling electronic structure methods and their applications, see e.g. [310, 316, 317], and focus instead on Fermi operator expansion techniques that target the expectation values of an non-interacting system by approximating the one-particle density matrix. In a diagonal representation of the Hamiltonian matrix H with eigenvalues ϵ_n and the eigenvectors $|n\rangle$, the one-particle density matrix is given by $F_\beta(H) = \sum_n F_\beta(\epsilon_n)|n\rangle\langle n|$, where the diagonal elements $F_\beta(\epsilon_n)$ are the Fermi-Dirac distribution at the inverse temperature β which give the occupation probability of each eigenstate in equilibrium. The general approach of Fermi operator expansion techniques is to avoid a a transition to the diagonal representation by instead directly approximating the one-particle density matrix $F_\beta(H)$ as a matrix function.

To motivate such Fermi operator expansion techniques assume the existence of a polynomial approximation of the Fermi-Dirac distraction such that $F_\beta(H) \approx \sum_{n=0}^{M} c_n H^n$ for some coefficients c_n. To see the beneficial features of such a representation, note first that individual entries of $F_\beta(H)$ can be computed $[F_\beta(H)]_{ij} = \langle i|F_\beta(H)|j\rangle$ requiring only that the operator is applied to one of the corresponding state vectors and subsequently taking the inner product. Evaluating the individual entries therefore can therefore be achieved using only matrix-vector multiplication. Note also that when the operator $F_\beta(H)$ is applied to an initial state vector, the increasing powers of H will propagate the state around in an expanding neighborhood of the initial state. These two features make is so that the polynomial expansion method naturally uses both the

assumed locality of the quantum system, but also targets the only the required expectation values. If the matrix H is spare, the the scaling will be linear, since the required spare matrix-vector multiplication is itself linear with the size of the matrix. In addition the multiplication step is readily parallelized. The method therefore works exceptionally well for truly localized states such as insulators with an insulating energy gap. While the above discussion serves to motivate the polynomial method and its beneficial features, a straightforward power iteration of the Hamiltonian can however be numerically unstable, but the situation is readily remedied by instead expanding the Hamiltonian in a suitably defined set of recursively defined orthogonal polynomials [316].

Having motivated and shown the essential features of the Fermi operator expansion techniques, we next turn our attention to our adaptations of such techniques. Motivated in part by the desire to investigate the odd-frequency pairing in inhomogeneous systems, we in Paper III extend and combine the Fermi operator expansion technique with the Chebyshev method for single particle wave-packet propagation widely used in quantum chemistry [318–321], resulting in a method that we call EPOCH that we also used to obtained the results of Paper IV. Importantly, the method is formulated within the BdG formalism of Sec. 7 and therefore applicable to superconducting systems. A central step is to extend the one-particle density matrix in time and consider the Equilibrium Propagator (EP) given by $L_\beta(H_{\text{BdG}}, t) = \mathrm{e}^{-iH_{\text{BdG}}t}F_\beta(H_{\text{BdG}})$. As we show in Paper III, the matrix elements of $L_\beta(H_{\text{BdG}}, t)$ are the lesser $\mathcal{G}^<(t)$, greater $\mathcal{G}^>(t)$, and anomalous Green's functions $\mathcal{F}(t)$. The other conventionally defined Green's functions, including the retarded, advanced, and time-ordered versions can also be found by taking the appropriate linear combinations of these Green's functions. The main result of Paper IV and the basis of the EPOCH method is that the EP can be directly computed from a series expansion containing the Legendre polynomials of the BdG Hamiltonian matrix $P_n(\tilde{H_{\text{BdG}}})$.

$$\begin{aligned} L_\beta(H_{\text{BdG}}, t) &= \frac{1}{i}\begin{pmatrix} \mathcal{G}^<(t) & \mathcal{F}(t) \\ \mathcal{F}^\dagger(t) & [\mathcal{G}^>(t)]^* \end{pmatrix} \\ &= \frac{1}{2}\sum_{n=0}^{\infty}(2n+1)(-i)^n(j_n(\tilde{t}) + if_{\tilde{\beta}}^n(\tilde{t}))P_n(\tilde{H_{\text{BdG}}})\,. \end{aligned} \tag{8.1}$$

A requirement is however that the Hamiltonian H_{BdG} is rescaled so as to fit the standard domain of the polynomial $P_n(x)$, achieved by a rescaling of the Hamiltonian and time accordingly by $\tilde{H} = H/\|H\|$ and $\tilde{t} = \|H\|t$. Eq. 8.1 directly generalizes the Chebyshev method wave-packet propagation method by extending the time-dependent part to also include the full quantum statistics of fermions. In addition to the spherical Bessel functions $j_n(\tilde{t})$, the time-dependence in the EPOCH methods therefore also contains projective transients $f_{\tilde{\beta}}^n(\tilde{t})$ that contains all the temperature dependence and account for the

quantum statistics. As we show, the $f^n_{\tilde{\beta}}(\tilde{t})$ can be generated from a recurrence relationship that we derive, so that the Green's functions can then be efficiently computed with a linear scaling similar to the Chebyshev method [318]. The additional details of the computations are presented in Paper III and not repeated here.

A limitation of polynomial Fermi operator expansion methods is that at low temperature the polynomials are unable to accurately represent the sharp cut-off of the Fermi surface in metals. The limitation generally requires that one goes beyond the polynomial class of functions. In particular, in rational pole expansion methods the Fermi operator $F_\beta(H) = (e^{\beta H} + 1)^{-1} \approx \sum_{n=1}^{N_p} R_n/(\beta z - P_n)$ is instead approximated by a set of N_p simple complex poles, at P_n with resides R_n [310, 322]. While there are several pole representations of the Fermi-Dirac distribution to choose from [323–325], recently derived sets of poles are distinguished by the fact that the number of required poles only scales with the logarithm of the inverse temperature [326, 327]. Such logarithmically convergent sets of poles have therefore greatly reduce the resulting computational complexity at low temperatures. In the method appendix of Paper V, we therefore show how to used the accompanying rational pole expansions within the the BdG formalism of Sec. 7 to compute both the normal and anomalous expectation values in a superconducting state from the matrix elements of the Fermi operator $F_\beta\left(H_{\text{BdG}}\right)$ of the BdG Hamiltonian matrix. A strong point of this approach is that it can also be used to compute the static response in the expectation values due to any perturbation λ to H_{BdG}. The reason is that for any matrix A_λ the derivative with respect to the λ of the inverse matrix involves just the change $\partial_\lambda A_\lambda$ and the product of two inverse: $\partial_\lambda A_\lambda^{-1} = -A_\lambda^{-1}[\partial_\lambda A_\lambda]A_\lambda^{-1}$ As we show in Paper V, the rational pole expansion can therefore be used to solve both the full non-linear and the linearized self-consistency for the pair potentials.

9. Summary of Results

As we have argued in this thesis, the recent new material classes of two-dimensional materials as well as certain classes of topological matter have greatly expanded the total number of materials with robust, large, even singular, DOS peaks, that have recently gathered large attention due to their extremely large ordering susceptibility, making them exceptional hosts of exotic ordered states, including superconductivity. In Sec. 3, we presented examples of concrete materials from these new classes of materials that include graphene, rhombohedral graphite, and twisted bilayer graphene (TBG).

Motivated by these developments, we considered the important question of competing orders near large DOS peaks. In Paper II, we show that while all possible conventional symmetry breaking ordered states are in fact equally enhanced from a large DOS peak near the Fermi level, superconductivity is in contrast enhanced by the DOS peak over a much wider region of the phase diagram when compared to all other possible conventional orders. A direct consequence is the large probability by which this difference will generate superconducting domes on the flanks of DOS peaks, accessible by doping or by electric gating. Since even in the case when a non-superconducting order is initially stronger, a shift in the chemical potential will drastically weaken the non-superconducting order when compared to any tendency towards a superconducting order. Thus uncovering the superconducting order on the flanks. We establish these results by deriving fully universal doping dependence relationships for the critical temperatures of conventional orders that are independent of microscopic details. That the results are completely general is one of the strong points, and we also rigorously derive criteria for when the results are applicable, showing that the results are true as long as the DOS peak is narrow compared to the energy scale of the interactions. We also show that the general results hold true to a very good approximation and over wide ranges of coupling strengths in full scale atomistic models. Specifically we consider both the completely flat topologically protected surface flat bands of ABC-stacked rhombohedral graphite and the van Hove singularity in heavily doped graphene, where for both systems we consider both superconducting and competing magnetic orders. In the case of rhombohedral graphite, we also show that the tuning of the chemical potential can equally well be accomplished by applying a displacement field on the graphite stack. The results of Paper II therefore show that the DOS peaks arising in many newly discovered condensed matter platforms not only have a strong ordering tendency but that they are also uniquely suited for unusual and high temperature forms of superconductivity.

We also point out that the results of Paper II are consistent with both recent renormalization group and quantum Monte Carlo calculations that explicitly consider the competition between many-body instabilities in graphene close to the van Hove filling [232, 233, 328], showing that superconducting orders compete especially favorably on the flanks of the van Hove filling, where in particular the six-fold symmetry of the honeycomb lattice ubiquitously promotes an unconventional time-reversal-breaking d+id chiral superconducting state [32–35, 329].

In Paper I, we further show that despite its exotic and unconventional nature the d+id-wave superconducting state proposed to appear in graphene doped close to the van Hove singularity is surprisingly robust against defects. In fact as we show, in the vicinity of either a single lattice vacancy or even a rotational symmetry breaking bivacancy, the recovery length of the d+id state is comparable to that of a conventional s-wave state which is directly protected by Anderson's theorem [302]. Further demonstrating that the d+id-wave state is quite resilient to defects, we show that while charge defects and lattice vacancies introduce a set of localized midgap states within the full energy gap of the d+id-state, the midgap states are very localized and have an energy that is always finite, keeping the superconducting gap intact. The impurity induced midgap states offer simultaneously an accessible experimental signature of the d+id-wave. Thus, despite the fact that attempts to significantly dope graphene closer to the van Hove singularity are also likely to introduce large amount of disorder, the disorder robustness of the chiral d+id-wave state means that a realization of this exotic topological superconducting state remains promising.

In the single graphene sheet, the chiral superconducting state is ubiquitously favored [32, 33, 35, 329], while as we rigorously show in Paper V, using full scale atomistic modeling, a nematic superconducting state is instead and unexpectedly favored in TBG close to the so-called magic twist angle. At this angle the long scale moiré pattern generates van Hove singularities and even flat band states with corresponding large peaks in the density of states. Both the correlated insulating and superconducting states within these flat bands have been of immense research focus since their experimental discovery [39, 40]. Simultaneously, the very large moiré patterns involved have challenged attempts to accurately describe the superconducting state in TBG. While several effective models have previously been developed, it has also led to a proliferation of models and predictions.

In Paper V, we therefore model each carbon atom with the added benefit that we are able to introduce unambiguous local interactions responsible for the superconducting state, but also that we maintain a full real space resolution. The general pairing mechanism that we employ is not only consistent and motivated by recent experiments, it is also the same pairing mechanism previously used for graphene, as in our Paper I. The results that we find for TBG can therefore also be directly compared to those of graphene but also to the high-temperature cuprate superconductors with which TBG shares many

distinct phase diagram features. Despite the very large 10^4 of carbon atoms within the moire unit cell and a dense k-point sampling, we solve both the linearized and the full non-linear gap equations using the linear scaling method described in Sec. 8. Importantly, we find experimentally relevant superconducting transition temperatures already for weak and highly realistic coupling strengths. Our combined approach also allows us to produce new insights by tracing the development of the nematic state. In particular, we rigorously show the symmetry imposed degeneracy at the critical temperature (T_c) is lifted below T_c, leading to a nematic state with a real valued order parameter. At the same time this analysis shows that the time-reversal-symmetry breaking d+id-wave has the largest energy within the degeneracy manifold. The appearance of a nematic superconducting state is consistent with recent experimental data, showing that the nematicity between the superconducting and the normal state is different [330]. With unprecedented resolution, we further show that the nematic superconducting phase is fully gapped and is spatially highly inhomogeneous with nematic ordering both on the full moire lattice scale developing a global C_2 axis and with an intricate vortex pattern in the local orientation of the d-wave pairing. We further tie the finite superconducting energy gap of the nematic superconducting order to an unusual and very strong π-locked Josephson coupling between the two layers. The atomic resolution, also allows us to show that the nematic state has clear signatures directly in the local density of states, offering a clear experimental signature that can for instance be measured using scanning probe microscopy.

In Paper IV, we present the very surprising result that exotic odd-frequency p-wave pairing not only survives but even thrives in a disordered normal metal-conventional superconductor (NS) junction, despite the anisotropy of the odd-frequency pairing. In fact, the odd-frequency pairing constitutes a growing fraction of the proximity-induced pair correlations in the N region, even compared to both the local and non-local isotropic pair correlations that are assumed to be disorder robust. To obtain these results, we perform fully quantum mechanical calculations on a large scale model dirty NS junction with random charge (Anderson) disorder. Prior to our work and given that most work has been done with in the quasi-classical framework where the anisotropic components automatically vanish in the dirty limit [279, 305], the odd-frequency p-wave correlations were almost completely ignored in such NS junctions. Our results therefore show that the true quantum mechanical behavior of such systems for both weak and very strong disorder is remarkably different, where the anisotropic odd-frequency p-wave correlations are robust and are even generated by disorder.

To obtain the odd- and even-frequency pair correlation in Paper IV, we used the EPOCH method that we developed and presented in Paper III (see also Sec. 8.1). The EPOCH method is a generalization of the widely used and efficient Chebyshev method for single particle wave-packet propagation method from quantum chemistry [318–321]. Our generalization extends the method

by incorporating the full equilibrium statistics of fermions as well as by capturing both the normal and anomalous Green's functions, where the anomalous Green's functions are required for superconducting systems and for odd-frequency superconductivity. The very favorable computational cost of the Chebyshev method is maintained in the EPOCH method. In fact, the propagation has the same general form as in the Chebyshev method but with the addition of a new projective part that we derive and which captures all of the quantum statistics and all temperature dependence. Since this projective mode is easily computed from a closed recurrence relationship and can be tabulated ahead of time, the EPOCH method scales linearly in the system degrees of freedom and can therefore readily and accurately be used to compute the time-domain Green's function even in very large systems, such as in Paper IV.

9.1 Conclusions and Outlook

In summary, the results of this thesis point towards new avenues for realizing exotic unconventional forms of superconductivity. We have shown that superconducting states are generally and especially favored close to peaks in the density of states that are readily created in for instance two-dimensional materials and in topological semimetals. Where at the same time, the recently recognized geometric contributions to the superfluid weight allow for a true superconducting state. We have also shown that even highly unconventional superconducting orders such as the chiral d+id in graphene and the odd-frequency p-wave pairing at NS junctions are remarkably robust towards disorder.

At the same time the general results of Paper II were derived within mean-field theory and do not include the effects of fluctuations. A future research direction is therefore to explore the extent to which these results are modified when many-body correlations and the effects of quantum fluctuations are included. Going beyond mean-field theory is in general difficult, especially when trying to sort out competing orders. A promising fact is that the BCS wave function is an exact ground state of certain interacting flat band models [207, 331], but one that does not directly address the order competition as a function of the band filling. Because the results of Paper II stem from the fundamental differences in the polarizabilities of the superconducting and non-superconducting ordering channels, we however speculate that similar conclusions will continue to hold even when beyond mean-field effects are included. In fact, the difference between the two channels might even become more pronounced, while still generally valid. A hint comes from the flow equations seen in functional renormalization group (FRG) theory where, at least to the one-loop corrections, the particle-particle and particle-hole channel susceptibilities directly enter in the flow equations [332, 333]. FRG has the added benefit of being in principle exact and treating the competition order between different channels on an equal footing. For systems with a singular DOS of a

flat dispersion, a careful choice of flow parameter is however required [334, 335].

In the case of graphene and twisted bilayer graphene (TBG), a further important question is to disentangle the factors that determine the competition between the chiral and nematic superconducting states. These two possibilities arise from the symmetry imposed degeneracy of the d-wave solutions that belong to the E irreducible representation and that undergo a further symmetry breaking below T_c. While several recent work show that coupling to another superconducting ordering channel or a Bosonic fluctuation can lead to a favoring of the nematic state in TBG [336–338], the results of Paper V show that the Nematic state is directly favored in the E irrep, corresponding to an unexpected sign change in the Landau free energy functional.

At the same time, TBG already gives an example of how van Hove singularities can be engineered in two-dimensional heterostructures and the rich physics that can emerge. The fact that periodic structures in two-dimensions necessarily have van Hove singularities also points to the general fact that they can be engineered or artificially created [339], pointing towards another possibly fruitful research direction. Already TBG analogs have been suggested by adding a relative twist angle in layered materials [340], such as twisted bilayer transition metal dichalcogenides [341].

The results of paper IV shows that odd-frequency p-wave pairing is both robust against and generated by disorder, but the finding also asks how to further measure these correlations and their implications for the superconducting state. A research question is therefore to develop a more general theory of the stability of finite time superconducting pair correlations, and simultaneously pursuing further experimental implications of these correlation. A natural starting point for such experimental signatures are dynamic measurements such as a the Meissner response [47] or signatures in Jospehson junctions [49, 280, 342]. Since odd-frequency pairing has been related to a superconducting fitness parameter and a suppression in T_c [293], one might even ask if odd-frequency pairing and its generation with disorder is also related to the over all stability of the superconducting state.

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