

MICROWAVE PROBES OF QUANTUM MATTER:  
PROBING QUANTUM SPIN LIQUIDS AND VAN DER WAALS  
HETEROSTRUCTURES USING SUPERCONDUCTING CIRCUITS

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I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

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# Abstract

Correlated ground states such as quantum spin liquids and unconventional superconductors are central to condensed matter physics. Probing their emergent properties is essential both for understanding them and for eventual applications. Advances in superconducting quantum circuits have produced microwave resonators with very high quality factors, achieved by isolating the resonator from dissipative degrees of freedom in its environment. Here I invert that design principle and ask: can a resonator coupled deliberately to a correlated material serve as a sensitive probe of it? I will describe two applications: to frustrated magnets and to van der Waals (vdW) heterostructures.

In Part II, I will focus on  $\text{TbInO}_3$ , a layered compound in which  $\text{Tb}^{3+}$  moments form a frustrated triangular lattice that may host a quantum spin liquid. Epitaxial films were grown only recently, and their small sample volume places them out of reach of the workhorse probes of frustrated magnetism such as neutron scattering and heat capacity. I will show that a NbTiN coplanar-waveguide resonator patterned directly onto such a film detects magnetic resonance of the Tb moments at microwave frequencies. The spectra resolve two distinct ground-state g-factors, which I assign to the inequivalent Tb sites created by an improper ferroelectric distortion. The magnetic susceptibility, recovered from the integrated spectral weight of the resonance, continues to grow down to 50 mK with no sign of ordering despite a Curie-Weiss scale of  $\sim 11$  K, placing a lower bound of 220 on the frustration index. I will then remove the requirement of fabricating on the sample at all, by developing a flip-chip platform in which a film or crystal is placed face down onto a prefabricated resonator chip. This qualitatively reproduces the  $\text{TbInO}_3$  spectrum and extends the technique to the Heisenberg pyrochlore  $\text{Gd}_2\text{Ti}_2\text{O}_7$ , where the harmonics of a single resonator map out a potential collective mode.

Switching to vdW heterostructures in Part III, I will focus on the superfluid stiffness of flatband vdW superconductors, a quantity that bears directly on phase fluctuations, pairing symmetry, and the quantum geometric contribution to the superfluid weight. I will present a hybrid architecture that integrates vdW heterostructures with high-impedance NbTiN resonators, enabling DC transport and microwave measurements on the same device, together with the fabrication problems that had to be solved to build it. Coupled to a bilayer graphene Josephson junction, the resonator resolves a Josephson inductance tunable over two orders of magnitude with gate voltage. The junction



inductance tuned by gate and by temperature spans the range expected for vdW superconductors. I will summarize our attempts to probe superfluid stiffness in Bernal bilayer graphene/WSe<sub>2</sub> heterostructures in which no superconducting state was observed. I will identify the features of the hybrid architecture most likely responsible for the absence of superconductivity, and outline future work on recently discovered candidate chiral superconductors in multilayer rhombohedral graphenes.

Quantum materials remain an active frontier, with new phases tying together topology, broken symmetry, and frustration continuing to emerge from a growing list of candidate compounds. I will close by arguing that superconducting resonators, applied across this landscape, can offer distinctive insights into unconventional phases of matter.

# Acknowledgments

I would like to start at the beginning, but in the Homeric tradition of starting stories *in medias res*, from the middle, I will start from the middle. A PhD can be a long and circuitous journey, and mine took place across two institutions: Stanford University and the University of Maryland (UMD) at College Park. The middle of my story begins at Stanford, where the research presented in this thesis was done over the last four years.

My deepest gratitude goes to my advisor, David Goldhaber-Gordon, who molded me into a confident scientist. I am unafraid to take on new scientific challenges because of David. A person's belief in themselves, in their abilities and in the quality of their ideas, is a precious thing. David nurtured my curiosity without judgment, and he was always eager to discuss whatever crazy idea I brought to him. He thinks a level deeper than most people and asks the right questions; I hope to do the same in my own career.

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Now to the beginning. My PhD journey started at the University of Maryland (UMD), College Park, in the group of Jimmy Williams. I came to UMD after a summer at NIST Gaithersburg working with Jake Taylor and Justyna Zwolak, and that summer was formative. Under their mentorship I learned the nitty-gritty of formulating a scientific problem, proposing a plan of action, executing it and writing the paper. When I was choosing grad schools, Jake helped me decide on UMD and recommended Jimmy, whose lab had just begun doing exciting work on topological insulators. I am glad I listened. Jimmy taught me how to reason through experimental data. Great artists see beauty in a common scene that others miss; Jimmy could see which features of a dataset mattered and which did not, and I have tried to learn that judgment. I thank Jay Sau and Ed Ott for many discussions about the non-linear dynamics of Josephson junctions. Learning about dynamical systems and their many quirks from one of the pioneers of the field was a privilege, and I am grateful to Ed for his feedback on my work and for teaching generations of students through his courses. Alicia Kollar mentored me during my last year at UMD, and she was kind enough to teach me and her students the basics of transmon and fluxonium measurements, which shaped how I later framed the resonator experiments with vdW heterostructures. It was a pleasure to work with Jimmy’s lab members — Rodney, Christie, Ming, Fan and Sungha — who helped me on projects throughout my time there. Rodney patiently mentored me on dilution fridges and nanofabrication, and I take on new challenges confidently because of him. Sungha and Sam always drew me into their company, and I thank them for their warm friendship; running into Sungha at APS still makes me nostalgic for Maryland. I thank Martin and Maya from Alicia’s group, and Ray, Nitin and Natalia from Vlad’s group, for their company and support. My friends in Maryland — Keshav, Sanket, Spandan, Nikhil, Goutam, Shubhayan, Naren, Sharmila, Aakansha, Pragya — kept me sane through the ups and downs of grad school and through the pandemic. I thank them for their friendship.

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# Contents

|                                                                                  |           |
|----------------------------------------------------------------------------------|-----------|
| <b>Abstract</b>                                                                  | <b>iv</b> |
| <b>Acknowledgments</b>                                                           | <b>vi</b> |
| <b>I Foundations</b>                                                             | <b>1</b>  |
| <b>1 Introduction</b>                                                            | <b>2</b>  |
| 1.1 Emergent phases in quantum materials . . . . .                               | 3         |
| 1.2 Superconducting circuits as sensors of quantum matter . . . . .              | 4         |
| 1.3 Thesis Outline . . . . .                                                     | 5         |
| <b>2 Probing many-body phases at microwave frequencies</b>                       | <b>7</b>  |
| 2.1 Order parameters and the Landau paradigm . . . . .                           | 8         |
| 2.2 Beyond Landau: topological order and fractionalization . . . . .             | 9         |
| 2.3 Excitations and linear response . . . . .                                    | 11        |
| 2.4 The probe landscape . . . . .                                                | 12        |
| 2.5 The microwave window: spin susceptibility and superfluid stiffness . . . . . | 13        |
| <b>3 Superconducting Circuits</b>                                                | <b>15</b> |
| 3.1 Superconductivity . . . . .                                                  | 15        |
| 3.2 London equations . . . . .                                                   | 16        |
| 3.3 Kinetic inductance . . . . .                                                 | 17        |
| 3.4 The superconducting resonator: storing photons in a box . . . . .            | 18        |
| 3.4.1 Coplanar transmission lines . . . . .                                      | 21        |
| 3.5 $S_{21}$ for hanger resonators . . . . .                                     | 23        |
| 3.5.1 Resonator terminated by a short: $\lambda/4$ resonator . . . . .           | 23        |
| 3.5.2 Resonator terminated by an arbitrary complex load . . . . .                | 27        |
| 3.6 Impedance of a Josephson junction . . . . .                                  | 32        |



|           |                                                                                                                          |           |
|-----------|--------------------------------------------------------------------------------------------------------------------------|-----------|
| 3.7       | Coupling resonators to condensed matter systems . . . . .                                                                | 34        |
| 3.7.1     | Resonators coupled to magnetic systems: spin resonance . . . . .                                                         | 36        |
| 3.8       | Summary . . . . .                                                                                                        | 38        |
| <b>II</b> | <b>Frustrated Magnetism</b>                                                                                              | <b>39</b> |
| <b>4</b>  | <b>Frustrated Quantum Magnets</b>                                                                                        | <b>40</b> |
| 4.1       | Atomic magnetism . . . . .                                                                                               | 41        |
| 4.1.1     | Term symbols . . . . .                                                                                                   | 42        |
| 4.2       | Paramagnetism . . . . .                                                                                                  | 43        |
| 4.2.1     | Free magnetic moments . . . . .                                                                                          | 43        |
| 4.2.2     | Partition function for a magnetic moment $J$ . . . . .                                                                   | 44        |
| 4.2.3     | Curie Law . . . . .                                                                                                      | 46        |
| 4.3       | Magnetic interactions . . . . .                                                                                          | 47        |
| 4.3.1     | Magnetic dipolar interaction . . . . .                                                                                   | 47        |
| 4.3.2     | Exchange interaction . . . . .                                                                                           | 49        |
| 4.3.3     | Superexchange . . . . .                                                                                                  | 50        |
| 4.3.4     | Exchange mediated by a Fermi liquid: RKKY interactions . . . . .                                                         | 51        |
| 4.4       | Magnetic Order: Non-frustrated magnetism . . . . .                                                                       | 51        |
| 4.4.1     | Curie-Weiss model . . . . .                                                                                              | 51        |
| 4.5       | Frustrated magnetism . . . . .                                                                                           | 55        |
| 4.5.1     | The origin of geometric frustration . . . . .                                                                            | 56        |
| 4.5.2     | Lattices prone to magnetic frustration . . . . .                                                                         | 58        |
| 4.5.3     | Experimental signatures . . . . .                                                                                        | 59        |
| 4.6       | Looking for frustrated magnetism: Complex oxides . . . . .                                                               | 60        |
| <b>5</b>  | <b>Microwave spin resonance in spin liquid candidate <math>\text{TbInO}_3</math></b>                                     | <b>62</b> |
| 5.1       | A new frontier: Epitaxy of frustrated magnet thin films . . . . .                                                        | 62        |
| 5.2       | $\text{TbInO}_3$ : A triangular-lattice anti-ferromagnet . . . . .                                                       | 63        |
| 5.3       | Probing magnetism in $\text{TbInO}_3$ by microwave spin resonance . . . . .                                              | 68        |
| 5.4       | Model for ground state eigenstates . . . . .                                                                             | 71        |
| 5.5       | Extraction of Magnetic Susceptibility . . . . .                                                                          | 73        |
| 5.6       | Discussion and Outlook . . . . .                                                                                         | 75        |
| <b>6</b>  | <b>Flip chip microwave spectroscopy of <math>\text{TbInO}_3</math> and <math>\text{Gd}_2\text{Ti}_2\text{O}_7</math></b> | <b>79</b> |
| 6.1       | Why flip-chip methods? . . . . .                                                                                         | 79        |
| 6.2       | Previous work on flip-chip methods . . . . .                                                                             | 82        |
| 6.3       | Vacuum finger for flip-chip assembly . . . . .                                                                           | 83        |

|                                           |                                                                                           |            |
|-------------------------------------------|-------------------------------------------------------------------------------------------|------------|
| 6.4                                       | Reference resonator . . . . .                                                             | 85         |
| 6.5                                       | Measurements on candidate spin liquid $\text{TbInO}_3$ . . . . .                          | 86         |
| 6.6                                       | Measurements on Heisenberg pyrochlore magnet $\text{Gd}_2\text{Ti}_2\text{O}_7$ . . . . . | 88         |
| 6.6.1                                     | Temperature dependence . . . . .                                                          | 90         |
| 6.7                                       | Refinements and outlook . . . . .                                                         | 91         |
| <b>III van der Waals Heterostructures</b> |                                                                                           | <b>93</b>  |
| <b>7</b>                                  | <b>Electronic correlations in 2D materials</b>                                            | <b>94</b>  |
| 7.1                                       | Moire materials . . . . .                                                                 | 95         |
| 7.2                                       | Non-moiré materials . . . . .                                                             | 96         |
| 7.3                                       | The zoo of correlated phases in flatband vdW materials . . . . .                          | 98         |
| 7.3.1                                     | Isospin polarization . . . . .                                                            | 99         |
| 7.3.2                                     | Topological order: anomalous Hall effects to fractional Chern insulators . . .            | 99         |
| 7.3.3                                     | Superconductivity . . . . .                                                               | 99         |
| 7.4                                       | Open problems in flatband vdW superconductivity . . . . .                                 | 100        |
| 7.4.1                                     | Phase fluctuations . . . . .                                                              | 101        |
| 7.4.2                                     | Pairing symmetry . . . . .                                                                | 102        |
| 7.4.3                                     | Quantum geometric contributions to the superfluid stiffness . . . . .                     | 102        |
| 7.4.4                                     | Pairing mechanism and its relation to isospin order . . . . .                             | 103        |
| <b>8</b>                                  | <b>Hybrid superconducting resonator architecture to probe vdW heterostructures</b>        | <b>104</b> |
| 8.1                                       | Motivation for a hybrid architecture . . . . .                                            | 105        |
| 8.2                                       | Design criteria . . . . .                                                                 | 106        |
| 8.3                                       | Fabrication of hybrid devices . . . . .                                                   | 108        |
| 8.4                                       | Challenges with hybrid device fabrication . . . . .                                       | 110        |
| 8.4.1                                     | Tenting during stack meltdown . . . . .                                                   | 110        |
| 8.4.2                                     | Spalling from strained superconducting contacts . . . . .                                 | 111        |
| 8.4.3                                     | Substrate leakage in gate lines . . . . .                                                 | 113        |
| 8.5                                       | A complete process flow for hybrid devices . . . . .                                      | 114        |
| <b>9</b>                                  | <b>A hybrid vdW Josephson junction</b>                                                    | <b>117</b> |
| 9.1                                       | Previous work on hybrid vdW JJ devices . . . . .                                          | 117        |
| 9.2                                       | Device Fabrication and Measurement Setup . . . . .                                        | 119        |
| 9.3                                       | Gate dependence of the critical current . . . . .                                         | 120        |
| 9.3.1                                     | Expected Josephson inductance . . . . .                                                   | 120        |
| 9.4                                       | Gate dependence of resonator response . . . . .                                           | 121        |
| 9.5                                       | Temperature dependence of resonator response . . . . .                                    | 124        |

|           |                                                                                        |            |
|-----------|----------------------------------------------------------------------------------------|------------|
| 9.6       | DC bias dependence of resonator response . . . . .                                     | 125        |
| 9.7       | Resonator frequency as a quantitative probe of junction inductance . . . . .           | 128        |
| 9.8       | Higher resonator harmonics and other gate-responsive modes . . . . .                   | 129        |
| 9.9       | Summary . . . . .                                                                      | 131        |
| <b>10</b> | <b>Progress towards superfluid stiffness measurements</b>                              | <b>133</b> |
| 10.1      | Previous work on superfluid stiffness measurements . . . . .                           | 133        |
| 10.2      | Measurements of a hybrid hallbar resonator device . . . . .                            | 134        |
| 10.3      | vdW impedance in the normal state . . . . .                                            | 136        |
| 10.4      | Data from an additional device . . . . .                                               | 138        |
| 10.5      | Missing superconducting state in BBG/WSe <sub>2</sub> heterostructures . . . . .       | 141        |
| 10.6      | Limitations of current approach to hybrid devices . . . . .                            | 142        |
| 10.7      | Design principles for future devices . . . . .                                         | 143        |
| <b>IV</b> | <b>Outlook</b>                                                                         | <b>145</b> |
| <b>11</b> | <b>Outlook on Future Experiments</b>                                                   | <b>146</b> |
| 11.1      | Microwave resonance in pyrochlore spin ices . . . . .                                  | 146        |
| 11.2      | Superfluid stiffness of rhombohedral graphene superconductors . . . . .                | 148        |
| 11.3      | Hybrid mm-waves probes of the superconducting gap . . . . .                            | 148        |
| 11.4      | Emergent excitations at superconductor-fractional Chern insulator interfaces . . . . . | 149        |
| 11.5      | Beyond exfoliation: focused-ion-beam microstructures . . . . .                         | 149        |
|           | <b>Appendices</b>                                                                      | <b>151</b> |
| <b>A</b>  | <b>S-parameter analysis using ABCD matrices</b>                                        | <b>152</b> |
| A.1       | ABCD Matrices . . . . .                                                                | 152        |
| A.1.1     | Definition of ABCD matrices . . . . .                                                  | 152        |
| A.1.2     | ABCD matrices for transmission lines . . . . .                                         | 154        |
| A.1.3     | Relation to S parameters . . . . .                                                     | 154        |
| A.1.4     | Impedance looking into an ABCD matrix . . . . .                                        | 154        |
| <b>B</b>  | <b>Derivation of the g-factor <math>g_J</math></b>                                     | <b>156</b> |
| <b>C</b>  | <b>Wafer Scale Marker Chips</b>                                                        | <b>158</b> |
| C.1       | SiO <sub>2</sub> /Si wafers . . . . .                                                  | 158        |
| C.1.1     | Fabrication recipe . . . . .                                                           | 158        |
| C.2       | Hybrid device wafers . . . . .                                                         | 160        |

|                                                                                      |            |
|--------------------------------------------------------------------------------------|------------|
| <b>D Stacking SOPs</b>                                                               | <b>161</b> |
| D.1 Exfoliation . . . . .                                                            | 161        |
| D.2 Searching for flakes . . . . .                                                   | 162        |
| D.3 Stacking . . . . .                                                               | 162        |
| D.3.1 Design principles for good hybrid stacks . . . . .                             | 163        |
| <b>E Nanofabrication Recipes</b>                                                     | <b>166</b> |
| E.1 Etching . . . . .                                                                | 166        |
| E.1.1 O <sub>2</sub> etch for graphite . . . . .                                     | 166        |
| E.1.2 CHF <sub>3</sub> /O <sub>2</sub> mesa and edge contact etch . . . . .          | 167        |
| E.1.3 CF <sub>4</sub> selective etch . . . . .                                       | 168        |
| E.1.4 XeF <sub>2</sub> hBN etch . . . . .                                            | 169        |
| E.1.5 NbTiN etch — fluorine chemistry . . . . .                                      | 169        |
| E.1.6 NbTiN etch — chlorine chemistry . . . . .                                      | 170        |
| E.2 Deposition . . . . .                                                             | 171        |
| E.2.1 Cr/Au normal contacts . . . . .                                                | 171        |
| E.2.2 NbTiN sputtering . . . . .                                                     | 171        |
| E.2.3 Ti/Nb/Al superconducting contacts . . . . .                                    | 172        |
| <b>F Fabrication Checklists</b>                                                      | <b>174</b> |
| F.1 Superconducting resonator fab for frustrated magnet devices . . . . .            | 174        |
| F.2 Superconducting fab for hybrid devices: superconducting circuit layers . . . . . | 175        |
| F.3 Hybrid JJ devices . . . . .                                                      | 176        |
| F.4 vdW fab for hybrid devices with superconducting gates . . . . .                  | 179        |
| F.5 vdW fab for hybrid devices with dual-graphite gates . . . . .                    | 182        |
| <b>G Microwave probe for VTI</b>                                                     | <b>186</b> |
| G.1 Structural design . . . . .                                                      | 186        |
| G.2 Microwave hardware . . . . .                                                     | 187        |
| G.3 Microwave-only PCB . . . . .                                                     | 187        |
| G.4 Cryogenic dc wiring and PCB . . . . .                                            | 188        |
| G.5 Hardware summary . . . . .                                                       | 189        |
| <b>H Pink Fridge</b>                                                                 | <b>190</b> |
| H.1 Grounding . . . . .                                                              | 190        |
| H.2 Electron Thermometry . . . . .                                                   | 190        |
| H.3 Cryogenic microwave wiring . . . . .                                             | 192        |
| H.4 Room temperature microwave setup . . . . .                                       | 194        |
| H.5 Hardware summary . . . . .                                                       | 196        |

|          |                                                           |            |
|----------|-----------------------------------------------------------|------------|
| <b>I</b> | <b>Miscellaneous Fabrications</b>                         | <b>197</b> |
| I.1      | Coax straightening tool . . . . .                         | 197        |
| I.2      | LN <sub>2</sub> trap holder for baking . . . . .          | 198        |
| <b>J</b> | <b>Matplotlib rcParams</b>                                | <b>199</b> |
| <b>K</b> | <b>Commonly Used Physical Constants in Uncommon Units</b> | <b>202</b> |
|          | <b>Bibliography</b>                                       | <b>203</b> |

# List of Figures

|     |                                                                                       |    |
|-----|---------------------------------------------------------------------------------------|----|
| 1.1 | Broad classes of quantum materials. . . . .                                           | 4  |
| 2.1 | Broken-symmetry phases and the Landau paradigm. . . . .                               | 8  |
| 2.2 | Topological order. . . . .                                                            | 10 |
| 2.3 | The probe landscape across energy scales. . . . .                                     | 14 |
| 3.1 | Types of 3D superconducting cavities. . . . .                                         | 19 |
| 3.2 | Types of planar superconducting resonators. . . . .                                   | 20 |
| 3.3 | Geometry of a coplanar waveguide. . . . .                                             | 21 |
| 3.4 | Hanger resonator $S_{21}$ response. . . . .                                           | 27 |
| 3.5 | Resonator properties under a complex load. . . . .                                    | 30 |
| 3.6 | Inductance of a Josephson junction. . . . .                                           | 33 |
| 3.7 | Coupling strategies for resonators to condensed matter systems. . . . .               | 34 |
| 3.8 | Zero-point current and voltage fluctuations for typical microwave resonators. . . . . | 36 |
| 4.1 | Origin of atomic magnetic moments. . . . .                                            | 41 |
| 4.2 | Paramagnetism of a free spin- $J$ moment. . . . .                                     | 46 |
| 4.3 | Types of Magnetic Interactions. . . . .                                               | 48 |
| 4.4 | Curie–Weiss susceptibility. . . . .                                                   | 52 |
| 4.5 | A map of antiferromagnetic ground states. . . . .                                     | 55 |
| 5.1 | Device schematic and basic principles of spin resonance detection. . . . .            | 64 |
| 5.2 | Frequency and temperature dependence of the spin resonance signal. . . . .            | 66 |
| 5.3 | Crystal-field model and c-axis displacement of $\text{Tb}^{3+}$ ions. . . . .         | 67 |
| 5.4 | Magnetic susceptibility from 20 mK to 2 K. . . . .                                    | 71 |
| 6.1 | Direct fabrication versus the flip-chip geometry. . . . .                             | 80 |
| 6.2 | Vacuum finger for flip-chip assembly. . . . .                                         | 83 |
| 6.3 | Flip-chip assembly process. . . . .                                                   | 84 |
| 6.4 | Reference resonator response. . . . .                                                 | 86 |

|      |                                                                                                     |     |
|------|-----------------------------------------------------------------------------------------------------|-----|
| 6.5  | Spin resonance of a $\text{TbInO}_3$ film in the flip-chip geometry. . . . .                        | 88  |
| 6.6  | Collective mode dispersion of $\text{Gd}_2\text{Ti}_2\text{O}_7$ mapped with CPW harmonics. . . . . | 89  |
| 6.7  | Temperature dependence of the $\text{Gd}_2\text{Ti}_2\text{O}_7$ response. . . . .                  | 91  |
| 7.1  | Three classes of correlated phase in flatband vdW materials. . . . .                                | 98  |
| 7.2  | Open problems in flatband vdW superconductivity. . . . .                                            | 101 |
| 8.1  | CAD layout of the hybrid resonator architecture. . . . .                                            | 105 |
| 8.2  | Tenting during stack meltdown. . . . .                                                              | 110 |
| 8.3  | Spalling of superconducting contacts. . . . .                                                       | 111 |
| 8.4  | Residual stress of Ti/Nb/Al contact metallizations. . . . .                                         | 112 |
| 8.5  | Contacts deposited with the stress-compensated recipe. . . . .                                      | 113 |
| 8.6  | Substrate leakage through the filter capacitors. . . . .                                            | 114 |
| 8.7  | Complete fabrication sequence for a hybrid vdW device. . . . .                                      | 116 |
| 9.1  | Device fabrication flow. . . . .                                                                    | 119 |
| 9.2  | Gate-tunable bilayer graphene Josephson junction terminating a microwave resonator. . . . .         | 121 |
| 9.3  | Gate tuning of the resonator frequency. . . . .                                                     | 122 |
| 9.4  | Resonator-based extraction of the Josephson inductance. . . . .                                     | 123 |
| 9.5  | Temperature dependence of the supercurrent and resonator response. . . . .                          | 125 |
| 9.6  | Bias dependence of the resonator response at different gate voltages. . . . .                       | 127 |
| 9.7  | Resonator frequency as a quantitative probe of junction inductance. . . . .                         | 129 |
| 9.8  | Gate-dependent modes at higher frequencies. . . . .                                                 | 131 |
| 10.1 | vdW hallbar embedded in hybrid resonator architecture. . . . .                                      | 135 |
| 10.2 | Simultaneous transport and microwave response of a hybrid Hall bar. . . . .                         | 136 |
| 10.3 | Load impedance presented to the resonator by a hybrid Hall bar. . . . .                             | 138 |
| 10.4 | Transport and microwave response of a second hybrid Hall bar over an extended gate range. . . . .   | 140 |
| 10.5 | Absence of superconductivity in two hybrid BBG/ $\text{WSe}_2$ Hall bars. . . . .                   | 142 |
| 10.6 | Fabrication of a dual-graphite-gated hybrid device. . . . .                                         | 144 |
| 11.1 | Four directions for future experiments. . . . .                                                     | 147 |
| A.1  | Definition and cascading of ABCD matrices. . . . .                                                  | 153 |
| A.2  | ABCD matrix terminated by a load impedance $Z_L$ . . . . .                                          | 155 |
| C.1  | Wafer-scale marker pattern for $\text{SiO}_2/\text{Si}$ chips. . . . .                              | 159 |
| C.2  | Marker pattern for hybrid device wafers. . . . .                                                    | 160 |

|     |                                                                   |     |
|-----|-------------------------------------------------------------------|-----|
| D.1 | Process flow for flake exfoliation. . . . .                       | 165 |
| E.1 | Effect of the O <sub>2</sub> etch on multilayer graphene. . . . . | 167 |
| G.1 | Custom microwave probe for the VTI. . . . .                       | 188 |
| H.1 | Electron thermometry from meso-wire resistance. . . . .           | 192 |
| H.2 | Cryogenic microwave wiring. . . . .                               | 193 |
| H.3 | Microwave wiring inside the fridge. . . . .                       | 194 |
| H.4 | Room-temperature microwave electronics. . . . .                   | 195 |
| I.1 | 3D-printed coax straightening tool. . . . .                       | 197 |
| I.2 | Trap holder for baking carbon powder traps. . . . .               | 198 |

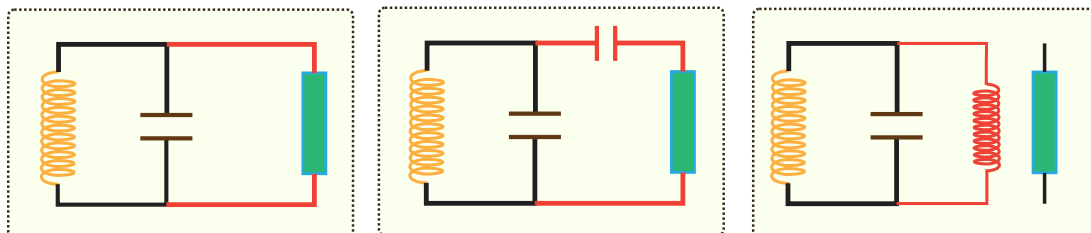


# List of Tables

|     |                                                                                                                                                           |     |
|-----|-----------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| E.1 | Plasma etch recipe: O <sub>2</sub> descum with cooldown step. . . . .                                                                                     | 167 |
| E.2 | Plasma etch recipe: O <sub>2</sub> descum, cycled CHF <sub>3</sub> etch with cooldown, and final O <sub>2</sub> descum. . . . .                           | 168 |
| E.3 | Plasma etch recipe: CF <sub>4</sub> etch with cooldown step. . . . .                                                                                      | 169 |
| E.4 | XeF <sub>2</sub> etch recipe. . . . .                                                                                                                     | 169 |
| E.5 | ICP plasma etch recipe: O <sub>2</sub> descum, CF <sub>4</sub> /O <sub>2</sub> /Ar etch, and final O <sub>2</sub> descum, with<br>cooldown steps. . . . . | 170 |
| E.6 | ICP plasma etch recipe: O <sub>2</sub> descum, Cl <sub>2</sub> /BCl <sub>3</sub> etch, and final O <sub>2</sub> descum, with<br>cooldown steps. . . . .   | 170 |
| E.7 | Electron-beam evaporation log: Cr/Au (5/75 nm) on the KJL evaporator. . . . .                                                                             | 171 |
| E.8 | Reactive magnetron sputter deposition recipe for NbTiN. . . . .                                                                                           | 172 |
| E.9 | E-beam deposition recipe: Ti/Nb/Al trilayer with static oxidation. . . . .                                                                                | 173 |
| G.1 | Hardware used in the VTI probe. . . . .                                                                                                                   | 189 |
| H.1 | Hardware used in the Pink Fridge microwave setup. . . . .                                                                                                 | 196 |
| K.1 | Commonly used physical constants in uncommon units. . . . .                                                                                               | 202 |

## Part I

# Foundations



# Chapter 1

## Introduction

Historians rely on the dominant material of a certain time period to demarcate distinct periods in the development of human civilization. Copper age, Bronze age, and Iron age thus correspond to periods in human history when it became possible to isolate, purify, process and shape these materials into objects of everyday use. The discovery of semiconductors in the early 20th century marked another such moment in human history. In particular, the development of silicon transistors and semiconductor technology led to a revolution in telecommunications, electrical appliances and computers. Hence, we are justified in referring to the 20th century as the Silicon Age. As we are passing into the second quarter of the 21st century, we can wonder what might be an appropriate name for this century.

A growing consensus among researchers seems to suggest that a study of quantum science and quantum materials is a fruitful direction for furthering technological development. The promise of quantum computers in solving currently computationally infeasible problems on classical computers is too strong to be ignored. It is then not a big surprise that many corporations and even governments have made it a priority to devote resources for the development of quantum computers. The United Nations declared 2025 as the International Year of Quantum Science and Technology [1]. It wouldn't be a surprise if future historians refer to the 21<sup>st</sup> century as the quantum century.

There is more to the quantum revolution than the engineering of quantum computers. At the frontier of material science lies the discovery of materials where long-range entanglement between the constituent degrees of freedom plays a central role in determining the materials' properties. Superconductors and Quantum Spin Liquids are examples of such materials, which we will focus on in this thesis. As the physical phenomena underlying the emergent states in these materials arise from counter-intuitive quantum effects, understanding these materials requires developing new probes and designing clever strategies to eke out the emergent properties of the ground state. There lies a gap between tools used in materials characterization which rely on classical sensors and the potential for incorporating quantum entanglement between sensors and quantum materials. We shall

aim to take the first steps towards bridging this gap by developing experimental strategies which use superconducting circuits, a building block of superconducting qubits, to probe quantum materials.

## 1.1 Emergent phases in quantum materials

Quantum physics plays a decisive role in the behavior of all materials [2]. Right from the chemical bonds which give structural integrity to crystalline lattices to the macroscopically degenerate ground state of a Bose-Einstein condensate, quantum physics provides a framework for us to model, understand and predict the properties of materials. In recent years, there has been a growing interest in the characterization of materials where quantum effects manifest themselves over a wide range of energy and length scales. Dubbed as quantum materials [2, 3, 4], this category of materials includes a wide range of materials such as superconductors, topological insulators, topological semi-metals, quantum spin liquids and so on.

What exactly characterizes a quantum material? We can use the following rough criterion: materials which have a distinctive physical property, say for example superconductivity, and for which the distinctive property does not have a classical description qualify to be referred to as *quantum materials*. At the heart of such distinctive properties is the entangled nature of the electronic wavefunction. Interactions associated with the spin, charge, lattice and orbital degrees of freedom compete with the kinetic energy and this competition favors novel phases. The delicate balance between these interactions also means that the ground state is anomalously sensitive to external stimuli. Depending on which interactions dominate, this competition stabilizes distinct classes of emergent phases, summarized in Fig. 1.1: broken-symmetry phases described by a local order parameter, topological phases classified by invariants of the band structure rather than any local order [5], and frustrated magnets in which no ordering pattern can satisfy all interactions at once, opening the door to entangled ground states such as quantum spin liquids [6, 7]. Experimental realization of quantum phases of matter and exerting control over their properties is central to realizing a new generation of electronic and optical devices which can potentially host unimaginable functionalities. Not only are these discoveries of intellectual value, but also quantum materials are poised to have a significant societal impact through their technological applications.

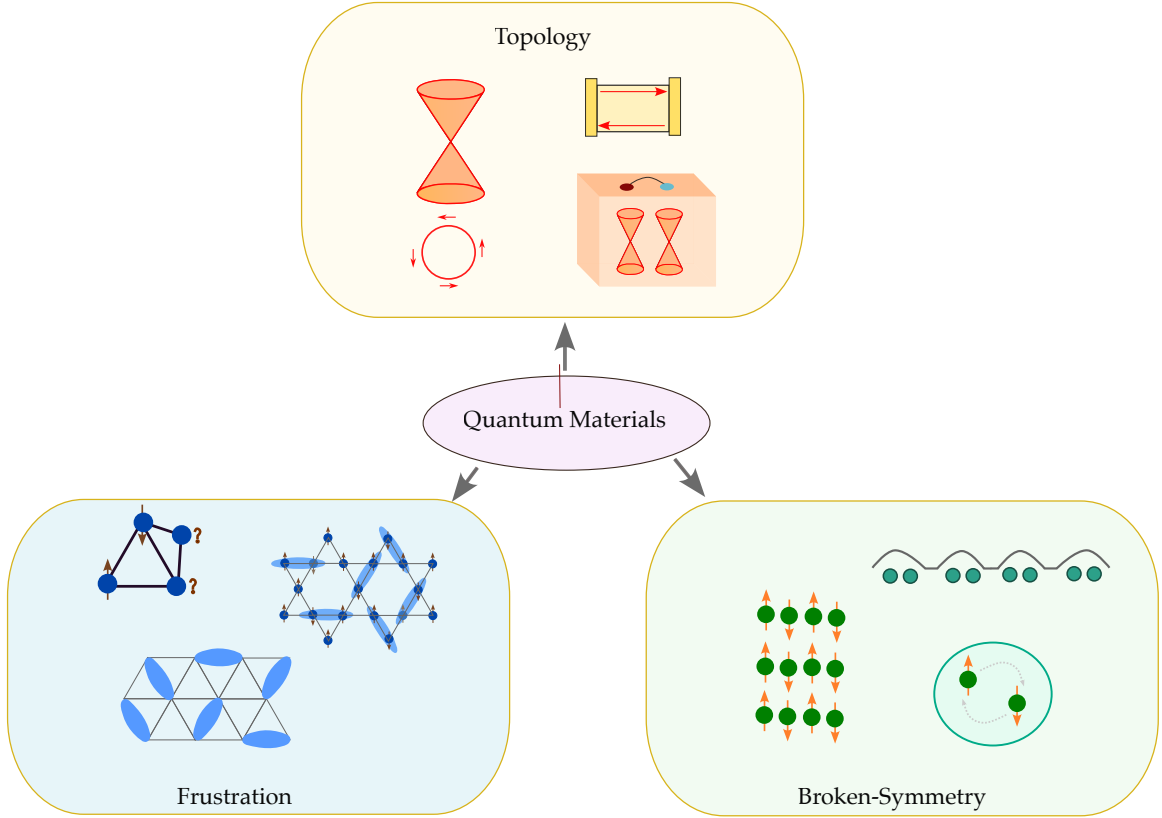


Figure 1.1: **Broad classes of quantum materials.** *Topology*: phases with a non-trivial topological invariant of the electronic band structure, which support spin-momentum-locked surface states with a Dirac dispersion; quantum Hall systems with dissipationless edge channels; and Dirac/Weyl semimetals with Fermi arcs on the surface. *Broken-Symmetry*: phases described by a local order parameter within the Landau paradigm, such as magnetic order (broken spin-rotation symmetry), charge density waves (broken lattice translation symmetry), and superconductivity (broken  $U(1)$  gauge symmetry), where electrons bind into Cooper pairs. *Frustration*: lattices on which competing interactions cannot be simultaneously satisfied, which can stabilize highly entangled ground states such as the resonating valence bond (RVB) state, a superposition of spin-singlet coverings of the lattice.

## 1.2 Superconducting circuits as sensors of quantum matter

Just as there are many classes of quantum materials, many distinctive probes of such materials have been developed which employ coupling to various charge, spin, lattice and orbital degrees of freedom [3]. We will cover many examples of such probes in chapter 2. The probes span a wide range of energies from low-frequency electrical conductivity at basically zero energy to X-ray scattering experiments at eV energies. We will be interested in the microwave i.e.  $\mu\text{eV}$  energy range in this thesis. As it turns out, a very sensitive detector and a mature set of experimental methods are

available to us at these energy scales — the superconducting microwave resonator.

What makes the superconducting microwave resonator so special and uniquely suited to the study of certain quantum materials? First, these resonators can concentrate electromagnetic fields within their footprint thereby enhancing the coupling to various observables of interest. Second, the energy scale offered at microwave frequencies is the right scale to study phenomena associated with mK to few K temperatures, typically achieved today in dilution cryostats. Third, with the right type of superconductors with a high enough critical temperature and resilience to magnetic field, we can use resonators as a probe of physical properties at mK to few K temperatures and from zero to few hundred mT magnetic fields. We can potentially map out the temperature-magnetic field phase diagram. However, challenges remain in designing appropriate devices to effectively probe properties of quantum materials. These challenges are not limited to resonator design, but also include choosing the coupling strategy to observables we care about, building a readout strategy for the material properties we seek to understand and finally implementing a microwave measurement setup capable of doing the desired measurements. By the end of this thesis, I hope to convey certain strategies to resolve these challenges, walk through the choices made to design appropriate devices and provide a guide to the interpretation of resonator characteristics in terms of material properties.

### 1.3 Thesis Outline

This thesis consists of two applications of superconducting circuits to the study of quantum materials: magnetic spin resonance in frustrated magnets (Part II) and a hybrid superconducting circuit architecture for probing superconductivity in van der Waals (vdW) heterostructures (Part III). Part I covers the foundations required to read the two later parts which can be read independently of each other. Part IV concludes with an outlook on future experiments.

Chapter 2 introduces the basic principles associated with collective phases in quantum materials: order parameters under the Landau paradigm, topological order beyond Landau theory, and commonly used probes of quantum materials. We will close by discussing what microwave frequencies can tell us about the dynamical spin susceptibility of frustrated magnets and the superfluid stiffness of vdW superconductors.

Chapter 3 introduces the main tool used in this thesis: *the superconducting resonator*. After a brief discussion of superconductivity, we will develop a formalism to analyze data from hanger-coupled superconducting resonators and discuss appropriate strategies for coupling resonators to materials' degrees of freedom. We will end with a discussion of magnetic resonance, which we will use in Part II to study frustrated magnetic systems.

Chapter 4 serves as an introduction to magnetic moments in solids. We will derive the susceptibility of a gas of free spin- $J$  moments and discuss the Curie–Weiss theory of ordered magnets at the mean-field level. After introducing the types of magnetic order, we will pivot to systems where

magnetic order is absent despite the presence of strong interactions — quantum spin liquids, spin ices, and spin glasses — which we will collectively refer to as frustrated magnets.

Chapter 5 discusses the first application of superconducting resonators to the quantum spin liquid candidate  $\text{TbInO}_3$ . While single-crystal studies of  $\text{TbInO}_3$  have been carried out over the past few years, epitaxial  $\text{TbInO}_3$  films were grown for the first time in Ref. [8]. We will couple these films to superconducting resonators and use spin resonance measurements to constrain the ground state of the  $\text{Tb}^{3+}$  moments.

Chapter 6 develops an alternate strategy for the study of frustrated magnets which does not require superconductor deposition or fabrication directly on the magnetic films. Using a flip-chip setup, we will study two frustrated magnets: the quantum spin liquid candidate  $\text{TbInO}_3$  and the Heisenberg pyrochlore antiferromagnet  $\text{Gd}_2\text{Ti}_2\text{O}_7$ .

Chapter 7 introduces vdW heterostructures assembled from 2D materials such as graphene, transition metal dichalcogenides (TMDs), and hBN. These heterostructures have become a fruitful platform in the search for correlated electronic phases. We will broadly review the classes of such phases, with a focus on superconductivity and the open questions surrounding it.

Chapter 8 brings back the superconducting resonator, now tasked with a new purpose: furthering our understanding of superconductivity in vdW heterostructures. We will develop a hybrid architecture capable of coupling vdW heterostructures to superconducting resonators. We will discuss the design criteria, challenges which arose during fabrication and solutions to those challenges.

Chapter 9 applies the hybrid architecture to measure the Josephson impedance of a vdW superconductor-normal-superconductor junction with Bernal bilayer graphene serving as the normal channel. Chapter 10 carries the hybrid architecture forward from junctions to Hall bars of Bernal bilayer graphene/ $\text{WSe}_2$  and rhombohedral graphene, reporting progress towards the application of the hybrid architecture developed in Chapter 8 to superfluid stiffness measurements of vdW superconductors.

Finally, Chapter 11 offers an outlook on future experiments enabled by the techniques developed in this thesis such as microwave resonance in pyrochlore spin ices and using mm-wave cavities for superconducting gap measurements of vdW superconductors.

## Chapter 2

# Probing many-body phases at microwave frequencies

One of the great triumphs of the first half of the 20th century was the discovery of the laws of quantum mechanics. Arguably, these laws along with the properties of fundamental particles (protons, neutrons and electrons) are sufficient to explain the behavior of all materials found in nature. However, knowing these laws does not bring any insights about commonly observed phenomena such as why metals are shiny, why liquids flow and solids don't, why some solids are transparent to light and so on. So then, how does one go about looking for unifying explanations of such phenomena from some common underlying principles? Condensed matter physics fills in this gap by providing a framework for the collective behavior of constituent atoms. Despite all materials being made up of electrons, protons, and neutrons, the ways in which these constituents organize are what lead to collective or many-body phases. In this chapter, we will begin with a basic description of many-body phases and unifying principles across the self-organization in these phases. We will then move on to studying the response of these phases to external perturbations and in the process introduce the concept of excitations of these phases. As we discussed in the previous chapter, one of the themes of this thesis is the probing of many-body phases through the lens of superconducting circuits. By the end of this chapter, we will identify two concrete observables: spin susceptibility and superfluid stiffness, which can be fruitfully probed at microwave frequencies.



## 2.1 Order parameters and the Landau paradigm

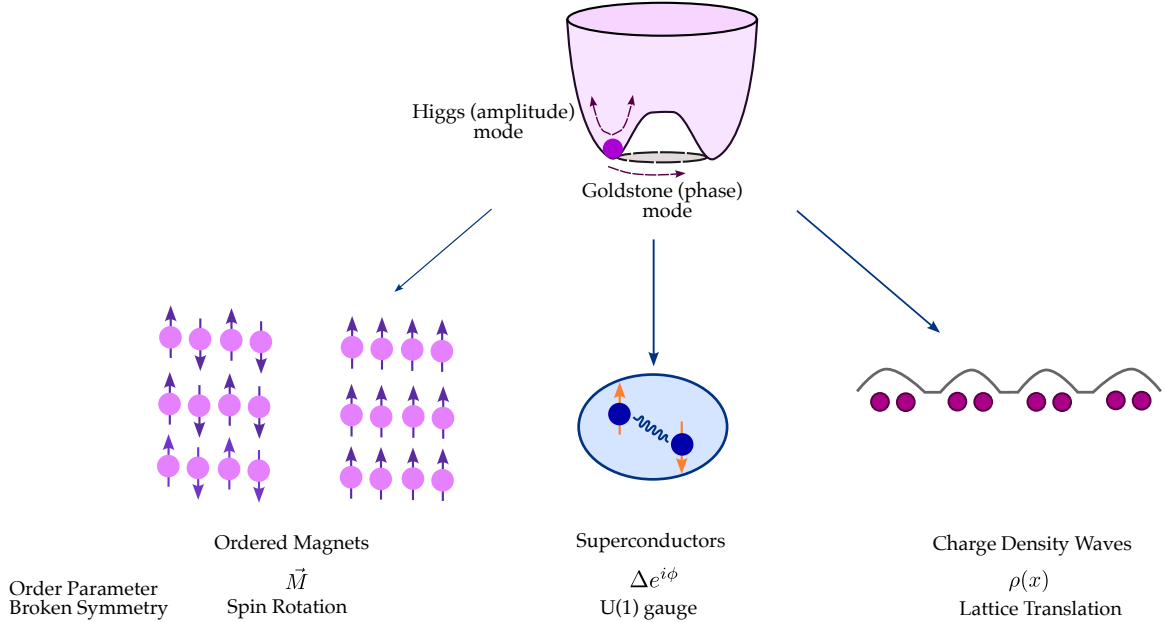


Figure 2.1: **Broken-symmetry phases and the Landau paradigm.** The Ginzburg–Landau free energy below a continuous phase transition takes the form of a “Mexican hat” in the space of the order parameter. The system spontaneously picks one of the degenerate minima (purple ball), breaking the symmetry of the free energy. Fluctuations about the minimum separate into two collective modes: a gapped amplitude (Higgs) mode along the radial direction and a gapless Goldstone mode along the flat phase direction, as guaranteed by Goldstone’s theorem. Three realizations are shown with their order parameters and broken symmetries: ordered magnets with magnetization  $\vec{M}$  (staggered magnetization for an antiferromagnet), breaking spin-rotation symmetry; superconductors with the complex pair amplitude  $\Delta e^{i\phi}$ , breaking  $U(1)$  gauge symmetry, with electrons bound into Cooper pairs; and charge density waves with a modulated charge density  $\rho(x)$ , breaking lattice translation symmetry.

If one word could encapsulate the excitement about condensed matter physics and quantum materials, it would be *emergence*. Superconductors, ordered magnets, topological insulators, Wigner crystals, Mott insulators, quantum spin liquids, charge density waves, and superfluids are all phases whose defining properties cannot be traced to any single atom or electron; they arise instead from the collective organization of some  $10^{23}$  interacting degrees of freedom [9, 2]. The first, and still most powerful, unifying description of such collective organization is due to Landau. In this framework, a phase of matter is characterized by the symmetries it spontaneously breaks, and the breaking is quantified by an *order parameter*. The order parameter is a real- or complex-valued function of the thermodynamic variables that vanishes identically in the disordered phase and acquires a nonzero

expectation value in the ordered phase [10]. Order parameters can be typically associated with emergent properties of the ordered phase. In a ferromagnet, the order parameter is the magnetization  $\vec{M}$ , which breaks spin-rotation symmetry; in an antiferromagnet it is the staggered magnetization on the ordering wavevector. In a superconductor the order parameter is the complex pair amplitude  $\Delta = |\Delta|e^{i\phi}$ , whose phase rigidity (energetic cost of spatial variations of  $\phi$ ) is directly responsible for zero resistance and the Meissner effect. Landau theory starts with the assumption that if a certain order parameter goes continuously to zero near a phase transition, then the free energy can be expanded in powers of the order parameter and its gradients. Known as the Ginzburg-Landau (GL) expansion, this series is constrained by symmetries satisfied by the order parameter. The GL expansion is remarkable as it can correctly predict the associated critical exponents with continuous phase transitions. Fig. 2.1 shows the characteristic form of the GL free energy together with three realizations of broken symmetry: ordered magnets, superconductors, and charge density waves. An ordered phase also holds collective excitations. When a continuous symmetry is spontaneously broken, Goldstone's theorem guarantees the existence of a massless collective mode. In quantifying the response of symmetry-broken phases to external dynamical perturbations, collective modes emerge as potential quasiparticles which can be excited from the ground state. Identifying an appropriate order parameter and the corresponding GL expansion is often enabled through the study of these collective excitations.

## 2.2 Beyond Landau: topological order and fractionalization

Landau's theory of phase transitions has been very successful at explaining experiments on most well-known phase transitions such as solid-liquid, ferromagnet-paramagnet, superconductor-metal, etc. The satisfactory nature of these results might lead one to conclude that all phase transitions are described by a Landau theory. Does that mean the physics of ordered phases in condensed matter is a solved problem and there is nothing left to be done? Before the discovery of the quantum Hall effect in 1980, this narrative was believed to be true. Around the same time, the theoretical descriptions of the BKT transition also emerged. High- $T_c$  superconductors along with many associated correlated phases such as strange metals and pseudo-gap phases were discovered. The fractional quantum Hall effect was seen in high-mobility GaAs quantum wells. These results required the development of theories beyond the Landau paradigm. What unifies phases which cannot be described by a Landau broken-symmetry theory? The easiest starting point is to consider topological aspects of the electronic wavefunction. For example, in the integer quantum Hall effect of 2D electron gases, the Chern number associated with an electronic band gives rise to an insulating bulk and a conductive edge. No symmetry is broken in realizing this state from an electron gas, but instead a topological winding of the electronic wavefunction in momentum space gives rise to the observed phenomenology. Similarly, in order to classify distinct phases which nevertheless

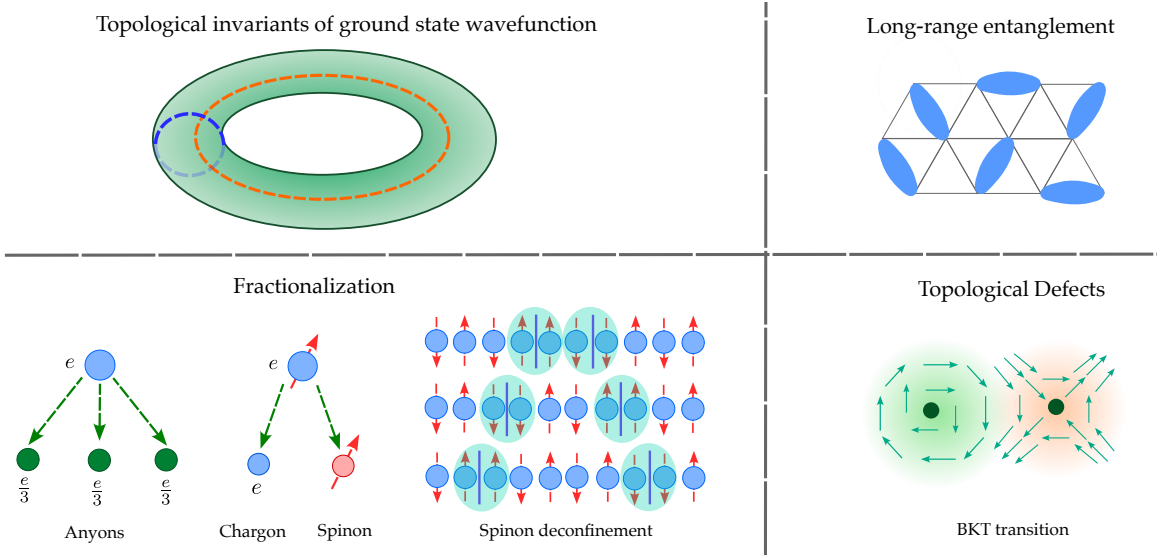


Figure 2.2: **Topological order.** *Topological invariants of the ground state wavefunction:* phases sharing the same symmetry are instead distinguished by topological invariants, illustrated by the two non-contractible loops of a torus. A topologically ordered ground state acquires a degeneracy that no local measurement can distinguish, reflecting the long-range entanglement of the ground state. *Long-range entanglement:* a resonating valence bond state is made of a coherent superposition of spin-singlet coverings of the lattice and realizes a highly-entangled ground state without breaking any symmetry. *Fractionalization:* the low-energy excitations carry quantum numbers that are fractions of those of the microscopic constituents: anyons of charge  $e/3$  in the  $\nu = 1/3$  fractional quantum Hall state, spin-charge separation of an electron into a chargon and a spinon, and spinon deconfinement in a one-dimensional antiferromagnet, where a single  $\Delta S = 1$  spin flip decays into two independently propagating  $S = 1/2$  domain walls. *Topological defects:* a vortex-antivortex pair of the  $XY$  model; the unbinding of such pairs drives the Berezinskii-Kosterlitz-Thouless (BKT) transition. A BKT transition is a phase transition without a symmetry-broken order parameter and is driven instead by the proliferation of topological defects.

share the same symmetry, we are led to introduce the concept of topological invariants [5]. These topological invariants essentially quantify the long-range entanglement of the ground state. Fig. 2.2 collects the concepts introduced in this section: topological invariants of the ground state, long-range entanglement, fractionalization, and topological defects. Topological order has the property of topological degeneracy which makes it highly attractive for quantum applications [5, 11]. As a result of topological degeneracy, the ground state of a many-body gapped system is robust against local perturbations. Since experimentally known sources of noise are typically local, perturbations by noise sources do not cause decoherence in qubits defined using topologically protected states. A second non-trivial aspect of topological order closely associated with topological degeneracy is the concept of fractionalization. In fractionalization, the quantum numbers of low-energy excitations of a many-body system are simple fractions of the quantum numbers associated with the non-interacting

constituent particles. For example, in fractional quantum Hall states such as the filling factor  $\nu = 1/3$  state, the electrical charge of the excitation is  $e/3$  where  $e$  is the charge of a bare electron. Even the spin of an electron can be fractionalized. In 1D spin chains with spin liquid states, a flipped spin can decay into two deconfined spin-1/2 spinon excitations [12]. Quantum spin liquids are magnetic incarnations of topologically protected phases [6, 13, 7]. In geometrically frustrated systems which we will discuss in Chapter 4, competing spin exchange interactions prevent the spins from ordering even at zero temperature. Instead the ground state is a massively entangled state consisting of superpositions between frustrated spin configurations. The excitations of this system are not the spin-1 magnons of an ordered magnet, but spin-1/2 spinons. Emergent gauge fields accompanying exotic excitations such as analogs of magnetic monopoles can also arise in such systems [13, 12].

### 2.3 Excitations and linear response

Whether a phase has a non-zero order parameter or has topological order without an order parameter, we experimentally probe it by applying an external perturbation and recording the response of the system. Depending on the precise nature of the perturbation, e.g. electric, magnetic, optical, neutron beams, etc., we can extract specific response functions of the ground state through these measurements. Linear response theory is the appropriate framework for understanding these measurements [14]. Let's consider an observable  $\hat{A}$  which is perturbed through a weak field  $h(t)$ . This corresponds to the presence of an additional term in the total Hamiltonian

$$H_1(t) = h(t)A(t) \quad (2.1)$$

When we calculate the evolution of quantum states under this perturbation, we can show that the change in expectation value of  $\hat{A}$  to first order is given by following simple formula

$$\delta\langle\hat{A}(t)\rangle = \int_{-\infty}^t dt' \chi(t, t') h(t'), \quad (2.2)$$

where the dynamical susceptibility  $\chi(t, t')$  is given by the following expression:

$$\chi(t) = \frac{i}{\hbar} \theta(t) \langle [\hat{A}(t), \hat{A}(0)] \rangle \quad (2.3)$$

$\theta(t)$  is the Heaviside step function. As the change in observable  $\delta\langle\hat{A}(t)\rangle$  is directly proportional to the applied field  $h(t)$ , the response is said to be linear and the corresponding theoretical framework is called linear response theory. Going to frequency space, we can simplify the above definition of

the generalized susceptibility for time-invariant systems into the following:

$$\delta\langle\hat{A}(\omega)\rangle = \chi(\omega)h(\omega) \quad (2.4)$$

If we include spatial degrees of freedom as well, the generalized susceptibility  $\chi(\vec{q}, \omega)$  is a function of a wave-vector  $\vec{q}$  and frequency  $\omega$ .  $\chi(\vec{q}, \omega)$  plays a central role in many-body physics as its poles locate the collective modes and the imaginary part captures the dissipation and lifetime of these collective modes. Through the fluctuation-dissipation theorem,  $\chi(\vec{q}, \omega)$  also connects to equilibrium fluctuations of the system [14]. Most experimental probes of quantum materials are, at their core, a measurement of some  $\chi(\vec{q}, \omega)$  in response to an external perturbation. A neutron measures the spin-spin correlation function; an optical photon measures the current-current correlation function at  $\vec{q} \approx 0$ ; a transport measurement takes the additional  $\omega \rightarrow 0$  limit.

## 2.4 The probe landscape

The experimentalist's toolbox can be organized along three axes: the energy (frequency) scale probed, the momentum resolution, and the coupling channel (charge, spin, or lattice) [3]. Fig. 2.3 arranges the principal probes of quantum materials along the first of these axes. At the high end of the energy scale, X-ray scattering and photoemission resolve internal atomic structure at the eV energy scale and above. Neutron scattering covers the meV range and is the gold standard for probing magnetic phenomena. A beam of neutrons carrying no charge and a spin-1/2 moment couples to magnetic moments which in turn affect the energy and momentum of the neutrons. The dynamical structure factor  $S(\vec{q}, \omega)$  measured by neutron scattering carries information about magnetic structure and excitations across the entire Brillouin zone. THz spectroscopy also covers the meV range and typically probes the zero momentum response of the charge degree of freedom. Low frequency quasi-DC transport sits at the opposite end of the energy range and measures the  $\omega \rightarrow 0$  charge conductivity of the material. Momentum resolution offers another equally sharp classification. On one extreme end, spatial resolution on the order of lattice spacing is provided by X-ray scattering techniques. Similarly, neutrons whose thermal de Broglie wavelength ( $\lambda_T \approx \frac{h}{\sqrt{2mk_BT}}$ ) is comparable to lattice constants in typical solids, map the dynamical structure factor  $S(\vec{q}, \omega)$  across the entire Brillouin zone. Angle-resolved photoemission (ARPES) is also capable of momentum resolution across the Brillouin zone. At the opposite extreme are long-wavelength probes such as optical and THz absorption, quasi-DC transport and the microwave resonator techniques described in this thesis. These long-wavelength probes are only capable of measuring  $\vec{q} \approx 0$  properties of materials. Between these two ends sit scanning probe techniques: scanning tunneling microscopy (STM), scanning NV microscopy, microwave impedance microscopy (MIM), scanning SQUID, etc [15]. These techniques, by virtue of their localized spatial sensitivity, can resolve properties right from the lattice scale of

$\sim 0.1$  nm in STM to  $\sim 1$   $\mu$ m for scanning SQUID. By Fourier duality, these scanning probes integrate broadly over momentum when scanning a narrow spatial range and are the natural choice for studying inhomogeneous materials. Surveyed this way, the landscape reveals a conspicuous gap on the energy scale. The characteristic energy scales of the phases studied from mK to a few K temperatures lie in the  $\mu$ eV range. This is exactly the energy of GHz and mm-wave photons. In this thesis, we will encounter two broad material systems: (a) frustrated magnets which have exchange couplings on the order of 10 K, yet fail to order even down to 50 mK; (b) vdW superconductors with critical temperatures on the order of 200–300 mK. As  $50$  mK  $\approx 1$  GHz, we can probe at energy scales appropriate to the physics of these material systems. Practically, we need a device element with the following requirements: (i) ability to store microwave photons from 50 mK to a few K temperatures; (ii) a coupling channel (electric/magnetic) to the generalized susceptibilities of interest; and (iii) readout architecture which encodes the material properties into easily measurable quantities of the device element. Today, drawing from advances in planar superconducting circuits, we have access to such a device element: the superconducting microwave resonator.

## 2.5 The microwave window: spin susceptibility and superfluid stiffness

The two parts of this thesis sit on opposite sides of the divide between broken-symmetry phases described by an order parameter and topological order in quantum spin liquids. In Part II, we will come across frustrated magnetic systems in which the measurable quantity is not an order parameter but the low-energy dynamics of the underlying spins in the ground state. By using the technical formalism of electron spin resonance, we will show that resonator measurements can be used to extract the magnetic susceptibility of these systems. In Part III, we will study superconductivity, an exemplary broken-symmetry phase, and seek to experimentally probe superfluid stiffness and hence the scale of relevant phase fluctuations in recently discovered vdW superconductors. As we shall see, probing these materials with the help of superconducting resonators at microwave frequencies has the potential to yield remarkable insights into the behavior of many-body phases and their excitations in these systems. Let's start by understanding the basic design, fabrication and measurement principles of superconducting circuits.

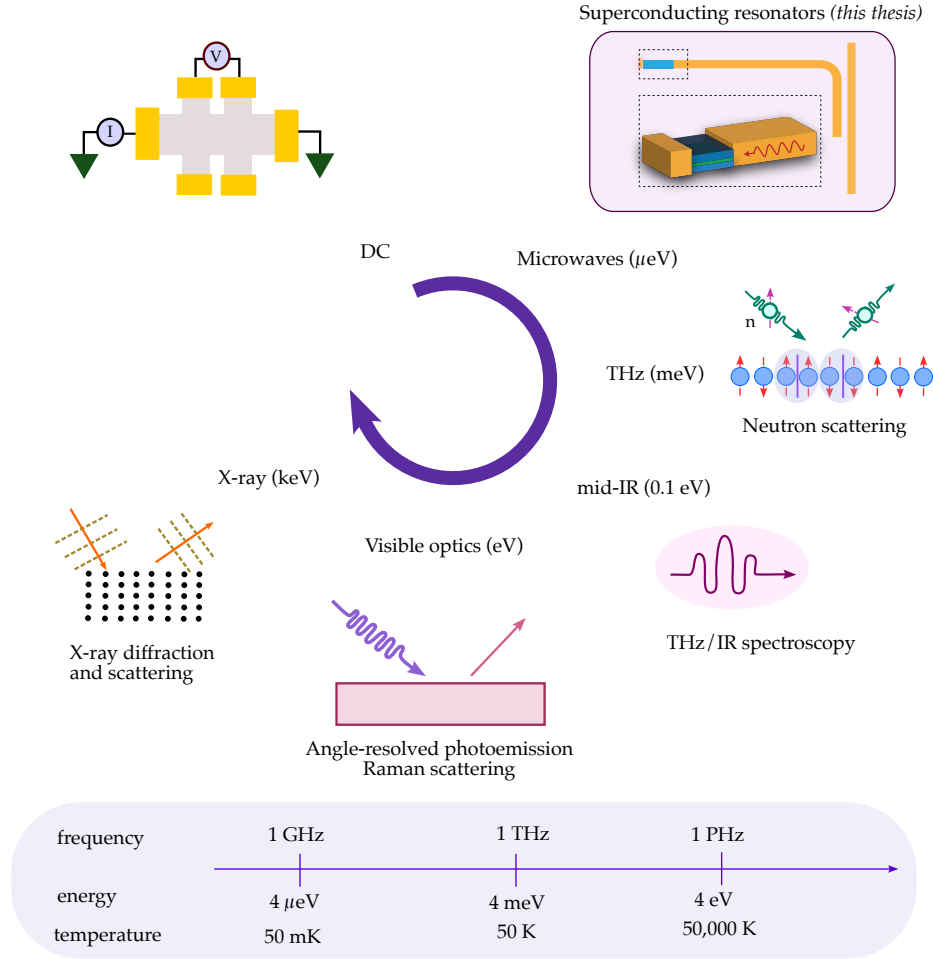


Figure 2.3: **The probe landscape across energy scales.** Probes of quantum materials arranged (clockwise) in order of ascending photon energy. Quasi-DC transport measures the  $\omega \rightarrow 0$  charge conductivity. Superconducting microwave resonators occupy the  $\mu\text{eV}$  window matched to the mK–K collective phenomena studied in dilution cryostats. Neutron scattering accesses the dynamical structure factor  $S(\vec{q}, \omega)$  at meV energies with momentum resolution across the Brillouin zone. THz and infrared spectroscopy probe the  $\vec{q} \approx 0$  charge and lattice response from meV to a few hundred meV. At eV scales, angle-resolved photoemission maps the occupied band structure and Raman scattering measures low-energy excitations such as phonons through inelastic light scattering. X-ray diffraction and scattering resolve structure at the lattice scale with keV photons. The bottom scale gives the conversion between frequency, energy, and temperature ( $1 \text{ GHz} \approx 4 \mu\text{eV} \approx 50 \text{ mK}$ ).

## Chapter 3

# Superconducting Circuits

In this chapter, we will briefly review superconducting circuits and introduce the primary technical probe of this thesis: the superconducting resonator. We will focus on understanding the properties of the superconducting resonator such as its frequency and intrinsic quality factor as being determined by the resonator’s environment. Such an approach naturally builds on the idea of using the resonator as a sensor, which will be used in the later chapters on experiments with various materials.

The chapter is organized as follows. We begin with a brief history of superconductivity and the London equations. In Sec. 3.3, we introduce kinetic inductance which controls the electrodynamic response of a superconducting film. We then introduce the superconducting resonator itself, contrasting three-dimensional cavities with the planar geometries used in this thesis, and specialize to the coplanar waveguide. The core of the chapter derives the transmission coefficient  $S_{21}$  of a hanger-coupled resonator, first for the familiar  $\lambda/4$  case and then for a resonator terminated by an arbitrary complex load. We will derive relations between a load impedance and the measured frequency and quality factors that we will rely on throughout Parts II and III. We close by deriving the inductance of a Josephson junction and by surveying the ways in which a resonator can be coupled to a condensed matter system. But first, let’s start with the phenomenon that makes these resonators even possible: superconductivity.

### 3.1 Superconductivity

Kamerlingh Onnes, motivated by a desire to investigate the universal applicability of van der Waals’ equation of state to the behavior of gases and liquids, set up a low-temperature physics laboratory at Leiden in the late 1880s [16]. After considerable effort and experimental ingenuity, he liquefied helium in 1908, which at the time was the last gas remaining to be liquefied. Onnes decided to investigate the resistivity of Pt wires and observed that the low temperature saturation resistivity depended sensitively on the impurity content of the wire. Mercury, being a liquid at room temperature,



can be readily purified by vacuum distillation. Hence, Onnes decided to investigate the resistance of mercury at liquid He temperatures and, in 1911, observed that the resistance drops to zero below 4.2 K. With this discovery began the field of superconductivity, which remains an active field of research even a century after the initial discovery. While the basic measurement does not require any sophisticated measurement apparatus beyond a multimeter and a cryostat (by today's standards), the discovery of the theoretical underpinnings involved in this particular correlated electron phenomenon has arguably been one of the crowning achievements of 20th century physics [17]. Today, the community continues to discover new superconductors at a steady pace, with tens of thousands of compounds known to be superconductors [18]. While superconductivity is a fascinating state of matter, the cryogenic temperatures required to maintain the superconducting state have restricted the use of bulk superconductors to applications in which the performance gain justifies the overhead of a cryostat. The most widespread of these is the superconducting magnet, which supplies the high and stable fields at the heart of nuclear magnetic resonance (NMR) spectrometers in analytical chemistry and of magnetic resonance imaging (MRI) scanners in medical diagnostics. A distinct set of practical applications began to emerge only after the discovery of the Josephson effect [19]. Superconducting quantum interference devices (SQUIDS) are the most sensitive magnetometers available [20]. Josephson junctions are used to define the voltage standard [21] and as a fundamental element in superconducting quantum processors [22].

### 3.2 London equations

As we will focus on high-frequency circuits made from superconductors later in this chapter, a good place to start is by understanding the response of the superconducting state to external electric and magnetic fields. The London equations are used to model the electrodynamics of superconductors [17]. We briefly review them in this section to establish a few concepts such as the superfluid density and penetration depth which we will encounter in later chapters. While a fully accurate description of a superconductor is possible using BCS theory, the conceptual simplicity of the London equations makes them a useful tool in designing superconducting circuits. The first London equation relates a supercurrent  $\vec{J}_s$  to the electric field  $\vec{E}$ .

$$\frac{\partial \vec{J}_s}{\partial t} = \frac{n_s e_s^2}{m_s^*} \vec{E} \quad (3.1)$$

Here,  $n_s$  is the density of Cooper pairs in the superconductor,  $e_s$  is the Cooper pair charge and  $m_s^*$  is the effective mass of the Cooper pair. Let's introduce  $\Lambda = \frac{m_s^*}{n_s e_s^2}$ . The second London equation describes the screening current generated in response to an external magnetic field, i.e. the Meissner effect.

$$\Lambda \nabla \times \vec{J}_s = -\vec{B} \quad (3.2)$$

Combining these two equations with Maxwell's equations, we can show that the magnetic field decays exponentially inside a bulk superconductor on a length scale  $\lambda_L = \sqrt{\frac{\Lambda}{\mu_0}} = \sqrt{\frac{m^*}{2\mu_0 n_s e^2}}$  known as the London penetration depth. Using the concept of the vector potential  $\vec{A}$ , we can combine both London equations into a single equation:

$$\vec{J}_s = -\frac{1}{\Lambda} \vec{A} \quad (3.3)$$

The above equation states that up to a scaling factor, the supercurrent induced in a superconductor is the same vector field as the vector potential  $\vec{A}$ . Note that since the vector potential is gauge dependent, we have to specify a gauge and this is known as the London gauge ( $\nabla \cdot \vec{A} = 0$ ,  $\vec{A}(\vec{r}) = 0$  with  $\vec{r}$  inside the superconducting bulk,  $\vec{A} \cdot \hat{n} = 0$  at a superconducting surface with normal  $\hat{n}$ ) [17]. At finite frequencies, a superconductor has a finite impedance with a real part from thermally excited quasiparticles and an imaginary reactive part from a generalization of the London equations to include non-local electrodynamics. This complex impedance can be calculated from the BCS theory of superconductivity and the results are known as the Mattis-Bardeen equations [23]. An excellent discussion of these equations is available in Gao's thesis [24]. For the experiments described in this thesis, we will work at temperatures  $T \ll T_c$  and frequencies  $\omega \ll \frac{\Delta}{\hbar}$  so that the real part of the complex impedance has a negligible effect on resonator dissipation. The imaginary part is known as the kinetic inductance and we will discuss it in the following section.

### 3.3 Kinetic inductance

A current in any metallic conductor induces a magnetic field around the conductor. Hence, any conductor can be regarded also as an inductor generating a flux from the flow of current. The reactive impedance corresponding to the inductance of a simple conductor like a straight wire is typically much smaller than the resistance at most frequencies from DC to even THz. In addition to this geometric inductance, the inertia of the charge carriers gives rise to a second contribution known as the kinetic inductance. Using Drude theory, it can be derived from the imaginary part of the frequency dependent complex conductivity:

$$\sigma(\omega) = \frac{ne^2\tau}{m^*} \frac{1}{1 + i\omega\tau} \quad (3.4)$$

If we invert the conductivity and interpret this as a sheet impedance for a film of thickness  $t$ , we get,

$$Z_{\square} = \frac{m^*}{ne^2\tau t} + i\omega \frac{m^*}{ne^2t} = R_0 + i\omega L_k \quad (3.5)$$

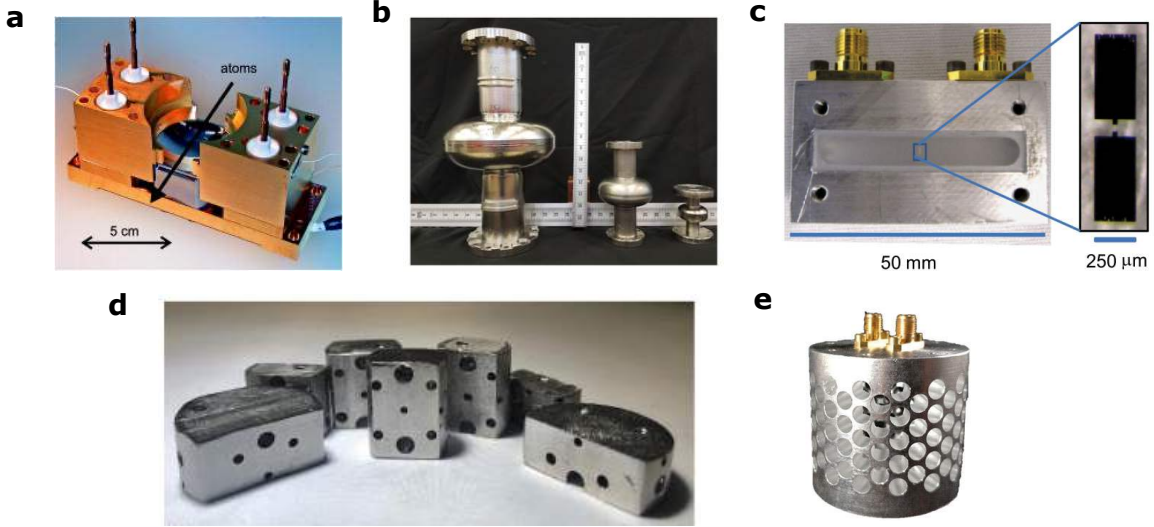
Here, we have introduced  $L_k$  to denote the kinetic inductance. Note that  $\omega L_k/R_0 = \omega\tau$ , and so for typical metals such as Au or Cu with scattering time  $\tau \approx 25$  fs, the reactive part is not a significant contribution to the complex impedance until frequencies  $\frac{1}{2\pi\tau} \approx 6$  THz. For superconductors, we can get a sense for the kinetic inductance by setting  $\tau \rightarrow \infty$  and the carrier mass/charge to be that of a Cooper pair. We get  $L_k = \frac{m^*}{2n_s e^2 t}$  where  $n_s$  is now the superfluid density, i.e. the density of Cooper pairs. Note that an accurate calculation of the reactive impedance requires the full Mattis-Bardeen equations. We can further simplify  $L_k$  by using the definition of the London penetration depth  $\lambda_L = \sqrt{\frac{m^*}{2\mu_0 n_s e^2}}$ .

$$L_k = \mu_0 \frac{\lambda_L^2}{t} \quad (3.6)$$

### 3.4 The superconducting resonator: storing photons in a box

The simplest way to store light is to trap it in a cavity between two mirrors. The lower the reflection losses and transmission losses in the cavity medium, the longer is the average time spent by the photon in the cavity before dissipating into the environment. In a Fabry-Pérot cavity, a photon bounces back and forth between two mirrors and interferes, leading to a standing wave at frequencies when an integer number of half-wavelengths fit between the two mirrors. The quality factor  $Q$  counts roughly the number of times the photon bounces back and forth between mirrors before a certain fraction of the energy is lost to the environment. Cavities enclosing single atoms played a foundational role in the development of cavity quantum electrodynamics (QED). Using cavity QED techniques involving optical cavities, entangled atom-photon states were investigated for the first time, demonstrating that individual quantum systems can be measured and manipulated while preserving their coherence [25, 26]. At RF and microwave frequencies, nature offers us a mirror better than any dielectric coating: the superconductor. At temperatures much lower than the critical temperature, the dissipative part of the surface impedance of a superconductor is many orders of magnitude lower than any metallic conductor like copper or gold. For example, Nb at 2 K and 1.5 GHz has a surface resistance of about 20 nΩ compared to about 10 mΩ for copper [27]. As a result, any closed superconducting box of appropriate dimensions becomes a high quality factor cavity. Nb superconducting radio frequency (SRF) cavities used in particle accelerator research routinely reach remarkable quality factors of about  $10^{10}$ – $10^{11}$  (at 1.5 GHz and 1 K) [28]. Such 3D cavities have also been adopted by the superconducting qubit community for circuit QED experiments [29]. Recent work on Nb coaxial cavities also showed high quality factors  $Q \approx 10^9$ , and these cavities were used for transmon readout [30]. In a 3D cavity, most of the electromagnetic field lives in the vacuum away from the superconducting surface where the primary loss mechanisms reside, giving rise to these exceptionally high quality factors. These losses arise from two-level systems in the surface oxides and from adsorbates on the surface. Fig. 3.1 shows representative examples of these geometries ranging from the Fabry-Pérot mirrors used in cavity QED to accelerator, transmon and seamless

multimode designs.



**Figure 3.1: Types of 3D superconducting cavities.** (a) Ultrahigh-finesse Fabry-Pérot cavity formed by two superconducting Nb mirrors for cavity QED experiments in which Rydberg atoms cross the cavity mode. (b) TESLA Nb superconducting radio frequency (SRF) accelerator cavities of successively higher frequencies; such cavities reach quality factors above  $10^{10}$ , with single-photon lifetimes up to 2 s. (c) The 3D transmon architecture: a machined aluminum rectangular waveguide cavity hosting a sapphire chip with a single Josephson junction transmon (zoom). (d) Seamless machined millimeter-wave cavities for hybrid circuit and cavity QED experiments. (e) A seamless multimode flute cavity, monolithically formed by overlapping holes drilled from the top and bottom of a superconducting block, evacuating lossy seams from the mode volume. Panel (a) reprinted from S. Kuhr *et al.*, Appl. Phys. Lett. **90**, 164101 (2007), with the permission of AIP Publishing. Panel (d) reprinted from A. Suleymanzade *et al.*, Appl. Phys. Lett. **116**, 104001 (2020), with the permission of AIP Publishing. Panel (b) reprinted with permission from Ref. [31]. Copyright (2020) by the American Physical Society. Panel (c) reprinted with permission from Ref. [32]. Copyright (2011) by the American Physical Society. Panel (e) reprinted with permission from Ref. [33]. Copyright (2021) by the American Physical Society.

While the three-dimensional mode volume of a 3D cavity can give rise to high quality factors, it comes with a limitation: a reduction in coupling to two dimensional systems like thin films and vdW heterostructures. Planar resonators invert this trade-off by confining most of the cavity field to the volume around a 2D plane. These planar resonators can be patterned from superconducting films deposited on a substrate. Quality factors are modest, with  $Q \approx 10^5$ – $10^6$  being typical for optimized lithographic and etching processes [34]. But the concentration of the electromagnetic field into a microscopic volume is precisely what a probe of thin films or 2D materials needs: the field enhancement compensates for the tiny volume of sample available, and the evanescent decay of the field typically over a few  $\mu\text{m}$  above the chip plane means the resonator senses the thin film while remaining blind to the bulk substrate beneath. Planar resonators come in two broad

families: distributed resonators and lumped-element resonators. Distributed resonators are sections of transmission line, such as a coplanar waveguide (CPW) or a microstrip, whose boundary conditions quantize the modes. A line shorted at one end and open at the other resonates when a quarter wavelength fits the line ( $\lambda/4$ ), with harmonics at odd multiples of the fundamental, while a line open at both ends resonates at half-wavelength ( $\lambda/2$ ) and all integer multiples of the fundamental. Lumped-element resonators instead build the oscillator from a discrete interdigitated capacitor and meander inductor, compressing the footprint below the wavelength at the price of a less controlled mode profile. The mode structure fixes where each field lives: the shorted end of a  $\lambda/4$  resonator is a current antinode, where the magnetic field peaks, and the open end is a voltage antinode, where the electric field peaks. Fig. 3.2 shows the various types of planar resonators.

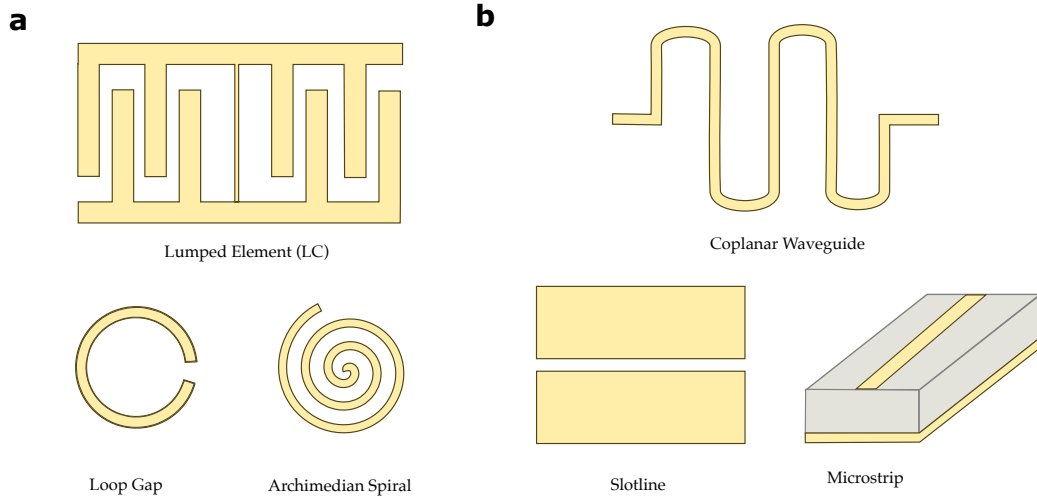


Figure 3.2: **Types of planar superconducting resonators.** (a) Quasi-lumped geometries: capacitance and inductance are supplied by distinct circuit elements with dimensions well below the wavelength: an interdigitated capacitor shunted by a strip inductor (lumped-element LC), a loop-gap resonator in which a single loop inductor closes on a narrow capacitive gap, and an Archimedean spiral, whose windings concentrate the microwave magnetic field at its center. (b) Distributed geometries: a section of transmission line resonates when an integer number of quarter- or half-wavelengths fits its length. Three kinds of distributed geometries are shown: a coplanar waveguide (CPW), a slotline and a microstrip. For a slotline, the mode lives in the slot between two ground planes. For a microstrip, the signal trace is separated from a backside ground plane by the substrate (gray). While a microstrip's mode lives inside the 3D volume of the substrate, since the ground plane is global, we can think of a microstrip as a quasi-2D resonator.

In order to make measurements of planar resonators, they are coupled to a wideband microwave feedline fabricated in proximity to the resonator. There are three main kinds of measurement

geometries: reflection, transmission and hanger. In a reflection geometry the resonator terminates a feedline and imprints itself on  $S_{11}$ ; in a transmission geometry it is embedded in series in the line; and in the hanger (or notch) geometry used throughout this thesis, the resonator is side-coupled (capacitively or inductively) to a feedline. One of the main advantages of the hanger geometry is that multiple resonators can be coupled to a feedline and each resonator appears as a narrow dip in the transmission coefficient  $S_{21}$ . A coplanar waveguide can be fabricated with a single-layer etch process, has a well-controlled impedance, and is free of deposited dielectrics that would add loss. In the next section, we will study coplanar transmission lines and resonators, which are primarily used for the experiments described in Parts II and III.

### 3.4.1 Coplanar transmission lines

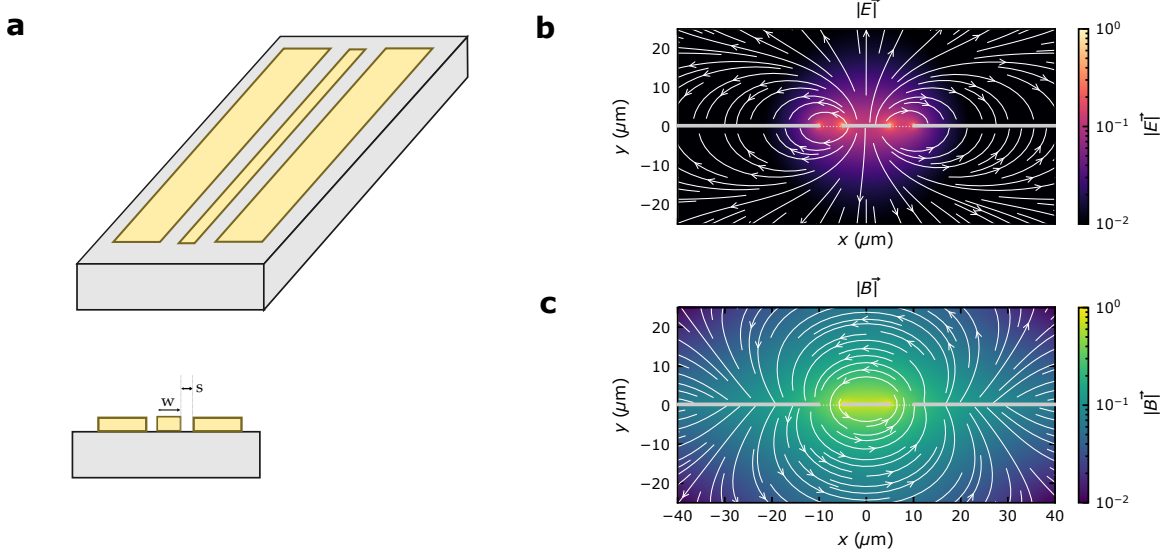


Figure 3.3: **Geometry of a coplanar waveguide.** (a) A coplanar waveguide consists of a center conductor of width  $w$  separated from two semi-infinite ground planes by gaps of width  $s$ , all patterned from a single superconducting film on a dielectric substrate (gray). The cross-section below defines  $w$  and  $s$ . (b) Magnitude (color, log scale, normalized) and direction (streamlines) of the electric field in the CPW cross-section, simulated using a finite-element solver for  $w = 10 \mu\text{m}$ ,  $s = 5 \mu\text{m}$  on a Si substrate ( $\epsilon_r = 11.5$ ). The electric field is concentrated in the two gaps between the center conductor and the ground planes. (c) Corresponding magnetic field, simulated with a uniform current density in the films: the field circulates around the current-carrying center conductor and peaks directly above and below it. Both fields decay evanescently within a few times  $(w + 2s)$  of the chip plane. This field confinement makes planar resonators sensitive probes of thin films placed on or near the surface.

Consider a coplanar waveguide as shown in Fig. 3.3. The simplest way to understand the coplanar structure of the waveguide is to imagine a coaxial cable for which the outer shield has been rolled out

into an infinite plane around the center conductor. Prior to the proposal of the coplanar waveguide by C.P. Wen [35], microwave waveguides on dielectric substrates such as microstrips had many disadvantages: the impedance would depend on the thickness of the substrate and shunt connections were not easily accessible as the ground plane was on the opposite side of the substrate. By moving both the center pin and the ground plane to one side of the substrate, the coplanar waveguide design alleviated the dependence on substrate thickness and was remarkably adaptable to fabrication processes used for integrated circuits. Let the direction of propagation along the coplanar waveguide be the  $z$ -axis. When an electromagnetic wave travels along the  $z$ -axis, time-varying electric  $\vec{E}$  and magnetic fields  $\vec{B}$  co-exist in the space around the waveguide. These fields can be decomposed into transverse components in the  $x$ - $y$  plane and longitudinal components along the  $z$ -axis. For a perfect TEM mode, the longitudinal components of  $\vec{E}$  and  $\vec{B}$  vanish. Using Maxwell's equations for a coplanar waveguide in a homogeneous medium, it is possible to show that TEM modes are valid solutions for such a waveguide [24]. However, real coplanar waveguides are fabricated on a substrate and conductors do have a finite surface impedance. As a result, perfect TEM solutions are not possible. Instead a coplanar waveguide supports quasi-TEM modes in which the longitudinal component is much smaller than the transverse components. The ratio of these two components is approximately  $w/\lambda$ , where  $w$  is the width of the center conductor and  $\lambda$  is the wavelength of the quasi-TEM mode. Typically,  $w \approx 1\text{--}100\text{ }\mu\text{m}$  while  $\lambda \approx \text{mm--cm}$  at microwave frequencies; the longitudinal components are a few percent or even smaller for most coplanar waveguide structures we will encounter in this thesis. From now on, we will assume perfect TEM modes travel along these coplanar waveguides for simplicity. Transmission lines are modeled as a cascade of distributed inductors and capacitors along with any dissipative elements using transmission line theory. Pozar's book, *Microwave Engineering*, is the standard reference for these topics [36]. We will review certain results to aid the design and modeling of specific superconducting circuits used in later chapters. For a transmission line with series inductance  $L$  and resistance  $R$ , and shunt capacitance  $C$  and conductance  $G$ , all per unit length, the telegrapher's equations give us the impedance  $Z_0$  and the propagation constant  $\gamma$ .

$$Z_0 = \sqrt{\frac{R + j\omega L}{G + j\omega C}} \quad (3.7)$$

$$\gamma = \sqrt{(R + j\omega L)(G + j\omega C)} \quad (3.8)$$

In the low-loss limit these reduce to  $Z_0 \approx \sqrt{L/C}$  and  $\gamma \approx \alpha + j\omega\sqrt{LC}$ , identifying the phase velocity  $v_p = 1/\sqrt{LC}$  and  $\beta = \omega/v_p$ . Note that  $L$  here is the *total* series inductance per unit length; for a superconducting line it contains both the geometric and the kinetic contributions (Sec. 3.3). Consider a transmission line with characteristic impedance  $Z_0$  and complex propagation constant



$\gamma = \alpha + j\beta$ . Let this transmission line be terminated with impedance  $Z_L$ . The impedance at length  $l$  from the termination is given as:

$$Z(l) = Z_0 \frac{Z_L + Z_0 \tanh(\gamma l)}{Z_0 + Z_L \tanh(\gamma l)} \quad (3.9)$$

### 3.5 $S_{21}$ for hanger resonators

We will derive a generalized  $S_{21}$  for hanger resonators capacitively coupled to a feedline and terminated by an arbitrary complex impedance  $Z_L$ . We will later see that well known cases such as termination by a short ( $\lambda/4$  resonator) and termination by an open end ( $\lambda/2$  resonator) are limiting cases which set  $Z_L = 0$  and  $Z_L \rightarrow \infty$  respectively.

#### 3.5.1 Resonator terminated by a short: $\lambda/4$ resonator

In this subsection, let's start by deriving the complex scattering coefficient  $S_{21}(\omega)$  for a hanger coupled  $\lambda/4$  resonator. We will assume that the resonator is coupled to a feedline through a capacitor  $C_c$ . We will see that  $S_{21}$  will trace out a circle in the complex plane and properties of this circle can be used to extract the resonator frequency, intrinsic quality factor, and coupling quality factor of the resonator. We will also discuss imperfections in transmission lines and how they affect the ideal  $S_{21}$  for a hanger coupled resonator. The derivations in this section are based on scattering coefficient theory in [37]. For a coplanar transmission line, the impedance of a section of length  $l$  shorted at one end is given as (set  $Z_L = 0$  in Eq. 3.9),

$$Z(l) = Z_r \tanh(\gamma l) \quad (3.10)$$

where  $\gamma = \alpha + j\beta$  is the propagation constant.  $\beta = \omega/v_p$  where  $v_p$  is the phase velocity of the transmission line. We will expand the  $\tanh$  around a frequency  $\omega_0$  such that  $\omega_0 l/v_p = \pi/2$ . Let  $\Delta = \omega - \omega_0$ . Note that  $\omega_0$  is not the actual resonance frequency of the  $\lambda/4$  mode as we will soon derive a small correction from the presence of a coupling capacitor.

$$Z(l) = Z_r \tanh(\alpha l + j\Delta l/v_p + j\pi/2) \quad (3.11)$$

$$= Z_r \coth(\alpha l + j\Delta l/v_p) \quad (3.12)$$

$$= \frac{Z_r}{\tanh(\alpha l + j\Delta l/v_p)} \quad (3.13)$$

$$\approx \frac{Z_r}{\alpha l + j\Delta l/v_p} \quad (3.14)$$

$$= \frac{Z_r}{\alpha l + j\pi\Delta/(2\omega_0)} \quad (3.15)$$



We have used the fact that the dissipative loss per unit length  $\alpha$  and the shift in frequency from the presence of the coupling capacitor  $\Delta$  are small quantities in order to expand  $\coth$  to first order. These assumptions are justified for resonators typically encountered in experiments. The total impedance  $Z_t$  presented to the feedline in a hanger geometry also includes a series contribution from a coupling capacitor  $C_c$ .

$$Z_t = Z(l) + \frac{1}{j\omega C_c} = \frac{Z_r}{\alpha l + j\pi\Delta/(2\omega_0)} + \frac{1}{j\omega C_c} \quad (3.16)$$

Resonance occurs when  $\text{Im } Z_t = 0$ . Let's simplify  $Z_t$  into its real and imaginary parts.

$$Z_t = \frac{Z_r}{\alpha l + j\pi\Delta/(2\omega_0)} + \frac{1}{j\omega C_c} \quad (3.17)$$

$$= \frac{Z_r(\alpha l - j\pi\Delta/(2\omega_0))}{(\alpha l)^2 + (\pi\Delta/(2\omega_0))^2} - \frac{j}{\omega C_c} \quad (3.18)$$

$$= \frac{Z_r\alpha l}{(\alpha l)^2 + (\pi\Delta/(2\omega_0))^2} - j \frac{Z_r\pi\Delta/(2\omega_0)}{(\alpha l)^2 + (\pi\Delta/(2\omega_0))^2} - \frac{j}{\omega C_c} \quad (3.19)$$

Let  $\omega = \omega_r$  such that the imaginary part of the above expression is zero. We will assume for now that we are in the low loss limit such that  $\alpha l \ll \frac{\pi|\omega_r - \omega_0|}{2\omega_0}$ .

$$\text{Im } Z_t = 0 \quad (3.20)$$

$$\frac{Z_r}{(\pi\Delta/(2\omega_0))} + \frac{1}{\omega_r C_c} = 0 \quad (3.21)$$

$$Z_r\omega_r C_c = -\frac{\pi(\omega_r - \omega_0)}{2\omega_0} \quad (3.22)$$

$$\omega_r = \frac{\pi}{2} \frac{1}{Z_r C_c + \frac{\pi}{2\omega_0}} \quad (3.23)$$

$$\omega_r = \omega_0 \frac{1}{1 + \frac{2\omega_0 Z_r C_c}{\pi}} \quad (3.24)$$

$$\omega_r \approx \omega_0 \left( 1 - \frac{2\omega_0 Z_r C_c}{\pi} \right) \quad (3.25)$$

To justify the low loss assumption we made before, we must have  $\alpha l \ll \omega_0 Z_r C_c$ . We will later see that  $\alpha l$  is approximately the inverse internal quality factor  $Q_i$  up to a  $O(1)$  scaling factor. So the assumption is approximately saying that  $Q_i \gg \frac{1}{\omega_0 Z_r C_c}$ . Now we will simplify the real part of  $Z_t$ .

$$\text{Re } Z_t = \frac{Z_r\alpha l}{(\alpha l)^2 + (\pi\Delta/(2\omega_0))^2} \quad (3.26)$$

$$\approx \frac{Z_r\alpha l}{(\pi\Delta/(2\omega_0))^2} \quad (3.27)$$

$$= \frac{Z_r\alpha l}{(\omega_0 Z_r C_c)^2} \quad (3.28)$$

Define  $Q_i$  and  $Q_c$  as follows. Note that we have not yet shown that these actually correspond to the internal and coupling quality factors respectively. Later, it will turn out when we derive the hanger  $S_{21}$  that these expressions indeed correspond to internal and coupling quality factors.

$$Q_i = \frac{\pi}{4\alpha l} \quad (3.29)$$

$$Q_c = \frac{\pi}{2\omega_0^2 C_c^2 Z_r Z_0} \quad (3.30)$$

Here, we have introduced  $Z_0$  as the impedance of the hanger feedline. We can rewrite the real part as,

$$\text{Re } Z_t = \frac{Z_0 Q_c}{2Q_i} \quad (3.31)$$

Going back to the imaginary part of  $Z_t$ , we are looking for an expansion around  $\omega = \omega_r$ . We have already shown that at  $\omega = \omega_r$ , the imaginary part vanishes. By a first order Taylor expansion,  $\text{Im } Z_t \approx (\omega - \omega_r) \frac{d \text{Im } Z_t}{d\omega} \Big|_{\omega_r}$ . We will work in the low-loss limit ( $\alpha l \ll 1$ ).

$$\frac{d \text{Im } Z_t}{d\omega} = \frac{1}{\omega^2 C_c} + \frac{Z_r}{\pi(\omega - \omega_0)^2 / (2\omega_0)} \quad (3.32)$$

When we evaluate the above derivative at  $\omega_r$ , the first term is  $\frac{1}{\omega_r^2 C_c}$  and the second term is  $\frac{\pi}{2\omega_0^3 Z_r C_c^2}$ . The second term is  $\frac{\pi}{2\omega_0 Z_r C_c}$  times the first term. We will make another assumption that the resonator is weakly coupled to the feedline, i.e.  $\omega_0 Z_r C_c \ll 1$ ; and so we can neglect the first term. Note that the second term can be written in terms of  $Q_c$  as  $\frac{\pi}{2\omega_0^3 Z_r C_c^2} = \frac{Z_0 Q_c}{\omega_0}$ .

$$\text{Im } Z_t \approx (\omega - \omega_r) \frac{Z_0 Q_c}{\omega_0} \quad (3.33)$$

$$= (\omega - \omega_r) \frac{Z_0 Q_c}{\omega_r} \quad (3.34)$$

Combining the real and imaginary parts, we get

$$Z_t \approx Z_0 Q_c \left[ \frac{1}{2Q_i} + j\delta \right] \quad (3.35)$$

where  $\delta = (\omega - \omega_r)/\omega_r$ . The  $S_{21}$  for a shunt impedance  $Z_t$  between the center pin and ground plane of a transmission line with impedance  $Z_0$  can be calculated using the ABCD matrix formalism.

Refer to Appendix A for a primer on ABCD matrices.

$$S_{21} = \frac{2}{2 + Z_0/Z_t} \quad (3.36)$$

$$= \frac{2}{2 + \frac{1}{Q_c} \left[ \frac{1}{2Q_i} + j\delta \right]^{-1}} \quad (3.37)$$

$$= \frac{\left[ \frac{1}{Q_i} + j2\delta \right]}{\frac{1}{Q_i} + \frac{1}{Q_c} + 2j\delta} \quad (3.38)$$

$$= \frac{\left[ \frac{Q_l}{Q_i} + j2Q_l\delta \right]}{1 + 2jQ_l\delta} \quad (3.39)$$

$$= 1 - \frac{Q_l/Q_c}{1 + 2jQ_l\delta} \quad (3.40)$$

where we have introduced the loaded quality factor  $\frac{1}{Q_l} = \frac{1}{Q_i} + \frac{1}{Q_c}$ . To handle imperfect reflections along the feedline which are observed in realistic measurement settings, a complex angle  $\phi$  is introduced as shown below.

$$S_{21} = 1 - \frac{Q_l e^{j\phi}/Q_c}{1 + 2jQ_l(\omega - \omega_r)/\omega_r} \quad (3.41)$$

Fig. 3.4 shows the response described by Eq. 3.41: the resonator appears as a narrow dip in the transmission amplitude on an otherwise flat background, accompanied by a rapid excursion in phase, and the same data trace out a circle in the complex plane whose diameter and off-resonant point encode  $Q_l/Q_c$ . The above functional form for  $S_{21}$  is sufficient to handle almost all measurements of hanger coupled resonators that we will discuss in this thesis. In practice, extracting quality factors from measured  $S_{21}$  traces is more subtle than the ideal lineshape suggests, and a substantial literature has grown around doing it correctly. The measured signal is dressed by the frequency-dependent gain and electrical delay of the full microwave chain, and impedance mismatches on the feedline rotate and distort the resonance circle in the complex plane. Fitting only the magnitude  $|S_{21}|$  discards half the information and biases the extracted  $Q_i$ ; the accepted practice is instead to fit the full complex data, exploiting the fact that Eq. 3.41 traces a circle in the complex plane. Ref. [24] gave the foundational geometric treatment of this circle; Ref. [38] showed that the naïve  $\phi$ -rotation treatment of asymmetric lineshapes deterministically overestimates  $Q_i$  and introduced the diameter correction method ( $Q_i^{-1} = Q_l^{-1} - \cos \phi/Q_c$ ) that removes this bias. Ref. [39] developed the algebraic circle fit and step-by-step background calibration algorithm that has become the community standard. Even with these methods, deviations persist: interference between the resonant signal and spurious background transmission paths produces Fano-type asymmetries that impose a systematic uncertainty on  $Q_i$  which grows with the coupling coefficient [40].  $Q_i$  itself is not a single

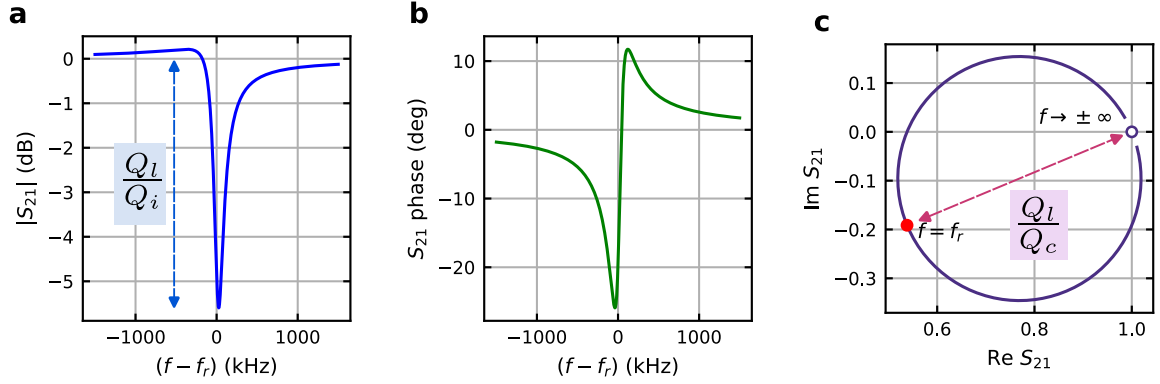


Figure 3.4: **Hanger resonator  $S_{21}$  response.** Complex transmission coefficient of a hanger-coupled resonator calculated from Eq. 3.41 for  $f_r = 1$  GHz,  $Q_i = Q_c = 10^4$ , and  $\phi = \pi/8$ . (a) Transmission amplitude  $|S_{21}|$  versus detuning from resonance: the resonator appears as a narrow dip on a  $|S_{21}| = 1$  background, with the residual transmission at resonance set by  $Q_l/Q_i$  (dashed arrow). The finite  $\phi$  produces the asymmetric lineshape. (b) Transmission phase across the resonance. (c) The same data in the complex plane, where  $S_{21}$  traces a circle: the off-resonant point sits at  $S_{21} = 1$  (open circle) and the resonance  $f = f_r$  lies diametrically opposite (filled circle). The circle diameter equals  $Q_l/Q_c$  (arrow).

number but depends on drive power and temperature through two-level system saturation, so quality factors are meaningfully compared only at matched photon number [34]. The fitting procedure used throughout this thesis follows this established approach. The complex  $S_{21}$  is fit to Eq. 3.41 along with a background model via non-linear least squares using the `lmfit` library [41], and  $Q_i$  is obtained via the diameter correction of [38]. The fitting code, along with the resonator measurement and analysis routines used, is available at <https://github.com/dgglab/microwave-resonators>. In the following subsection, we will show that terminating a resonator by a load impedance  $Z_L$  keeps the functional form for  $S_{21}$  while changing the resonance frequency  $\omega_r$  and the quality factors. Our goal is then to derive these changes in resonance frequency and quality factors as a function of  $Z_L$ .

### 3.5.2 Resonator terminated by an arbitrary complex load

Consider a coplanar waveguide with impedance  $Z_r$  and length  $l$ . One end of the resonator is terminated by a load  $Z_L$  while the other end is capacitively coupled to another transmission line through a coupling capacitor  $C_c$ . Let  $Z(l, Z_L)$  be the impedance of the resonator as seen by the coupling capacitor. The total impedance  $Z_t$  between the center pin and the ground plane for the transmission line is

$$Z_t = \frac{1}{j\omega C_c} + Z(l, Z_L) \quad (3.42)$$

Using transmission line theory, we can calculate  $Z(l, Z_L)$ .

$$Z(l, Z_L) = Z_r \frac{Z_L + Z_r \tanh(\gamma l)}{Z_L \tanh(\gamma l) + Z_r} \quad (3.43)$$

The propagation constant  $\gamma$  for the resonator transmission line is  $\gamma = \alpha + j\beta = \alpha + j\frac{\omega}{v_p}$ .  $v_p$  is the phase velocity along the resonator transmission line. In order to find resonances corresponding to  $Z_t$ , we set the imaginary part of  $Z_t$  to zero. This is heuristically justified in the low loss limit where in the absence of loss,  $Z_t \rightarrow 0$  implies the center pin for the transmission line is shorted to the ground plane. As a result,  $S_{21} \rightarrow 0$ , which we can interpret as the resonator dip in transmission.

$$\text{Im } Z_t = 0 \quad (3.44)$$

$$\text{Im} \left[ \frac{1}{j\omega C_c} + Z_r \frac{Z_L + Z_r \tanh(\gamma l)}{Z_L \tanh(\gamma l) + Z_r} \right] = 0 \quad (3.45)$$

$$\text{Im} \left[ \frac{1}{j\omega C_c Z_r} + \frac{Z_L/Z_r + \tanh(\gamma l)}{Z_L/Z_r \tanh(\gamma l) + 1} \right] = 0 \quad (3.46)$$

Let  $\theta$  be a complex number such that  $\tanh(\theta) = Z_L/Z_r$ . We can simplify the above expression using a trigonometric identity for the hyperbolic tangent.

$$\text{Im} \left[ \frac{1}{j\omega C_c Z_r} + \frac{\tanh(\theta) + \tanh(\gamma l)}{\tanh(\theta) \tanh(\gamma l) + 1} \right] = 0 \quad (3.47)$$

$$\text{Im} \left[ \frac{1}{j\omega C_c Z_r} + \tanh(\theta + \gamma l) \right] = 0 \quad (3.48)$$

$$\frac{1}{\omega C_c Z_r} + \text{Im} [\tanh(\theta + \gamma l)] = 0 \quad (3.49)$$

$$\text{Im} [\tanh(\theta + \gamma l)] = -\frac{1}{\omega C_c Z_r} \quad (3.50)$$

Let's consider a few simple cases to build our intuition on the resonance condition. In typical superconducting circuits, resonators are weakly coupled to the transmission line. Hence, we have small coupling capacitors of 1–10 fF, which leads to  $\frac{1}{\omega C_c Z_r} \gg 1$ .

1. **Shorted load** ( $Z_L = 0$ ): We then have  $\theta = 0$  and using  $\gamma = \alpha + j\beta$ ,

$$\text{Im} [\tanh(\alpha l + j\beta l)] = -\frac{1}{\omega C_c Z_r} \quad (3.51)$$

In the limit of low intrinsic loss,  $\alpha l \ll 1$ ,

$$\tan(\beta l) = -\frac{1}{\omega C_c Z_r} \quad (3.52)$$

For typical superconducting circuits,  $\frac{1}{\omega C_c Z_r} \gg 1$  implies,

$$\beta l = (2n + 1) \frac{\pi}{2} \quad (3.53)$$

$$\omega = (2n + 1) \frac{\pi v_p}{2l} \quad (3.54)$$

These are the modes for a  $\lambda/4$  resonator as only the odd harmonics of  $\frac{\pi v_p}{2l}$  are present.

2. **Open load ( $Z_L \rightarrow \infty$ ):** We then have  $\theta = j\pi/2$ . By using similar arguments as in the shorted load case, we get,

$$\beta l + \pi/2 = (2n + 1) \frac{\pi}{2} \quad (3.55)$$

$$\omega = \frac{n\pi v_p}{l} \quad (3.56)$$

These are the modes of a  $\lambda/2$  resonator.

3. **Purely reactive load ( $Z_L = jX$ ):** The previous cases were intuitive and are well-known in the literature. But now, when we turn to arbitrary complex impedances, we will see the value of our generalized approach. Let's start with purely reactive impedances. We have  $\theta = j \tan^{-1}(X/Z_r) = j\chi$ . Similarly,

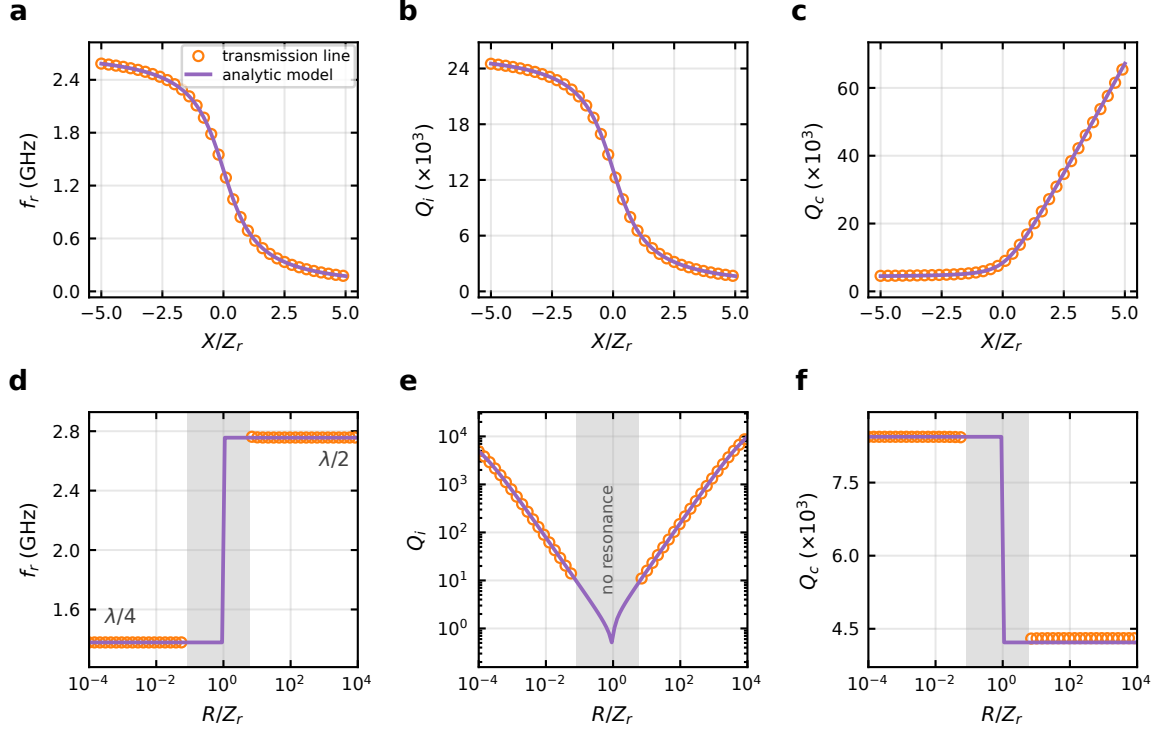
$$\beta l + \chi = (2n + 1) \frac{\pi}{2} \quad (3.57)$$

$$\omega = \frac{v_p}{l} \left[ (2n + 1) \frac{\pi}{2} - \chi \right] \quad (3.58)$$

$$\omega = \frac{v_p}{l} \left[ n\pi + \frac{\pi}{2} - \chi \right] \quad (3.59)$$

$$\omega = \frac{v_p}{l} \left[ n\pi + \frac{\pi}{2} - \tan^{-1} \left( \frac{X}{Z_r} \right) \right] \quad (3.60)$$

The angle  $\chi = \tan^{-1}(X/Z_r)$  enters the resonance condition as an additional phase shift on top of the phase accumulated by the electromagnetic wave traveling along the resonator, and it takes either sign:  $\chi \in (-\pi/2, \pi/2)$ . Consider the mode continuously connected to the  $\lambda/4$  fundamental ( $n = 0$ ). An inductive load ( $X > 0$ ,  $\chi > 0$ ) lengthens the effective line and pushes the mode down in frequency; setting  $\chi = \pi/2$  recovers the  $\lambda/2$  spectrum of the previous case, whose fundamental is now the  $n = 1$  member. A capacitive load ( $X < 0$ ,  $\chi < 0$ ) shortens the effective line and raises the frequency, approaching twice the  $\lambda/4$  value as  $\chi \rightarrow -\pi/2$ . In both directions the size of the shift is set by the reactance relative to the resonator impedance:  $|X| \gg Z_r$  gives phase shifts approaching  $\pm\pi/2$ , while  $|X| \ll Z_r$  leaves the mode essentially unshifted. Fig. 3.5(a–c) shows this interpolation for a representative resonator.



**Figure 3.5: Resonator properties under a complex load.** Resonance frequency and quality factors of a  $\lambda/4$  hanger resonator terminated by a load  $Z_L = R + jX$ , comparing the full transmission-line calculation (open circles) with the analytic model of Eqs. 3.66–3.68. The transmission-line points are generated by evaluating the exact  $Z_t$ , computing the complex  $S_{21}$ , and fitting it using the circle-fit method. Parameters:  $Z_r = 2 \text{ k}\Omega$ ,  $l = 1200 \text{ }\mu\text{m}$ ,  $v_p = 7 \times 10^6 \text{ m s}^{-1}$ ,  $\alpha = 5 \times 10^{-2} \text{ m}^{-1}$  and  $C_c = 5 \text{ fF}$ , which give  $f_r = 1.38 \text{ GHz}$ ,  $Q_i = 1.3 \times 10^4$  and  $Q_c = 8.4 \times 10^3$  for a shorted termination. The load enters only through the complex angle  $\theta = \tanh^{-1}(Z_L/Z_r) = \eta + j\chi$ : the phase  $\chi$  adds to the phase accumulated along the line, while  $\eta$  adds to the loss. (a–c) Purely reactive load  $Z_L = jX$ , for which  $\eta = 0$  and  $\chi = \tan^{-1}(X/Z_r)$ . An inductive load ( $X > 0$ ) pushes  $f_r$  down toward the  $\chi \rightarrow \pi/2$  limit whereas a capacitive load ( $X < 0$ ) raises  $f_r$  towards  $2f_r$ .  $Q_i$  tracks  $f_r$  keeping the decay rate ( $f_r/Q_i$ ) constant in our model while  $Q_c$  scales inversely and grows as the mode is pushed to lower frequency and couples more weakly through the fixed  $C_c$ . (d–f) Purely resistive load  $Z_L = R$ , which contributes  $\eta = \tanh^{-1}(R/Z_r)$  and switches  $\chi$  from 0 to  $-\pi/2$  as  $R$  crosses  $Z_r$ . The resonator therefore crosses over from the  $\lambda/4$  mode to the  $\lambda/2$  mode at twice the frequency, with  $Q_c$  halving across the crossover, while  $Q_i$  falls from its intrinsic-loss-limited value on either side. In the shaded region the load is close to impedance matched to the line and the resonator is highly damped. Essentially all of the stored energy is absorbed by the load and no resonance survives to be fitted. This region also bounds the validity of Eqs. 3.66–3.68, which are first order in  $\alpha l + \eta$ .

4. **Arbitrary complex load  $Z_L$ :** Let  $\theta = \eta + j\chi$ . The total complex impedance  $Z_t$  is given as:

$$Z_t = \frac{1}{j\omega C_c} + Z(l, Z_L) \quad (3.61)$$

$$= \frac{1}{j\omega C_c} + Z_r \frac{Z_L/Z_r + \tanh(\gamma l)}{Z_L/Z_r \tanh(\gamma l) + 1} \quad (3.62)$$

using the definition for the complex angle  $\theta = \tanh^{-1}(Z_L/Z_r)$

$$= \frac{1}{j\omega C_c} + Z_r \frac{\tanh(\theta) + \tanh(\gamma l)}{\tanh(\theta) \tanh(\gamma l) + 1} \quad (3.63)$$

$$= \frac{1}{j\omega C_c} + Z_r \tanh(\gamma l + \theta) \quad (3.64)$$

$$= \frac{1}{j\omega C_c} + Z_r \tanh(\alpha l + \eta + j(\beta l + \chi)) \quad (3.65)$$

If we compare the above equation to Eq. 3.10 and the subsequent results of the previous section, we see that the load impedance  $Z_L$  modifies the results for a shorted resonator by changing the real and imaginary parts of the propagation constant as:  $\alpha \rightarrow \alpha + \frac{\eta}{l}$  and  $\beta \rightarrow \beta + \chi/l$ . Hence, we can use the results derived in the previous section to immediately write down the resonance frequency and the coupling quality factors using the  $\lambda/4$  mode as a reference point when  $\theta = \eta + j\chi = 0$ .

$$\omega_r(\theta) \approx \omega_r(0) \left( 1 - \frac{2\chi}{\pi} \right) \quad (3.66)$$

Similarly, the internal and coupling quality factors are also modified as follows:

$$Q_i(\theta) = Q_i(0) \frac{1}{1 + 4\eta Q_i(0)/\pi} \left( 1 - \frac{2\chi}{\pi} \right) \quad (3.67)$$

$$Q_c(\theta) = Q_c(0) \frac{1}{(1 - \frac{2\chi}{\pi})} \quad (3.68)$$

Equations 3.66–3.68 are the central results of this section. As we will later see in Part III on vdW heterostructures, by using the extracted resonator frequency and quality factors from measurements and these equations, we can reconstruct the complex impedance from the vdW heterostructure (including any parasitic components such as gate and contact lines) coupled to the resonator.



### 3.6 Impedance of a Josephson junction

In this section, we will derive the inductance of a Josephson junction. We will revisit the measurement of the JJ inductance in Chapter 9, where we will compare the theoretical estimates from this section to the experimentally inferred inductances from the resonator frequency shift. The supercurrent flowing through a Josephson junction (JJ) is related to the phase  $\phi$  across the two superconductors forming the junction. For a tunnel junction, the current phase relation is given as follows:

$$I(\phi) = I_c \sin(\phi) \quad (3.69)$$

In principle, we can write down more complicated current phase relations for SNS junctions depending on the physical characteristics of the normal region N. A second Josephson relation relates the potential difference  $V$  across the junction to the time derivative of the phase  $\phi$ .

$$V = \frac{\Phi_0}{2\pi} \frac{d\phi}{dt} = \frac{\hbar}{2e} \frac{d\phi}{dt} \quad (3.70)$$

where  $\Phi_0 = h/2e$  is the superconducting flux quantum. If we now use Eq. 3.69 to calculate the time derivative  $\frac{d\phi}{dt} = \frac{dI/dt}{I_c \cos(\phi)}$  and substitute it in Eq. 3.70, we get

$$V = \frac{\Phi_0}{2\pi} \frac{1}{I_c \cos(\phi)} \frac{dI}{dt} \quad (3.71)$$

Recall that for an ideal inductor, the flux across the inductor  $\Phi$  is related to the current as  $\Phi = LI$ , where  $L$  is defined as the inductance. Using Faraday's law, the voltage across the inductor is given as  $V = L \frac{dI}{dt}$ . Comparing these two expressions, we see that a JJ behaves as an inductor with an inductance  $L_J$  such that

$$L_J(\phi) = \frac{\Phi_0}{2\pi} \frac{1}{I_c \cos(\phi)} \quad (3.72)$$

For a JJ in the absence of a current bias, the phase  $\phi$  sits at  $\phi = 0$  and we get the JJ inductance as  $L_J = \frac{\hbar}{2eI_c}$ . With a finite DC bias  $I_{dc}$  such that  $I_{dc} < I_c$ , the equilibrium value of the phase occurs at  $\phi = \phi_0$  where  $\sin(\phi_0) = I_{dc}/I_c$ . We can show this using the tilted washboard potential, in which the phase  $\phi$  lives on a potential landscape  $U(\phi)$ :

$$U(\phi) = -\frac{\Phi_0 I_c}{2\pi} \cos(\phi) - \frac{\Phi_0 I_{dc}}{2\pi} \phi \quad (3.73)$$

Minimizing the potential energy  $U(\phi)$ , we get  $\sin(\phi_0) = I_{\text{dc}}/I_c$ . We can now calculate the inductance of a JJ in the presence of a finite DC current bias  $I_{\text{dc}}$  as

$$L_J(\phi_0) = \frac{\Phi_0}{2\pi} \frac{1}{I_c \cos(\phi_0)} \quad (3.74)$$

$$= \frac{\Phi_0}{2\pi} \frac{1}{I_c \sqrt{1 - I_{\text{dc}}^2/I_c^2}} \quad (3.75)$$

$$= \frac{\Phi_0}{2\pi} \frac{1}{\sqrt{I_c^2 - I_{\text{dc}}^2}} \quad (3.76)$$

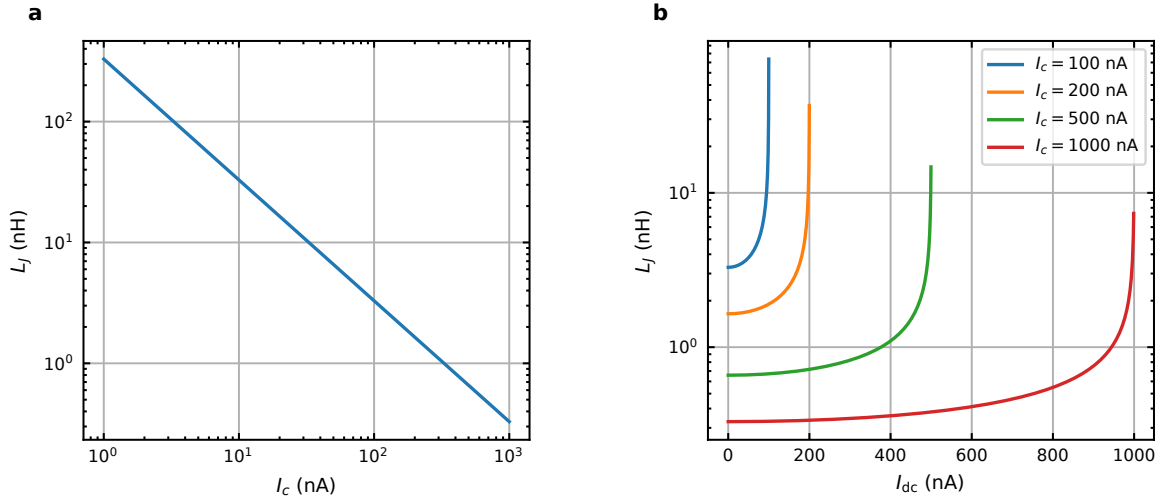


Figure 3.6: **Inductance of a Josephson junction.** (a) Inductance of a Josephson junction (JJ)  $L_J$  calculated as a function of the JJ's critical current  $I_c$ . (b)  $L_J$  as a function of an applied DC current  $I_{\text{dc}}$  for various critical currents as shown in the legend.  $L_J$  remains approximately constant as a function of  $I_{\text{dc}}$  right until the critical current of the JJ where it diverges to large values.

Fig. 3.6(a) shows the calculated inductance as a function of the critical current. For critical currents ranging from 1 nA to 1  $\mu$ A, the JJ inductance varies from 300 nH to 300 pH. Fig. 3.6(b) shows the dependence of the JJ inductance on an external DC bias current.  $L_J$  stays close to the zero-bias value until  $I_{\text{dc}}$  approaches  $I_c$ , where it diverges.

### 3.7 Coupling resonators to condensed matter systems

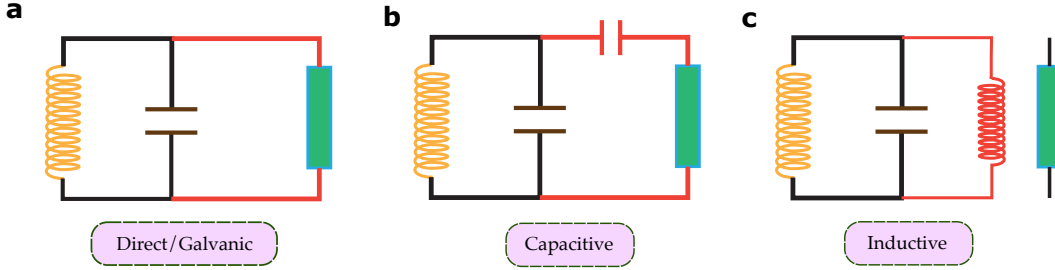


Figure 3.7: **Coupling strategies for resonators to condensed matter systems.** Three ways of placing a system of interest (green) into the electromagnetic environment of a superconducting resonator, drawn here as a lumped  $LC$  oscillator (orange inductor, black capacitor) and the coupling element is shown in red. (a) *Galvanic* coupling: the system is wired directly into the resonator so that the microwave current of the mode flows through it, and the resonator responds to changes in the system impedance. This is the natural geometry for quantities carried by current flow such as the kinetic inductance of a superconductor or the Josephson inductance of a junction. (b) *Capacitive* coupling: the system is connected through a coupling capacitor and samples the microwave electric field, so the resonator senses quantities associated with charge and electric-field fluctuations, such as the electronic compressibility (quantum capacitance) of a two-dimensional electron system. (c) *Inductive* coupling: the system is galvanically isolated and responds to the microwave magnetic field, either through a mutual inductance or simply by sitting within the mode volume. Magnetic-dipole sensitive excitations such as isolated spins, spin waves, and magneto-plasmons can be detected using inductive coupling.

In the preceding sections, we have derived basic equations concerning resonator measurements and the changes in resonator properties from coupling to arbitrary complex loads. From this formalism, we can see that the resonator frequency and quality factors make it a probe of any system in the electromagnetic environment of the resonator. The high quality factors arising from superconductivity mean that we can be sensitive to small changes in frequency and dissipation. The central challenge in adapting the resonator as a sensitive detector of condensed matter phases is the following: how do we establish an appropriate coupling to the system of interest such that the coupling is sensitive to the observable we care about *without* significantly degrading the quality factor of the resonator? Fig. 3.7 shows three broad classes of available strategies. In *galvanic* coupling, the system under study is wired directly into the resonator, say by terminating the current antinode of a  $\lambda/4$  mode, so that the resonator's microwave current flows through the system. This is the natural choice for quantities carried by current flow: the kinetic inductance and superfluid stiffness of a superconductor, the Josephson inductance of a junction, or the superconducting gap through its dissipative response. In *capacitive* coupling, the system is connected through a coupling capacitor and samples the resonator's electric field; the resonator then senses quantities associated with

charge and electric-field fluctuations, such as the electronic compressibility (or quantum capacitance) of a two-dimensional electron system. In *inductive* coupling, the system responds primarily to the resonator's microwave magnetic field either through a mutual inductance or simply by placing it within the mode volume. The resonator senses magnetic-field coupled excitations of isolated spins, spin waves, and magneto-plasmons. Of the three, this thesis employs the inductive route in Part II and the galvanic route in Part III. The characteristic impedance  $Z_r$  of the resonator determines the strength of the electric and magnetic fields for a given photon number (i.e. resonator power), and therefore determines which coupling, electric or magnetic, dominates for a particular resonator geometry. For a mode of frequency  $\omega_r$ , the zero-point fluctuations of voltage and current are as follows [42]:

$$V_{\text{zpf}} = \omega_r \sqrt{\frac{\hbar Z_r}{2}} \quad (3.77)$$

$$I_{\text{zpf}} = \omega_r \sqrt{\frac{\hbar}{2Z_r}} \quad (3.78)$$

Voltage fluctuations grow with  $\sqrt{Z_r}$  while current fluctuations shrink as  $1/\sqrt{Z_r}$ . High-impedance resonators therefore maximize coupling to capacitive and galvanic loads through strong electric fields while low-impedance resonators maximize the microwave magnetic fields. Conventional coplanar waveguide geometries for superconductors such as Al or Nb are limited to  $Z_r \sim 10\text{--}100\,\Omega$ . Ultra-thin disordered films and Josephson junction arrays evade this bound through kinetic inductance, reaching several  $\text{k}\Omega$  [43, 44, 45]. In Chapter 8, we will use NbTiN ultra-thin films ( $< 10\text{ nm}$ ) to develop a galvanically coupled architecture for vdW heterostructures. Fig. 3.8 shows the magnitude of the zero-point voltage and current fluctuations across the microwave band, for characteristic impedances spanning conventional coplanar waveguides to high-impedance designs. Note that the dependence of these values on the resonator design is captured completely through the resonator frequency and its characteristic impedance.

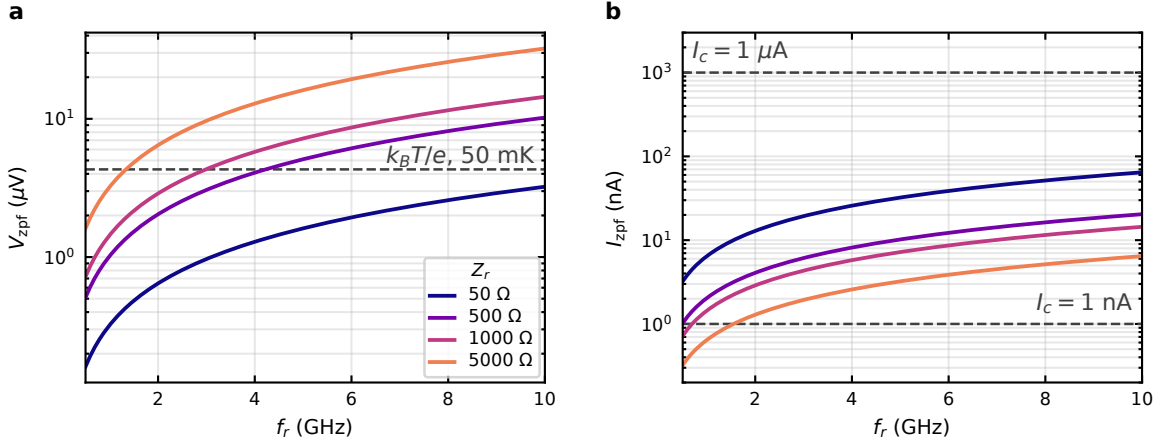


Figure 3.8: **Zero-point current and voltage fluctuations for typical microwave resonators.** Zero-point fluctuations of (a) voltage and (b) current for a resonator mode of frequency  $f_r$ , plotted for characteristic impedances spanning conventional coplanar waveguides (50  $\Omega$ ) to the high-impedance resonators (5 k $\Omega$ ).  $V_{zpf}$  grows as  $\sqrt{Z_r}$  while  $I_{zpf}$  falls as  $1/\sqrt{Z_r}$ , so the choice of impedance trades electric-field coupling against magnetic-field coupling. The dashed line in (a) marks the thermal voltage  $k_B T / e = 4.3 \mu\text{V}$  at 50 mK. The dashed lines in (b) bracket the approximate range of critical currents of the Josephson junctions measured in Chapter 9, 1 nA to 1  $\mu\text{A}$ .

### 3.7.1 Resonators coupled to magnetic systems: spin resonance

The microwave photons stored in a resonator can be brought into resonance with excitations of a material when the frequency of some excitation is tuned to be equal to the resonator frequency. For isolated, non-interacting spins, the relevant excitation is set by the Zeeman splitting,

$$E_Z = g\mu_B B, \quad (3.79)$$

where  $g$  is the Landé  $g$ -factor,  $\mu_B$  is the Bohr magneton and  $B$  is the magnitude of an externally applied field. A handy conversion: for  $g = 2$ ,  $g\mu_B/h \approx 28 \text{ GHz T}^{-1}$ , i.e. about 2.8 GHz at 100 mT. Modest laboratory fields of tens to hundreds of mT therefore bring the Zeeman splitting directly through the band of typical coplanar resonators. This resonance condition,  $hf_r = g\mu_B B$ , is the basis of electron spin resonance (ESR), a spectroscopy with a long history in analytical chemistry and solid-state physics, where it is used to fingerprint paramagnetic centers, radicals, and transition-metal and rare-earth ions through their  $g$ -factors and linewidths. Conventional ESR spectrometers employ 3D microwave cavities and  $\sim \text{mm}^3$  sample volumes [46]. The planar superconducting resonator implements the same physics with a mode volume smaller by many orders of magnitude, trading sample generality for the sensitivity needed to detect spins in thin films or 2D systems [47]. The geometry of the coupling follows from the mode structure of the coplanar waveguide. The microwave magnetic field  $B_{mw}$  circulates around the center conductor, so a film placed on (or under)

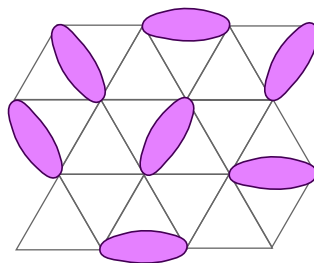
the resonator sits in this field throughout the length of the line. A static field  $B_0$  is applied in the plane of the film and perpendicular to  $B_{mw}$ , as required to drive the magnetic-dipole transitions between the Zeeman-split levels. Because the field decays evanescently over a length set by the lithographic dimensions ( $\approx \mu\text{m}$  scale), the resonator addresses all spins within the film, its interfaces, and the top few microns of the substrate. As a result, the resonator is sensitive not only to thin films, but also to every paramagnetic defect and impurity in the mode volume, a point that we will return to in Chapter 5. A single spin couples to the resonator's magnetic zero-point fluctuations with a strength of only tens of Hz, far too weak to resolve [47]. An ensemble of  $N$  spins, however, couples collectively with an enhanced strength  $g_{\text{ens}} = g_s \sqrt{N}$ , where  $g_s$  is the single-spin coupling rate; for the  $\sim 10^{12}$  moments within the mode volume of our devices this collective coupling is appreciable, but still small compared to the spin linewidth  $\Gamma$ , placing the experiments of this thesis in the weak-coupling regime  $g_{\text{ens}} \ll \Gamma$  [42]. In this regime, the spins act on the resonator as a weak, tunable admittance: the resonator frequency shifts in proportion to the dispersive part of the spin susceptibility,  $\Delta f \propto \chi'(f_r)$ , and the decay rate acquires a contribution proportional to the absorptive part,  $\Delta\kappa \propto \chi''(f_r)$ . For our parameters the frequency pull is too small to be resolved in the weak-coupling regime, and so the decay rate measured as a function of applied field,  $\kappa(B_0)$ , is the experimental observable. As  $B_0$  tunes a population of spins through the resonance condition, photons are absorbed and the resonator line broadens. This method of extracting spin resonance will be used as the primary experimental tool in Part II. The measured resonance line carries quantitative information beyond the  $g$ -factor read off from its position. The thermal polarization of a spin population at temperature  $T$  scales as  $\tanh(hf_r/2k_B T)$ , so the signal grows toward low temperature. The lineshape distinguishes broadening mechanisms: a Lorentzian indicates homogeneous broadening by spin relaxation and mutual interactions, while a Gaussian indicates inhomogeneous broadening by a distribution of local environments. Most importantly, the area under  $\Delta\kappa(B_0)$  is proportional to the static magnetic susceptibility of the participating moments, so tracking the integrated spectral weight versus temperature turns the resonator into a susceptometer for films far too thin for conventional magnetometry. This is the toolkit deployed in Chapter 5 to follow the Tb moments of  $\text{TbInO}_3$  down to 20 mK, and in flip-chip form in Chapter 6. Finally, nothing in this detection scheme is specific to free spins. Any excitation with a magnetic-dipole matrix element and an energy tunable through  $hf_r$ , for example, spin waves in ordered magnets [48, 49], crystal-field transitions [46], or the continua of fractionalized excitations proposed for quantum spin liquids [6, 50], can contribute to  $\chi''(f_r)$  and is detected by the resonator in exactly the same way. The resonator can be regarded as a low-energy ( $\mu\text{eV}$ ) probe of the dynamic magnetic susceptibility, complementary to inelastic neutron scattering at meV energies, and it is in this spirit that we apply it to frustrated magnets in Part II.

### 3.8 Summary

In this chapter, we developed the formalism to analyze measurements of hanger resonators. Two results are carried through the rest of the thesis. The first is Eq. 3.41, the complex transmission coefficient of a hanger-coupled resonator, which we use to extract resonator frequency and quality factors from measured data. The second is the set of relations in Eqs. 3.66–3.68, which translate a complex load impedance at the end of the resonator into shifts of resonator frequency and quality factors. Together they make the resonator a probe of whatever occupies its electromagnetic environment: the reactive part of that environment moves the resonance frequency, while the dissipative part broadens the line. Part II applies this inductively, using the microwave magnetic field of a coplanar resonator to perform spin resonance on frustrated magnets, where the field-dependent decay rate  $\kappa(B_0)$  is the observable. Part III applies it galvanically, embedding van der Waals heterostructures into high-impedance NbTiN resonators, so that the microwave current of the mode flows through the sample and the extracted frequency and quality factors report the complex impedance of the channel directly.

## Part II

# Frustrated Magnetism





## Chapter 4

# Frustrated Quantum Magnets

Magnetism has been known to humans since the dawn of recorded history. In fact, magnetic phenomena predate the notion of purely electrostatic forces and electrically charged objects. The earliest evidence of humans using naturally occurring magnets, known as lodestones, dates back to the ancient Sumerian and Egyptian civilizations of the fourth millennium BC [51]. By the first millennium BC, Chinese navigators had discovered that a freely suspended lodestone could function as a compass [51]. Lodestones consist primarily of  $\text{Fe}_3\text{O}_4$ , in which the partially filled d sub-shell of the iron atoms gives rise to local magnetic moments. In a ferromagnet, these moments align along a common direction. It is not difficult, however, to envision a magnetic order built from more intricate repeating arrangements of moments. Yet despite the conceptual ease of writing down such an order, ordered magnetic systems that are not ferromagnetic were not discovered until the second half of the twentieth century.

The theoretical framework for anti-ferromagnetic order was first proposed by Louis Néel in 1932 [52]. Expanding on the idea of a uniform molecular field, a concept invented by Weiss to explain ferromagnetism, Néel worked out the theory of magnets with a non-uniform ‘local’ molecular field. Starting from equal and opposite molecular fields on two interleaving sub-lattices, he predicted a state in which the sub-lattice moments are equal in magnitude and opposite in direction. This phase transition occurs at a temperature known as the Néel temperature  $T_N$ . For  $T < T_N$ , an anti-ferromagnetic state with equal and opposite moments on two sub-lattices exists, which transitions into a paramagnetic state at high temperatures. While anti-ferromagnetism could be indirectly inferred from measurements such as magnetic susceptibility as a function of temperature, direct evidence of the anti-parallel moments only came from the development of a new measurement technique — neutron diffraction. In 1949, pioneering experiments on MnO by Shull and Smart revealed the existence of diffraction peaks which only emerged below the Néel temperature [53]. Since no crystallographic transition was expected from the behavior of non-magnetic diffraction peaks, it was unambiguously established that magnetic sub-lattices had emerged below the Néel temperature.

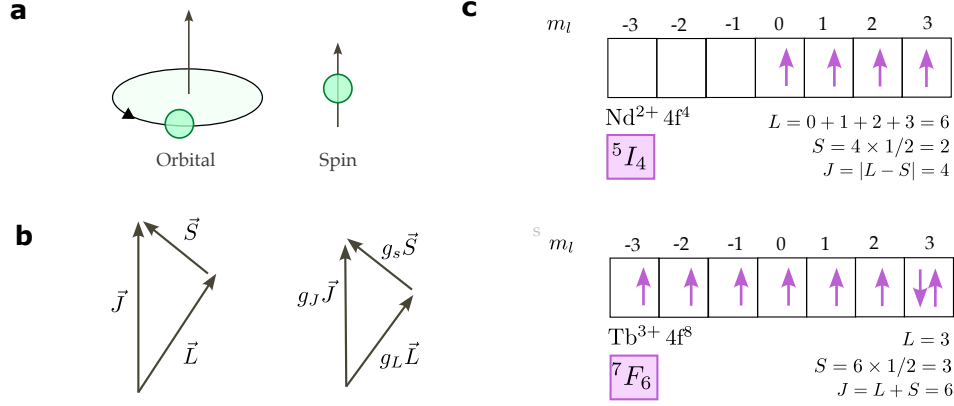


Figure 4.1: **Origin of atomic magnetic moments.** (a) There are two kinds of magnetic moments: orbital and spin. Orbital motion of an electron around the nucleus is a closed current loop and carries a moment  $\mu = IA$  directed along the loop normal. The electron additionally carries an intrinsic spin moment. (b) Vector model underlying the Landé  $g$ -factor. On the left, the orbital and spin angular momenta add as  $\vec{J} = \vec{L} + \vec{S}$ . On the right, the corresponding magnetic moments add as  $g_J \vec{J} = g_S \vec{S} + g_L \vec{L}$ . (c) Hund's-rule filling of the  $4f$  shell for two rare-earth ions, with the seven orbitals labeled by  $m_l$ . For Nd<sup>2+</sup>  $4f^4$  the four electrons occupy the orbitals of largest  $m_l$  with parallel spins, giving  $L = 6$ ,  $S = 2$ , and, since the shell is less than half filled,  $J = |L - S| = 4$ : the term symbol is  $^5I_4$ . For Tb<sup>3+</sup>  $4f^8$  one orbital is doubly occupied, leaving six unpaired spins, so  $L = 3$ ,  $S = 3$ , and, the shell now being more than half filled,  $J = L + S = 6$ : the term symbol is  $^7F_6$ . The Tb<sup>3+</sup> moment is the one measured in Chapter 5.

Beyond systems with perfectly ordered magnetic moments, there exists a larger class of systems in which magnetic order is absent down to the lowest accessible temperatures despite the presence of strong interactions between the moments. The incompatibility of a simple ordered magnetic state from geometric constraints of the underlying lattice gives rise to a class of magnets known as frustrated magnets. In this chapter, we will learn about the essential requirements on the magnetic moments, their interactions and the underlying lattice which can lead to frustrated magnets. At the end, a guide on where we can fruitfully look for such materials among the vast database of material systems will be given. But first, let's start by understanding why magnetic order occurs in solids at all.

## 4.1 Atomic magnetism

We begin by understanding the origin of magnetic moments at the level of individual atoms. In elementary electromagnetism, the concept of a magnetic moment originates from studying the magnetic field produced by closed current loops. A magnetic moment  $\mu$  produced by a current  $I$  circulating

in a loop which encloses an area  $A$  is defined as follows:

$$\mu = IA \quad (4.1)$$

At the core of the magnetic moment is the principle that the motion of an electric charge creates a magnetic field. A magnetic moment therefore is a useful concept which abstracts away the details of this motion while preserving enough information to calculate the resultant magnetic field.

The study of elementary particles such as electrons, protons and neutrons shows another source of magnetic moments in nature which goes beyond spatial motion. Known as the spin, it can be vaguely understood as spinning of the elementary particle around an axis. However, such a picture is overly simplistic for at least a couple of reasons: (i) as far as we know, certain particles such as the electron do not have any internal structure and (ii) spinning around an axis requires the notion of an axis tied to the particle pointed along a fixed direction. However, experimentally, the spin can be quantized in any given spatial direction which makes it impossible to interpret the ‘quantum’ spin as some spatial classical spin around an axis. As such, it is best for practical applications to treat the spin on the same level as any other effective magnetic moment without pondering too much on the origin of the moment.

Each individual electron has a spin  $1/2$  magnetic moment. The  $1/2$  refers to the experimentally deduced fact that the electron wavefunction described by a spinor needs to rotate by two full spatial rotations i.e.  $720^\circ$  to get back to an identical state [54]. As these electrons are filled in the s,p,d,f... sub-shells, they acquire another magnetic moment from the orbital motion of the electron around the nucleus. The angular quantum number  $l$  of these subshells — s ( $l = 0$ ), p ( $l = 1$ ), d ( $l = 2$ ) and so on leads to a magnetic moment directly proportional to  $l$ . Since a typical atom has multiple electrons filled across many shells and sub-shells, it is helpful to introduce a total spin quantum number  $S$  and a total angular momentum quantum number  $L$ . The Pauli exclusion principle, the Aufbau principle and Hund’s rules dictate the order in which electrons fill up sub-shells in the ground state electronic configuration of atoms [55, 56].

### 4.1.1 Term symbols

Term symbols ( $^{2S+1}L_J$ ) are a notational device introduced in atomic physics to capture the electronic configuration of an atom. Since these term symbols are often used to describe the magnetic moments of atoms in solid-state magnets, it will be helpful for us to review how these symbols are derived from bare electronic configurations. The total angular quantum number  $J = L + S$  can take values from  $L + S$  to  $|L - S|$  according to the rules of angular momentum addition in quantum mechanics [54].  $2S + 1$  is the spin multiplicity i.e. the number of spin split levels corresponding to a particular term symbol.

**Exercise: Term symbol for hydrogen atom** Let’s start with the simplest atom, the Hydrogen

atom in its ground state. Its electronic configuration is  $1s^1$ . Since there is only one electron, the total spin quantum number is  $S = 1/2$ . As the electron sits in the s sub-shell, the total angular momentum is  $L = 0$ . The total angular momentum  $J = L + S = 1/2$ . The term symbol for the ground state of the hydrogen atom is  $^2S_{1/2}$ .

**Exercise: Term symbol for a filled shell - He** For He, there are two electrons in the s sub-shell and the ground state electronic configuration is  $1s^2$ . Due to the exclusion principle, the total spin quantum number is  $S = 1/2 + (-1/2) = 0$ . Since both electrons are in the s sub-shell,  $L = 0$ . Also,  $J = L + S = 0$ . The term symbol for the ground state of He is  $^1S_0$ . This example illustrates an important point: the total spin and orbital momentum of a fully filled sub-shell is zero. Hence, we only need to consider the outermost electrons in writing down the term symbol.

**Exercise: Term symbol for an alkali metal - Na** The electronic configuration is  $[Ne]3s^1$ . As there is only one outermost electron, the total spin is  $S = 1/2$ . Being in s sub-shell leads to  $L = 0$  and hence  $J = 1/2$ . The term symbol is  $^2S_{1/2}$ , same as that of hydrogen.

**Exercise: Term symbol for rare-earth element - Nd** Nd has the electronic configuration  $[Xe]4f^46s^2$ . We only need to consider electrons in the f sub-shell as the s sub-shell is fully filled. Due to Hund's rules, each electron occupies a separate orbital indexed by the azimuthal quantum number  $m_l$  and the spin points along the same direction. For f sub-shell,  $m_l$  can take values as  $-3, -2, -1, 0, 1, 2, 3$ . According to Hund's rules, the occupied orbitals must maximize the total  $L = \sum m_l$ . Therefore, the four electrons occupy orbitals corresponding to  $m_l = 0, 1, 2, 3$  and hence the total orbital quantum number  $L = 0 + 1 + 2 + 3 = 6$ .  $L = 6$  is written as  $I$  in the  $S, P, \dots$  notation. As there are four electrons across the four orbitals and the spin points in the same direction,  $S = 4 \times 1/2 = 2$ . As the sub-shell is less than half-filled, the total angular momentum  $J$  takes the value  $|L - S| = 4$ . Hence, the term symbol is  $^5I_4$ .

## 4.2 Paramagnetism

### 4.2.1 Free magnetic moments

We now derive the thermodynamic properties such as bulk magnetization and susceptibility for a solid containing atoms with non-zero magnetic moments. For simplicity, assume that there are no interactions between these moments. Each moment has a spin angular momentum  $S$ , orbital momentum  $L$  and total angular momentum  $J$ . In the presence of an externally applied magnetic field, the Hamiltonian is given as follows:

$$H = g_s \mu_B \vec{B} \cdot \vec{S} + g_l \mu_B \vec{B} \cdot \vec{L} \quad (4.2)$$

$g_s$  and  $g_l$  are the Landé factors,  $\mu_B$  is the Bohr magneton and  $\vec{B}$  is an externally applied magnetic field. In cases where there are no interactions and  $\vec{J} = \vec{L} + \vec{S}$  is a good quantum number, we can

simplify the above Hamiltonian as

$$H = g_J \mu_B \vec{B} \cdot \vec{J} \quad (4.3)$$

Here  $g_J$  is Landé factor for the moment  $J$  and given by the following complicated expression:

$$g_J = g_s \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} + g_L \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} \quad (4.4)$$

Appendix B provides a derivation of the above expression.

### 4.2.2 Partition function for a magnetic moment $J$

We will derive thermodynamic properties of an ensemble of magnetic moments  $J$  interacting with a magnetic field  $\vec{B}$  using tools from statistical mechanics. For simplicity, we will assume that this magnetic field points along the z-direction and has magnitude  $B$ . The partition function for a single spin- $J$  moment  $Z$  is given as

$$Z = \sum_{m_J=-J}^J \exp(-\beta g_J \mu_B B m_J) \quad (4.5)$$

$\beta = \frac{1}{k_B T}$  is the usual inverse temperature. Let  $x = \beta g_J \mu_B B$  and  $y = e^x$ . Assume  $J$  is integer for now.

$$Z = 1 + y + y^2 \cdots + y^J + y^{-1} + y^{-2} \cdots + y^{-J} \quad (4.6)$$

$$= (1 + y + y^2 \cdots + y^J) + (1 + y^{-1} + y^{-2} \cdots + y^{-J}) - 1 \quad (4.7)$$

$$= \frac{y^{J+1} - 1}{y - 1} + \frac{y^{-J-1} - 1}{y^{-1} - 1} - 1 \quad (4.8)$$

$$= \frac{y^{J+1} - 1}{y - 1} - \frac{y^{-J} - y}{y - 1} - 1 \quad (4.9)$$

$$= \frac{y^{J+1} - 1 - y^{-J} + y - y + 1}{y - 1} \quad (4.10)$$

$$= \frac{y^{J+1} - y^{-J}}{y - 1} \quad (4.11)$$

$$= \frac{y^{1/2} (y^{J+1/2} - y^{-J-1/2})}{y - 1} \quad (4.12)$$

$$= \frac{y^{J+1/2} - y^{-J-1/2}}{y^{1/2} - y^{-1/2}} \quad (4.13)$$

$$= \frac{\sinh(x(J+1/2))}{\sinh(x/2)} \quad (4.14)$$

The partition function for half-integer  $J$  can be derived in a similar manner. We have the following result,

$$Z = \frac{\sinh(x(J + 1/2))}{\sinh(x/2)} \quad (4.15)$$

We can now derive the magnetization and susceptibility from appropriate derivatives of the free energy function  $F = -\frac{1}{\beta} \log Z$ .

$$M = -\frac{\partial F}{\partial B} \quad (4.16)$$

$$= \frac{1}{Z\beta} \frac{\partial Z}{\partial B} \quad (4.17)$$

$$= \frac{g_J \mu_B}{Z} \frac{\partial Z}{\partial x} \quad (4.18)$$

$$= g_J \mu_B \frac{\sinh(x/2)}{\sinh(x(J + 1/2))} \times \left[ \frac{(J + 1/2) \cosh(x(J + 1/2)) \sinh(x/2) - (1/2) \sinh(x(J + 1/2)) \cosh(x/2)}{(\sinh(x/2))^2} \right] \quad (4.19)$$

$$= g_J \mu_B [(J + 1/2) \coth(x(J + 1/2)) - (1/2) \coth(x/2)] \quad (4.20)$$

$$= g_J \mu_B J \left[ \frac{2J + 1}{2J} \coth(x(J + 1/2)) - \frac{1}{2J} \coth(x/2) \right] \quad (4.21)$$

It is conventional to define a new function known as Brillouin function defined as:

$$B_J(y) = \frac{2J + 1}{2J} \coth\left(\frac{2J + 1}{2J} y\right) - \frac{1}{2J} \coth\left(\frac{y}{2J}\right) \quad (4.22)$$

With the definition, the magnetization of spin-J moment can be written down as:

$$M = g_J \mu_B J B_J(y) \quad (4.23)$$

where  $y = xJ = \beta g_J \mu_B B J$ .

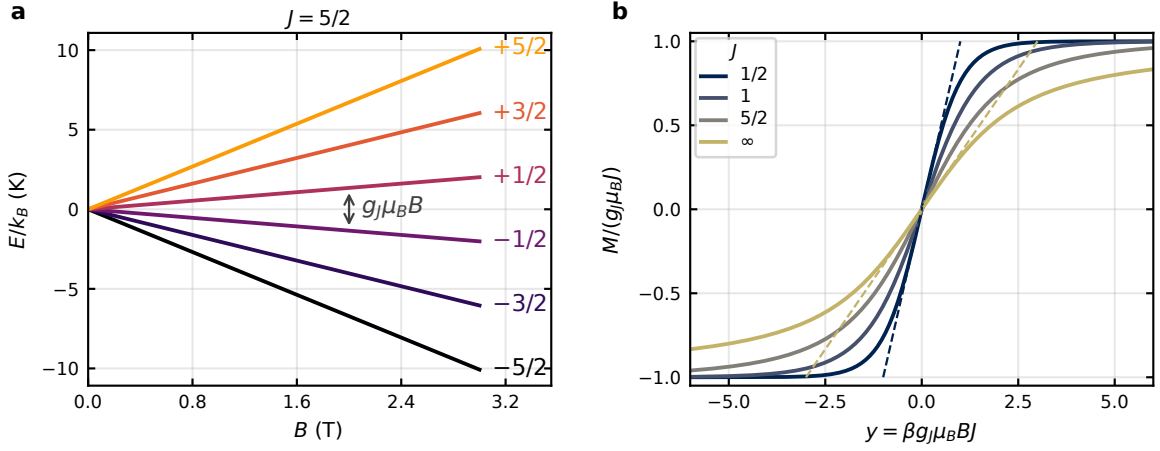


Figure 4.2: **Paramagnetism of a free spin- $J$  moment.** (a) Zeeman splitting of a  $J = 5/2$  multiplet in an applied field, from  $H = g_J \mu_B \vec{B} \cdot \vec{J}$  with  $g_J = 2$ . The  $2J + 1$  states, labeled by  $m_J$ , disperse linearly in  $B$  with a uniform level spacing  $g_J \mu_B B$  (arrow). These are the states summed over in the partition function of Eq. 4.15. (b) Magnetization of a free moment,  $M/g_J \mu_B J = B_J(y)$ , against the reduced field  $y = \beta g_J \mu_B B J$ , for  $J = 1/2, 1, 5/2$  and  $J \rightarrow \infty$ . The moment saturates once the Zeeman energy exceeds the thermal energy,  $|y| \gtrsim 1$ , and the approach to saturation is slower the larger the moment. Two limits are worth noting:  $B_{1/2}(y) = \tanh y$ , and  $J \rightarrow \infty$  recovers the classical Langevin function  $\coth y - 1/y$ , for which the quantization of  $m_J$  has been washed out entirely. Dashed lines are the small-field tangents of slope  $(J + 1)/3J$ ; this linear response is the Curie law of Eq. 4.34, which is accurate only for  $|y| \ll 1$ .

### 4.2.3 Curie Law

We can now compute the magnetic susceptibility  $\chi$  from the magnetization derived in the previous section.

$$\chi = \frac{\partial M}{\partial B} \quad (4.24)$$

$$= g_J \mu_B J \frac{dy}{dB} \frac{dB_J(y)}{dy} \quad (4.25)$$

$$= \beta (g_J \mu_B J)^2 \frac{dB_J(y)}{dy} \quad (4.26)$$

$$= \beta (g_J \mu_B J)^2 \left[ - \left( \frac{2J+1}{2J} \right)^2 \operatorname{csch}^2 \left( \frac{2J+1}{2J} y \right) + \left( \frac{1}{2J} \right)^2 \operatorname{csch}^2 \left( \frac{1}{2J} y \right) \right] \quad (4.27)$$

In practice, magnetic susceptibility is measured by applying a small magnetic field  $B$  such that  $y = xJ \ll 1$ . We can use a Taylor expansion for the hyperbolic cosecant to simplify the above expression [57].

$$\operatorname{csch}(z) = \frac{1}{z} - \frac{z}{6} + O(z^3) \quad (4.28)$$

On squaring the above expression and keeping terms lower than  $O(y^2)$

$$\operatorname{csch}^2(z) \approx \frac{1}{z^2} - \frac{1}{3} \quad (4.29)$$

Using the above expansion in Eq. 4.27, we get

$$\chi = \beta(g_J\mu_B J)^2 \left[ -\left(\frac{2J+1}{2J}\right)^2 \left(\frac{2Jy}{2J+1}\right)^2 + \frac{1}{3} \left(\frac{2J+1}{2J}\right)^2 + \left(\frac{1}{2J}\right)^2 \left(\frac{2Jy}{1}\right)^2 - \frac{1}{3} \left(\frac{1}{2J}\right)^2 \right] \quad (4.30)$$

$$= \beta(g_J\mu_B J)^2 \left[ -1 + 1 + \frac{(2J+1)^2 - (2J)^2}{3(2J)^2} \right] \quad (4.31)$$

$$= \beta(g_J\mu_B J)^2 \frac{(J+1)}{3J} \quad (4.32)$$

$$= \beta(g_J\mu_B)^2 \frac{J(J+1)}{3} \quad (4.33)$$

We have a succinct expression for the susceptibility of a spin-J moment. Note that the susceptibility is inversely proportional to temperature, a characteristic property of paramagnets. We have derived a generalized form of the Curie law of magnetic susceptibility valid for a magnetic moment with an arbitrary spin J.

$$\chi = \beta(g_J\mu_B)^2 \frac{J(J+1)}{3} \quad (4.34)$$

The story of magnetic materials would be complete at this point if no interactions existed between the constituent magnetic moments. Fortunately for us, moment to moment interactions are quite common in solid state systems and in fact there are a multitude of mechanisms which give rise to these interactions. We will explore them in the next section.

## 4.3 Magnetic interactions

Magnetic moments interact in solid state systems as a result of magnetic fields produced either directly by the moment or through electrostatic forces encountered by the electric charge associated with the magnetic moment. We first begin by understanding the direct moment-moment interaction through the magnetic field.

### 4.3.1 Magnetic dipolar interaction

Each magnetic moment acts as a tiny magnetic dipole and creates a magnetic field in its surrounding environment. If a second magnetic moment is placed in this magnetic field, the second moment



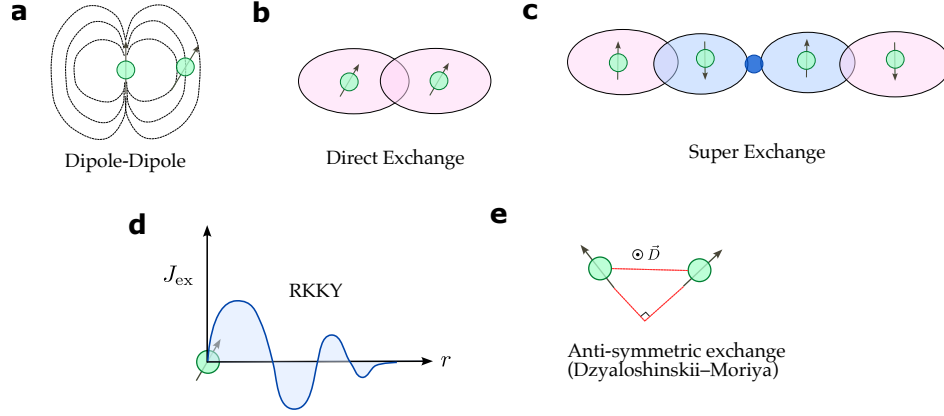


Figure 4.3: **Types of Magnetic Interactions.** (a) *Dipole-dipole coupling* Each moment sources a magnetic field, sketched here as field lines, and a second moment placed in that field lowers its energy by aligning with it. (b) *Direct exchange* between orbitals on neighboring magnetic atoms. Where the wavefunctions overlap, the Pauli principle correlates the spin configuration with the spatial symmetry of the two-electron state, and the resulting singlet-triplet splitting sets the exchange constant. (c) *Superexchange* Two magnetic cations with no direct orbital overlap are coupled through the filled  $p$  orbital of an intermediate oxygen anion. The electron delocalization gained through virtual hopping favors antiferromagnetic order. (d) *RKKY Interactions* A localized moment polarizes the surrounding conduction electrons, and the polarization oscillates in space as  $J_{\text{ex}}(r) \propto \cos(2k_F r)/r^3$  for a spherical Fermi surface of radius  $k_F$ . (e) *Antisymmetric (Dzyaloshinskii-Moriya) Exchange* Arising from spin-orbit coupling on a bond without inversion symmetry, it contributes a term  $\vec{D} \cdot (\vec{S}_1 \times \vec{S}_2)$ , with the Dzyaloshinskii-Moriya vector  $\vec{D}$  here pointing out of the page.

experiences a force which tries to reduce the total energy of the system. This interaction energy is known as the magnetic dipolar interaction and is captured by the following expression [58]:

$$E_d = \frac{\mu_0}{4\pi r^3} \left[ \vec{\mu}_1 \cdot \vec{\mu}_2 - \frac{3}{r^2} (\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r}) \right] \quad (4.35)$$

$\vec{\mu}_1, \vec{\mu}_2$  are the magnetic moments and  $\vec{r}$  is the vector connecting the location of the two moments. Let's make a crude estimate of the strength of this interaction. Assume  $\mu_1 = \mu_2 \approx 1\mu_B$  and a typical separation between atoms  $r \approx 0.1\text{ nm}$ . We get  $E_d \approx 9 \times 10^{-24}\text{ J}$ . When converted to temperature  $E_d \approx \frac{\mu_0 \mu^2}{4\pi r^3} \approx 600\text{ mK}$ , which is a tiny energy scale compared to room temperature. Since ferromagnetism does occur at room temperature in many materials like iron, cobalt, iron oxides and so on, this suggests that the dipolar interaction is too weak to explain experimentally observed magnetic interactions.

### 4.3.2 Exchange interaction

The calculation estimating the dipolar interaction between magnetic moments raises a conundrum: if the magnetic field interactions between magnetic moments are so small compared to typical energy scales where magnetism is observed, there must be some other force which leads to enhanced interactions between magnetic moments. Since the electrons creating these magnetic moments also carry an electric charge, the electrostatic forces seem like a natural candidate to explain the observed strength of magnetic interactions. However, no law or principle in classical electrodynamics was experimentally observed which could be invoked to couple magnetic moments with electrostatic forces. Despite the unification of the electric and magnetic fields via a Faraday tensor in Einstein's special theory of relativity, we are still left without a mechanism to explain magnetic interactions.

Further progress had to wait until the discovery of quantum mechanics and in particular quantum statistics. Heisenberg and Dirac independently showed that it is actually the Pauli exclusion principle and the Fermi exchange statistics of the underlying electrons which create a new term in the Hamiltonian which we today refer to as the Heisenberg exchange interaction.

$$H_{\text{ex}} = -J_{\text{ex}} \mathbf{S}_1 \cdot \mathbf{S}_2 \quad (4.36)$$

Here,  $J_{\text{ex}}$  quantifies the strength of the exchange interaction.

The following discussion is adapted from [58]. Here, we will sketch only the essential features to estimate the magnitude of the exchange interaction. Consider two electrons with spatial coordinates  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . These two electrons are occupying two spin degenerate wavefunctions  $\psi_a(\mathbf{r})$  and  $\psi_b(\mathbf{r})$ . Let  $\chi_S$  and  $\chi_T$  be spin-only anti-symmetric and symmetric wavefunctions respectively for the two electrons. As the total wavefunction is required to be anti-symmetric, we have two possible wavefunctions:

$$|\Psi_S\rangle = \frac{1}{\sqrt{2}} [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)] \chi_S \quad (4.37)$$

$$|\Psi_T\rangle = \frac{1}{\sqrt{2}} [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)] \chi_T \quad (4.38)$$

Let  $E_S$  and  $E_T$  be the corresponding expectation values for the above two wavefunctions. We can show that an effective Hamiltonian can be written down as follows:

$$H = \frac{1}{4}(E_S + 3E_T) - (E_S - E_T) \mathbf{S}_1 \cdot \mathbf{S}_2 \quad (4.39)$$

The second term is the exchange interaction. We can see why it is called 'exchange' by looking at the different  $(E_S - E_T)$  in terms of the constituent single particle wavefunctions.

$$E_S - E_T = 2 \int \psi_a^*(\mathbf{r}_1) \psi_b^*(\mathbf{r}_2) \mathcal{H} \psi_a(\mathbf{r}_2) \psi_b(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 \quad (4.40)$$

where  $\mathcal{H}$  is the full Hamiltonian containing the kinetic energy of the two electrons, Coulomb attraction between the electrons and positive cores, and the Coulomb repulsion between two electrons. Since the labels  $a$  and  $b$  specifying which electron is contained in which orbital are exchanged in calculating this expectation value, the corresponding interaction is called the exchange interaction. Since  $\mathcal{H}$  contains Coulomb terms on the order of  $e^2/(4\pi\epsilon_0 r)$  with  $r$  being some characteristic length scale, the exchange energy is significantly larger than the magnetic dipolar interaction energy we estimated in the previous subsection. To get a sense of scale  $e^2/(4\pi\epsilon_0 r)$  at  $r = 1 \text{ nm}$  is already on the order of  $1 \text{ eV} \approx 10000 \text{ K}$ . However, this estimate is an oversimplification and the spatial extent of the orbitals including the precise nature of the orbital overlap reduces the actual strength of the exchange interaction to  $100 - 1000 \text{ K}$ .

Direct exchange is the exchange interaction between electrons on neighboring atoms. In elemental magnets such as transition metals Fe, Co, Ni or the rare-earth metals, one might think that direct exchange plays a decisive role in determining the total strength of the exchange interaction. However, the reality is more complicated as the atoms are located spatially too far apart for effective direct exchange to take place. Instead, the conduction electrons play a major role in determining the experimentally observed exchange interaction.

### 4.3.3 Superexchange

Superexchange refers to an indirect exchange mechanism which proceeds via an intermediate ion between two magnetic atoms. It was observed that certain ionic compounds such as MnO have anti-ferromagnetic ground states despite no direct bond being present between adjacent  $\text{Mn}^{2+}$  ions. The simplest example to illustrate the superexchange process is to consider two d orbitals containing a single unpaired electron coupled through a filled p orbital. By allowing the electrons to hop on and off the p orbital, we can see that there is an energetic advantage to anti-alignment of the spins on the d orbitals. The anti-alignment allows for electron delocalization which reduces the overall energy of the system. This tendency to anti-align is captured by writing down an anti-ferromagnetic exchange interaction between the spins.

Later when we encounter complex oxides, superexchange will play a dominant role in determining the interaction between the constituent magnetic ions. The sign and magnitude of superexchange depends on the length of metal-oxygen (M-O) bonds and the M-O-M bond angle. Anti-ferromagnetic superexchange is most efficient when the M-O-M bond angle is close to  $180^\circ$ . Goodenough-Kanamori rules are used to predict the sign of the exchange interactions and are a valuable tool in predicting if a particular compound will be ferromagnetic or anti-ferromagnetic based only on the atomic structure of the material [59].

### 4.3.4 Exchange mediated by a Fermi liquid: RKKY interactions

The interaction between isolated magnetic moments and the conduction band in a metal leads to another exchange mechanism. A localized magnetic moment creates spatial oscillations in spin polarization around the location of the moment. This polarization can couple to another localized magnetic moment in the vicinity of the first moment. Since this mechanism does not involve direct coupling between localized moments, it is known as indirect exchange. Another name for this interaction is an abbreviation of the discoverers of this mechanism: RKKY (Ruderman, Kittel, Kasuya and Yosida). RKKY interaction between two moments separated by distance  $r$  is given by:

$$J_{RKKY}(r) = C \frac{\cos(2k_F r)}{r^3} \quad (4.41)$$

The above functional form assumes a spherical Fermi surface with radius  $k_F$ . The cosine term leads to oscillations in the sign of the interaction and can lead to either ferromagnetic or anti-ferromagnetic interactions depending on the value of  $r$ . As such, a distribution of such localized moments in a metal with varying separations leads to a distribution of ferromagnetic and anti-ferromagnetic couplings in the same material. We will encounter RKKY mechanism again in the context of spin glasses in a later section.

In addition to these commonly encountered interaction mechanisms, there are other mechanisms such as double exchange involving ions showing mixed valency (e.g.  $\text{Mn}^{3+}$ ), biquadratic exchange involving higher order terms in the Hubbard model, and Dzyaloshinskii-Moriya anisotropic exchange arising from spin-orbit interactions [58].

## 4.4 Magnetic Order: Non-frustrated magnetism

In the previous section, we came across a variety of mechanisms that give rise to moment-moment interactions. At low temperatures, an ordered arrangement of spins can reduce the total ground state energy with these interactions. The phase transitions associated with these interactions can be understood at the mean-field level using Curie-Weiss models, which we will discuss next.

### 4.4.1 Curie-Weiss model

Consider spin- $J$  moments on a lattice, coupled to their  $z$  nearest neighbors and to an external field:

$$H = -J_{\text{ex}} \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j - \vec{B} \cdot \sum_i \vec{S}_i \quad (4.42)$$

Here  $J_{\text{ex}}$  is the exchange constant introduced in Section 4.3.2, sub-scripted to keep it distinct from the total angular momentum  $J$ . The interaction term makes this a many-body problem. The mean-field approximation replaces the neighbors of site  $i$  by their thermal average, so that each spin sees

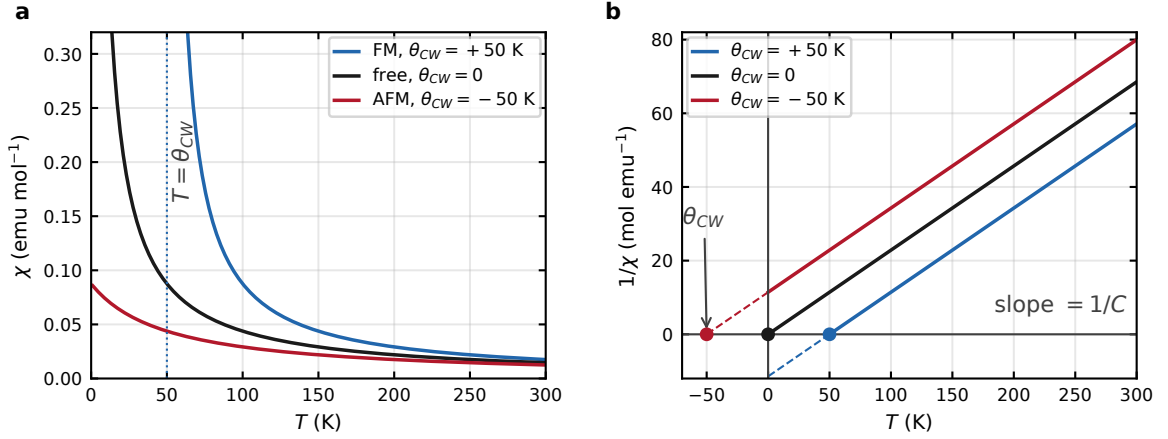


Figure 4.4: **Curie–Weiss susceptibility.** (a) Susceptibility  $\chi = C/(T - \theta_{CW})$  of a mean-field magnet for the three signs of the Curie–Weiss constant, all at the same Curie constant  $C$ : ferromagnetic coupling ( $\theta_{CW} = +50$  K), non-interacting moments ( $\theta_{CW} = 0$ , the Curie law of Eq. 4.34), and antiferromagnetic coupling ( $\theta_{CW} = -50$  K). Ferromagnetic coupling drives the susceptibility to diverge as  $T \rightarrow \theta_{CW}$  from above (dotted line), whereas antiferromagnetic coupling suppresses it below the free-moment value at every temperature. Above roughly 150 K the three curves are barely distinguishable, and the mean-field form in any case only applies above an ordering transition. (b) The same three cases plotted as  $1/\chi$ , which linearises the Curie–Weiss form: each is a straight line of slope  $1/C$  whose intercept on the temperature axis is  $\theta_{CW}$  (circles). Solid segments span the physically accessible region; dashed segments are the extrapolation from that region back to the intercept. Both the size of the moment, through  $C = N\mu^2/3k_B$ , and the sign and strength of the exchange, through  $\theta_{CW} = J_{\text{ex}}zJ(J+1)/3k_B$ , are read directly off this plot, which is why susceptibility data are almost always presented in inverted form.

an effective field built from the magnetization it is itself helping to produce:

$$H_{MF} = -J_{\text{ex}}z\langle\vec{S}\rangle \cdot \vec{S}_i - \vec{B} \cdot \vec{S}_i \quad (4.43)$$

We work in the density-matrix formalism, which handles the thermal averaging cleanly and generalizes without modification to the crystal-field Hamiltonians we meet in later chapters. The thermal density matrix is

$$\rho_{th} = \frac{\exp(-\beta H_{MF})}{\text{Tr}\{\exp(-\beta H_{MF})\}} \quad (4.44)$$

with  $\langle\vec{S}\rangle = \text{Tr}\{\vec{S}_i\rho_{th}\}$ . No approximation has been made beyond the mean-field replacement itself. Two simplifications now make the problem tractable. First, take the field along  $z$  with magnitude  $B$ , so that

$$H_{MF} = -J_{\text{ex}}z\left(\langle S \rangle_x S_{ix} + \langle S \rangle_y S_{iy} + \langle S \rangle_z S_{iz}\right) - BS_{iz} \quad (4.45)$$

Second, work at high temperature,  $\beta J_{\text{ex}}z$ ,  $\beta B \ll 1$ , so the exponential can be expanded as  $\exp(-\beta H_{MF}) = 1 - \beta H_{MF} + \mathcal{O}(\beta^2)$ . This is the regime in which a Curie–Weiss fit to measured

data is meaningful: well above any ordering temperature, and well above the Zeeman scale of the measurement field.

Since  $H_{MF}$  commutes with  $S^2$  and  $S_{iz}$ , evaluate the traces in the basis  $|m\rangle$  of  $S_{iz}$  eigenstates, with  $m$  running from  $-J$  to  $+J$  over  $2J+1$  values. Two elementary facts then collapse the algebra: the transverse operators are purely off-diagonal,  $\langle m|S_{ix}|m\rangle = \langle m|S_{iy}|m\rangle = 0$ , and

$$\sum_{m=-J}^J m = 0, \quad \sum_{m=-J}^J m^2 = \frac{J(J+1)(2J+1)}{3} \quad (4.46)$$

The first sum sets the  $\mathcal{O}(\beta)$  term of the normalization to zero. Keeping terms to  $\mathcal{O}(\beta)$ ,

$$\text{Tr}\{\exp(-\beta H_{MF})\} = (2J+1) + \mathcal{O}(\beta^2) \quad (4.47)$$

$$\text{Tr}\{S_{iz} \exp(-\beta H_{MF})\} = \beta (J_{\text{ex}} z \langle S \rangle_z + B) \frac{J(J+1)(2J+1)}{3} + \mathcal{O}(\beta^2) \quad (4.48)$$

Dividing one by the other gives the self-consistent equation for  $\langle S \rangle_z$ , which is all we need since the susceptibility of interest is for a field along  $z$ :

$$\langle S \rangle_z = \frac{\beta (J_{\text{ex}} z \langle S \rangle_z + B) J(J+1)}{3} + \mathcal{O}(\beta^2) \quad (4.49)$$

Collecting the  $\langle S \rangle_z$  terms and solving,

$$\langle S \rangle_z = \frac{B J(J+1)}{3k_B} \frac{1}{T - J_{\text{ex}} z \frac{J(J+1)}{3k_B}} \quad (4.50)$$

The interaction has done something simple but consequential: it has shifted the pole of the response away from  $T = 0$ , where the free-moment result of the previous section put it.

To convert to a susceptibility for  $N$  spins, use the magnetization  $\langle m \rangle_z = N g \mu_B \langle S \rangle_z$  and restore the physical Zeeman coupling with  $B \rightarrow g \mu_B B$ :

$$\chi(T) = \frac{\partial \langle m \rangle_z}{\partial B} = \frac{N (g \mu_B)^2 J(J+1)}{3k_B} \frac{1}{T - J_{\text{ex}} z \frac{J(J+1)}{3k_B}} \quad (4.51)$$

Comparing with the standard Curie-Weiss form  $\chi = C/(T - \theta_{CW})$  identifies the Curie constant,

$$C = \frac{N (g \mu_B)^2 J(J+1)}{3k_B} = \frac{N \mu^2}{3k_B} \quad (4.52)$$

where  $\mu = g\mu_B\sqrt{J(J+1)}$  is the “size” of the spin- $J$  moment, and the Curie-Weiss constant,

$$\theta_{CW} = J_{\text{ex}} z \frac{J(J+1)}{3k_B} \quad (4.53)$$

Setting  $J_{\text{ex}} = 0$  recovers the Curie law of Eq. 4.34.

Figure 4.4 shows susceptibility  $\chi$  as a function of temperature  $T$ . Panel (a) plots  $\chi(T)$  for the three signs of  $\theta_{CW}$  at fixed  $C$ . Ferromagnetic coupling ( $J_{\text{ex}} > 0$ ) pushes the pole to positive temperature and the susceptibility diverges on approaching it from above; antiferromagnetic coupling ( $J_{\text{ex}} < 0$ ) moves the pole to negative temperature and suppresses  $\chi$  below its free-moment value everywhere. Above roughly 150 K the three curves are barely distinguishable. In Panel (b), we plot  $1/\chi$  and the Curie-Weiss form is a straight line whose slope is  $1/C$  and whose intercept on the temperature axis is  $\theta_{CW}$ .

Within mean-field theory the magnitude  $|\theta_{CW}|$  also sets the temperature at which order appears. That two temperatures which mean-field theory equates are found to differ by orders of magnitude in real materials is the central experimental signature of frustration, and we return to it quantitatively in Section 4.5.

Some further points to note from this result:

1. For a fixed  $J_{\text{ex}}$ , the measured Curie-Weiss constant depends on the magnitude of the spin- $J$  moment. Hence, when using  $\theta_{CW}$  as a proxy for  $J_{\text{ex}}$ , we must incorporate the  $J(J+1)$  factor. The correct expression is

$$J_{\text{ex}} = \frac{3k_B\theta_{CW}}{zJ(J+1)} \quad (4.54)$$

If the aim is to maximize  $J_{\text{ex}}$  in materials where what we actually measure is  $\theta_{CW}$ , the following rules are useful:

- (a) maximize  $\theta_{CW}$ ;
  - (b) choose low co-ordination number ( $z$ ) compounds, i.e. honeycomb ( $z = 3$ ) > square, tetrahedral ( $z = 4$ ) > triangular ( $z = 6$ );
  - (c) choose  $J$  as low as possible, i.e. spin-1/2 moments are preferable to high- $J$  moments; e.g. for  $J = 6$ ,  $J(J+1)/3 = 14$ , so  $J_{\text{ex}}$  is over an order of magnitude smaller than the measured  $\theta_{CW}$ .
2. Observe that we can write  $\theta_{CW} \sim J_{\text{ex}} z |\mu|^2$  where  $|\mu|^2 \sim J(J+1)$ . In this analysis we have neglected the effect of crystal fields. If the effect of crystal fields is to reduce the magnitude  $|\mu|$  of the moment as the temperature is lowered, then one would expect  $\theta_{CW}$  to show a similar dependence. A Curie-Weiss fit over a high-temperature window and one over a low-temperature

window will then return different values of both  $C$  and  $\theta_{CW}$ , even with the exchange held fixed. We encounter exactly this complication in the  $\text{Tb}^{3+}$  moments of Chapter 5.

## 4.5 Frustrated magnetism

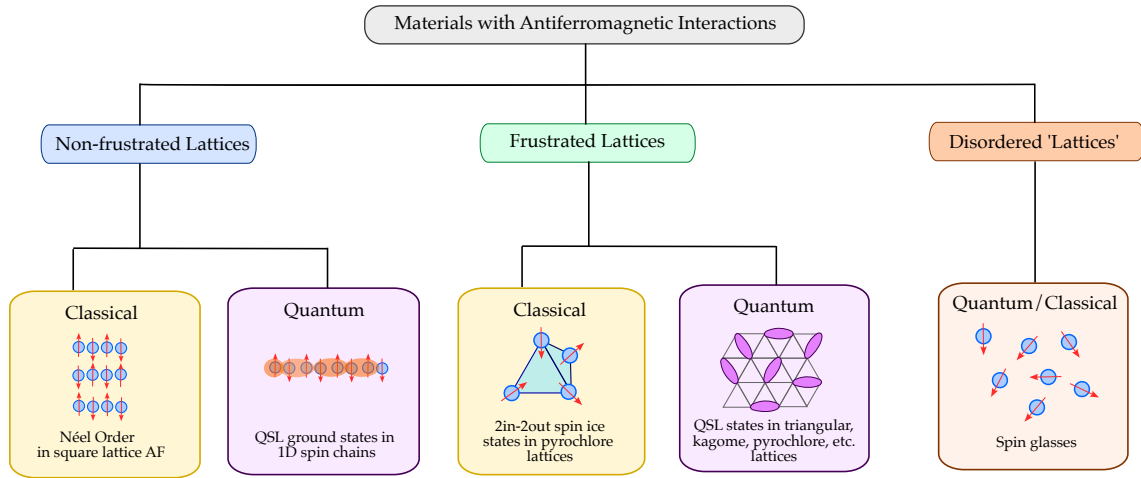


Figure 4.5: **A map of antiferromagnetic ground states.** Classification of materials with antiferromagnetic interactions, branching first on the lattice and then on the size of the quantum fluctuations. On a non-frustrated, bipartite lattice every bond can be satisfied at once. The square-lattice antiferromagnet freezes into the two-sublattice Néel state with a unique ground state and magnetic Bragg peaks below  $T_N$ . Lowering the spin and the dimensionality changes nothing about which bonds can be satisfied, but it does change whether the ordered state survives: in the  $S = 1/2$  Heisenberg chain, zero-point fluctuations destroy long-range order at any temperature, leaving a resonating pattern of nearest-neighbor singlets whose excitations are deconfined spinons rather than magnons. Frustration removes the possibility of satisfying every bond at all. Classically this leaves a macroscopically degenerate manifold in place of a unique ground state, as in the spin ices, where Ising moments on the corner-sharing tetrahedra of the pyrochlore lattice obey a two-in / two-out rule on every unit and retain a residual entropy down to the lowest temperatures. Once the moments are small enough to tunnel between those degenerate configurations, the system can instead settle into a quantum spin liquid: a long-range entangled superposition of many singlet coverings, sought on the triangular, kagome and pyrochlore lattices, and the state of interest for the  $\text{TbInO}_3$  films of Chapter 5. Frustration need not come from the lattice at all. A random distribution of moments coupled by an oscillating interaction such as RKKY carries a random mixture of ferromagnetic and antiferromagnetic bonds, and the resulting spin glasses freeze cooperatively without ever developing long-range order. Note that spin liquids appear on both the non-frustrated and the frustrated branch: geometric frustration is sufficient to destroy magnetic order, but it is not necessary.

The Curie-Weiss theory of the previous section makes a prediction that magnets order at the scale given by the Curie-Weiss constant. A material with antiferromagnetic exchange has  $\theta_{CW} < 0$



and on cooling to  $T \sim |\theta_{CW}|$ , we expect to see an ordered ground state, typically a Néel state. For MnO, the material that established the basic phenomenology of antiferromagnetism, this is exactly what happens [53].

However, for a large class of antiferromagnets, ordering does not happen at low temperatures. The mineral herbertsmithite,  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ , has an exchange constant of roughly 17 meV, close to 200 K, and shows no magnetic order down to 50 mK [60]. The interactions are enormous compared to the mK energy scale, and yet the spins refuse to pick a configuration. Ref. [61] proposed a simple figure of merit to quantify the level of discrepancy between the ordering scale and the interaction scale, the frustration index  $f$  given as follows:

$$f = \frac{|\theta_{CW}|}{T_N} \quad (4.55)$$

where  $T_N$  is the experimentally observed ordering temperature.  $T_N$  is replaced by the lowest temperature at which measurements occur where no transition to long-range order is observed experimentally. Mean-field theory predicts  $f \approx 1$ ; a value  $f \gtrsim 10$  is the conventional threshold for calling a material frustrated, and the best candidates reach  $f > 100$ .

Two distinct mechanisms: geometrical frustration and quantum fluctuations conspire to give large frustration indices in materials. Figure 4.5 organizes the observed ground states for materials containing moments with antiferromagnetic interactions. The first is geometry: on some lattices, the antiferromagnetic bonds simply cannot all be satisfied at once, so there is no unique classical ground state to order into. The second is quantum mechanics: even when a classical ground state exists, zero-point fluctuations can be strong enough to melt it. The two mechanisms reinforce each other, and the most interesting materials are those where both are at work.

### 4.5.1 The origin of geometric frustration

The canonical example for geometric frustration is three Ising spins on a triangle with antiferromagnetic coupling between each pair. If we satisfy the first bond by making two spins antiparallel, the third spin now faces two neighbors pointing in opposite directions. Whichever way it points, one of its two bonds is left unsatisfied. There is no arrangement that minimizes every term in the Hamiltonian simultaneously. Instead of the twofold degeneracy of an unfrustrated antiferromagnet, the triangle has six ground states, all with the same energy.

Nothing about this argument referred to the chemistry of the magnetic atom or the moment size. What produced the degeneracy was the odd-membered loop, and so materials in which frustration arises this way are called *geometrically frustrated*. Tiling the plane or filling space with such loops multiplies the degeneracy: rather than a single ground state, one obtains a manifold whose size grows exponentially with the number of spins. The system is free to wander within it instead of

ordering.

The fate of the ground state in this degenerate manifold depends on the size of the moments. Large, strongly anisotropic moments cannot tunnel between the degenerate configurations, and the system simply explores the manifold thermally and then falls out of equilibrium. The spin ices are the cleanest realization [62, 63] of being stuck in one of the realizations of a classical ground state within a macroscopically degenerate ground state manifold. Ising moments sit on the corner-sharing tetrahedra of the pyrochlore lattice with a local easy axis along the line joining each site to the tetrahedron centers, and the ground-state condition on each tetrahedron is that two moments point in and two point out. There are six such configurations per tetrahedron out of sixteen, and because the tetrahedra share corners the constraint cannot be used to build a unique global state. Specific-heat measurements on  $\text{Dy}_2\text{Ti}_2\text{O}_7$  recover a residual entropy close to the entropy estimated for configurations of protons in water ice, which is where the name spin ices comes from [61].

When the size of the magnetic moment is small, the energetic cost to change the direction of the moment is also lower ( $\sim JS^2$  where  $S$  is the size of the moment). If the energy difference between two equivalent states is small enough for quantum tunneling between the degenerate configurations to be appreciable, the system need not freeze into any one of them. It can instead form a coherent superposition of many, and the resulting state is a *quantum spin liquid*: a ground state with no magnetic order at any temperature, no broken symmetry to label it by, and long-range entanglement between distant spins [6, 13, 7]. Anderson proposed the first such wavefunction, a resonating superposition of nearest-neighbor singlet coverings, as an alternative to the Néel state for  $S = 1/2$  [64]. Its most striking consequence is that the excitations are not magnons. Breaking one singlet creates two spin-1/2 objects which, in a genuine spin liquid, can move apart independently. These fractionalized excitations are called spinons, and detecting them is the central experimental problem of the field.

Frustration does not strictly require a frustrating lattice. Quantum fluctuations grow as the spin and the dimensionality are reduced, and in the  $S = 1/2$  Heisenberg chain, a perfectly bipartite system in which every bond can be satisfied, they are strong enough to destroy long-range order at any temperature and leave deconfined spinons behind. Geometric frustration is a sufficient route to a spin liquid, not a necessary one, which is why Figure 4.5 places spin liquids on both the frustrated and unfrustrated branches.

A third class arises when the frustration comes from disorder rather than geometry. Dilute moments in a metal are coupled by the RKKY interaction, whose sign oscillates with separation, so a random distribution of impurity spacings produces a random mixture of ferromagnetic and antiferromagnetic bonds. Around any closed loop the product of bond signs is then as likely to be negative as positive, and a negative product is exactly the condition for frustration. These systems do not order, but neither do they remain static: below a freezing temperature  $T_f$  the spins lock cooperatively into one of many metastable configurations, with slow dynamics, aging and memory

effects rather than a sharp thermodynamic transition [65]. Given the similarity of slow spin dynamics to what is observed in ‘optical’ (i.e. soda-lime) glasses, these materials are referred to as spin glasses.

### 4.5.2 Lattices prone to magnetic frustration

Since geometrical frustration is a property of the lattice, the search for frustrated magnets begins with identifying lattices prone to magnetic frustration. The relevant question for any lattice is whether its bonds can be partitioned into two sublattices such that every bond connects one to the other. Such bipartite lattices are unfrustrated: the square lattice is the standard example, and the two-sublattice Néel state satisfies all four bonds at every site. The honeycomb and simple cubic lattices are bipartite for the same reason. Frustration requires loops of odd length, which is to say triangles.

The triangular lattice is built from *edge-sharing* triangles, and although the Ising model on it is macroscopically degenerate, the classical Heisenberg antiferromagnet is not: the three-sublattice  $120^\circ$  structure satisfies every bond as well as it can be satisfied, and the ground state is unique up to global rotations. Frustration on the triangular lattice weakens order and reduces the ordered moment, but it does not by itself prevent order. The kagome lattice is built from *corner-sharing* triangles, and here the counting changes qualitatively. Each triangle can be satisfied independently of its neighbors because they share only a single site, so the ground-state manifold retains an extensive degeneracy even for Heisenberg spins, and the coordination number drops from  $z = 6$  to  $z = 4$ .

In 3D, the pyrochlore lattice is a network of corner-sharing tetrahedra, the 3D analogue of the kagome lattice, and it inherits the same extensive degeneracy. The pyrochlore lattice can also be viewed as an alternating stack of kagome and triangular planes along the [111] direction. It is by some margin the most frustrated three-dimensional lattice known, which is why the magnetic pyrochlore oxides have supplied so many of the field’s canonical materials, from spin ices to spin liquid candidates [63, 66].

The following three separate considerations can be used to guide a search for frustrated magnets. First is the corner-sharing geometry. Corner-sharing triangles and tetrahedra decouple the ground-state constraints on neighboring units and produce degeneracies that grow with system size, whereas edge-sharing units often permit conventional order. Second, low coordination number. The mean-field result of Section 4.4.1 gives  $J_{\text{ex}} = 3k_B\theta_{CW}/zJ(J+1)$ , so for a fixed measured  $\theta_{CW}$  a low- $z$  lattice implies a larger exchange constant per bond. The kagome lattice at  $z = 4$  therefore buys a stronger microscopic interaction than the triangular lattice at  $z = 6$  for the same Curie-Weiss temperature, and fewer neighbors also means a weaker mean field, which is precisely what suppresses ordering. Third, low dimensionality tends to disfavor an ordered ground state. Quantum fluctuations are more effective the fewer neighbors each spin has and the lower the dimension. Two-dimensional layers with continuous spin symmetry cannot develop long-range order at any finite temperature at all through the Mermin-Wagner theorem [67], so a quasi-2D material orders only through weak

interlayer coupling.

Frustration can also be produced on an unfrustrated lattice by competing further-neighbor exchange; the square lattice with both nearest-neighbor  $J_1$  and next-nearest-neighbor  $J_2$  antiferromagnetic couplings is frustrated near  $J_2/J_1 \approx 1/2$  [68]. Conversely, a frustrated lattice is no guarantee of a frustrated ground state, because the anisotropic and further-neighbor terms discussed in Section 4.3.2 can generically lift the degeneracy at some low energy scale.

### 4.5.3 Experimental signatures

Frustrated magnets are defined by what they fail to do, which makes their experimental identification a process of accumulating negative results and then eliminating expectations based on ordered states [69].

Magnetic susceptibility is typically the first measurement which can be used to identify the frustration index. A conventional antiferromagnet shows a clear cusp in  $\chi(T)$  at  $T_N$ , below which the susceptibility falls as the sublattice moments lock into place. A frustrated magnet instead continues to follow the Curie-Weiss form of Eq. 4.51 straight through  $T \sim |\theta_{CW}|$  and  $\chi$  keeps growing as the temperature is lowered rather than saturating or turning over. In practice the low-temperature susceptibility of real samples is often contaminated by a Curie tail from a small concentration of weakly coupled defect spins, and in herbertsmithite the Cu-Zn site mixing that produces such orphan spins has been a persistent complication in interpreting the intrinsic response [60].

The absence of order must then be established directly, since a susceptibility measurement cannot exclude a small ordered moment. Neutron diffraction can be used to find magnetic Bragg peaks and muon spin rotation can probe any static internal fields of order  $10^{-2} \mu\text{T}$  [6]. Instead of sharp Bragg peaks, diffuse scattering in reciprocal space is observed [63].

Inelastic neutron scattering can measure the dynamical structure factor  $S(\vec{q}, \omega)$  and therefore probe the excitations directly. An ordered magnet has sharp magnon branches: a single spin flip is a well-defined  $\Delta S = 1$  quasiparticle with a definite dispersion. A spin liquid does not. Because a neutron flipping one spin creates a *pair* of spin-1/2 spinons which then share the transferred energy and momentum in any proportion, the spectral weight is spread into a broad continuum bounded by kinematic limits rather than concentrated on a dispersion curve. This continuum is the most direct evidence for fractionalization available. It has been measured with quantitative precision in the  $S = 1/2$  Heisenberg chain, where the two-spinon and higher-order contributions account for the full spectral weight [70], and it is observed on the kagome lattice in single-crystal herbertsmithite, where the excitations form a continuum with no sign of the spin waves expected of an ordered state [71]. The same signature motivates the material of this thesis:  $\text{TbInO}_3$  shows a broad, gapless continuum of magnetic excitations at the triangular-lattice zone boundary and no static order down to temperatures two orders of magnitude below its exchange scale [72].

Thermodynamic and transport probes provide complementary constraints. Specific heat measures the entropy released on cooling, and a classically degenerate manifold retains some of it: this is how the residual entropy of spin ice was found [61]. In a quantum spin liquid the low-temperature specific heat instead follows a power law set by the spinon density of states, so that a gapless spin liquid with a spinon Fermi surface is expected to show a linear term  $C \sim \gamma T$  in an electrical insulator, where no such term has any business being. Because spinons are mobile and carry energy, the same physics predicts a residual linear term in the thermal conductivity,  $\kappa/T \rightarrow \text{constant}$  as  $T \rightarrow 0$ , which would be a spectacular signature: heat conducted through an insulator by fractionalized magnetic excitations. However, evidence of signatures of spinons in heat conductivity has not been established conclusively. A residual linear term was reported in the organic triangular-lattice candidate  $\text{EtMe}_3\text{Sb}[\text{Pd}(\text{dmit})_2]_2$  and interpreted as evidence for highly mobile gapless excitations [73], but a later measurement on the same compound found a vanishingly small residual term and concluded that the excitations responsible for the specific-heat anomaly are localized rather than itinerant [74]. The quality of samples plays a crucial role in observation of these experimental signatures, and hence working with material platforms where materials with low defect densities are possible is necessary to draw useful conclusions.

## 4.6 Looking for frustrated magnetism: Complex oxides

The field of frustrated magnetism would be quite boring if the simplified phenomenology we described before did not occur in real materials. Fortunately for us, there are many well-studied classes of materials in which frustrated magnetism occurs in a variety of incarnations such as spin ices and quantum spin liquids. A particular material class that we will encounter in the next two chapters is oxides.

Realizing frustrated magnetism places many stringent demands on the material system that realizes it. We need magnetic moments that are well localized, exchange interactions whose magnitude is large and whose sign is set by the crystal geometry, a lattice that supports frustration, and experimental synthesis knobs that can tune the frustrated magnetic state. Complex oxides, which we define here as compounds with one or many transition metal and rare-earth cations and oxygen anions, can satisfy many of these requirements simultaneously. Hence, it is no surprise that the canonical frustrated magnets described in the previous sections are overwhelmingly oxides.

Complex oxides are typically electrical insulators. In a transition metal oxide, the  $d$  electrons occupy narrow electronic bands and the on-site Coulomb repulsion is large compared to the hopping energy; such Mott insulators host localized moments rather than itinerant electrons [75]. This localization matters for frustration: itinerant magnets typically have RKKY interactions of oscillating sign and magnitude between the spins, and as a result may not support geometrical frustration. The oxygen ions not only balance the cation charge but also mediate superexchange interactions,

whose sign and strength follow from the cation-oxygen-cation bond angle through the Goodenough-Kanamori rules [59]. These exchange mechanisms supply the crucial antiferromagnetic interactions which lead to frustrated magnetism. In rare-earth oxides, the story acquires additional flavors: the  $4f$  moments are even more strongly localized, the exchange scales are smaller, and the crystal electric field splits the free-ion multiplet. As a result, the effective low-energy moment including its size and anisotropy is a strong function of the local environment of the ion. We will encounter exactly this physics in the  $\text{Tb}^{3+}$  moments of  $\text{TbInO}_3$  in chapter 5.

Finally, complex oxides form many series of iso-structural families with groups of transition metal or rare-earth ions. For example, in the pyrochlore titanates  $\text{A}_2\text{Ti}_2\text{O}_7$ , the A cation can take most of the lanthanide series. Across such an iso-structural family, the strength of the exchange interaction, the size of the magnetic moment, and the crystal field can be varied systematically while keeping the geometry fixed. This tuning knob has made the pyrochlores a playground for frustrated magnetism, hosting spin ices, spin liquids, and spin glasses within a single structure type [63, 66]. In chapter 6, we will discuss measurements of  $\text{Gd}_2\text{Ti}_2\text{O}_7$  with isotropic  $\text{Gd}^{3+}$  moments.

## Chapter 5

# Microwave spin resonance in spin liquid candidate $\text{TbInO}_3$

This chapter is adapted from Ref. [76]. In this chapter, we use superconducting resonators to probe spin resonance at microwave frequencies in a quantum spin liquid candidate  $\text{TbInO}_3$ . Films of  $\text{TbInO}_3$  were synthesized for the first time in Ref. [8] and in this chapter, we use these films to understand the mK ground state of the Tb moments.

### 5.1 A new frontier: Epitaxy of frustrated magnet thin films

The ability to grow thin films with exquisite control over parameters such as film composition, layer thickness, and crystal structure is a big advantage of working with complex oxides. Growth methods such as pulsed laser deposition (PLD) and molecular beam epitaxy (MBE) for complex oxide thin films have reached a level of maturity [77, 78, 79] such that materials with complex compositions can be grown epitaxially with low defect densities. In these techniques, the film is assembled essentially one atomic layer at a time on a single-crystal substrate, with in-situ diagnostics such as reflection high-energy electron diffraction (RHEED) providing real-time feedback on the growth. The substrate through its lattice constant and symmetry can modify the properties of the film grown on top. The choice of substrate selects the film orientation and can potentially impose a biaxial strain set by the lattice mismatch.

Epitaxy offers the frustrated-magnetism community several knobs that bulk synthesis cannot. Epitaxial strain acts as a continuous, symmetry-selective tuning parameter: straining a frustrated lattice perturbs the balance of competing exchange interactions and crystal fields directly, and can lift or restore the degeneracies at the heart of frustration. Film thickness provides a handle on dimensionality, interpolating between three-dimensional and quasi-two-dimensional limits of a

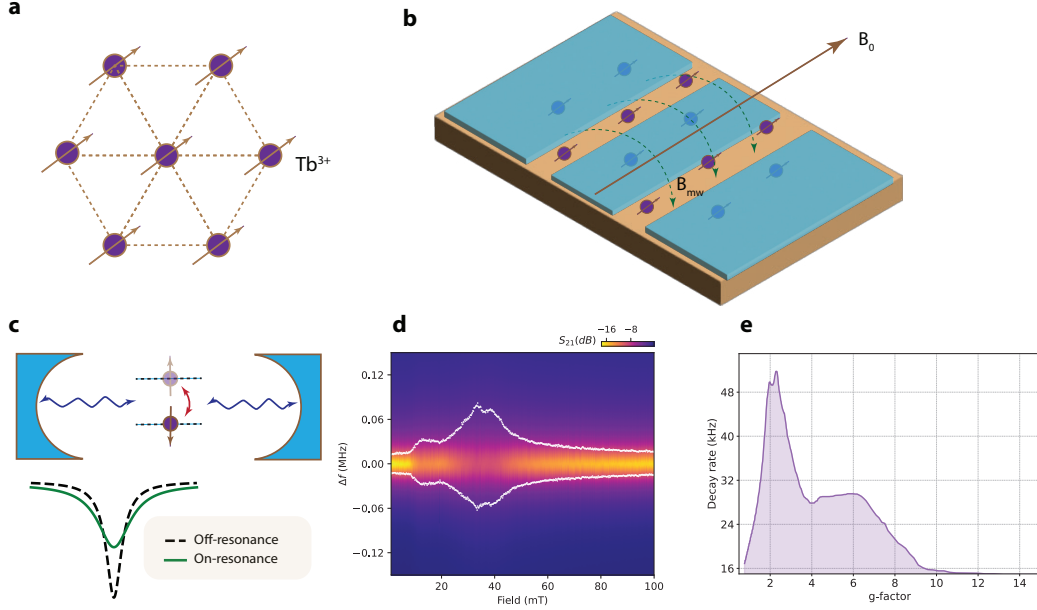
frustrated lattice. Epitaxial stabilization can create metastable phases that cannot be synthesized in bulk, enlarging the space of candidate frustrated materials. Finally, thin films are device compatible: a film of thickness  $t \sim 1\text{-}100\text{ nm}$  can be integrated directly with planar superconducting circuits, placing the frustrated magnet within the microwave field of a resonator. This is precisely the geometry we will exploit in chapters 5 and 6.

Frustrated magnets have arrived relatively late to the oxide epitaxy program, which historically focused on ferroelectrics, manganites, and superconductors [78, 80]. Spin ice films of  $\text{Ho}_2\text{Ti}_2\text{O}_7$  grown on yttria-stabilized zirconia (YSZ) provided an early demonstration that frustration physics survives in the thin-film limit [81], and epitaxial pyrochlore iridates have since become a platform for combining frustration with strong spin-orbit coupling [82]. Most relevant to us, the experiments in the current and the following chapter build on recent developments in epitaxial growth of frustrated magnet thin-films by the Mundy group at Harvard. Thin films of the quantum spin liquid candidate  $\text{TbInO}_3$  were grown on YSZ substrates by oxide MBE [8], preserving the frustrated Tb sublattice of the bulk while opening the door to resonator-based measurements. Experiments using these films are the subject of this chapter. Pyrochlore titanates and vanadates films have also been synthesized recently [83, 84]. In the next chapter, we will probe  $\text{Gd}_2\text{Ti}_2\text{O}_7$ , a Heisenberg pyrochlore frustrated magnet.

## 5.2 $\text{TbInO}_3$ : A triangular-lattice anti-ferromagnet

Broken-symmetry ground states are associated with fascinating properties such as ferromagnetic order and superconductivity. Less-studied but equally interesting are states in which global symmetry breaking is prevented by frustration and quantum fluctuations. Quantum spin liquids (QSLs) are canonical realizations of this, where the lattice geometry imposes frustration among localized magnetic moments, and the exchange interaction between moments introduces quantum fluctuations [6, 7]. In theoretical models, the effective dimensionality of the spin lattice plays a key role in the realization of QSLs. In 1D antiferromagnetic spin chains, quantum fluctuations alone suffice to yield QSL states, as corroborated experimentally in a variety of materials [85, 86]. In contrast, in 3D antiferromagnets (AFs), an ordered Néel ground state can be stabilized even in the presence of frustration and quantum fluctuations, in accordance with the Mermin-Wagner theorem [87, 85]. It is in 2D layered AFs with lattices such as triangular, honeycomb, and kagome that the tension between quantum fluctuations and magnetic ordering can lead to QSL ground states [6, 7]. Hence, 2D AFs with frustrated lattice geometry appear promising targets for experimentally realizing QSLs. Accordingly, materials such as Herbertsmithite [60], 2D-organic salts [88],  $\alpha\text{-RuCl}_3$  [89, 90], 1T-TaSe<sub>2</sub> [91], YbMgGaO<sub>4</sub> [92], and KYbSe<sub>2</sub> [93] have been extensively investigated with a wide range of techniques.





**Figure 5.1: Device schematic and basic principles of spin resonance detection.** (a)  $\text{Tb}^{3+}$  ions with a partially filled  $4f^8$  subshell form a frustrated triangular lattice. At low temperatures ( $T \lesssim 10$  K), each  $\text{Tb}^{3+}$  is in a doublet state. (b) Schematic of the coplanar microwave resonator fabricated by etching a NbTiN superconductor (blue) deposited on a  $\text{TbInO}_3$  film (golden). The microwave magnetic field  $B_{mw}$  points along paths concentric with the center pin of the waveguide. An external static magnetic field  $B_0$  is applied in the plane of the film such that the static field is perpendicular to the microwave field. (c) A spin embedded in a coplanar microwave resonator interacts with the resonator's electromagnetic field. When the frequency of the resonator is equal to the Zeeman splitting of a spin or the energy of a collective excitation, a resonant exchange occurs between photons in the resonator and the spins. This process causes an increase in the decay rate of the resonator. (d)  $S_{21}$  (dB) of the microwave feedline coupled to the resonator as a function of  $B_0$  and frequency. The white dots are a guide to the eye and track the resonator width. (e) The decay rate of the resonator as a function of an extracted  $g$ -factor, where  $g = \frac{hf}{\mu_B B_0}$ , where  $f$  is the frequency of the resonator and  $\mu_B$  is the Bohr magneton. Prominent broad resonances are centered around  $g = 2.1$  and  $g = 4 - 9$ .

Here, we focus on a layered hexagonal antiferromagnet,  $\text{TbInO}_3$ , where the rare-earth  $\text{Tb}^{3+}$  ion has a local magnetic moment. Magnetic susceptibility of bulk single-crystal  $\text{TbInO}_3$  anomalously continues to follow a naive Curie-Weiss form down to 450 mK, far below the Curie-Weiss temperature [72]. Inelastic neutron scattering measurements on both powder [72] and single-crystal [94] samples have confirmed the lack of conventional magnetic order at temperatures down to two orders of magnitude lower than the energy scale set by the exchange interaction ( $\theta_{\text{CW}} \sim 15$  K). This failure to order has been attributed to the arrangement of Tb moments in a frustrated 2D lattice, and has been suggested to reflect a spin liquid ground state [95]. An additional subtlety is that Tb sites are spatially shifted in a periodic pattern along the  $c$ -axis of the unit cell, leading to improper

ferroelectricity [95, 8]. This combination of magnetic frustration, large spin-orbit coupling, lattice distortion, and the resultant local crystal fields is unique to  $\text{TbInO}_3$  among spin liquid candidate materials.

Whereas single crystals of  $\text{TbInO}_3$  have been extensively studied since their first synthesis in 2018, growth of thin films could bring important opportunities such as using interfaces to introduce novel functionalities or break symmetries, and for inducing strain [96]. Furthermore, nanofabrication of functional devices is far easier on thin films compared to bulk crystals. Motivated by these advantages, epitaxial thin films of  $\text{TbInO}_3$  were recently synthesized for the first time [8, 97]. Characterizing magnetic order and fluctuations in thin films requires new approaches, as workhorse measurements of heat capacity and neutron scattering are technically challenging to apply to thin films. Near-DC magnetic susceptibility measurements on such films are challenging but possible. Recently, both macroscopic and scanning SQUIDs were used to characterize  $\text{TbInO}_3$  films and found that the Tb moments do not fully order down to 44 mK [8].

Here, we set out to develop a complementary probe of magnetic order and fluctuations in thin films, and apply it to  $\text{TbInO}_3$ . Inspired by progress in the field of hybrid quantum systems based on circuit quantum electrodynamics [98], we develop a microwave magnetic resonance technique which is compatible with thin films and capable of measurements down to millikelvin temperatures. Using planar superconducting resonators, we probe spin and collective magnetic excitations in  $\text{TbInO}_3$  thin films. From a resonant response as a function of magnetic field, we extract two distinct g-factors associated with the moments in  $\text{TbInO}_3$ , and compare them with a simple model based on superpositions of crystal-field eigenstates of  $\text{Tb}^{3+}$  moments. Why two distinct g-factors?  $\text{TbInO}_3$  in both bulk and thin film form has been shown to be an improper ferroelectric [95, 8]. Since the g-factor is a sensitive probe of the local environment of a magnetic moment, we associate the two g-factors with the two types of Tb sites under the known ferroelectric distortion. We extract the integrated spectral weight of each resonant feature, which is proportional to the magnetic susceptibility of the associated population of moments. In this way we show that Tb moments fluctuate down to 20 mK, extending previous reports of magnetic frustration in this material system to almost three orders of magnitude below the exchange interaction energy scale ( $\sim 11$  K).

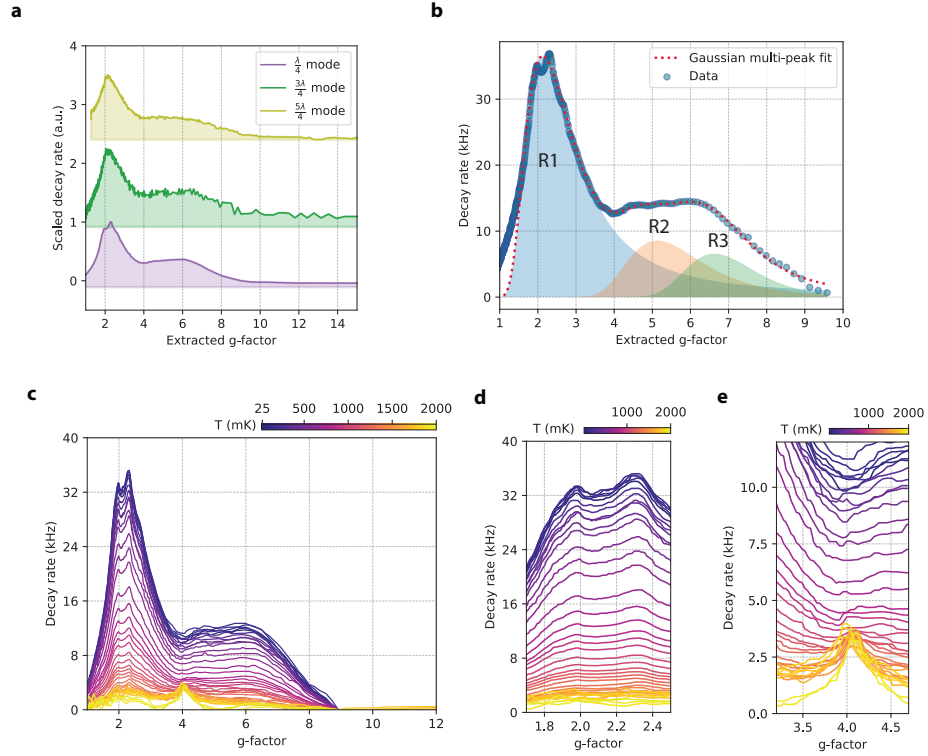


Figure 5.2: **Frequency and temperature dependence of the spin resonance signal.** (a) Decay rate of the resonator measured as a function of magnetic field for  $\lambda/4$ ,  $3\lambda/4$  and  $5\lambda/4$  modes of the same resonator. The corresponding frequencies are  $f$ ,  $3f$  and  $5f$ . An extracted g-factor ( $g = hf/(\mu_B B_0)$ ) is used as the x-axis. The response is qualitatively similar across the three modes when plotted as a function of  $g$ . (b) A multi-peak Gaussian model with three major components gives a good fit to the signal measured at the lowest temperature ( $\sim 18$  mK). We denote these three major components as R1 ( $g = 2.13 \pm 0.01$ ), R2 ( $g = 5.1 \pm 0.9$ ) and R3 ( $g = 6.6 \pm 0.5$ ). (c) Temperature dependence of the decay rate vs g-factor as a function of sample temperature from 18 mK to 2 K. (d) Two narrow resonances at  $g = 1.95$  and  $g = 2.3$  are observed on top of R1. (e) A third narrow resonance at  $g = 4.1$  has a very different phenomenology: suppressed for  $T \lesssim 800$  mK, but present at higher temperatures.

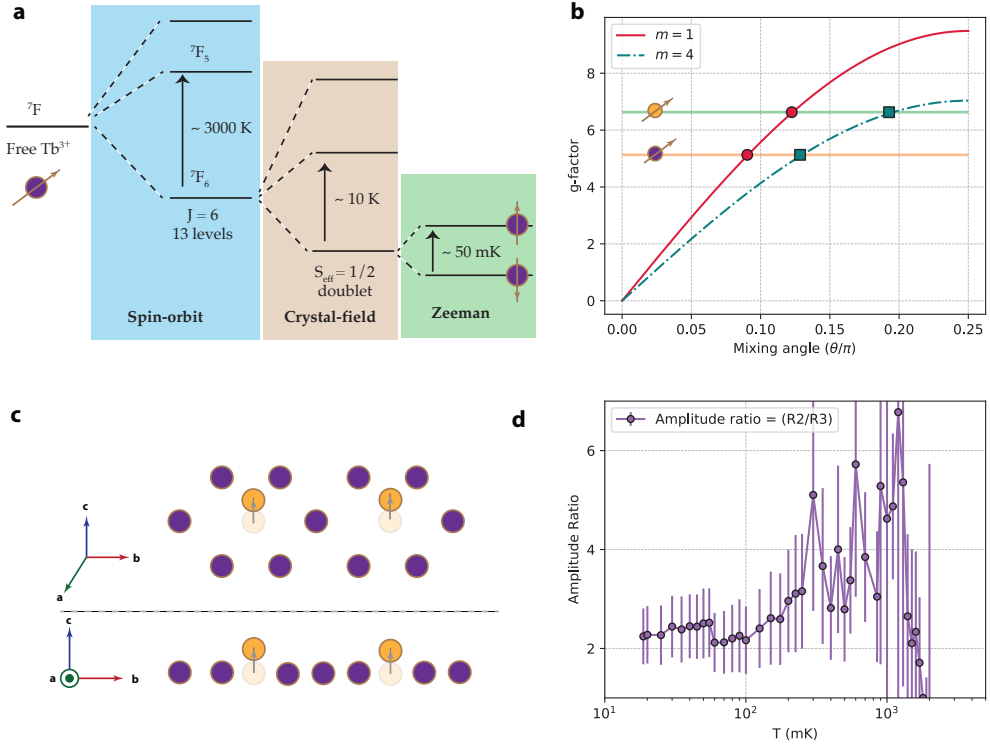


Figure 5.3: **Crystal-field model and c-axis displacement of Tb<sup>3+</sup> ions.** (a) The hierarchy of energy scales that govern the ground state of a single Tb<sup>3+</sup> ( $4f^8$ ,  $L = 3$ ,  $S = 3$ ) ion, neglecting coupling to other Tb<sup>3+</sup> sites. A large spin-orbit coupling from the high-Z Tb nucleus implies  $J = L + S$  is a good quantum number and the atomic term <sup>7</sup>F<sub>6</sub> with  $J = 6$  is the ground state.  $J = 0, \dots, 5$  states are separated by  $\sim 3000$  K from the ground state. The <sup>7</sup>F<sub>6</sub> state with  $J = 6$  is a collection of  $2J + 1 = 13$  levels. The crystal field from nearby ions further splits these into a doublet ground state separated from the lowest-lying crystal field excited level at 10 K. We apply an external magnetic field to finally split this doublet, adjusting the field so the splitting matches the resonator frequency. Note that the splittings are not drawn to scale. (b)  $g$ -factor calculated using a simple crystal-field model that mixes the  $m_J = -6, \dots, 6$  components of the  $J = 6$  moment, yielding a ground-state doublet built from either  $m_J = \pm 1, \pm 2$  states (solid line) or  $m_J = \pm 4, \pm 5$  states (dash-dot line). The mixing angle  $\theta$  parametrizes the superposition between the two constituent  $m_J$  states in each of these scenarios. For either assignment of the constituents of the ground-state doublet, the two  $g$ -factors for R2 and R3 as extracted in the previous figure can be matched by setting two different values of the mixing angle, as represented by red circles ( $m_J = \pm 1, \pm 2$ ) and teal squares ( $m_J = \pm 4, \pm 5$ ). (c) Displacement of 1/3 of the Tb ions along the  $c$ -axis leads to a distortion of the triangular lattice and hence the local crystal field environment. As a result, two flavors of Tb ions exist, each with a distinct crystal-field environment. (d) Amplitude ratio of the two Tb-moment peaks R2 ( $g = 5.1 \pm 0.9$ ) and R3 ( $g = 6.6 \pm 0.5$ ), extracted from the Gaussian fit model. At low temperatures, the amplitude ratio is close to 2. This suggests two classes of Tb moments with distinct  $g$ -factors are present in the film in a 2:1 ratio of concentration.

### 5.3 Probing magnetism in $\text{TbInO}_3$ by microwave spin resonance

We grow  $\text{TbInO}_3$  films on a yttria-stabilized zirconia (YSZ)  $\langle 111 \rangle$  substrate using molecular beam epitaxy (MBE) as described in [8]. The YSZ substrate ensures epitaxial growth of  $\text{TbInO}_3$  with the  $c$ -axis perpendicular to the substrate surface. We then use reactive magnetron sputtering with Nb and Ti targets in an Ar/ $\text{N}_2$  environment to deposit superconducting NbTiN films onto the  $\text{TbInO}_3$  films. Finally, we use photolithography followed by reactive plasma etching to pattern the superconducting film into a microwave feedline capacitively coupled to a  $\lambda/4$  co-planar waveguide (CPW) resonator. Additional details on crystal structure, growth, fabrication and measurement are provided in the methods section and supplementary information [99].

$\text{TbInO}_3$  has a hexagonal unit cell in which layers of magnetic  $\text{Tb}^{3+}$  ions are separated by layers of non-magnetic  $[\text{InO}_5]^{7-}$  corner-sharing trigonal bipyramid polyhedra [72, 94, 100]. A  $c$ -axis lattice constant of  $12.3 \text{ \AA}$ , far larger than the Tb-Tb intra-layer separation of  $3.65 \text{ \AA}$ , coupled with the compactness of  $f$ -orbitals, implies quasi-2D interactions between adjacent Tb moments. Fig. 5.1a schematically shows an ideal triangular lattice of Tb ions. Each Tb is in a  $3+$  oxidation state, corresponding to an incompletely filled  $f$ -subshell with electronic configuration  $4f^8$ . For bulk crystals, a careful analysis of powder and single-crystal magnetic susceptibility along with assignment of crystal fields based on neutron scattering and Raman spectroscopy have led to a common conclusion that an effective non-Kramers magnetic doublet state exists at low temperatures ( $\lesssim 5 \text{ K}$ ) [72, 94, 100]. The failure of this doublet to globally order has been attributed to frustration associated with antiferromagnetic coupling on a triangular lattice. We probe this doublet state using microwave spin resonance.

Within the mode volume of a microwave resonator, electric and magnetic fields at the resonator frequency are strongly enhanced. These fields can couple to spins and other collective excitations of a material placed within the mode volume, so the field enhancement can compensate for the low volume of the material to be probed. Such a resonator can be described as a damped harmonic oscillator with frequency  $f$  and energy loss rate  $\kappa$ . The field enhancement is given by the quality factor  $Q = \frac{f}{\kappa}$ . Resonators in planar rather than three dimensional geometry are particularly well suited to coupling to thin films: the electromagnetic field produced by the resonator falls off on a length scale set by its lithographic features, typically microns, so a resonator fabricated or placed atop a thin film of interest will probe that film as well as the top portion of the underlying substrate, but will be insensitive to the bulk of the substrate. We deposit NbTiN on  $\text{TbInO}_3$  films, then lithographically pattern the NbTiN to form superconducting planar resonators. Fig. 5.1b schematically shows a coplanar waveguide with a center conductor surrounded by a ground plane on top of the  $\text{TbInO}_3$  film. Since the  $22 \text{ nm}$  thickness of the film is much smaller than the  $10 \text{ }\mu\text{m}$  width of the center conductor, Tb spins through the entire film thickness are coupled to the resonator, as are any

free spins at interfaces or within the top  $\approx 10\text{ }\mu\text{m}$  of the substrate. We achieve quality factors  $Q = \frac{f}{\kappa} \sim 10^5$ , comparable to those reported for microfabricated planar superconducting resonators on more conventional substrates [101].

A spin interacting with an external magnetic field is described by the Zeeman Hamiltonian:  $H = g\mu_B \vec{B} \cdot \vec{S}$  where  $g$  is the g-factor,  $\mu_B$  is the Bohr magneton,  $\vec{B}$  is an externally applied magnetic field and  $\vec{S}$  is the quantum mechanical spin operator. We apply an external static magnetic field  $B_0$  in the plane of the film. As a result, the two spin eigenstates are split by  $\Delta E = g\mu_B B_0$ . We typically apply fields on the order of 10–300 mT, corresponding to splittings  $\frac{\Delta E}{h} = 0.28\text{--}8.4\text{ GHz}$  (for  $g = 2$ ), making resonators designed in the microwave GHz range ideal for our measurements. We use a resonator with a fundamental frequency  $f = 1.064\text{ GHz}$ . Upon tuning the external magnetic field, spins with different g-factors are independently coupled to the same resonator with the resonance condition  $hf = g\mu_B B_0$ . In resonance, the microwave field in the resonator drives transitions between the two spin eigenstates, which have a nonzero population difference set by temperature as  $\tanh\left(\frac{hf}{2kT}\right)$ . As a result of these transitions, the decay rate  $\kappa$  of the resonator gets an additional contribution which can be measured (see Fig. 5.1c). The resultant spin-photon hybridization also causes a shift in the resonator frequency, but since we are in the weak coupling limit [98] this frequency change is too small to be detected. Hence, we rely on measuring the decay rate of the resonator as a function of  $B_0$  to detect spin resonance.

Fig. 5.1d shows the raw transmission coefficient  $S_{21}$  (dB) of our microwave setup as a function of frequency and magnetic field. At a given magnetic field, a narrow dip appears at the resonator frequency  $f_0$ . In the plot, we shift the center of the resonance dip to zero at each magnetic field to highlight changes in the resonator width. The resonator width quantified into a decay rate of the resonator (see Methods for fitting and analysis of the resonator profile) changes as a function of the magnetic field. When the magnetic field is near a resonance condition for spins in the mode volume ( $hf = g\mu_B B$ ), the resonator decay rate is enhanced. To make a transparent connection to the underlying spins interacting with the resonator, we plot the decay rate as a function of an extracted g-factor defined as  $g = \frac{hf}{\mu_B B_0}$  in Fig. 5.1e. We observe a prominent broad peak centered around  $g = 2.1$ , and another broad peak with a spread of g-factors from 4–9.

A  $\lambda/4$  CPW resonator also has higher modes at  $3f$  and  $5f$ , in our case at 3.2 GHz and 5.3 GHz, respectively. In Fig. 5.2a, we plot the decay rate for  $f$ ,  $3f$  and  $5f$  modes as a function of the extracted g-factor. We observe that resonances (enhanced decay rate) occur at the same extracted g-factor for the three resonator modes: a feature that occurs at magnetic field  $B_0$  for a resonator mode at frequency  $f$  occurs at magnetic fields  $3B_0$  and  $5B_0$  when measured at  $3f$  and  $5f$ . This pattern allows us to rule out explanations other than magnetic resonance, for example loss due to superconducting vortices or parasitic cavity modes. Hence, a linear in magnetic field splitting described by a constant g-factor is indeed a good phenomenological descriptor of the observed resonances.

The width of a spin resonance signal is tied to the spin relaxation time. A narrow resonance

( $< 1$  mT) typically indicates localized spins on defect centers with long relaxation times, whereas broader resonances indicate that other interactions such as dipole-dipole and anisotropic exchange determine the linewidth. Moreover, the broadening mechanism also determines the functional form of the lineshape. For homogeneously-broadened lines, a Lorentzian lineshape is commonly used. On the other hand, when the local environment of individual sites is different, an inhomogeneously broadened line with a Gaussian lineshape is used. In Fig. 5.2b, a multi-peak Gaussian with three components gives the best fit to the data. Fitting with two Gaussians is not sufficient to capture the broad shoulder from  $g = 4 - 9$  and with three peaks, we see a good agreement between the data and the fit. We denote these three major components as R1 ( $g = 2.13 \pm 0.01$ ), R2 ( $g = 5.1 \pm 0.9$ ) and R3 ( $g = 6.6 \pm 0.5$ ). The R1 resonance is also observed on a second resonator fabricated on the same chip, with the  $\text{TbInO}_3$  film removed by ion milling to extract the YSZ substrate response [99]. Hence, R1 must be a result of defects or impurities in the YSZ substrate. On the other hand, g-factors corresponding to R2 and R3 are not seen from the resonator coupled only to the YSZ substrate, so they must arise from the  $\text{TbInO}_3$  film or in principle its interface with the substrate.

Fig. 5.2c shows the temperature dependence of the spin resonance signal from 18 mK to 2 K. With increasing temperature, the response is diminished by the decrease in polarization of the participating spins in the small applied magnetic field. We first focus on the identification of the g-factors corresponding to the narrow lines in our dataset. We show these narrow lines originate from impurities or defects in the superconducting film and the YSZ substrate. Figs. 5.2d and e show a zoom-in around the g-factor ranges where narrow lines are observed. The  $g = 1.9$  line (Fig. 5.2d) also occurs in a separate  $\text{NbTiN}$  resonator fabricated on silicon, showing that it does not reflect spins in either our thin film of interest or the YSZ substrate. We associate this feature with  $\text{Nb}^{4+}$  defects present on the surface of the superconducting film [99]. These defect spins have been recently reported in  $\text{NbTiN}$ /sapphire films through a similar resonator measurement [102]. The  $g = 2.3$  line (Fig. 5.2d) also occurs in the second resonator on the same YSZ chip, where the  $\text{TbInO}_3$  film was removed by ion milling to aid in background subtraction. However, it does not occur in another resonator on an otherwise-unprocessed YSZ substrate (no  $\text{TbInO}_3$  ever deposited) [99]. This suggests the feature arises from modification of the YSZ substrate during the growth of the  $\text{TbInO}_3$ . YSZ has been shown to conduct oxygen ions at high temperatures [103]. A g-factor slightly larger than 2 is consistent with an oxygen vacancy defect with spin-orbit coupling of intermediate strength in comparison to crystal fields [104, 105]. Finally, a third sharp resonance at  $g = 4.1$  has a temperature dependence quite different from that of all our other resonances: instead of fading with increasing temperature, it is absent for temperatures lower than  $\sim 800$  mK and emerges only at higher temperatures. Since ESR spectroscopy of Fe impurities in other materials has identified  $g = 4.1 - 4.3$  resonances as associated with the  $\text{Fe}^{3+}$  state [106, 107], we identify this resonance with Fe impurities in the YSZ substrate. From the magnitude of the signal at 2 K, we estimate a 60–840 ppm concentration of Fe impurities in the YSZ substrate [99]. We speculate that the

disappearance of the resonance signal below 800 mK could be caused by the  $\text{Fe}^{3+}$  impurity moments entering a spin glass state.

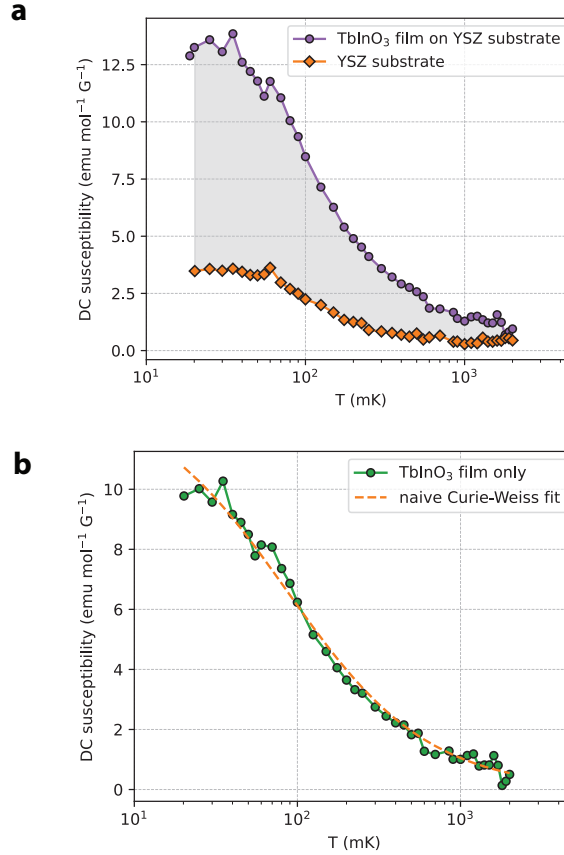


Figure 5.4: **Magnetic susceptibility from 20 mK to 2 K.** (a) Magnetic susceptibility inferred by calculating the area under the decay rate vs magnetic field curve. Since the resonator is also sensitive to signals from the substrate, we fabricate a second resonator on the same chip in a region where the  $\text{TbInO}_3$  has been removed by ion milling. The susceptibility is reported on the same y-axis scale with  $\text{TbInO}_3$  plus substrate (purple squares) and substrate alone (orange diamonds) at temperatures from 20 mK to 2 K. (b) The difference between the two values at each temperature is our best measure of the susceptibility of the  $\text{TbInO}_3$  film. We observe a non-saturating susceptibility which is well-described by a naive Curie-Weiss law down to 50 mK, below the Curie-Weiss scale from that same fit, and 220 times below the Curie-Weiss scale extracted from higher-temperature data. Susceptibility may start to saturate between 20 and 50 mK.

## 5.4 Model for ground state eigenstates

Having assigned the narrow lines ( $g \approx 1.9, 2.3$ , and 4.1) to various interfacial defects and bulk impurities, we now focus on the origin of the broad resonances (R2 and R3) in our spectra. We start



with the energy level scheme of each constituent Tb ion. Rare earth ions are simpler to model than transition metal ions, as they have a clear hierarchy in the magnitude of energy scales (Coulomb  $\gg$  spin-orbit  $\gg$  crystal-fields  $\gg$  hyperfine). This hierarchy makes the identification of a ground state manifold unambiguous from first principles.

Fig. 5.3a shows the hierarchy of energy scales from the atomic levels to the doublet ground state for each  $\text{Tb}^{3+}$ . The 3+ oxidation state has an outer electronic configuration of  $4f^8$ . By Hund's rules, we get the total orbital angular momentum  $L = 3$  and total spin angular momentum  $S = 3$ . The high atomic number of the rare earth atoms leads to a large spin-orbit interaction which couples  $L$  and  $S$  into a total angular momentum  $J = |L - S|, \dots, L + S$ . Since the f-subshell is more than half-filled, the sign of the spin-orbit interaction dictates that  $J = 6$  is the ground state. The  ${}^7F_6(2S+1L_J)$  ground state is separated from the  $J = 5$  state by  $\sim 3000$  K [46]. The  $J = 6$  level itself is composed of  $2J + 1 = 13$   $m_J$  states with  $m_J = -6, \dots, 6$ . Crystal fields imparted by the local environment of the ion cause a splitting of the  $J = 6$  multiplet into singlet and doublet states [100]. Inelastic neutron scattering and Raman spectroscopy on  $\text{TbInO}_3$  single crystals have established a doublet ground state separated by a low-lying crystal field (CF) level at roughly 10 K [72, 94, 100]. Since our experiment is conducted in the 20 mK to 2 K range, the higher CF levels are unoccupied and the physics is dominated by the properties of the ground state doublet. When we apply a static magnetic field, this doublet state is split, and the field can be tuned so this splitting matches the resonator frequency  $f = 1 \text{ GHz} \sim 50 \text{ mK}$ .

Which  $m_J$  states participate in this doublet, and their relative weight, remain to be identified. The trigonal symmetry of each Tb site restricts the  $m_J$  quantum numbers that can participate to give a doublet state [100]:  $m_J = 0, \pm 3, \pm 6$  states are required to be singlets. We are left with  $m_J = \pm 1, \pm 2, \pm 4, \pm 5$ , an eigenspace spanned by 8 states, which can potentially exist in a superposition to give a doublet state. At this point, the g-factors extracted from our spin resonance measurements provide further constraints. Spin resonance involves absorption of photons which carry angular momentum  $\pm 1\hbar$ . This leads to another constraint that doublets observed in ESR must incorporate  $m_J$  states which differ by  $\pm 1$ .

We propose an ansatz that mixes the  $m_J$  states, parameterized by a single mixing angle  $\theta$ :

$$|\psi_{m,+}(\theta)\rangle = c|\phi_{m,+}\rangle + s|\phi_{m+1,+}\rangle \quad (5.1)$$

$$|\psi_{m,-}(\theta)\rangle = c|\phi_{m,-}\rangle - s|\phi_{m+1,-}\rangle \quad (5.2)$$

where  $|\psi_{m,\pm}\rangle$  is a candidate doublet ground state,  $c = \cos(\theta)$ ,  $s = \sin(\theta)$  and  $|\phi_{m,\pm}\rangle = \frac{1}{\sqrt{2}}(|m\rangle \pm |-m\rangle)$ . Each  $|\psi_{m,\pm}\rangle$  state mixes  $\pm m$  and  $\pm(m+1)$  states:  $|\psi_{1,\pm}\rangle$  mixes  $m = 1$  and  $m = 2$ , whereas  $|\psi_{4,\pm}\rangle$  mixes  $m = 4$  and  $m = 5$ . Fig. 5.3b shows the calculated g-factor as a function of mixing angle for  $m = 1$  and  $m = 4$ .

Recall that we observe two different g-factors for the resonances R2 and R3 (Fig. 5.2b). The g-factor is a sensitive probe of the local environment of each Tb site, so the different g-factors

may reflect two non-equivalent Tb sites in the film.  $\text{TbInO}_3$  belongs to a class of hexagonal  $\text{ABO}_3$  compounds which includes hexagonal manganites [108] and ferrites [109] that undergo a structural transition into an improper ferroelectric phase. The existence of such a structural distortion and the corresponding domain structure in  $\text{TbInO}_3$  have been established by scanning transmission electron microscopy (STEM) imaging of bulk single crystals and thin films [8, 110]. Fig. 5.3c shows a schematic of the Tb site distortion: 1/3 of the Tb sites are shifted along the c-axis. If we posit that the different g-factors are associated with different mixing angles on the inequivalent sites, R2 and R3 both lie in the range that can be accounted for by either  $|\psi_{1,\pm}\rangle$  or  $|\psi_{4,\pm}\rangle$ , for suitable choices of mixing angles in each case: in Fig. 5.3b, matching mixing angles are marked by circles for  $|\psi_{1,\pm}\rangle$ , and squares for  $|\psi_{4,\pm}\rangle$ .

Fig. 5.3d shows the amplitude ratio of R2 and R3 as extracted from multi-peak Gaussian fitting. For a given temperature, amplitude is proportional to the number density of the moments participating in the resonance. We experimentally observe an amplitude ratio close to 2. This matches a naive expectation of the density ratio of two classes of Tb sites that are rendered inequivalent by the improper ferroelectric distortion. The fact that the sample does not consist of a single ferroelectric domain initially gave us pause: STEM imaging has shown two kinds of structural domains with a typical domain size ranging from 20–40 nm [8]. Since the resonator is sensitive to all spins within a characteristic length set by the resonator dimensions ( $\sim 5 - 10 \mu\text{m}$ ), we expect our measurement to represent an average over these structural domains. The structural domains are related to each other by a reflection in the  $ab$  plane, which transforms  $m_J$  quantum numbers as  $m \rightarrow -m$ . Since our ansatz for the ground state doublets involves symmetric and anti-symmetric combinations of  $\pm m$  states, the wavefunctions  $|\psi_{m,\pm}\rangle$  of the doublet states only acquire a global phase under this transformation. This means that not only the g-factors of the two inequivalent Tb sites but also the relative density of sites associated with those g-factors should be preserved across domain boundaries, consistent with our observation of an amplitude ratio close to 2 rather than 1.

We have aimed to explain the experimental observations with a minimum set of parameters, so our ansatz is designed to capture only the simplest superpositions consistent with visible transitions in ESR. The actual doublets could combine not just two but three or even all four of the allowed magnitudes of magnetic quantum numbers  $|m| = 1, 2, 4, 5$ . Experiments which can measure the complete angular dependence of the g-factor or even g-factors along high-symmetry directions of the crystal lattice would allow more specific assignment of the doublet ground states.

## 5.5 Extraction of Magnetic Susceptibility

The integrated area under the spin resonance line as a function of magnetic field is directly proportional to the low-frequency magnetic susceptibility [111]. By applying an in-plane magnetic field, we measure the in-plane ( $ab$  plane) magnetic susceptibility as a function of temperature. Note that

recently-reported measurements on  $\text{TbInO}_3$  films using a scanning SQUID were sensitive to the out-of-plane (c-axis) susceptibility down to 44 mK, whereas measurements of in-plane susceptibility using a commercial SQUID were performed down to 400 mK [8]. Here, we extend the temperature range for in-plane susceptibility down to 20 mK. As the YSZ substrate itself has magnetic impurities and defects, we ion-mill off a section of the  $\text{TbInO}_3$  film and fabricate a second resonator device on the same chip, with identical geometrical parameters. Such a device on the same chip allows us to subtract the background susceptibility of the YSZ substrate and thus extract a susceptibility of the  $\text{TbInO}_3$  film alone. We convert the spectral weight from the resonance curve into  $\text{emu mol}^{-1} \text{ G}^{-1}$  units for direct comparisons to DC susceptibility reported by others [99]. In temperature ranges overlapping other measurements, our extracted in-plane susceptibility is within a factor of 2–3 of previously reported values [72, 8]. We attribute any remaining inconsistency in the absolute magnitude of the susceptibility to approximations made by us in estimating the participation ratio of the spins coupled to the resonator.

Fig. 5.4a shows the extracted susceptibility for the  $\text{TbInO}_3/\text{YSZ}$  device and the control YSZ device. For both cases, we observe susceptibility increases with decreasing temperature. Above 2 K, the spin resonance signal is difficult to detect (see Fig. 5.2c) due to the decrease in thermal polarization of the participating spins and the reduction in quality factor of the resonator at higher temperatures. For all temperatures between 20 mK and 2 K, the extracted susceptibility from the  $\text{TbInO}_3/\text{YSZ}$  device is strictly larger than that of the YSZ device. Fig. 5.4b shows the result of subtraction between these two curves as the susceptibility we attribute to the  $\text{TbInO}_3$  film alone. The susceptibility increases with decreasing temperature at least down to 50 mK, with possible indication of saturation below that, and can be fit to a naive Curie-Weiss form  $\left(\chi(T) = \frac{C}{T - \theta_{\text{CW}}^{LT}}\right)$  as shown in Fig. 5.4b. From the fit to data between 20 mK and 2 K, we obtain a Curie-Weiss constant  $\theta_{\text{CW}}^{LT} = -86 \pm 5 \text{ mK}$ , far lower in magnitude than that extracted from higher temperature (2 K–300 K) measurements,  $\theta_{\text{CW}} \sim -11 \text{ K}$ . A similar reduction in  $|\theta_{\text{CW}}|$  was reported for polycrystalline  $\text{TbInO}_3$  when the researchers fit to their lowest-temperature data from 400 mK to 1 K rather than to their higher-temperature data [72]. When an antiferromagnet orders, susceptibility saturates or decreases as temperature is lowered below the ordering temperature. Between 50 mK and our base temperature of 20 mK, susceptibility may be starting to saturate, or the sample may not fully thermalize during ESR measurements. However, down to 50 mK we don't observe any decay or saturation of the susceptibility, so we conclude that no ordering transition occurs in  $\text{TbInO}_3$  down to that temperature, 220 times lower than the Curie-Weiss scale  $|\theta_{\text{CW}}| \sim 11 \text{ K}$  extracted from high-temperature (2 – 300 K) susceptibility measurements [99, 8]. The degree of frustration in magnetic materials is commonly quantified by a frustration index  $f = |\theta_{\text{CW}}|/T_{\text{ord}}$ , where  $T_{\text{ord}}$  is the ordering temperature [112, 99]. Our measurements show that the frustration index in  $\text{TbInO}_3$  is at least 220, one of the highest values reported in the search for candidate materials to host QSL states (see [99] for a table of frustration indices). Our microwave measurements of in-plane

susceptibility complement recent commercial and scanning SQUID measurements of these  $\text{TbInO}_3$  films [8, 99], not only probing susceptibility in a completely independent way but extending in-plane susceptibility an order of magnitude lower in temperature to match the range of out-of-plane susceptibility measurements. The scanning SQUID-based out-of-plane susceptibility peaks around 1 K and slowly decreases from the peak value with further decreasing temperature [8]. An exponential decrease in susceptibility along the moment axis that would be expected below an ordering transition is not observed. Coupled with our in-plane susceptibility results, this suggests that the Tb moments have an easy-plane anisotropy, consistent with previous studies on powder and single-crystal samples [72].

## 5.6 Discussion and Outlook

Transition metal and rare-earth oxides have historically played a prominent role in the discovery of correlated phases of matter. The presence of energetically favorable couplings between charge, spin, orbital and lattice degrees of freedom in such materials catalyzes novel ground states [96].  $\text{TbInO}_3$  is exemplary in this regard, as all these factors are at play in the determination of the ground state.

Fluctuating Tb moments with a high frustration index as shown by these measurements and others [8, 72, 94, 100] indicate a high degree of magnetic frustration in  $\text{TbInO}_3$ . The geometric distortion of Tb sites differentiates two subsets of Tb ions. One subset occupies a honeycomb lattice, the other a triangular lattice, each of these being a lattice geometry prone to magnetic frustration. What the ultimate ground state of such a dual-flavored magnetic system on distinct frustrated lattices would look like remains an open question. Moreover, since the ground state eigenstates are composed of f-orbital states, the exchange interaction is likely strongly anisotropic, i.e. bond direction dependent. A honeycomb lattice of Tb moments along with anisotropic exchange raises an interesting connection to the Kitaev honeycomb spin model, which displays canonical QSL states [113].  $\text{TbInO}_3$  and other rare-earth hexagonal  $\text{ABO}_3$  oxides with magnetic frustration could fruitfully join the more widely-studied iridates and  $\alpha\text{-RuCl}_3$  [114, 72] in this context.

Finally, we emphasize that the microwave resonator technique described here is widely applicable to a large class of insulating materials with magnetic frustration [63]. Advances in the field of circuit quantum electrodynamics as implemented by planar resonators have enabled hybrid spin-photon magnetic systems [98]. Such resonators can probe not only local, nearly-free spins but also collective deconfined excitations such as spinons that have been proposed in certain QSL models [50, 115, 116]. In conclusion, the combination of new measurement techniques and thin film growth provides a rich landscape for the discovery and characterization of frustrated magnets, including spin liquid candidates.

## Methods

### Growth and Device Lithography

Thin films of  $\text{TbInO}_3$  were grown by MBE on YSZ substrates [8]. NbTiN films were deposited by magnetron co-sputtering of Nb and Ti targets in an  $\text{Ar}/\text{N}_2$  environment. Direct-write photolithography with 385 nm light was used to expose AZ1512 resist (1.4  $\mu\text{m}$  thickness) and subsequently developed in MF319 developer solution for 1 min. After optical inspection and a 30 s oxygen descum, the NbTiN film was etched in a reactive-ion etcher with an  $\text{SF}_6/\text{Ar}$  plasma. The resist was finally removed in acetone and isopropanol.

### Cryogenic measurement setup

Each chip with patterned resonators was glued onto a custom-designed copper sample holder with mini-SMP connectors for microwave excitation and measurement. The sample holder is screwed onto a microwave click-in plate at the bottom of a top-loading probe used with a commercial He3-He4 dilution cryostat (Leiden Cryogenics, CF-CCS81). The click-in plate is thermally anchored to the mixing chamber of the cryostat with a minimum base temperature of 14 mK. In the main text, we report the temperature of a calibrated ruthenium oxide thermometer in proximity to the sample as the temperature of the sample. The minimum temperature as measured by the sample thermometer is 18 mK. A 100  $\Omega$  resistive heater on the mixing chamber of the cryostat is used to control sample temperature from base to 2 K. A PID loop ensures temperature stability with an error less than 0.1 %. Temperature stability was found to be crucial when sweeping the magnetic field at a given temperature as any change in temperature also leads to a change in the decay rate of the resonator by generation of thermal quasi-particles in the superconductor.

Microwaves are sent to the sample holder via lossy CuNi semi-rigid coax cables thermally anchored at the 4 K, Still, 50 mK and mixing chamber plates of the cryostat. The input line is heavily attenuated by cryogenic attenuators (XMA Corp.) with attenuation of 20 dB (4 K), 20 dB (Still), 20 dB (50 mK) and 6 dB (mixing chamber) to thermalize the signal line of the coax with the shield. On the output side, a cryogenic isolator (Quinstar) is mounted at the mixing chamber and is further connected to a cryogenic microwave amplifier (Cosmic Microwave, CITLF3) with a gain of 35 dB in the frequency range 1 – 5 GHz. A chain of three room temperature low-noise microwave amplifiers (Mini-Circuits, ZX60-83LN-S+) provides additional gain of about 60 dB. Measurements are performed with a vector network analyzer (Rohde & Schwarz, ZNB8) with an IF bandwidth of 500 Hz and with 1–5 averages per frequency trace. A doubly-isolated superconducting magnet (American Magnetics) capable of supplying fields up to 10 T mounted on the still plate ( $\sim 1$  K) is used to apply the static magnetic field. The field was ramped slowly at 0.25 – 0.5  $\text{mT s}^{-1}$  with a 1–3 second wait between adjacent field points to prevent any inductive heating and avoid sudden introduction of vortices in the superconducting film. OFHC Cu and brass screws were used in the construction

of the sample holder to avoid any stray fields from magnetic components near the sample. This is crucial in reporting g-factors as we use the absolute value of the magnetic field along with the resonator frequency to calculate the g-factor.

### Fitting of resonator $S_{21}$ and extraction of resonator properties

The superconducting resonator is capacitively coupled in a hanger geometry to an on-chip broadband microwave feedline. The coupling strength to the feedline is quantified by a coupling quality factor  $Q_c$  and it is chosen to be such that the resonator is critically coupled to the feedline, i.e. the internal quality factor  $Q_i$  is such that  $Q_i \sim Q_c$ . This enables us to extract small changes in the width, i.e. the decay rate of the resonator, with high sensitivity. The  $S_{21}$  magnitude and phase as measured by the VNA is fit to a model for hanger resonators [38, 117]:

$$S_{21}(\omega) = 1 - \frac{2 \frac{Q_l}{Q_c} e^{i\phi}}{1 + 2iQ_l \frac{\delta\omega}{\omega}} \quad (5.3)$$

where  $\omega = 2\pi f$  is the angular frequency,  $Q_l$  is the loaded quality factor,  $Q_c$  is the coupling quality factor,  $\phi$  is a phase that accounts for imperfections (e.g. reflections due to imperfect impedance matching) in the resonator coupling and  $\delta\omega = \omega - \omega_0$  is the offset from the resonator frequency  $\omega_0$ . The internal quality factor is then extracted by the diameter correction method [38] as:

$$\frac{1}{Q_i} = \frac{1}{Q_l} - \frac{\cos(\phi)}{Q_c} \quad (5.4)$$

Instead of the quality factor  $Q_i$ , we report the equivalent decay rate defined as  $\kappa = \frac{f}{2Q_i}$  in the main text. We subtract the zero field decay rate when reporting the decay rate as a function of temperature. The zero field decay rate is an intrinsic property of the resonator and does not arise from spin resonance. We use the non-linear least squares fitting numerical package `lmfit` to fit both real and imaginary components of the measured  $S_{21}$  [41]. A further median filter with a 3–5 point window is applied to the decay rate vs magnetic field to remove single point jumps (likely due to superconducting vortices) from the dataset.

Note that the information about various loss mechanisms for photons in the resonator is contained in the internal quality factor  $Q_i$ . These loss mechanisms include a finite resistive impedance of the superconductor at temperatures close to  $T_c$ , electric-dipole coupled two-level systems in the surface oxide of the superconductor or at superconductor-substrate interfaces, superconducting vortices and magnetic-dipole coupled spins. Out of all these loss mechanisms, only the spins are expected to have a response that requires tuning into a resonance condition ( $g\mu_B B = hf$ ) as described in the main text. As a result, by tuning the magnetic field and extracting the decay rate, we are able to separate out the spin-resonance contribution from other non-resonant loss mechanisms.

When the magnetic field is swept, the resonator frequency discontinuously jumps at certain non-repeatable magnetic fields potentially due to the introduction of vortices in the resonator CPW or the surrounding ground plane. In order to mitigate this problem, we use an automatic peak-finding algorithm that does a broad frequency scan (50 MHz range) around the expected resonator frequency to find the resonator dip and then does a finer scan (3 MHz range) to accurately measure the resonator profile. This peak-finding algorithm is performed at each magnetic field and temperature point in our dataset. Additionally, sweeping the magnetic field from higher fields to zero causes a reduction in the number of these jumps. A combination of such measurement strategies enables us to accurately and efficiently extract the resonator properties as a function of magnetic field and temperature without confounding background signals.

## Chapter 6

# Flip chip microwave spectroscopy of $\text{TbInO}_3$ and $\text{Gd}_2\text{Ti}_2\text{O}_7$

In the previous chapter, we saw the application of coplanar microwave resonators fabricated from superconducting NbTiN films grown directly on  $\text{TbInO}_3$  thin films. We targeted one particular frustrated magnet ( $\text{TbInO}_3$ ) and performed an in-depth study of the spin resonance properties of the underlying films and the growth substrate. While such an approach is appropriate for a material system for which one wants an in-depth characterization, it would be pragmatic to also have a platform capable of performing high-throughput spin resonance measurements utilizing superconducting resonators on thin films and potentially single crystals. In this chapter, we explore one such approach which uses a flip-chip geometry: thin films or single crystals of frustrated magnets are placed on top of a prefabricated resonator chip, and the composite chip assembly is then used for cryogenic spin resonance measurements.

We first motivate the flip-chip geometry against direct fabrication and review its use in the circuit QED literature. We then describe the vacuum-finger assembly tool built for this purpose. With that in hand we turn to measurements, first on quantum spin liquid candidate  $\text{TbInO}_3$  and then on the pyrochlore magnet  $\text{Gd}_2\text{Ti}_2\text{O}_7$ .

### 6.1 Why flip-chip methods?

Our goal is to use superconducting resonators as probes of magnetic excitations in thin films and single crystals. There are two routes to coupling a resonator to a sample of interest. In direct fabrication, the resonator is patterned onto the sample itself: a superconducting film is deposited on the material under study and subsequently defined by lithography. In the flip-chip approach,



the resonator is fabricated on a separate host substrate, and the sample is mechanically placed face-down on top of the completed resonator. Fig. 6.1 contrasts the two geometries. The choice between these routes shapes nearly every practical aspect of the experiment, from which materials can be measured at all to how quickly a series of samples can be screened. We begin by enumerating the advantages of flip-chip methods over direct fabrication.

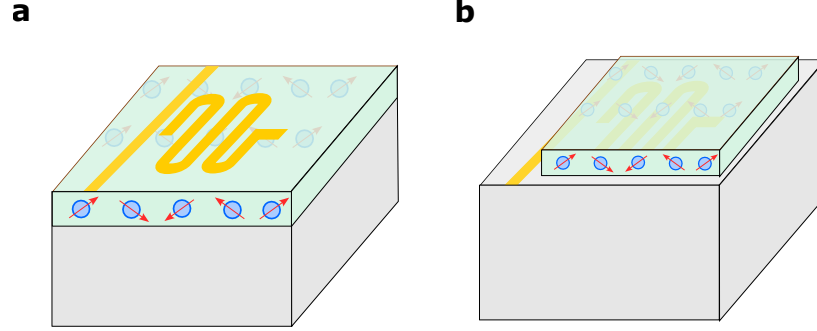


Figure 6.1: **Direct fabrication versus the flip-chip geometry.** Two routes to coupling a superconducting resonator to a magnetic sample, drawn for a quarter-wave coplanar meander and its feedline. Only the center pin is shown in gold color for simplicity. In direct fabrication (a), the superconducting film is deposited onto the magnetic film itself and the resonator is patterned in place, so that the conductors and the spins share an interface and the microwave field enters the sample where it is strongest. The cost is that every step of the process, from superconductor deposition at elevated temperature through resist coating, lithography and etching, can potentially degrade the material under study, and the achievable quality factor is tied to the dielectric losses of whichever substrate the sample happened to be grown on. In the flip-chip geometry (b), the resonator is fabricated and characterized on its own host substrate and the sample is afterwards placed face-down on the finished device, so that the spin-bearing surface faces the resonator plane. No lithography is performed on the sample, one calibrated resonator chip serves an entire family of samples, and the assembly can be dissolved afterwards to recover both pieces. The field must traverse a separation between the resonator plane and the sample which is set stochastically by surface roughness, trapped dust particles and tilt. As the field decays evanescently over a length of order the conductor and gap width, the coupling is both weaker than in (a) and not known *a priori*.

1. **No fabrication on sample:** Direct fabrication requires the growth of a superconducting film on the film or single crystal of interest followed by a full lithographic sequence of resist coating, e-beam or optical patterning and etching. Each step of the process carries a potential for degrading the sample: superconductor deposition at elevated temperatures can cause oxygen loss and vacancy formation in complex oxide films, while resist interfaces and plasma chemistry can alter the chemical composition of the material we intend to probe. Even if we disregard the chemical incompatibility, these fabrication processes can also cause physical surface damage leading to defect formation right at the interface where the coupling to the resonator is the strongest.

2. **Resonator quality factor is decoupled from the sample:** The resonator chip can be fabricated with an optimized process associated with a particular combination of a superconducting film and the substrate, leading to the highest achievable quality factors. Direct fabrication ties resonator performance to the losses associated with the sample substrate, and the fabrication process must be re-established for every material.
3. **High-throughput:** A single fabrication run of resonator chips serves an entire family of samples. Exchanging films is a simple assembly process instead of a slow and long fabrication process involving a cleanroom and multiple lithography and etching tools. Hence, flip-chip enables rapid screening of multiple growth runs, composition and thickness series against the same calibrated resonator design.
4. **Non-destructive and reversible assembly:** Most flip-chip methods involve gluing the two substrates with a physical process which is reversible using certain solvents. For example, if PMMA is used as a glue, we can separate the two chips easily by soaking the chips in acetone. As such, the samples can be detached from the resonator chip and re-measured using other characterization tools such as X-ray diffraction, Raman scattering, SQUID magnetometry, etc. The resonator itself can also be measured after the disassembly, establishing a baseline post flip-chip measurement.
5. **In-situ referencing:** The resonator chip can be much larger than the sample of interest and we can have resonators which are not covered by the sample. These resonators, with an identical design and which undergo the same fabrication process, serve as a baseline for any changes from the presence of the sample. For example, simultaneous measurements of such reference resonators enable us to correctly attribute field- or temperature-dependent changes in resonator properties to those originating from the sample.
6. **Tolerance to irregular sample geometry:** Flip-chip methods do not impose any strong constraints on sample size or geometry. As long as the sample covers a significant fraction of the spatial extent of a typical resonator ( $\sim 1 \text{ mm}^2$ ), the resonator has the potential to probe the sample.

At the same time, flip-chip methods come with their own set of trade-offs that must be considered. The chip separation is uncontrolled and can be limited by microscopic dust particles between the two chips. Moreover, uncertainty in the tilt degree of freedom further contributes to our ignorance of the precise sample geometry that is being probed. As the microwave field decays evanescently away from the resonator plane, we suffer from reduced sensitivity at large gaps and tilts between the resonator plane and the sample. A lack of an epitaxial interface between the superconducting film and the sample means that interfacial phenomena that could arise from the coupling of superconductivity to the sample are absent. In a flip-chip assembly, the resonator only serves as a probe of excitations

in the sample and does not directly influence the underlying interaction physics of the spins in the sample. We return to the first and third of these limitations in the final section of this chapter, Sec. 6.7, where controlled spacers and modified resonator geometries offer quantitative paths to mitigate them.

## 6.2 Previous work on flip-chip methods

Flip-chip methods involving planar superconducting resonators were first applied to investigate the spin resonance of defects in solid state systems such as  $Cr^{3+}$  in  $Al_2O_3$  (ruby) and N substitution centers (P1 centers) in diamond [118, 119]. Motivated by long coherence times observed through traditional spin resonance techniques for some of these solid-state defects, these early efforts were geared towards the prospect of realizing a solid-state quantum memory for superconducting qubits. Ref. [120] studied the  $g$ -factor anisotropy of  $Er^{3+}$  defects in  $Y_2SiO_5$  crystals by varying the angle between the resonator field and the crystallographic axes of the crystal. In addition to demonstrating strong coupling between resonator photons and spin ensembles, follow-up work on P1 centers by Ref. [121] measured spin relaxation times and diffusion dynamics through pump-probe pulsed methods.

Two features distinguish the present work from this body of literature. First, the samples there are dilute paramagnetic defects in an otherwise inert host, so the spins are non-interacting and the resonance is a single-ion Zeeman transition of known  $g$ -factor. Here, the samples are dense, strongly interacting magnets in which the excitation spectrum is itself the object of study. Second, those experiments sought to use the spins as a memory whereas in our samples, we are probing either the dressed magnetic moment from the presence of crystal fields or a collective excitation from the presence of interactions. The resonator reports the absorptive part of the spin susceptibility through its decay rate rather than hybridizing with the spins.

### 6.3 Vacuum finger for flip-chip assembly

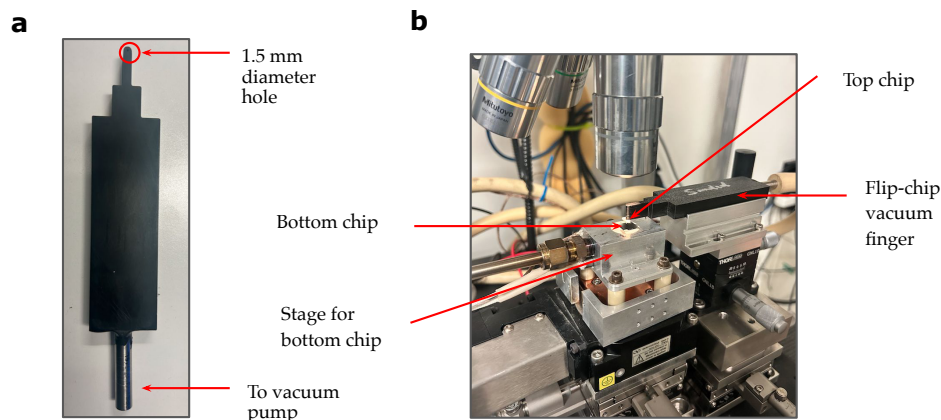


Figure 6.2: **Vacuum finger for flip-chip assembly.** (a) The 3D-printed vacuum finger. A 1.5 mm hole at the tip, circled, holds a chip by suction, and the tube at the opposite end connects to a diaphragm pump. The body is printed to the same width as the glass slides used for polymer stamps in the lab, so it mounts on the stamp stage of the group’s 2D-material stacker in place of a stamp and requires no modification to the tool. (b) The finger in use on the stacker. The sample, or top chip, is held face-down at the finger tip, while the resonator chip sits on its own vacuum stage below; the finger is carried on the translation stage at right and the two chips are aligned and brought into contact under the long-working-distance objective visible above. Because the finger and the stage hold their chips on independent vacuum lines, releasing the finger vacuum after contact leaves the sample behind on the resonator chip, and the finger can then be retracted without disturbing the assembly.

In order to assemble chips in a flip-chip geometry, I built a vacuum finger which was integrated with the 2D material stacker used by the group for van der Waals heterostructures [122]. Fig. 6.2 shows the vacuum finger with a suction hole for holding chips on the finger and a tube with a vacuum port which is connected to a pump. The vacuum finger was 3D printed using a Prusa Core One printer and black ASA filament. A suction hole of 1.5 mm diameter was designed to provide vacuum suction for holding samples on the finger. The width of the vacuum finger was chosen to be the same as the glass slides used for polymer stamps in the lab. As a result, the vacuum finger can be used in place of a polymer stamp without any modifications to the stamp stage of the stacker. The vacuum suction is produced by the same diaphragm pump used for all other vacuum suction ports on the stacker.

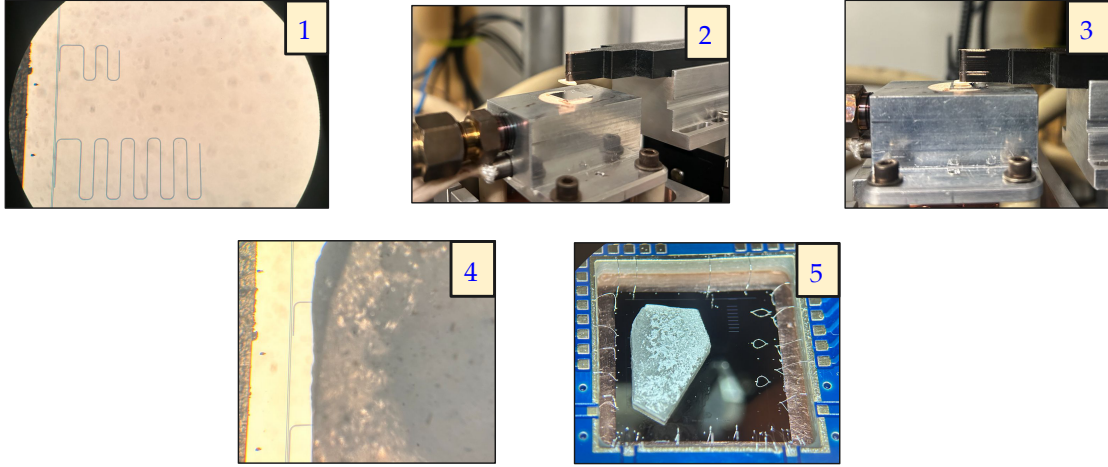


Figure 6.3: **Flip-chip assembly process.** The five stages of a flip-chip assembly, in order. (1) The bare resonator chip viewed through the alignment microscope, with two quarter-wave meander resonators of different length coupled to the common feedline running down the left of the field of view. The resonator to be covered is centered in the field before the sample is introduced. (2) The vacuum finger, carrying the sample face down, approaching the resonator chip on the stage below. We use a stepper motor for motion on the stamp stage. (3) The finger is lowered until the sample contacts the resonator chip, at which point the finger vacuum is released. (4) The composite assembly viewed through the sample after the finger has been retracted. The meander and feedline of the resonator are visible at the left, and the edge of the placed sample runs vertically across the field, so that both the placement relative to the resonator and the presence of trapped particulates or a large gap can be judged optically before the assembly is committed. (5) The finished assembly, glued, wire-bonded into its sample holder and ready to load into the dilution refrigerator. From this point, the flip-chip assembly is handled exactly like a conventional single-chip sample.

The flip-chip assembly proceeds as follows:

1. Place the resonator chip on the sample stage and turn on the sample stage vacuum.
2. Adjust the sample stage so that the resonator of interest is in the center of the optical field of view of the camera.
3. Place the vacuum finger on the stamp stage and turn on the stamp stage vacuum.
4. Pick up the sample chip with the vacuum finger, sample face down, and confirm that it is held flat against the finger.
5. Focus on the resonator chip and align the edge of the sample to the resonator's location.
6. Lower the finger until the sample makes contact with the resonator chip, then release the stamp stage vacuum so that the sample remains on the resonator chip.

7. Retract the finger and inspect the assembly optically to verify placement and to look for trapped particulates or interference fringes indicating a large gap.
8. Secure the assembly with a glue, either PMMA or GE varnish. I lower the vacuum finger again so that it can push down on the sample chip while I use a small wire as a brush to apply the glue.
9. Wire-bond the composite chip and load it into the dilution refrigerator. The composite assembly is bonded and mounted exactly like any single-chip sample.

The resonators used in this chapter are quarter-wave coplanar waveguide meanders patterned from NbTiN on high-resistivity Si, with a footprint of order  $1\text{ mm} \times 1\text{ mm}$  and a fundamental frequency near 1 GHz. This is the same resonator design and fabrication process described in Chapter 5. The resonator chip is calibrated through a separate cooldown in the absence of any flip-chip sample. Only the sample on top of the resonator chip change as we investigate various materials.

## 6.4 Reference resonator

Before placing anything on top of a resonator it is worth establishing what the resonator does on its own, because every claim made in the rest of this chapter is a claim about a difference from that baseline. Fig. 6.4 shows the decay rate of an uncovered resonator as a function of applied in-plane field and of the extracted  $g$ -factor  $g = hf/\mu_B B_0$ .

A single resonance appears near  $g \approx 1.9$ , and away from it the trace is flat and featureless across the whole range  $g = 1$  to 10. We attribute this peak to paramagnetic defects in the surface oxide of the NbTiN film itself rather than to anything in the substrate. The same feature appears in the directly fabricated devices of Chapter 5, where it was identified by its presence on a NbTiN resonator patterned on bare silicon, and it is therefore independent of both the  $\text{TbInO}_3$  film and the YSZ substrate [76]. Surface spins at  $g \approx 2$  are a generic feature of nitride superconducting resonators and have been characterized in some detail in NbTiN and NbN films by other groups [102, 123]. Their origin is generally assigned to defects in the native niobium oxide that forms on the exposed surfaces of the film.

The uncovered resonator provides a baseline that has experienced an identical fabrication history, an identical field sweep and an identical thermal cycle, so any feature that appears in a covered resonator and is absent here can be assigned to the sample with confidence. At the same time, any sharp feature at  $g \approx 2$  should be treated as a background contribution regardless of what the sample is. The flatness of the baseline away from  $g \approx 2$  makes the flip-chip measurement quantitative rather than merely suggestive.

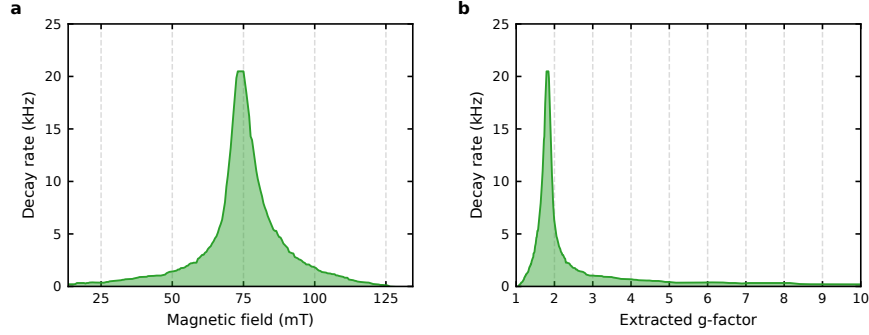


Figure 6.4: **Reference resonator response.** Decay rate of an uncovered resonator on the flip-chip host chip, plotted (a) against the applied in-plane field and (b) against the extracted  $g$ -factor  $g = hf/\mu_B B_0$ . A single resonance appears near  $g \approx 1.9$ , corresponding to a field of about 75 mT at this mode frequency, and away from it the response is featureless out to  $g = 10$ . We assign the peak to paramagnetic defects in the surface oxide of the NbTiN film rather than to the substrate, on the basis that the same feature is present in devices fabricated directly on  $\text{TbInO}_3$  and on bare silicon in Chapter 5. Because this resonator is uncovered but otherwise identical to those measured in the rest of the chapter, it serves as the baseline against which the sample contributions are defined.

## 6.5 Measurements on candidate spin liquid $\text{TbInO}_3$

The natural first test of the flip-chip platform is a sample whose directly fabricated answer is already known. In Chapter 5 we patterned NbTiN resonators onto  $\text{TbInO}_3$  films grown on YSZ and measured the spin resonance spectrum of the  $\text{Tb}^{3+}$  moments [76]. Here we take a separate but nominally identical  $\text{TbInO}_3$  film from the same growth effort, place it face down on a prefabricated resonator chip using the assembly of Sec. 6.3, and investigate whether the same spectrum is reproduced.

Fig. 6.5a shows the decay rate of the  $\lambda/4$  mode as a function of the extracted  $g$ -factor. The qualitative structure is similar to what was reported for the directly fabricated devices. A large peak centered near  $g \approx 2$  followed by a broad shoulder that persists out to  $g \approx 8$  before falling to the background. Fig. 6.5b repeats the measurement on the  $\lambda/4$ ,  $3\lambda/4$  and  $5\lambda/4$  modes of the same resonator. The features occur at the same extracted  $g$ -factor in all three, which is to say that a feature appearing at field  $B_0$  for the fundamental appears at  $3B_0$  and  $5B_0$  for the harmonics. This is the same internal consistency check applied in Chapter 5, and it rules out field-dependent loss mechanisms such as vortex motion or parasitic cavity modes.

Fig. 6.5c fits the base-temperature trace to the same three-component Gaussian model used in Chapter 5, and recovers the same three resonances: R1 near  $g \approx 2$ , which the reference measurement of the previous section assigns to defects in the NbTiN, together with the two broad components R2 and R3 at  $g \approx 5$  and  $g \approx 6.6$  that were attributed to the two inequivalent Tb sites created by the improper ferroelectric distortion. The flip-chip geometry therefore reproduces the essential result of the direct-fabrication measurement. Therefore, a resonator that never touched the sample during

fabrication and which is separated from it by an uncontrolled gap, still resolves the crystal-field doublets of the Tb moments.

However, the quantitative agreement is not perfect, and the difference can be explained as follows. Relative to Fig. 5.2 of Chapter 5, R2 and R3 are noticeably weaker here in comparison to R1. There are multiple possible explanations, which we discuss below.

The first possible explanation is inadequate thermalization. In the flip-chip geometry the sample is held to the resonator chip only by a thin glue layer, and its thermal link to the mixing chamber is correspondingly poorer than that of a film with a superconductor deposited directly on it. Since the spin signal scales with the thermal polarization  $\tanh(\hbar f/2k_B T)$ , a sample sitting at a higher effective temperature than the thermometer reports would show a suppressed Tb response while leaving R1 unaffected. The second explanation is imperfect coupling to the  $\text{TbInO}_3$  film. The microwave field decays evanescently away from the resonator plane, so tilt and trapped particulates that increase the gap reduce the fraction of the field that reaches the film. This too would suppress R2 and R3 selectively, since R1 arises from spins in the resonator's own surface oxide or defects in the bulk YSZ substrate and is less sensitive to such imperfections.

The third is that the sample signal is not suppressed at all and R1 is simply larger. This possibility is favored by the absolute magnitudes rather than the ratios. Comparing against Fig. 5.2 of Chapter 5, the peak decay rate at R1 is roughly a factor of two larger in the flip-chip measurement, while R2 and R3 have comparable absolute magnitudes in the two experiments. If the Tb signal were being suppressed by poor thermalization or a large gap, we would expect R2 and R3 to shrink in absolute terms; instead they are essentially unchanged, and it is R1 that has grown. Hence, we suspect that particular resonator chip carries a higher density of NbTiN surface defects or YSZ bulk defects than the chip used in Chapter 5, which is unsurprising given that the two were fabricated in separate runs.

Distinguishing these possibilities is straightforward in principle and worth investigating in future experiments. Controlled-spacer measurements outlined in Sec. 6.7, in which a series of assemblies at known standoff distances are made, can potentially map the observed signal as a function of the spacer gap.



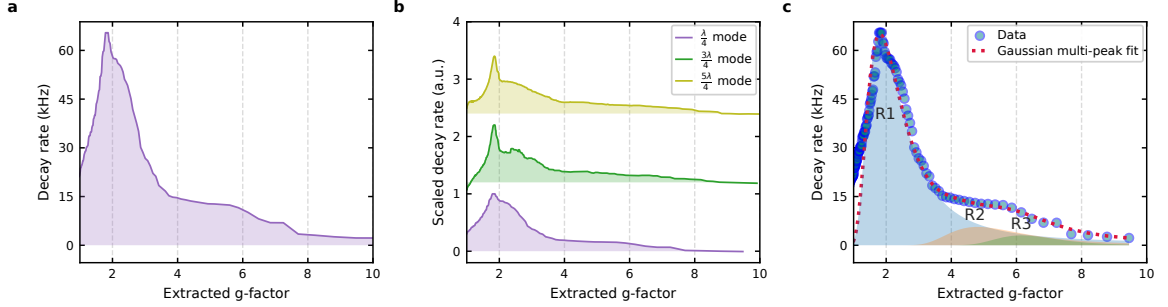


Figure 6.5: **Spin resonance of a  $\text{TbInO}_3$  film in the flip-chip geometry.** (a) Decay rate of the  $\lambda/4$  mode as a function of the extracted  $g$ -factor  $g = hf/\mu_B B_0$ , for a resonator covered by a  $\text{TbInO}_3$  film placed face-down in the flip-chip geometry. A large peak near  $g \approx 2$  is followed by a broad shoulder extending to  $g \approx 8$ . (b) The same measurement on the  $\lambda/4$ ,  $3\lambda/4$  and  $5\lambda/4$  modes of the same resonator, scaled and offset vertically for clarity. The features occur at the same extracted  $g$ -factor for all three modes, so that a feature at field  $B_0$  for the fundamental recurs at  $3B_0$  and  $5B_0$  for the harmonics; this scaling is the signature of a magnetic resonance and excludes field-dependent losses such as vortex motion or parasitic modes. (c) The base-temperature trace fitted to the three-component Gaussian model of Chapter 5, recovering R1 near  $g \approx 2$  from defects in the  $\text{NbTiN}$  film, and the broad components R2 and R3 associated with the two inequivalent Tb sites. The spectrum reproduces that of the directly fabricated devices of Chapter 5, with R2 and R3 weaker relative to R1. As discussed in the text, the absolute magnitudes suggest this reflects a larger defect contribution on this resonator chip rather than a suppressed sample signal.

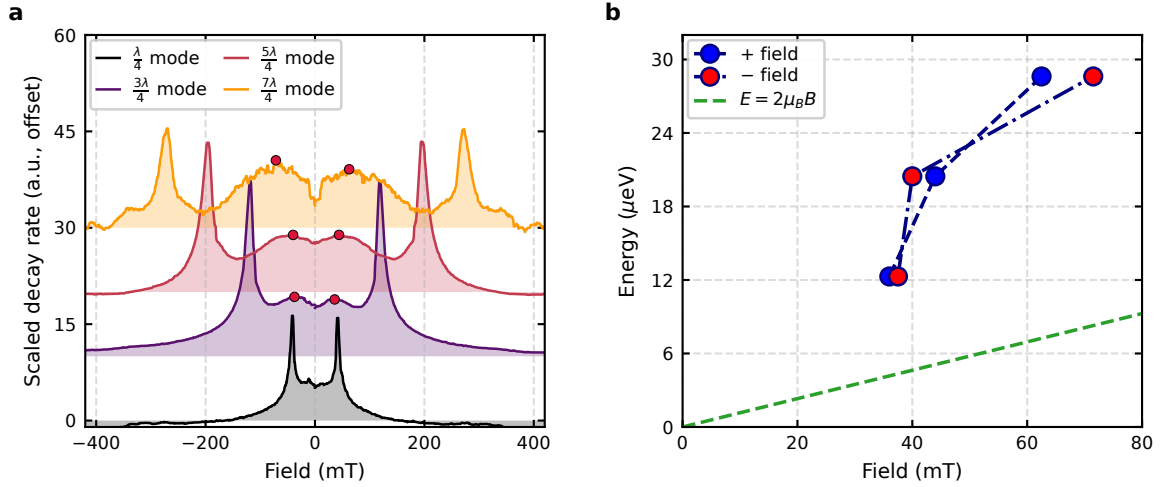
## 6.6 Measurements on Heisenberg pyrochlore magnet $\text{Gd}_2\text{Ti}_2\text{O}_7$

The pyrochlore oxides  $A_2B_2O_7$  host two interpenetrating networks of corner-sharing tetrahedra formed by the  $A$  and  $B$  sites [63]. As discussed in Sec. 4.5.2, corner-sharing tetrahedra are the three-dimensional analogue of the corner-sharing triangles of the kagome lattice and represent a maximally frustrated geometry for antiferromagnetic exchange. For a single tetrahedron with antiferromagnetic exchange, no spin configuration can simultaneously satisfy all six bonds. In the titanate family  $A_2\text{Ti}_2\text{O}_7$ , Ti sits in the +4 oxidation state with an empty  $d$  shell, so all magnetism originates from the  $A$  site. This makes the titanates a clean series in which the rare-earth  $A$  site can be varied while holding the lattice and the non-magnetic sublattice fixed, and the local crystal-field environment of the  $A$  site then selects between isotropic, easy-axis and easy-plane single-ion anisotropy.

$\text{Gd}_2\text{Ti}_2\text{O}_7$  is the closest thing this family offers to a textbook frustrated Heisenberg antiferromagnet.  $\text{Gd}^{3+}$  is a half-filled  $4f$  shell,  $S = 7/2$  with  $L = 0$ , so the moment is very nearly isotropic and the physics is set by exchange and dipolar interactions rather than by single-ion anisotropy. Curie–Weiss fits to the bulk susceptibility give  $\theta_{CW} \approx -10$  K with no ordering down to  $\approx 1$  K [124, 125, 126], a frustration index of about 10. Below 1 K, specific heat and susceptibility measurements on bulk crystals reveal one or more ordering transitions into a partially ordered state [127]. Our objective is

to look for signatures of this sub-kelvin ordering in  $\text{Gd}_2\text{Ti}_2\text{O}_7$  *films*, and to characterize the collective excitations of the sub-kelvin ground state.

A quarter-wave coplanar resonator supports modes not only at its fundamental  $f_r$  but also at the odd multiples  $3f_r$ ,  $5f_r$ ,  $7f_r$  and so on. Here each mode interrogates the sample at a different photon energy while everything else about the measurement is held fixed. Repeating a field sweep on four modes therefore samples the excitation spectrum at four energies, converting the resonator into a coarse but genuine spectrometer in energy. Fig. 6.6a shows the decay rate of the first four odd modes, at approximately 1, 3, 5 and 7 GHz, as a function of in-plane field swept through both polarities, for a resonator covered by a  $\text{Gd}_2\text{Ti}_2\text{O}_7$  film at base temperature. Two distinct kinds of resonances are present in every trace.



**Figure 6.6: Collective mode dispersion of  $\text{Gd}_2\text{Ti}_2\text{O}_7$  mapped with CPW harmonics.** (a) Decay rate versus in-plane field for the first four odd modes of a single quarter-wave resonator covered by a  $\text{Gd}_2\text{Ti}_2\text{O}_7$  film. Every trace shows a pair of sharp, narrow peaks symmetric about zero field whose position moves outward in proportion to the mode frequency. A resonance field that scales with  $f_r$  is the signature of a fixed  $g$ -factor, and these are the NbTiN surface defects at  $g \approx 1.9$  identified on the uncovered reference resonator in Sec. 6.4. Beneath them, at fields below the defect resonance, lies a much broader feature that is absent from the reference and is therefore the sample contribution. The peak positions are marked with circles. (b) Excitation energy against field, obtained by pairing each marked peak field with that mode's photon energy  $hf_r$ . Blue and red markers denote sweeps to positive and negative field respectively, and the spread between the two polarities at a given energy indicates the uncertainty of the peak extraction. The fundamental is omitted because at 1 GHz the broad feature and the defect resonance fall at similar fields and cannot be separated. The dashed line is the free spin Zeeman energy  $E = 2\mu_B B_0$ . The measured mode lies three to four times above this line across the accessible range, corresponding to an effective slope of order  $450 \mu\text{eV T}^{-1}$  and an effective  $g$ -factor near 8, which rules out a single-ion Zeeman transition of an isolated  $\text{Gd}^{3+}$  moment. We suspect that this feature is a collective excitation of the partially ordered ground state below 1 K.

The first is a pair of sharp, narrow peaks symmetric about zero field, whose position moves outward as the mode frequency increases, from roughly 40 mT at the fundamental to roughly 270 mT at  $7\lambda/4$ . A resonance field proportional to  $f_r$  is the defining property of a fixed  $g$ -factor, and the progression corresponds to  $g \approx 1.9$ . This is not a signal from the sample. The same peak appears on the uncovered reference resonator of Sec. 6.4, and we assign it to paramagnetic defects in the surface oxide of the NbTiN film itself, consistent with the film contribution identified in Chapter 5.

The second feature is a much broader enhancement at lower field, absent from the reference resonator and therefore originating in the sample. It is quite wide in field which tells us immediately that the lifetime of this resonance is quite short. At 3, 5 and 7 GHz the maximum of the broad feature is extracted as the peak of the resonance and is marked by circles in Fig. 6.6a. Pairing each marked peak field with its mode's photon energy  $hf_r$  converts these traces into a dispersion relation, plotted in Fig. 6.6b. The fundamental does not contribute a point: at 1 GHz the broad feature and the defect resonance fall at similar fields and cannot be separated. Each is measured at both field polarities, and the two agree to within a few mT, which is both a measure of the peak-extraction uncertainty and a useful check that the feature tracks  $|B_0|$  as a magnetic resonance rather than following a drift or a hysteretic instrumental artifact.

The observation of this broad feature is incompatible with a single-ion Zeeman transition of an isolated  $\text{Gd}^{3+}$  moment, whose half-filled shell would give  $g$  very close to 2. We suspect that what we are measuring through the broad resonance is a collective mode of ground state, whose energy at a given field is set by the ordering pattern and the exchange constants rather than by the bare moment. Extracting those parameters would require theoretical modeling of the sub-kelvin ground state of  $\text{Gd}_2\text{Ti}_2\text{O}_7$ , which could be the subject of future studies.

### 6.6.1 Temperature dependence

Fig. 6.7 shows the decay rate as a function of magnetic field as we warm up the sample from 50 mK to 1.6 K. Both features identified in the previous section weaken monotonically with increasing temperature, until by roughly 1 K neither is distinguishable from the background.

These results are consistent with thermal depolarization. The absorption from a two-level spin system is proportional to the population difference between the two states, which for a splitting matched to the resonator is  $\tanh(hf_r/2k_B T)$ , so the signal saturates once  $k_B T \ll hf_r$  and falls off smoothly once the thermal energy exceeds the photon energy. The relevant scale  $hf_r/k_B$  is  $\sim 50$  mK at the fundamental and  $\sim 350$  mK at  $7\lambda/4$ , so over the range measured here every mode passes from fully polarized to essentially unpolarized. A monotonic decay is expected regardless of any ordering transitions.

The temperature dependence is therefore consistent with the collective mode of the previous section but does not, on its own, establish its origin. Bulk  $\text{Gd}_2\text{Ti}_2\text{O}_7$  is known to order below about 1 K: specific heat identifies transitions near 1.0 K and 0.7 K [124, 126] whereas neutron diffraction

resolves the low-temperature state as a partially ordered antiferromagnet in which not all of the Gd sublattices develop a moment [125]. It is tempting to connect the disappearance of our signal near 1 K to that transition, but a paramagnetic response would fade over the same range due to thermal depolarization. Separating the two would require either a sharper determination of the onset than thermal depolarization permits, concurrent thermodynamic probes of the transition or magnetic susceptibility measurements on the same samples.

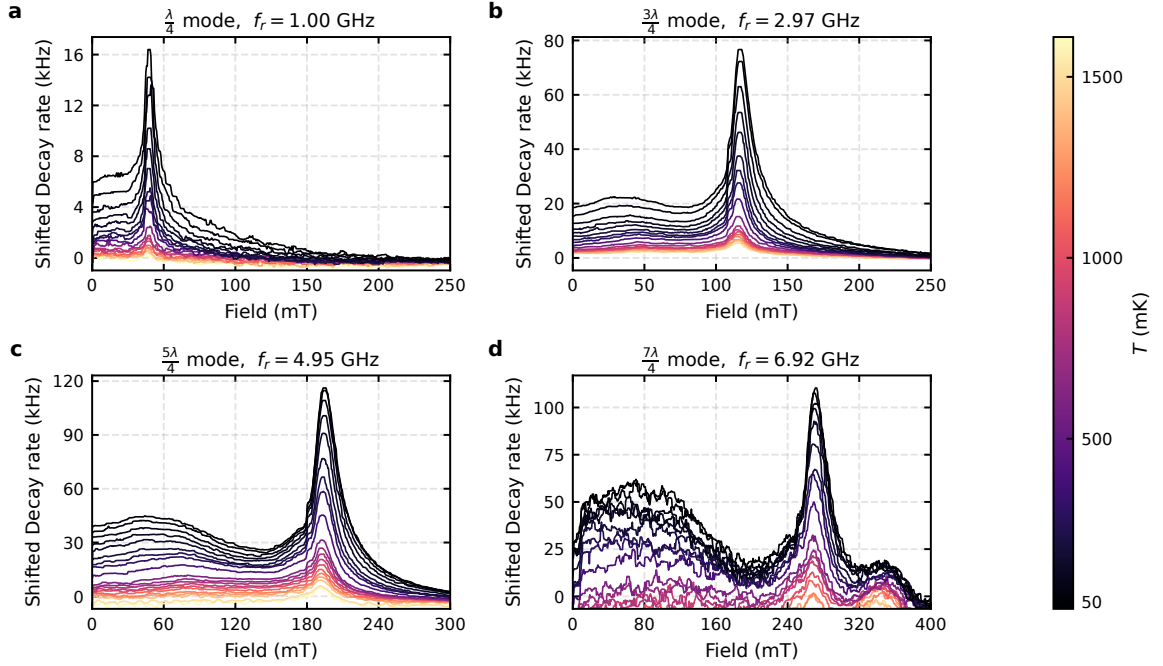


Figure 6.7: **Temperature dependence of the  $\text{Gd}_2\text{Ti}_2\text{O}_7$  response.** Decay rate versus in-plane field for the (a)  $\lambda/4$ , (b)  $3\lambda/4$ , (c)  $5\lambda/4$  and (d)  $7\lambda/4$  modes of the resonator covered by a  $\text{Gd}_2\text{Ti}_2\text{O}_7$  film, with sample temperature from 50 mK to 1.6 K encoded by the color scale at right. A constant offset has been removed from each trace so that all share a common baseline at the largest field. In every mode the sharp defect resonance, at  $\sim 40$ , 117, 190 and 270 mT respectively, and the broad low-field feature attributed to the sample both weaken monotonically as the temperature is raised. This behavior is consistent with thermal depolarization as the absorption follows the population difference  $\tanh(hf_r/2k_B T)$ , and  $hf_r/k_B$  ranges from  $\sim 50$  mK at the fundamental to  $\sim 350$  mK at  $7\lambda/4$ , so all four modes depolarize over the range shown.

## 6.7 Refinements and outlook

In this section, we will discuss limitations in the flip chip technique, and possible refinements in future experimental setups.

**Controlling the gap.** The dominant uncontrolled parameter is the separation  $d$  between the resonator plane and the sample, together with the tilt across the sample footprint. Because the

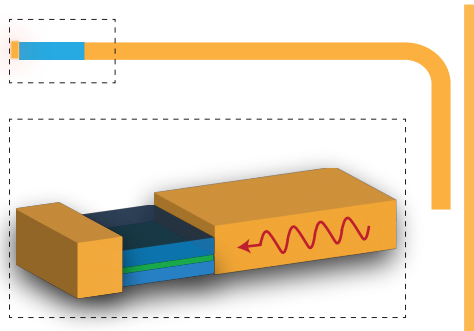
CPW field decays evanescently over a length set by  $w + 2s$ , the coupling to the sample falls off steeply with  $d$ , and an unknown  $d$  means the integrated spectral weight cannot be converted into an absolute spin density. Two routes are available. The first is to make  $d$  deliberate rather than accidental by patterning spacers of known height. Evaporated dielectric pillars (e.g. SU8 resists) of calibrated thickness can serve as well-defined standoffs on the resonator chip. A series of chips with different spacer heights would then map out the coupling versus  $d$  curve directly, calibrating the coupling strength for future measurements.

**Recovering interfacial coupling.** The absence of an epitaxial interface means the resonator probes the sample without perturbing it. It does, however, close off the interfacial physics such as proximity-induced superconductivity at the superconductor-frustrated magnet interface. Flip-chip and direct fabrication are therefore complementary rather than competing depending on the scientific goals. A natural order of applications is to use flip-chip for survey spectroscopy across a materials family and direct fabrication for the one or two compositions that the survey identifies as worth an epitaxial interface.

**Extending the frequency coverage.** Using higher harmonics of the resonator gave four points on a dispersion curve from a single  $Gd_2Ti_2O_7$  device. A finer sampling in frequency is possible by reducing the fundamental resonator frequency to lower frequencies such as 100 MHz. Another possibility is to fabricate multiple resonators at incommensurate frequencies coupled to the same hanger feedline. Such modifications can turn the coarse dispersion of Fig. 6.6 into a well-resolved  $E(B)$  curve.

# Part III

## van der Waals Heterostructures



## Chapter 7

# Electronic correlations in 2D materials

The isolation of single layer, i.e. atomically thick, materials came as a surprise. Thermodynamic arguments on the stability of free standing layers of graphene had suggested that 2D layers would just curl up into soot, fullerenes or carbon nanotubes to save energy [128, 129, 130]. And yet, using graphite crystals thinned down using Scotch tape, Geim, Novoselov, and others demonstrated the presence of isolated graphene flakes [131]. Around the same time as the discovery of graphene, it was shown that other layered materials including transition-metal dichalcogenides (TMD) such as MoS<sub>2</sub>, NbSe<sub>2</sub>, insulators such as hBN and high- $T_c$  superconductors such as BSCCO could be exfoliated into few-layer flakes using the same mechanical exfoliation process [132]. By exfoliating single crystals of a variety of layered materials onto oxidized silicon wafers, it is now possible to isolate few-layer flakes and crucially make these flakes visible down to the monolayer limit [133]. Once the process of isolating thin flakes was established, field-effect transistors were realized shortly after [131, 132]. In addition to the single atomic layer thickness, graphene flakes have exceptional crystalline quality and in most typical flakes, the entire flake is a single crystal without any dislocations and very few point defects [134]. As a result, charge carriers can travel ballistically for thousands of atomic spacings without a scattering event [128]. High quality samples have always served as a fertile ground for the discovery of new physics and graphene delivered spectacularly on this promise.

Early experiments showed an ambipolar electric field effect [131] such that both positive and negative charge carriers could be tuned to densities as high as  $10^{13} \text{ cm}^{-2}$  and mobilities exceeding  $10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at room temperature. The linear electronic dispersion near the Dirac point of graphene gives rise to unconventional electronic properties. While most electrical conductors we know have free carriers described by the Schrodinger equation with massive charged particles, the presence of the linear dispersion means that we have to resort to a relativistic Dirac equation for the

description of electrons in graphene. Despite the fact that there is nothing particularly relativistic about the motion of electrons around graphene's carbon atoms, the effective bandstructure gives rise to massless quasiparticles with a linear dispersion. The observation of a relativistic analogue of the quantum Hall effect in graphene and the significance of the intrinsic Berry phase around the Dirac point established graphene as a platform for the study of relativistic quasiparticles and quantum electrodynamics in two dimensions [135].

The carrier mobility in the first-generation graphene devices was limited by the roughness of the underlying amorphous  $\text{SiO}_2$  substrate and the presence of adsorbates both on the open surface and the substrate interface. A breakthrough came through the development of dry transfer techniques which used another 2D material, hexagonal Boron Nitride (hBN) as a single crystal dielectric for graphene [136]. And thus, the field of vdW heterostructures was born and in principle, any combination of 2D materials could be engineered into a heterostructure just like a set of lego blocks [137]. Today, with dielectrics such as ultrathin hBN combined with graphite gate with very low charge disorder, graphene channels with record high mobilities approaching  $10^7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  are possible [138].

Until this point in our discussion of graphene, electronic correlations have played a minor role. An exception is the Fractional quantum Hall effect, which has been observed in graphene and indeed fractional Landau levels require electron-electron interactions [139]. Barring this exception and despite the novelty of Dirac quasiparticles, once we incorporate the linear dispersion in theory, almost all experimental observations until about 2018 could be explained within the framework of single particle physics. A paradigm shift occurred in 2018 with the discovery of correlated physics in two layers of graphene, with a twist!

## 7.1 Moire materials

The correlated electron problem at its core is a competition: the Coulomb interaction between electrons ( $U$ ) vs the kinetic energy in electronic bands with characteristic bandwidth  $W$ . When  $U/W \gtrsim 1$ , the independent electron approximation fails and the ground state is determined by interactions. The resulting phases include Mott insulators, magnets, charge-ordered crystals, and unconventional superconductors. Historically, this regime was reached through materials chemistry: transition metal oxides, heavy fermion compounds, and organic salts realize narrow bands through atomic orbital character and crystal structure.

The success of single particle models in explaining observed electronic phenomena in graphene and other vdW heterostructures gave confidence to theorists that simple tight-binding models of these heterostructures could be a reliable guide for predicting their electronic properties. It is important to note this distinction between graphene and traditional correlated materials. Since the bandstructure directly involves atomic orbitals with considerable complexity such as spin-orbit



couplings, crystal fields and internal degeneracy (e.g. d and f orbitals), a complete calculation of the electronic bands requires sophisticated approaches such as density functional theory. Graphene on the other hand consists only of relatively simple p orbitals, has low spin orbit couplings and crystal fields do not play a major role in electronic properties.

The layered nature of vdW materials implies they can be potentially stacked in interesting ways such as a twist between neighboring atomic layers and stacking of heterogeneous layers (e.g. graphene and TMDs). Superposing 2D meshes leads to moiré patterns which can create aesthetically pleasing patterns. A key development was the realization that these moiré patterns can greatly alter the electronic properties of the underlying layers [140]. As early as 2010, STM measurements had observed spatially resolved moiré patterns in CVD graphene. The tunneling spectroscopy as a function of bias showed peaks in the density of states flanking the minimum at the Dirac point. These peaks correspond to van Hove singularities in the bandstructure and their position as a function of bias depends on the twist angle. Two theoretical proposals, by Suárez Morell *et al.* [141] and Bistritzer and MacDonald [142] predicted that an almost magical cancellation of the band dispersion occurs in two layers of graphene twisted at an angle of around  $1.1^\circ$ . At the core of this cancellation is a quantum interference effect where the interlayer and intralayer hopping amplitudes balance in such a way that the carrier velocity goes to zero. In the continuum limit, the bandstructure was predicted to consist of a flat band isolated from remote bands by a few meV.

Experimental efforts based on these predictions finally bore fruit in 2018 with the discovery of correlated insulators and superconductivity in magic angle twisted bilayer graphene (MATBG) [143, 144]. In heterostructures involving twisted vdW materials, the interference pattern between the lattice of two layers defines a moiré superlattice with a period significantly larger than atomic lattice constants. This additional periodicity zone folds the electronic bands into a smaller moiré Brillouin zone (mBZ). In twisted bilayer graphene, the zone folded moiré bands have a degeneracy of four from spin and valley degrees of freedom. In Ref. [143], the surprising observation was the presence of additional insulators at partial integer fillings of the moiré band. For example, non-interacting physics would predict that a half-filled band is a metal, but on half-filling the moiré bands, insulators were observed. Hence, these insulators are called correlated insulators. On doping the half-filled insulators, superconductivity was observed [144]. Superconductivity from a doped insulator state is reminiscent of the phase diagram of high- $T_c$  cuprate superconductors [87] and hence these discoveries in MATBG attracted significant interest from the condensed matter physics community.

## 7.2 Non-moiré materials

Moiré engineering is not the only route to correlations in vdW systems, and it is worth separating two different classes of non-twisted materials. The first class is what we will call *intrinsic* correlated vdW materials: layered compounds whose bulk parents were already known as correlated materials

and which have since been thinned to the monolayer limit. Here the narrow bands come from the atomic physics of partially filled  $d$  orbitals. Metallic TMDs such as 2H-NbSe<sub>2</sub> and 2H-TaS<sub>2</sub> host charge density waves (CDW) coexisting with superconductivity. In monolayer NbSe<sub>2</sub>, the CDW is strongly enhanced while  $T_c$  falls from 7.2 K in the bulk to roughly 3 K in monolayers [145, 146]. The broken inversion symmetry of the monolayer generates an Ising spin-orbit field that pins spins out of plane and pushes the in-plane critical field several times beyond the Pauli limit [147]. 1T-TaS<sub>2</sub> takes a rather different route: its star-of-David CDW reconstruction leaves one unpaired electron per cluster and the resulting narrow band Mott-localizes into an insulator that has been suggested as a candidate quantum spin liquid [148, 149]. Cr<sub>2</sub>Ge<sub>2</sub>Te<sub>6</sub>, CrI<sub>3</sub> and Fe<sub>3</sub>GeTe<sub>2</sub> retain magnetic order down to the monolayer limit and CrI<sub>3</sub> shows a layer number dependent alternation between ferromagnetic and antiferromagnetic interlayer coupling [150, 151]. Monolayer Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+ $\delta$</sub>  has a superconducting critical temperature similar to the bulk cuprate [152]. The correlated phase in these materials is derived from a correlated phase which exists in the bulk. Their carrier densities are also high, typically  $\gtrsim 10^{14} \text{ cm}^{-2}$ , so a typical dielectric gate can move the chemical potential by only a small fraction of the bandwidth. As a result, the resultant phases are only tunable by chemical changes or unconventional gating methods such as ionic-liquid gating [153].

The second class has been discovered in the last few years and is different from these *intrinsic* correlated vdW materials. For example, in graphene multilayers with no twist and no moiré superlattices, flat bands are produced by an externally applied displacement field. In rhombohedral (ABC) stacked  $N$ -layer graphene at high displacement field, the low-energy states live on the two non-dimer sublattices at the outer surfaces and disperse as  $E \sim k^N$  leading to a flat band bottom with a high density of states [154]. Rhombohedral trilayer graphene displays a cascade of isospin-polarized quarter-, half- and three-quarter-metal phases together with two superconducting pockets, one of which borders a spin-polarized normal state and survives in-plane fields far beyond the Pauli limit [155]. Bernal bilayer graphene (BBG) shows an isospin cascade and superconductivity near  $D \approx 1 \text{ V nm}^{-1}$  with  $T_c$  of order 30 mK [156], enhanced by roughly an order of magnitude and extended over a much larger region of the  $n$ - $D$  plane when the bilayer is proximitized by a monolayer of WSe<sub>2</sub> [157, 158, 159]. Four, five and six layer rhombohedral graphenes have since produced quantum anomalous Hall states [160, 161, 162], fractional Chern insulators [163, 164, 165, 166, 167], and superconductivity carrying signatures of spontaneous time-reversal symmetry breaking [168, 169], alongside a broader family of correlated and broken-symmetry phases [155, 170, 171, 172, 173, 174, 175, 176, 177, 178]. The correlated physics of these systems is driven by the similar ingredient as the moiré materials: a narrow, high-density-of-states band with nontrivial Berry curvature at low carrier density. They also carry a practical advantage over twisted systems. Because no alignment is required, there is no twist-angle disorder, and spatial inhomogeneity is set instead by strain and stacking-domain structure.

In order to distinguish the physics of moiré materials and non-twisted rhombohedral graphenes

from that of intrinsic vdW correlated materials, we will refer to the former collectively as *flatband vdW materials*. As the name suggests, the defining feature is the presence of a flat band, engineered by twist or by stacking order along with high displacement fields, rather than correlations being inherited from bulk bands.

### 7.3 The zoo of correlated phases in flatband vdW materials

Dozens of correlated phases are now known in flatband vdW materials. In this section, we will try to get a bird's eye view of these phases. It is best to group not by material but by the nature of the phase. Three recurring themes cover most of the experimental landscape and are sketched in Fig. 7.1: spontaneous isospin (spin-valley) polarization, interaction driven topological order and superconductivity. They are not independent of one another, and much of what follows is an account of how each grows out of the one before it. Note that these themes are not exhaustive, and there are many phases such as charge density waves [145], generalized Wigner crystals [179], multi-ferroics [173], etc which occur outside of the classification suggested below.

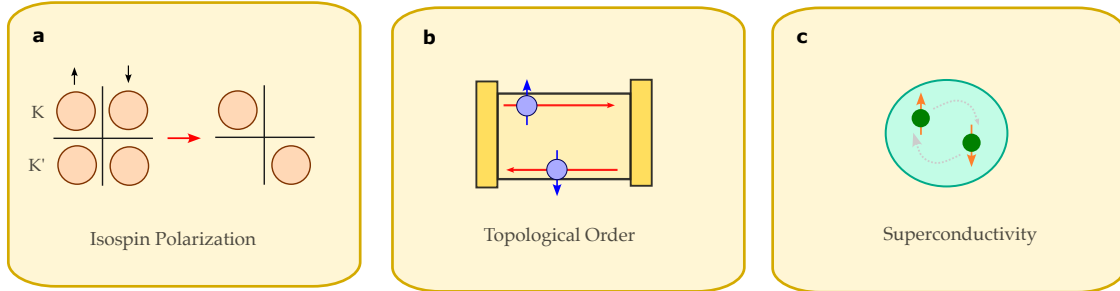


Figure 7.1: **Three classes of correlated phase in flatband vdW materials.** (a) *Isospin polarization*. The flat bands of graphene and TMD systems carry a fourfold degeneracy of spin and valley, drawn here as a grid whose rows are the  $K$  and  $K'$  valleys and whose columns are the two spin projections. On the left all four flavors are equally occupied in the non-interacting limit. Exchange coupling can instead make it favorable to depopulate some of the flavors and redistribute the carriers among the rest, leaving a partially polarized configuration such as the two-flavor state on the right. (b) *Topological order*. When a polarized flat band carries a nonzero Chern number, the gapped bulk is accompanied by chiral channels that carry current along the sample boundary between contacts. (c) *Superconductivity*. Carriers bind into Cooper pairs, drawn here as a two-electron bound state, which condense into a state with global phase coherence. The three classes are not independent of one another: the topological states arise when isospin polarization acts on a band that already carries Berry curvature, and superconductivity in these materials appears predominantly at the boundaries of isospin-ordered regions.

### 7.3.1 Isospin polarization

Electrons in graphene and TMD flatbands carry a fourfold degeneracy of spin and valley, collectively termed as isospin. When the bandwidth is reduced, exchange interaction favors spontaneous polarization of the isospin, analogous to Stoner ferromagnetism [180]. The Stoner criterion for ferromagnetism states  $UD(\epsilon_F) > 1$ , where  $U$  is the exchange energy and  $D(\epsilon_F)$  is the density of states at the Fermi energy. Since the density of states is large for flatbands, even a modest exchange energy can tip the criterion in favor of a ferromagnetic phase. In the language of isospins, such an isospin ferromagnet is also referred to as an isospin polarized phase, and Fig. 7.1a shows the transfer of carriers between flavors that defines it. We have encountered isospin phases before in our discussion of correlated insulators in MATBG. The insulators at the integer filling of the moiré band are isospin polarized phases, though the precise nature of the polarization remains unknown. Compressibility using scanning probe techniques in MATBG revealed a cascade of transitions in which the isospin flavors polarize sequentially and a reset of the Hall densities occurs at each transition [181]. A similar situation occurs even without a moiré pattern in rhombohedral graphenes. As a function of density and displacement field, we get a phase diagram consisting of quarter-metal, half-metal and full-metal isospin polarized phases [155, 169].

### 7.3.2 Topological order: anomalous Hall effects to fractional Chern insulators

The flat bands of these systems frequently carry finite Chern numbers or valley-contrasting Berry curvature, so isospin polarization can convert band topology into observable topological order [182]. The consequence, sketched in Fig. 7.1b, is a gapped bulk with dissipationless channels running along the sample edge and a Hall conductance quantized at zero applied field. Orbital ferromagnetism accompanied by a large anomalous Hall effect was first observed in twisted bilayer graphene aligned to hBN [183], followed by full quantization of the anomalous Hall conductance [184] and by quantum anomalous Hall (QAH) states built from intertwined moiré bands in TMD heterobilayers [185]. The most striking recent development is the zero-field fractional quantum anomalous Hall (FQAH) effect, in which fractionally quantized Hall conductance and topological order appear without any external magnetic field. FQAH states were observed nearly simultaneously in twisted  $\text{MoTe}_2$  [186, 187] and in rhombohedral pentalayer graphene aligned to hBN [163].

### 7.3.3 Superconductivity

Superconductivity in flatband vdW materials, the third of the classes in Fig. 7.1, seems to be ubiquitous across a wide range of material platforms such as twisted multilayer graphenes [144], non-twisted rhombohedral graphenes [156, 168, 169] and twisted TMDs [188]. The superconducting regions in the density-displacement field phase diagram seem to be intimately connected to the isospin physics

of Fig. 7.1a, as they predominantly occur adjacent to isospin transitions [156, 170, 168, 169]. In MATBG and higher layer twisted graphenes, superconductivity occurs always adjacent to correlated insulating phases [181]. The situation is slightly complicated for non-twisted rhombohedral graphenes and TMDs where only some of the transition regions host superconductivity. A unifying picture about which isospin polarized phases favor superconductivity is absent, as the isospin order itself is tricky to extract from current measurements.

## 7.4 Open problems in flatband vdW superconductivity

The primary method for discovery of superconductivity in vdW materials is electrical transport. The zero resistance state can be used to map out the  $n$ - $D$  phase diagram and to extract the critical temperature. Beyond these measurements, attempts to probe other properties of the superconducting state through transport do not always yield crisp results. Extraction of the superconducting critical field is obscured by 2D vortex physics. Nematicity as inferred from in-plane critical field measurements may suffer from non-idealized current flow due to spatial disorder in the sample. Hence, building new techniques which can probe the superconducting state beyond transport is crucial for a better understanding of superconductivity in these systems.

The techniques used on bulk superconductors that go beyond transport such as heat capacity, thermal conductivity, magnetic susceptibility, penetration depth by mutual inductance, and  $\mu$ SR are almost all extensive, and the small size of vdW samples makes them unrealistic. Certain techniques such as tunneling spectroscopy through an hBN barrier or an STM tip [189], scanning magnetometry with SQUIDS, and microwave measurements of the kinetic inductance are possible with appropriate experimental setups [190, 191]. In this part of the thesis, we will focus on kinetic inductance measurements. We have already encountered it in Sec. 3.3, as one of the fundamental properties of superconductors. The kinetic inductance and its inverse, known as superfluid stiffness  $K_s$ , can be used to answer some of the open problems in superconductivity of flatband vdW systems. Three of these are illustrated in Fig. 7.2 and are taken up in the subsections that follow, together with a fourth, the pairing mechanism, on which the stiffness bears less directly.

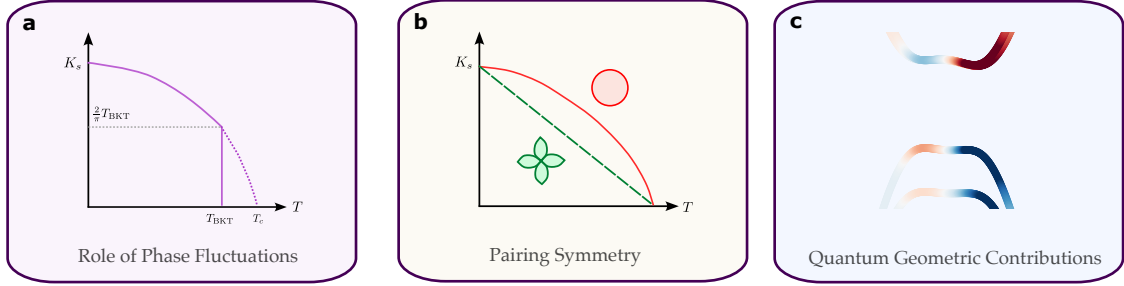


Figure 7.2: **Open problems in flatband vdW superconductivity.** (a) *The role of phase fluctuations.* In two dimensions, the superconducting transition is of Berezinskii-Kosterlitz-Thouless (BKT) type. The superfluid stiffness  $K_s$  falls with temperature and then drops discontinuously to zero where it meets the universal line  $K_s = (2/\pi)T_{\text{BKT}}$ , marked by the dotted horizontal. Above  $T_{\text{BKT}}$  the pairing amplitude may survive up to a higher mean-field  $T_c$ , indicated by the dotted continuation, without supporting global phase coherence. (b) *Pairing symmetry.* The low-temperature behavior of  $K_s(T)$  is governed by the population of thermally excited quasiparticles and therefore by the structure of the gap. s-wave pairing symmetry gives an activated suppression  $\delta K_s \sim e^{-\Delta/k_B T}$  while a nodal symmetry leads to power law dependence of  $K_s \sim K_0 + aT^n$  ( $n = 1$  is shown on the plot). (c) *Quantum geometric contributions.* In a flatband, the dominant contribution to  $K_s$  is through quantum geometry. In the schematic, the Berry curvature magnitude for Bernal bilayer graphene/WSe<sub>2</sub> bands is shown in the high  $D$  limit where superconductivity is known to occur. The significant Berry curvature in these bands suggests potentially large quantum geometric contributions to  $K_s$ . Understanding this contribution requires an absolute measurement of  $K_s$ .

#### 7.4.1 Phase fluctuations

A basic quantity characterizing superconducting order is the superfluid stiffness  $K_s$  and the associated temperature scale  $T_\theta$  [192, 193]. Superfluid stiffness captures the rigidity of the order parameter and the response of the superconductor to external magnetic fields. A superconductor with high superfluid stiffness has a higher energy cost to create phase fluctuations and expels magnetic fields readily. On the other hand, low superfluid stiffness is characterized by a low cost of phase fluctuations and weak screening of external magnetic fields. Elemental superconductors such as Al and Nb have  $T_\theta \approx 10^4$  K, much higher than their few-kelvin critical temperatures. It was established early on in the cuprates and other high- $T_c$  superconductors that the superfluid stiffness is anomalously low compared to elemental superconductors. Thermal fluctuations of the phase decide whether a superconducting condensate survives at a given temperature: the Cooper pairs themselves are believed to form at temperatures above  $T_c$ , and they only condense for temperatures below  $T_\theta$ . Fig. 7.2a makes this concrete for a two-dimensional superconductor, where the condition is sharpened into the Nelson–Kosterlitz criterion and the transition occurs when the falling stiffness meets the universal line  $K_s = (2/\pi)T$ . The vdW flatband superconductors introduced in this chapter also occur at anomalously low densities, so it seems highly likely that the superfluid stiffness itself is low, and

with it that the gap between the pairing scale and the phase-coherence scale is wide.

### 7.4.2 Pairing symmetry

The most basic unresolved question is the symmetry of the order parameter: is the gap an isotropic spin-singlet  $s$ -wave, as in an elemental BCS superconductor, or does it change sign around the Fermi surface, carry finite angular momentum, or vanish at nodes? The circumstantial case for unconventional pairing is strong. Superconductivity in these systems appears adjacent to isospin-ordered normal states rather than out of a featureless Fermi liquid. Most theoretical mechanisms proceed from a repulsive interaction, which generically favors a sign-changing order parameter in a nonzero angular momentum channel.

A superfluid stiffness measurement offers a simple route to extracting pairing symmetry, as the low-temperature behavior of  $K_s(T)$  is governed by the thermally excited quasiparticle population and therefore by the gap structure. A fully gapped superconductor gives an activated suppression,  $\delta K_s \sim e^{-\Delta/k_B T}$ , whereas line nodes give  $\delta K_s \propto T$ . The two cases are contrasted in Fig. 7.2b, and what distinguishes them is the shape of the curve as  $T \rightarrow 0$  rather than its absolute scale, which is a considerable practical advantage in a geometry where the absolute stiffness is hard to calibrate. Penetration depth measurements, which effectively measure the superfluid stiffness, have been used in the past to establish  $d$ -wave pairing in YBCO [194].

### 7.4.3 Quantum geometric contributions to the superfluid stiffness

In a conventional single-band superconductor the superfluid stiffness is set by the ratio of the superfluid density to the effective mass,  $K_s \sim n_s \hbar^2 / m^*$ . Since the effective mass in a flatband is ill-defined, the quantitative value of the stiffness cannot be given by that particular expression. The resolution is that this expression is incomplete for a multiband system. The superfluid weight contains a second contribution which depends not on the band energies but on the geometry of the Bloch wavefunctions through the quantum metric  $g_{\mu\nu}(\mathbf{k})$ , the real part of the quantum geometric tensor whose imaginary part is proportional to the Berry curvature. Fig. 7.2c indicates this schematically as structure carried by the bands beyond their dispersion. Peotta, Törmä and co-workers showed that in the flat-band limit the superfluid weight is proportional to the integral of the quantum metric over the Brillouin zone and is bounded below by the Chern number,  $D_s \gtrsim |C|$  [195, 196] ( $D_s \sim K_s$  and is the stiffness in normalized units). Subsequent work has sharpened these bounds using symmetry and topology and applied them to MATBG, where the geometric term is predicted to dominate the conventional term. [197, 198, 199, 200, 201].

#### 7.4.4 Pairing mechanism and its relation to isospin order

The origin of Cooper pairing of electrons in flatband vdW superconductors remains unsettled. For BBG and rhombohedral graphene, the candidate mechanisms include acoustic-phonon-mediated pairing and charge-fluctuation-assisted pairing [202], virtual tunneling into the proximate WSe<sub>2</sub> layer [203], Kohn-Luttinger pairing in which overscreening of the repulsive Coulomb interaction generates an attractive channel at finite angular momentum [204, 205, 206, 207], pairing generated directly by strong short-range repulsion, where correlated multi-particle tunneling processes about the atomic limit bind two itinerant carriers together without invoking overscreening [208], and pairing mediated by fluctuations of the adjacent isospin order, in analogy with spin-fluctuation pairing in the cuprates and iron pnictides [209, 210]. The stiffness depends on this question only indirectly, through the pairing symmetry of Sec. 7.4.2, since different mechanisms favor different angular momentum channels.

The remaining chapters take up the resolution of these open questions directly by building an experimental technique capable of measuring the superfluid stiffness of flatband vdW superconductors.



## Chapter 8

# Hybrid superconducting resonator architecture to probe vdW heterostructures

The study of two-dimensional materials over the past two decades has been a driving force in the discovery of new condensed matter phases and has led to myriad applications in electronics, photonics and quantum materials. As discussed in the previous chapter, superconductivity in flatband van der Waals (vdW) superconductors is an exciting frontier. In this chapter, we develop a hybrid architecture that combines superconducting microwave resonators with vdW heterostructures, with the goal of measuring the superfluid stiffness of flatband vdW superconductors.

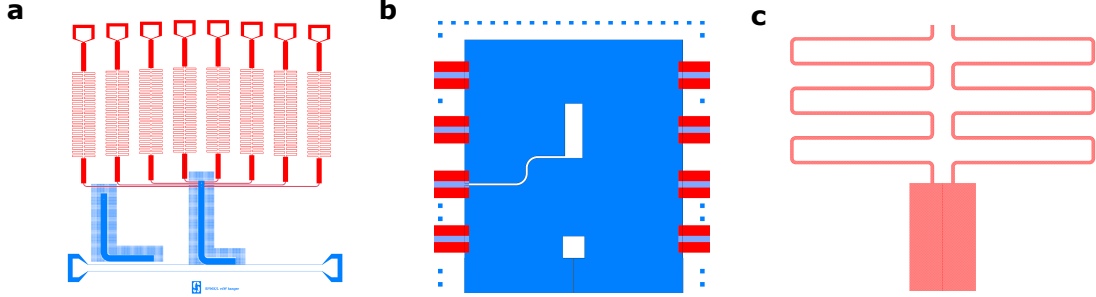


Figure 8.1: **CAD layout of the hybrid resonator architecture.** (a) Full  $5 \times 5$  mm chip. Blue denotes the microwave layer: the  $50 \Omega$  feedline running along the bottom edge with a tapered launch at either end, two hanger resonators, and the arrays of vortex traps that surround them. The left resonator is the reference resonator, which is never connected to a device and serves as an in-situ control on film properties and thermal cycling; the central resonator is the main resonator used for the hybrid experiments. Red denotes the DC layer: eight lines, each terminated by an LCL filter and a wirebond pad, which carry the two gate biases and the Hall bar probe connections. (b) Zoom on the terminating end of the main resonator, where the vdW stack is melted down. The meandering trace brings the resonator center pin into the device region and ends on a contact pad; the larger rectangle is the pre-patterned superconducting back gate,  $8 \times 20 \mu\text{m}$ . The eight DC coplanar waveguides approach from the left and right, four on each side, and the dotted rows above and below are vortex traps. (c) Zoom on a single LCL filter, showing the serpentine nanowire inductors and the interdigitated fingers that form the shunt capacitor. The inductors are  $200 \text{ nm}$  wide and several hundred microns long, giving of order  $100 \text{ nH}$  each, and the two inductors of a given filter are deliberately made unequal in length so that their parasitic  $\lambda/2$  modes are not degenerate. Note throughout that this is an image of the etch mask, so the filled regions are those removed during fabrication and the unfilled regions are where the superconducting film remains.

## 8.1 Motivation for a hybrid architecture

The interplay between the confinement of electronic systems to dimensions lower than three and the possibility of interaction-induced symmetry-breaking makes vdW materials a rich playground for the discovery of unconventional phases of matter [211]. A striking example of such a phase is superconductivity. Since the discovery of superconductivity in magic-angle twisted bilayer graphene (MATBG) in 2018 [144], several other vdW systems have been shown to superconduct [212]. Yet the nature of the superconducting state remains largely undetermined. The central open question is the pairing symmetry of the superconducting gap. Recent superfluid stiffness measurements of MATBG using high-frequency circuits suggest a nodal gap, though moiré disorder and the superconducting proximity effect preclude a simple interpretation [191]. Extending such measurements to cleaner vdW systems is necessary to answer questions about the origin of the pairing interaction, its consequences for the pairing symmetry, and ultimately to sort this growing family of superconductors into unifying classes that can guide theory [201].

VdW superconductors are almost exclusively probed through quasi-DC transport. Dissipationless conductivity, however, is not the only characteristic property of a superconductor. Perfect diamagnetism is an equally defining hallmark of the superconducting state. It stems from the phase coherence of the condensate of Cooper pairs and, specifically, from the “stiffness” of that phase to external electromagnetic perturbations. At the level of an electrical circuit, this stiffness manifests as an inductance and is referred to as the kinetic inductance (KI) of the superconductor. Because the temperature dependence of the stiffness is set by the low-energy quasiparticle spectrum, KI measurements provide direct evidence for the symmetry of the order parameter and for the presence of nodes in the superconducting gap.

The kinetic inductance of a superconductor is  $L = \frac{m^*}{2n_s e^2}$ , where  $m^*$  is the effective mass,  $n_s$  is the superfluid density and  $e$  is the electron charge. KI scales inversely with superfluid density. VdW superconductors have typical densities of order  $10^{11} \text{ cm}^{-2}$  and therefore a large KI in the range of 1–10 nH. This is a large enough inductance to shift the resonance frequency of a GHz microwave circuit by tens of MHz, which is readily resolvable. Our strategy is therefore to embed the vdW device directly into a superconducting microwave resonator and to extract the KI, and hence the superfluid stiffness, from the resonator response. To address the questions of pairing symmetry outlined above, these measurements must be performed as a function of temperature, carrier density and magnetic field.

## 8.2 Design criteria

To enable KI measurements across a wide range of vdW superconductors, we set out to build a universal circuit architecture satisfying the following requirements.

1. **Critical temperature ( $T_c$ ):** The superconducting circuit layer must have a critical temperature much higher than that of the vdW superconductor of interest, so that any temperature dependence we observe can be attributed unambiguously to the vdW material rather than to the circuit. Since most vdW superconductors have  $T_c \sim 0.1\text{--}1 \text{ K}$ , we seek a film with  $T_c > 5 \text{ K}$ . We use NbTiN, for which our ultra-thin films reach  $T_c \approx 10 \text{ K}$ .
2. **Substrate:** The superconducting film on the chosen substrate must support microwave circuits with high quality factors. We use high-resistivity silicon, on which bare NbTiN resonators routinely achieve  $Q_i \sim 10^5 - 10^6$ .
3. **Substrate compatibility with vdW stack transfer:** vdW stacks are assembled by dry pickup with polymer stamps. The circuit substrate must therefore survive a final stack melt-down and the subsequent nanofabrication of the stack into a device. This requirement couples the microwave design to the surface chemistry left behind by the circuit-layer etch, and, as described in Sec. 8.4, proved to be the single largest obstacle in practice.

4. **Quasi-DC measurements:** The circuit must support quasi-DC transport on a standard six-probe Hall bar concurrently with microwave measurements. This allows every microwave observation to be cross-checked against a conventional transport signature on the same device and in the same cooldown.
5. **Frequency:** The resonator frequency  $f_r$  must be high enough that the kinetic inductance of the vdW superconductor produces a substantial frequency shift, and must lie within the bandwidth of standard cryogenic microwave amplifiers. At the same time,  $hf_r$  must remain well below the gap of the vdW superconductor to avoid high-frequency depairing of Cooper pairs. Taking  $2\Delta \sim 3.5k_B T_c$  places this ceiling around 70 GHz per kelvin of  $T_c$ , so a fundamental mode near 1 GHz leaves ample margin for a vdW superconductor with  $T_c \sim 0.1\text{--}1$  K while still permitting frequency-dependent studies on the higher harmonics of the same resonator.
6. **Quality factor:** The internal quality factor  $Q_i$  should be as large as possible in order to resolve small frequency shifts. The coupling quality factor  $Q_c$  should be designed so that the resonator is close to critically coupled ( $Q_i \approx Q_c$ ). We target  $Q_c \sim 10^4$ , which gives a linewidth of order 100 kHz. This is comfortably narrow compared to the 10–50 MHz shifts expected from the kinetic inductance of the vdW superconductor.
7. **Contact transparency:** To minimize the degradation of quality factor caused by imperfect interfaces to the vdW system, the contacts must be as transparent as possible, i.e. have the lowest achievable contact resistance. As we show in Chapter 3, a resistance appearing in series with the resonator termination degrades  $Q_i$  extremely rapidly, so this requirement is considerably more stringent here than in standard transport devices.
8. **Dual gating:** Independent top and bottom gates are required in order to control the carrier density and the displacement field of the vdW system independently.

An additional constraint that cuts across several of the above is the resonator impedance  $Z_r$ . As discussed in Chapter 3, the fractional frequency shift produced by a given change in kinetic inductance grows with  $Z_r$ , and the zero-point current fluctuations at the current antinode shrink as  $Z_r$  increases. The latter matters because the critical currents of vdW superconductors are small, typically 1–100 nA; a high-impedance resonator therefore perturbs the condensate less at a given photon number. We also require  $Z_r$  to exceed the normal-state resistance of the vdW channel, which for BBG is 30–100  $\Omega$  outside the superconducting dome. Both considerations point to  $Z_r \sim 1\text{--}2$  k $\Omega$ , an order of magnitude above the 50  $\Omega$  of a conventional CPW.

Finally, the feedline itself is kept at 50  $\Omega$  to avoid spurious reflections that would distort the resonator lineshape and complicate fitting. On a high-sheet-inductance film this requires a wide center pin (30–40  $\mu\text{m}$ ) with a narrow gap (1–2  $\mu\text{m}$ ) to ground. This is geometrically the opposite limit from the high-impedance device resonator. It illustrates how much of the design freedom in these circuits comes from the geometry rather than from the film itself.

### 8.3 Fabrication of hybrid devices

We chose to focus initially on a single vdW system: Bernal bilayer graphene (BBG) proximitized by the transition metal dichalcogenide WSe<sub>2</sub>, in which superconductivity was demonstrated recently [157]. Spin-orbit coupling inherited from WSe<sub>2</sub>, combined with the quasi-flat bands of BBG at high displacement field, is believed to be essential to the superconducting state. Because no particular twist angle is required, the system is free of moiré disorder. Stack assembly is also considerably easier than for twisted graphene superconductors, which allows a higher throughput of test devices while the circuit architecture is being optimized.

#### Superconducting circuit layer

The resonators are patterned from NbTiN films grown on high-resistivity Si by reactive magnetron sputtering (see Appendix E). We use ultra-thin films ( $< 10$  nm) in order to obtain a large sheet kinetic inductance and hence a high resonator impedance. Reducing the film thickness trades off against  $T_c$ , and the deposition was optimized by first maximizing  $T_c$  and then maximizing sheet inductance at fixed  $T_c$ , by tuning the Nb:Ti and N<sub>2</sub>:Ar ratios. The resulting films have  $T_c \approx 10$  K and sheet inductances of order  $10^2$  pH per square, corresponding to a London penetration depth of several hundred nanometers and a Pearl length far exceeding the device dimensions.

Circuit patterning proceeds at the wafer scale. The film is deposited on a 4-inch wafer, Ti/Pt alignment markers are patterned and lifted off well away from any future superconducting features, and the wafer is diced into  $15 \times 15$  mm mother chips (Appendix C). The coplanar waveguide layer is then defined by electron beam lithography and a slow etch using either a fluorine or a chlorine chemistry (Appendix E), after which the mother chips are diced into the final  $5 \times 5$  mm chips shown in Fig. 8.1(a). Batching the process in this way lets us produce of order nine superconducting circuit layer chips in one fabrication run. The subsequent vdW fabrication has a much lower yield, and this batching ensures that it is never limited by the availability of substrates with the patterned hybrid architecture.

The device resonator has a 200 nm center pin separated from the ground plane by 50  $\mu$ m, giving  $Z_r \approx 2$  k $\Omega$ . It is patterned in the first etch as a  $\lambda/2$  resonator with both ends open. Once the vdW device is fabricated at one end, the source contact ties that end to the ground plane through the device, converting the mode into a  $\lambda/4$  resonance at half the original frequency. On a blank chip we measure the device resonator at 2.2085 GHz and the reference resonator at 3.7002 GHz, consistent with the intended  $\sim 1$  GHz fundamental once the device is in place. The reference resonator, which is never shorted by a device, provides an in-situ control for film properties, thermal cycling and loss mechanisms that are not specific to the vdW stack. The ground plane and the region surrounding both resonators are perforated with square and holey flux traps to pin vortices during out-of-plane field sweeps.

## Filtering the DC lines

One of the requirements of the architecture is simultaneous DC and microwave measurement. Quasi-DC transport uses a Hall bar geometry, whose voltage probes are galvanically connected to the channel and hence to the resonator. Without intervention, these arms act as antennae that radiate the microwave mode out of the device, spoiling  $Q_i$ . We therefore terminate each DC line with an LCL filter, consisting of a shunt capacitor flanked by two series inductors. The filter acts as a low-pass element and reflects microwaves back toward the resonator. We adapted the on-chip nanowire inductor approach from circuit QED architectures developed for quantum dot based semiconductor qubits [213]. Simulations indicate that  $L_{\text{filter}} > 100 \text{ nH}$  and  $C_{\text{filter}} > 1 \text{ pF}$  are sufficient to keep  $Q_i > 10^5$  even in the presence of eight DC lines and two gates.

The large sheet inductance of NbTiN makes these inductors easy to realize on-chip: etching the film into a nanowire 200 nm wide and several hundred microns long yields inductances of order 100 nH in a footprint of a few hundred microns. The shunt element is an interdigitated finger capacitor. Fig. 8.1(c) shows the resulting layout. Two practical points constrain this design. First, a nanowire of this length supports its own  $\lambda/2$  modes in the 8–9 GHz range; we deliberately make the two inductors of a given filter unequal in length so that these parasitic modes are not degenerate and cannot provide a clean transmission path past the filter. Second, the finger spacing of the shunt capacitor sets the closest approach between a biased conductor and the ground plane anywhere on the chip, which turns out to determine the maximum usable gate voltage (Sec. 8.4.3). A thin Nb layer, co-deposited with the superconducting contacts, is added on top of the DC lines to push their  $\lambda/2$  modes to higher frequency and away from the resonator harmonics of interest.

## Choosing a contact etch recipe

The vdW stack is melted down onto a pre-patterned NbTiN back gate at the shorted end of the device resonator (Fig. 8.1(b)), a pad of  $8 \times 20 \mu\text{m}$ . Device fabrication then proceeds through three lithography steps, which define the edge contacts, the top gate and finally the mesa. The full sequence is set out in Sec. 8.5.

The critical materials problem in this sequence is the contact etch, which must remove the top hBN and stop cleanly on the graphene without consuming it.  $\text{XeF}_2$  is perfectly selective to hBN over graphene, but its etch rate on the underlying silicon is of order  $\mu\text{m}$  per minute, which is unacceptable on a substrate that also carries the resonator. We therefore developed  $\text{CF}_4$  and  $\text{CHF}_3/\text{O}_2$  recipes instead: pure  $\text{CF}_4$  etches hBN at  $\sim 90 \text{ nm}$  per 30 s while consuming essentially no graphene, whereas  $\text{CHF}_3/\text{O}_2$  is slower (8.5 nm per 30 s) and removes roughly a monolayer of graphene in the same time. Reducing the  $\text{O}_2$  flow improves the selectivity of the latter at the cost of etch rate.

## 8.4 Challenges with hybrid device fabrication

Integrating vdW heterostructures onto a superconducting circuit chip introduced several failure modes that do not arise in either field on its own. Three dominated the yield: failure to melt stacks down reliably onto the circuit substrate, spalling of the superconducting contacts, and premature leakage on the gate lines. Each was eventually traced to a specific and, in retrospect, unsurprising cause.

### 8.4.1 Tenting during stack meltdown

Early attempts to melt stacks down onto patterned circuit chips failed in a variety of ways: stacks wrinkled, floated away entirely during the polymer dissolution, or tented. Tenting is both the most common of these failures and the most informative, and is shown in Fig. 8.2(a). Part of the stack lies conformally on the substrate while another part is lifted off it, the raised region being immediately recognizable under the microscope by the interference fringes produced by the air gap beneath. The stack itself appears undamaged: within the tented region the layers remain continuous and show no optical evidence of tearing, which places the fault at the interface rather than in the heterostructure. The picture this suggests is sketched in Fig. 8.2(b). Surface adsorbates, leftover resist and roughness prevent contact over part of the footprint, and the stack bridges these regions and stands off the surface like a tent.

Tenting over the pre-patterned back gate initially suggested that the topography of the gate was to blame, but the same failures occurred on regions of bare silicon with no gate underneath, ruling out topography as the primary cause.

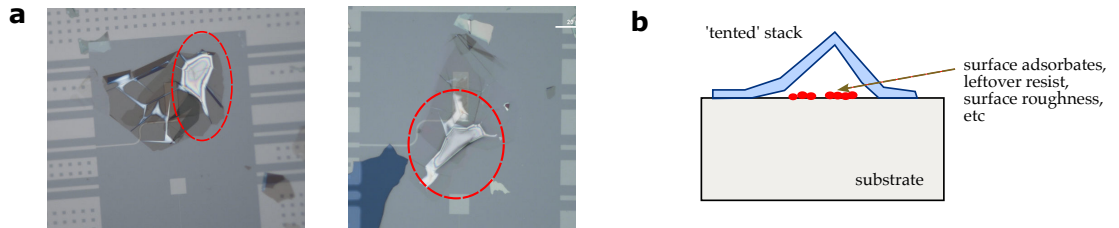


Figure 8.2: **Tenting during stack meltdown.** (a) Optical images of two vdW stacks melted down onto patterned circuit chips. The regions circled in red are lifted off the substrate and display interference fringes from the air gap beneath them, while the surrounding areas of the same stack lie conformally on the surface. We refer to stacks with this morphology as tented. Note that the tented regions show no optical evidence of damage to the stack itself, so the defect is one of adhesion rather than of the heterostructure. (b) Schematic cross-section of a tented region. Surface adsorbates, leftover resist and roughness, indicated in red, prevent the stack from making contact over part of its footprint, so that it bridges the contaminated area and stands off the substrate. Since tenting occurs on bare silicon as readily as over the pre-patterned back gate, the topography of the circuit layer is not the primary cause.

Sweeping the surface with an AFM tip before meltdown resolved the problem locally, which identified the culprit as a surface contaminant rather than a bulk property of the substrate. AFM cleaning is not practical to scale to the areas and stack counts we require, so we looked for the origin of the contamination. The circuit layer is etched in  $\text{CF}_4/\text{O}_2/\text{Ar}$ , a chemistry that leaves a partial fluoropolymer film on exposed silicon and renders the surface hydrophobic. Notably, the same recipe leaves much less residue when etching  $\text{SiO}_2$ , because the oxygen liberated from the oxide suppresses fluoropolymer formation. This is consistent with the observation that meltdowns on oxide substrates had never given us trouble.

The fix is a short HF dip immediately before meltdown, which we think lifts off the fluorocarbon layer along with the native oxide beneath it. This restored reliable adhesion, and we now routinely melt stacks down onto patterned chips. The dip must be kept short: extended HF exposure of above 5 minutes attacks the exposed circuit layer and reintroduces failures of its own. EKC265, a commercial fluorocarbon residue stripper used in superconducting device processing [214], provides an alternative route but did not reliably improve our meltdowns.

#### 8.4.2 Spalling from strained superconducting contacts

The second failure mode is the spalling of superconducting contacts, in which the deposited metal relieves its residual stress by lifting off the surface, taking the underlying 2D material with it. Figure 8.3 follows a single device through the three stages of the contact step and shows where the damage appears. After the contact lithography and etch the device is intact. After deposition of the Ti/Nb/Al trilayer, parts of the film have already buckled away from the substrate. After liftoff, sections of the contact arms are visibly raised and the traces are severed. The failure is therefore not a liftoff artefact but is present as soon as the metal is on the chip.

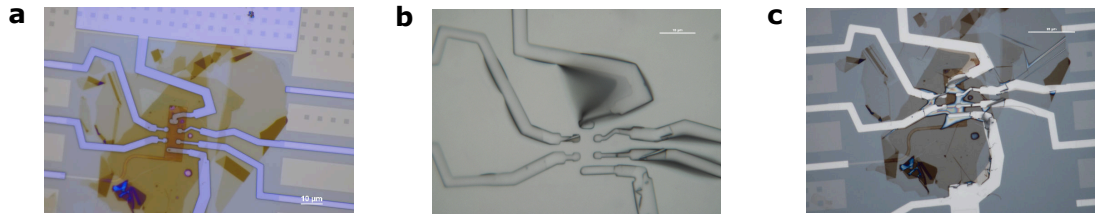


Figure 8.3: **Spalling of superconducting contacts.** The same device imaged at three stages of the contact step for a high-stress metallization. (a) After the contact lithography and selective etch, before deposition. The vdW stack, the etch windows and the underlying circuit layer are all intact. (b) After deposition of the Ti/Nb/Al trilayer and before liftoff. The buckled, wrinkled region near the center of the device is metal that has already delaminated from the surface. (c) After liftoff. Sections of the contact arms are raised off the substrate and the traces are broken. Since the damage is already present in (b), the mechanism is the relief of residual film stress at deposition rather than mechanical disruption during liftoff.



The driving force is the residual tensile stress of electron-beam evaporated Nb. Above a critical thickness the stored elastic energy exceeds the adhesion energy of the interface and the film delaminates. The effect was consistently worse on hBN than on silicon, reflecting the weaker adhesion of metals to a vdW surface. To put this on a quantitative footing we measured the residual stress of a series of trilayer recipes by wafer bowing on 4-inch wafers, shown in Fig. 8.4. The stress rises steeply with the Nb fraction of the film, and the recipes at the high-Nb end are precisely those that spalled in practice.

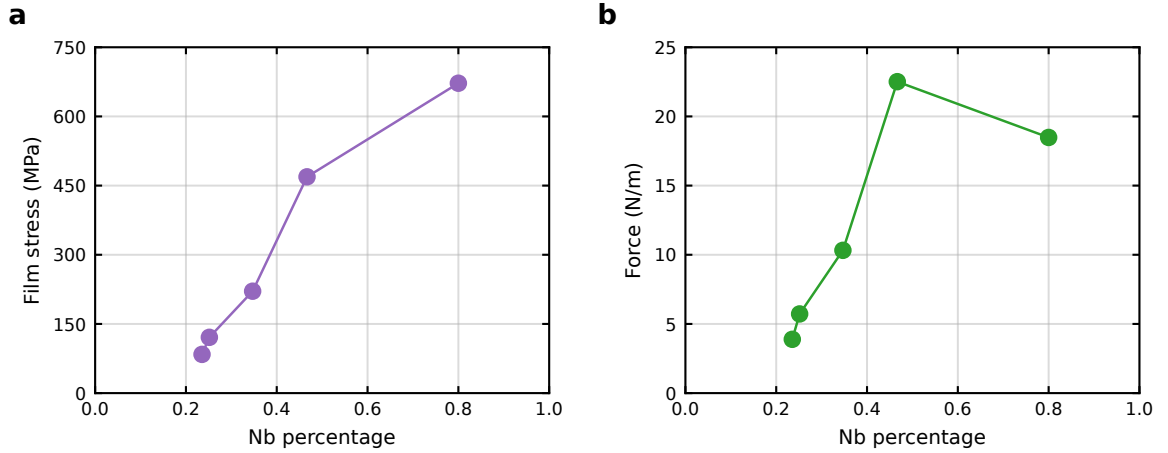


Figure 8.4: **Residual stress of Ti/Nb/Al contact metallizations.** Stress extracted from wafer bowing measurements on 4-inch wafers, plotted against the Nb fraction  $t_{\text{Nb}}/t_{\text{total}}$  of the trilayer, where  $t_{\text{total}} = t_{\text{Ti}} + t_{\text{Nb}} + t_{\text{Al}}$ . (a) Film stress, which is tensile throughout and rises steeply with Nb content, from below 100 MPa at a Nb fraction of 0.23 to roughly 650 MPa at 0.80. This is the trend that motivates the aluminium cap: Nb grows under tensile stress and Al under compressive stress, so increasing the Al fraction at fixed Nb thickness partially compensates the two and lowers the net stress of the stack. (b) The corresponding force per unit width, that is the product of the film stress and the total thickness. This combination rather than the stress alone sets the elastic energy per unit area available to drive delamination. It is not monotonic in Nb fraction because the recipes differ in total thickness as well as in composition.

The optimized recipe follows directly from this. We settled on a 3 nm Ti / 10 nm Nb / 30 nm Al trilayer, in which the compressive Al cap offsets the tensile Nb. Its Nb fraction of 0.23 places it at the low-stress end of the series in Fig. 8.4, and it does not spall, whereas recipes of comparable total thickness dominated by Nb do. Two further changes helped. Reducing the deposition rate from  $10 \text{ \AA s}^{-1}$  to  $5 \text{ \AA s}^{-1}$  eliminated spalling on silicon, though not on hBN. Rounding sharp corners in the contact layout to a 500 nm radius removed the stress concentrators at which delamination nucleates. Figure 8.5 repeats the three-stage sequence of Fig. 8.3 with the optimized recipe on a comparable device, and no delamination is visible at any stage.

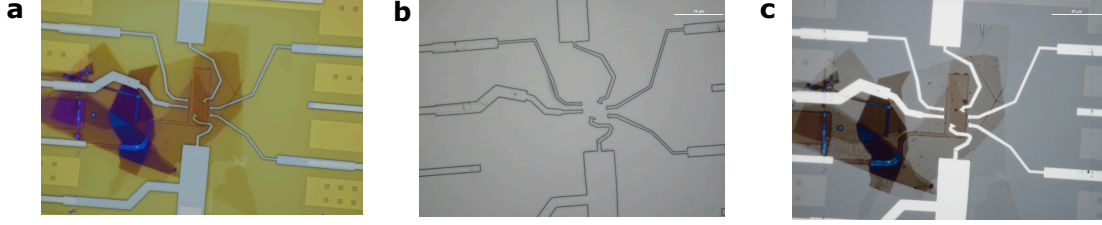


Figure 8.5: **Contacts deposited with the stress-compensated recipe.** The same three stages as Fig. 8.3, for a device contacted with the optimized 3 nm Ti / 10 nm Nb / 30 nm Al trilayer. (a) After the contact lithography and etch. (b) After deposition. The film lies flat across the whole device, with none of the buckling seen in Fig. 8.3(b). (c) After liftoff, with continuous contact arms and no raised regions.

Because the Al cap is a normal metal at the relevant temperatures, it suppresses the  $T_c$  of the contact through the proximity effect, so the stress compensation is not free. Using the Usadel-based treatment of superconductor-normal bilayers [215], we estimate that at the interface transparency characteristic of our depositions the suppression is modest and leaves the contact  $T_c$  at about 2-3 K depending on the Al thickness. Note that this is well above that of the vdW superconductor, so the trilayer still satisfies criterion 1 of Sec. 8.2.

### 8.4.3 Substrate leakage in gate lines

Two of the on-chip DC lines carry the bottom and top gate biases. Measurements on early devices showed the onset of gate leakage at around 5 V. This is on the low side for the 10–20 nm hBN dielectrics in the stack, and it is low enough to prevent us from reaching the displacement fields at which superconductivity appears in BBG/WSe<sub>2</sub>.

We eventually traced the leakage not to the hBN but to the silicon substrate itself, and specifically to the closest approach anywhere on the chip between a biased conductor and the ground plane. This occurs not at the device but in the interdigitated capacitors of the LCL filters, where the finger spacing had been set to 500 nm in order to maximize the filter capacitance. The substrate is nominally intrinsic silicon, so this route to ground was not anticipated, but residual dopants evidently supply enough carriers for conduction to set in once the field between the conductors becomes large.

To test this directly we fabricated chips carrying only the filter pattern, with the gap  $g$  between the fingers and the ground plane varied systematically, and measured the DC leakage current (Fig. 8.6). The behaviour is clean. Below breakdown the current is a few tens of pA, corresponding to resistances of hundreds of G $\Omega$ , and at breakdown it rises abruptly by orders of magnitude. The breakdown voltage increases monotonically with gap, from about 11.5 V at  $g = 1 \mu\text{m}$  to about 21 V at  $g = 4 \mu\text{m}$ , while chips with the original 500 nm spacing were shorted to ground from the outset.

We settled on  $g = 3\,\mu\text{m}$ , which interpolates to a leakage onset of 17–20 V. This costs some filter capacitance but is comfortably sufficient for the gate voltages we need.

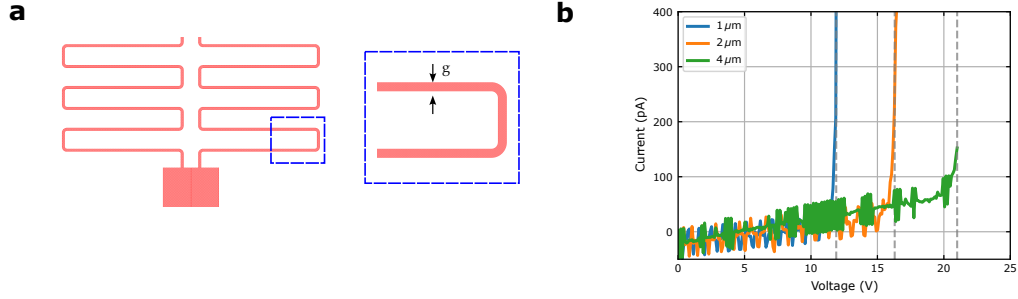


Figure 8.6: **Substrate leakage through the filter capacitors.** (a) Mask layout of an LCL filter. The inset shows the gap  $g$  between the interdigitated fingers and the surrounding ground plane, which is the closest approach between a biased conductor and ground anywhere on the chip. Early designs set  $g = 500\text{ nm}$  to maximize the filter capacitance. (b) Leakage current against applied voltage, measured on test chips carrying only the filter pattern, for  $g = 1, 2$  and  $4\,\mu\text{m}$ . Below breakdown the current is a few tens of pA, corresponding to resistances of hundreds of G $\Omega$ . Dashed lines mark the onset of runaway conduction at approximately 11.5, 16 and 21 V respectively, so the breakdown voltage rises monotonically with gap. Chips with  $g = 500\text{ nm}$  were shorted to ground before any bias was applied and are not shown. Note that conduction of this kind is not expected in the nominally intrinsic silicon used here, especially at mK temperatures, and we attribute it to breakdown through residual dopants in the substrate.

A second, superficially similar failure mode is worth distinguishing, since it cost us several devices before it was identified. On some chips we observed leakage of 0.5–1 M $\Omega$  between an electrically open DC line and the ground plane. This is orders of magnitude more conductive than substrate breakdown, and crucially it is present already at zero bias. This turned out to be caused by drifting etch rates in the RIE: an incomplete etch leaves a thin conductive residue bridging the trenches. Because the symptom at the device level looks like a leaking gate, the diagnostic that separates the two is to bias a line that is not connected to anything. Any leakage observed on an open line cannot be a property of the stack and must arise from irregularities in the superconducting circuit layer fabrication process.

## 8.5 A complete process flow for hybrid devices

With the meltdown, spalling and leakage problems resolved, the vdW fabrication has converged on a reproducible sequence of three lithography steps. Figure 8.7 follows a single device through it. A step-by-step checklist is given in Appendix F and the individual process recipes in Appendix E.

The starting point is a stack melted down onto the pre-patterned back gate at the terminating end of the resonator. The contacts are defined first, using a bilayer EL6 / 950 A3 resist and an

electron beam write that splits the pattern by feature size, with a fine beam current for the contact fingers and a coarse one for the filters and other large features. After development in cold water:IPA, the exposed top hBN is removed in the RIE with an  $O_2$  descum followed by the selective  $CF_4$  etch described above, stopping on the graphene. The Ti/Nb/Al trilayer is then evaporated in a single pump-down. A Ti getter step precedes the deposition to reduce the residual water and oxygen in the chamber, the high Nb rate is stabilized behind a closed shutter before the sample is exposed, and a static oxidation at the end caps the aluminium with a controlled oxide. Liftoff is done in acetone followed by an IPA rinse, with gentle drying in a single direction.

The top gate follows the same lithography and the same metallization, differing only in that the RIE step is an  $O_2$  descum alone with no hBN etch, since the gate sits on top of the stack rather than contacting the graphene edge. Using the same stress-compensated trilayer for both steps means that a single optimized deposition serves the contacts and the gate.

The mesa etch defines the channel and is the last step. A single layer of 950 Å  $Al_6$  protects the device while everything outside it is etched away. This etch has to clear not only the stack but also the superconducting back gate underneath, so that the regions outside the mesa are fully isolated, and it is therefore run as repeated cycles of the  $CHF_3/O_2$  recipe until it does. Stripping the resist gives the finished device.

Optical inspection after every write, etch, deposition and liftoff is part of the flow rather than an optional check. Most of the failure modes of Sec. 8.4 were diagnosed by comparing images taken before and after a single step, which is how the spalling in Fig. 8.3 was localized to the deposition rather than to the liftoff.

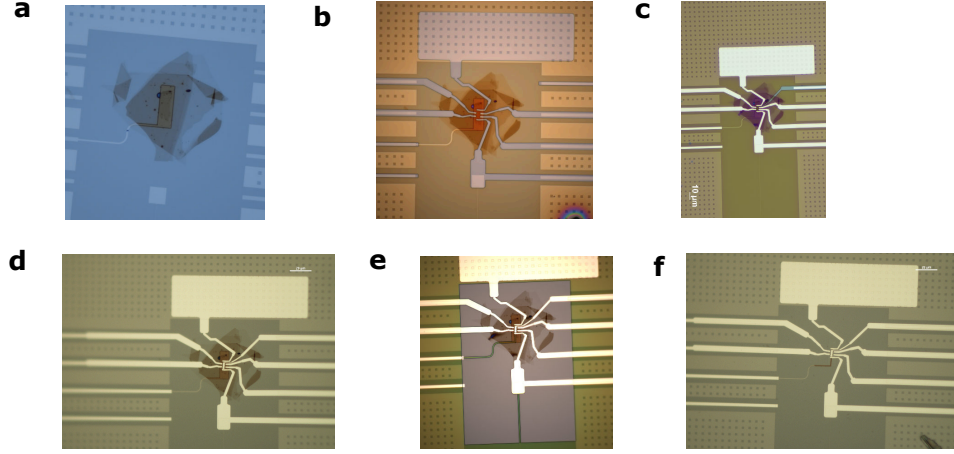


Figure 8.7: **Complete fabrication sequence for a hybrid vdW device.** Optical images of a single device at each stage of the vdW process flow. (a) The stack after meltdown onto the pre-patterned superconducting back gate at the terminating end of the resonator. (b) After the contact write and the selective  $\text{CF}_4$  etch, which removes the top hBN and stops on the graphene. (c) After deposition and liftoff of the Ti/Nb/Al contacts, with the developed resist window for the top gate write already in place. (d) After liftoff of the top gate, which uses the same metallization as the contacts. (e) After the mesa write, with resist protecting the channel while the surrounding material, including the superconducting back gate, is etched away. (f) The finished device after the resist strip. Step-by-step checklists are given in Appendix F and the process recipes in Appendix E.

The stacking and fabrication problems that dominated the early part of this work have now been resolved with optimized processing recipes. Tenting during meltdown, spalling of the superconducting contacts and substrate leakage on the gate lines each turned out to have a specific cause and a specific fix. We now have a reproducible process flow for building hybrid vdW devices on a superconducting circuit chip. Nothing in this fabrication flow is specific to BBG/WSe<sub>2</sub>, and adapting to another vdW superconductor requires only minimal changes. The measurement of the devices is the subject of Chapter 10.

## Chapter 9

# A hybrid vdW Josephson junction

The previous chapter established a process flow for building vdW devices on a superconducting circuit chip, but left open the question of what the resulting architecture can actually resolve. Answering that requires a device whose inductance is known independently, and a Josephson junction is the natural choice. A JJ is an inductor of inductance  $L_J = \Phi_0/(2\pi I_c)$ , and in a vdW junction the critical current  $I_c$  is tunable with a gate and measurable directly at DC. Embedding such a junction at the terminating end of the resonator therefore gives a load that can be swept in situ over a wide range and whose inductance is known from transport. The junctions are also of interest in their own right due to their myriad applications. The Josephson junction is the primary non-linear inductor at the heart of superconducting qubits [216], and JJs are used as active elements in quantum-limited amplifiers [217, 218] and high-frequency bolometers [219]. Given this range of applications, the ability to model, extract and predict the junction inductance accurately is valuable independently of what it tells us about our own measurement chain.

Single-crystal vdW materials have ultrahigh carrier mobility and low charge disorder, and considerable effort has therefore gone into studying JJs that incorporate vdW materials as the normal element in SNS junctions. The characterization of these junctions coupled to resonant microwave circuits is a more recent development, which we review in the next section.

### 9.1 Previous work on hybrid vdW JJ devices

Ref. [220] was one of the early demonstrations of embedding a monolayer graphene JJ into a coplanar waveguide superconducting resonator. The device architecture consisted of a top gated JJ with galvanic NbTiN contacts to the resonator center pin and ground plane on two sides of the JJ. The resonator center pin was shunted to the ground plane with a large capacitor which allowed galvanic access at both DC and microwave frequencies. As the critical current approaches zero near the charge neutrality point of graphene, the JJ inductance increases significantly, thereby causing a

strong downshift in resonator frequency. The authors show that the change in resonator frequency can be accurately captured by adding an additional inductance  $L_J$  given by the following expression for JJ inductance:

$$L_J = \frac{\Phi_0}{2\pi I_c} \quad (9.1)$$

where  $\Phi_0$  is the superconducting flux quantum and  $I_c$  is the critical current. Further work by the same set of authors in Ref. [221] considered both ballistic and diffusive junctions. They also probed the microwave power dependence of  $L_J$  and saw non-linear resonator characteristics at high powers. In contrast to power-independent dissipation in standard JJs such as aluminum oxide tunnel junctions, they introduced a power-dependent dissipation  $\delta\kappa = \gamma\sqrt{P}$  and attributed it to low-lying subgap states within the induced superconducting gap in the graphene JJ.

Transmons involving a graphene JJ were first demonstrated in [222, 223]. The JJ consisted of an hBN encapsulated graphene heterostructure proximitized by Ti/Al electrodes and coupled to a superconducting Al backgate. The authors performed two-tone spectroscopy and coherent control of the qubit state using cQED techniques. The voltage tunability of the critical current allows tuning of the qubit frequency over a wide frequency range, from 6 GHz to 12 GHz in [223]. The qubit frequency also exhibited oscillations as a function of gate voltage which were associated with Fabry-Perot oscillations at p-n interfaces as well as with universal conductance fluctuations. With Rabi oscillation and Ramsey interferometry measurements, an energy relaxation time  $T_1 \approx 12 - 36$  ns and a dephasing time  $T_2^* \approx 55$  ns were measured. Since  $T_2^*$  is close to  $2T_1$ , qubit coherence is limited by energy relaxation. A strong dependence of the energy relaxation time on gate voltage was not observed, in contrast to other gate tunable transmons involving semiconductor heterostructures. The authors attributed the short coherence times to decay channels not directly associated with the graphene JJ. Rather, the capacitive coupling between the qubit capacitor and backgate was suggested as a prominent decay channel. An additional feature of graphene JJs is that the superconducting contacts used for the JJ can be magnetic field resilient type-II superconductors such as MoRe and NbTiN. In Ref. [222], MoRe contacts were used in a graphene JJ and the transmon along with the readout resonator were fabricated out of NbTiN. The authors demonstrate only a slight increase in the qubit linewidth from 350 to 425 MHz as an in-plane magnetic field is applied from 0 to 1 T.

In conclusion, recent work on incorporating graphene JJs into microwave circuits has shown such circuits can be a probe of electrodynamic properties of the JJ channel. Early demonstrations of qubits have measured short qubit coherence times, on the order of 10–50 ns, as compared to standard AlOx tunnel junctions. While all these experiments involved a monolayer graphene channel, in the following sections, we will investigate how the hybrid architecture discussed in the previous chapter can be applied to bilayer graphene JJs.



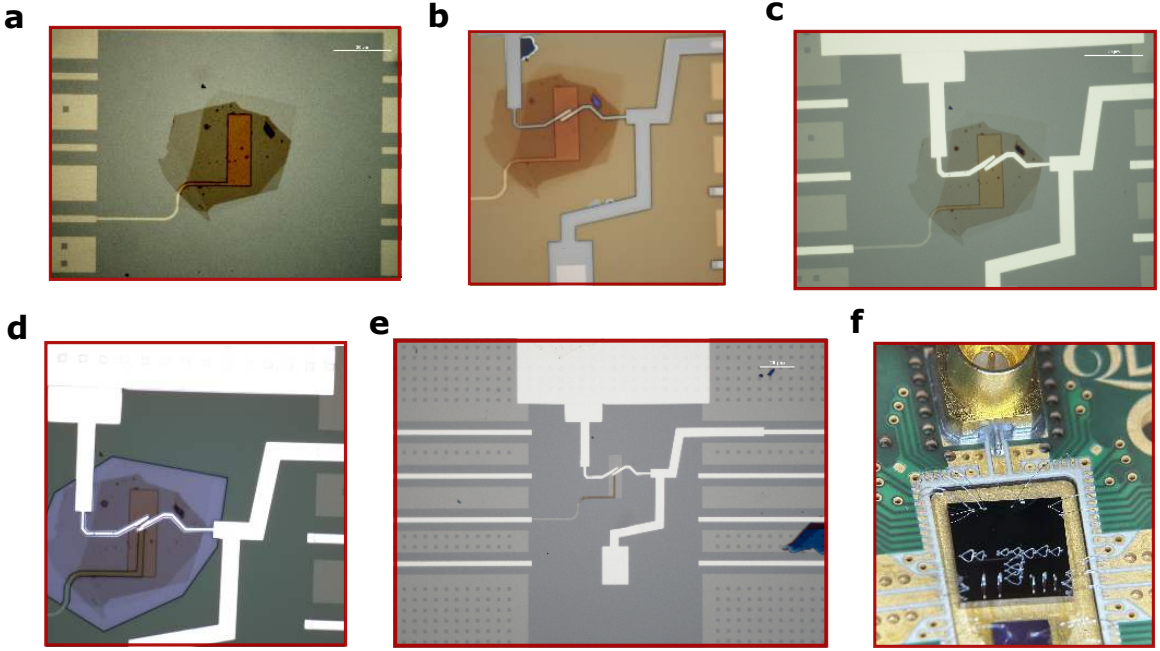


Figure 9.1: **Device fabrication flow.** (a) Optical image of the van der Waals stack after melt-down onto the superconducting back gate. (b) Image after the contact lithography write and selective  $\text{CF}_4$  etch exposing the graphene edge. (c) Image after superconducting contact deposition (Ti/Nb/Al) and lift-off. (d) Image after the mesa write defining the junction geometry. (e) Optical image of the completed device. (f) Wire-bonded device mounted on the PCB. The feedline is bonded to the mini-SMP connectors on the left and right, and the DC lines (source and back gate) are connected through the top row of pads on the chip. Bonds across the feedline, resonators, and DC lines suppress slot-line modes.

## 9.2 Device Fabrication and Measurement Setup

In order to calibrate the sensitivity of our hybrid resonator architecture to changes in inductance, we fabricated resonator devices terminated by a bilayer graphene Josephson junction. The stack was assembled using dry transfer techniques onto a NbTiN superconducting back gate. We etched contact patterns on top of the superconducting back gate using a  $\text{CF}_4$  etch recipe (fully selective to etch hBN over graphene) and made superconducting Ti/Nb/Al (3/20/45 nm) contacts with e-beam deposition. In the same step, the source contact of the junction was also connected to the center pin of a coplanar waveguide resonator. In order to do simultaneous DC measurements, the source contact branches off to a DC line and is connected to a separate bondpad through an LCL low-pass filter (see Chapter 8 for a complete description of the filter architecture). The JJ channel was defined by etching away the rest of the stack using a  $\text{CHF}_3/\text{O}_2$  mesa etch recipe. Fig. 9.1 shows optical images of the device through the different steps of the fabrication process. The final sample is glued using GE varnish onto a Qdevil PCB consisting of standard low frequency pads for transport



measurements as well as high frequency mini-SMP connectors for microwave measurements. The sample is then loaded onto a cryogenic probe and inserted into a dilution cryostat. The probe has RC and  $\pi$  filters for low frequency lines as well as a microwave click-in plate with SMP connectors. The click-in plate connects the sample to coaxial microwave lines inside the cryostat. The input high-frequency line is heavily attenuated ( $> 66$  dB) using cryogenic attenuators (XMA Corp.) at various stages of the cryostat. The output high-frequency line consists of a circulator at the mixing chamber stage and a cryogenic amplifier (Cosmic Microwave, CITLF3) at the 4 K stage. Unless specified otherwise, all measurements were carried out at a base temperature of 50 mK.

### 9.3 Gate dependence of the critical current

We can change the Fermi energy and the transparency of the channels involved in a bilayer graphene JJ by tuning the back gate away from the charge neutrality point (CNP). These changes manifest themselves as a gate tunable critical current of the JJ. Fig. 9.2 shows  $dV/dI$  of the junction as a function of the backgate voltage  $V_{bg}$  and an applied DC current bias  $I_{dc}$ . The DC current bias is swept from negative to positive values. We define the critical current  $I_c$  as the current at which the junction switches from the superconducting state to the normal state. Similarly, the re-trapping current  $I_r$  is defined as the current at which the junction switches from the normal state to the superconducting state. With our chosen direction of sweeping the current bias,  $I_c > 0$  and  $I_r < 0$ . Fig. 9.2 shows the extracted  $I_c$  and  $I_r$  as a function of  $V_{bg}$ . A minimum critical current of 5 nA is observed near the CNP which increases to 2.5  $\mu$ A at  $V_{bg} = -6$  V. We attribute the asymmetry in  $I_c$  between positive and negative gate voltages to p-n junctions formed near the contacts. Due to a work function difference between the contact metal and the bilayer graphene, a heavily p or n doped region can exist near the contact region. The doping of this region is only weakly modulated by the back gate, and hence when the channel is tuned from p to n type using the backgate, p-n junctions are inevitably formed. The normal state resistance near the CNP exhibits oscillations with  $V_{bg}$  which we attribute to Fabry-Perot cavities associated with these p-n junctions or to disorder-induced universal conductance fluctuations. Fig. 9.2 shows a zoom-in of the critical current dependence near the CNP.

#### 9.3.1 Expected Josephson inductance

The JJ has an inductance inversely proportional to the critical current,  $L_J = \Phi_0/(2\pi I_c)$ . Since the critical current approaches zero near the CNP, we expect a large increase in the junction inductance. Fig. 9.2(e) shows the expected  $L_J$  as a function of the back gate voltage  $V_{bg}$ . The highest critical current occurs at  $V_{bg} = -6$  V and corresponds to  $L_J = 0.12$  nH, while the lowest critical current near the CNP at  $V_{bg} = -0.1$  V corresponds to  $L_J \approx 50$  nH.  $L_J$  changes over two orders of magnitude and hence we expect a significant change in the resonator frequency from the additional reactive impedance associated with  $L_J$ .

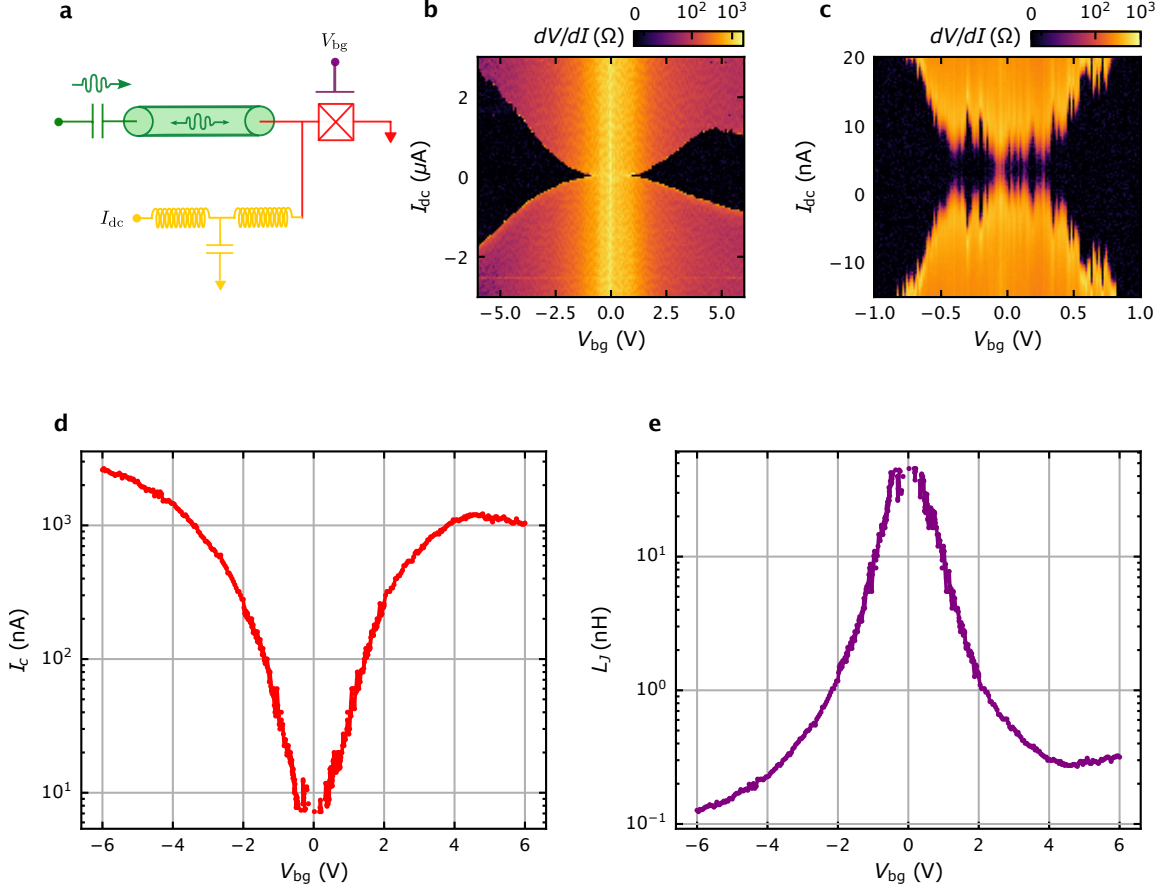


Figure 9.2: **Gate-tunable bilayer graphene Josephson junction terminating a microwave resonator.** (a) Circuit schematic: a coplanar-waveguide resonator (green) is terminated by a bilayer graphene Josephson junction (red, crossed box), with carrier density tuned by the back-gate voltage  $V_{bg}$ . A dc current bias  $I_{dc}$  is applied through an on-chip low pass filter (yellow) for quasi-dc characterization. (b) Differential resistance  $dV/dI$  as a function of  $I_{dc}$  and  $V_{bg}$ . The dark region ( $dV/dI \approx 0$ ) marks the bias range with a supercurrent, which narrows near charge neutrality.  $I_{dc}$  is swept from negative to positive values. (c) High-resolution measurement around the charge-neutrality point, showing a suppressed but finite switching current ( $\sim 5$  nA) with mesoscopic fluctuations as a function of  $V_{bg}$ . (d) Critical current  $I_c$  extracted from the switching of  $dV/dI$  vs  $I_{dc}$ , tunable over more than two orders of magnitude (from below 5 nA at charge neutrality to  $\sim 2.5$   $\mu$ A at high hole doping). (e) Josephson inductance  $L_J = \hbar/2eI_c$  estimated from (d), spanning  $\sim 0.1$  nH at high doping to 50 nH near charge neutrality.

## 9.4 Gate dependence of resonator response

The  $\lambda/4$  resonance frequency of the resonator is designed to be close to 1.1 GHz. However, preliminary  $S_{21}$  measurements at  $V_{bg} = 0$  showed no significant dip in transmission which would correspond to a resonance. In order to find the location of the resonance, we took  $S_{21}$  measurements

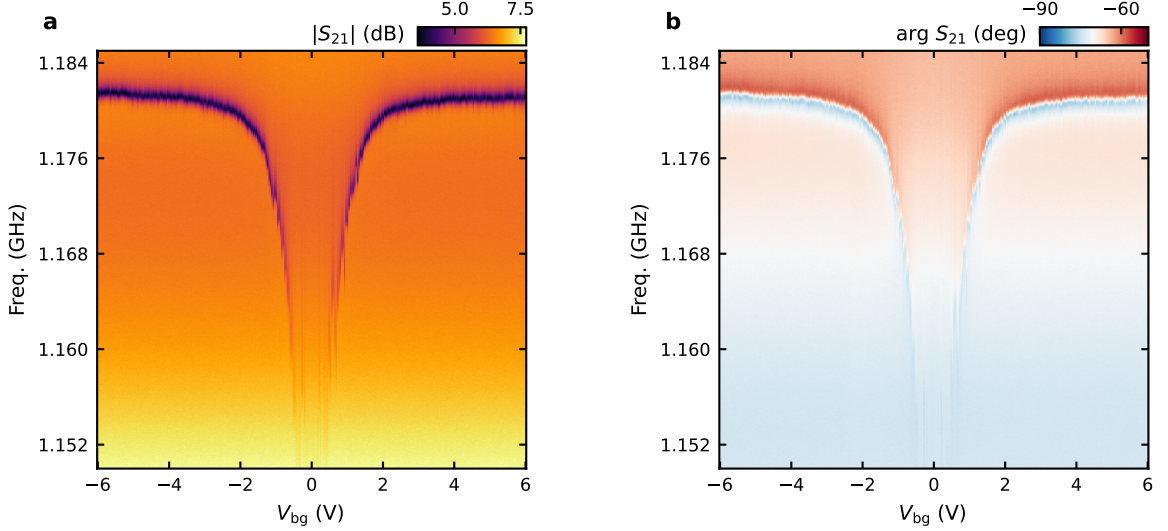


Figure 9.3: **Gate tuning of the resonator frequency.** (a) Magnitude and (b) phase of the feedline transmission  $S_{21}$  as a function of probe frequency and back-gate voltage  $V_{bg}$ . The resonance appears as a dip in  $|S_{21}|$  accompanied by a phase shift. At large  $|V_{bg}|$  the resonance sits near 1.181 GHz; as the junction approaches charge neutrality, the increasing Josephson inductance  $L_J$  pulls the resonance down by tens of MHz and the dip broadens and fades, consistent with the suppressed critical current and enhanced losses near the charge neutrality point.

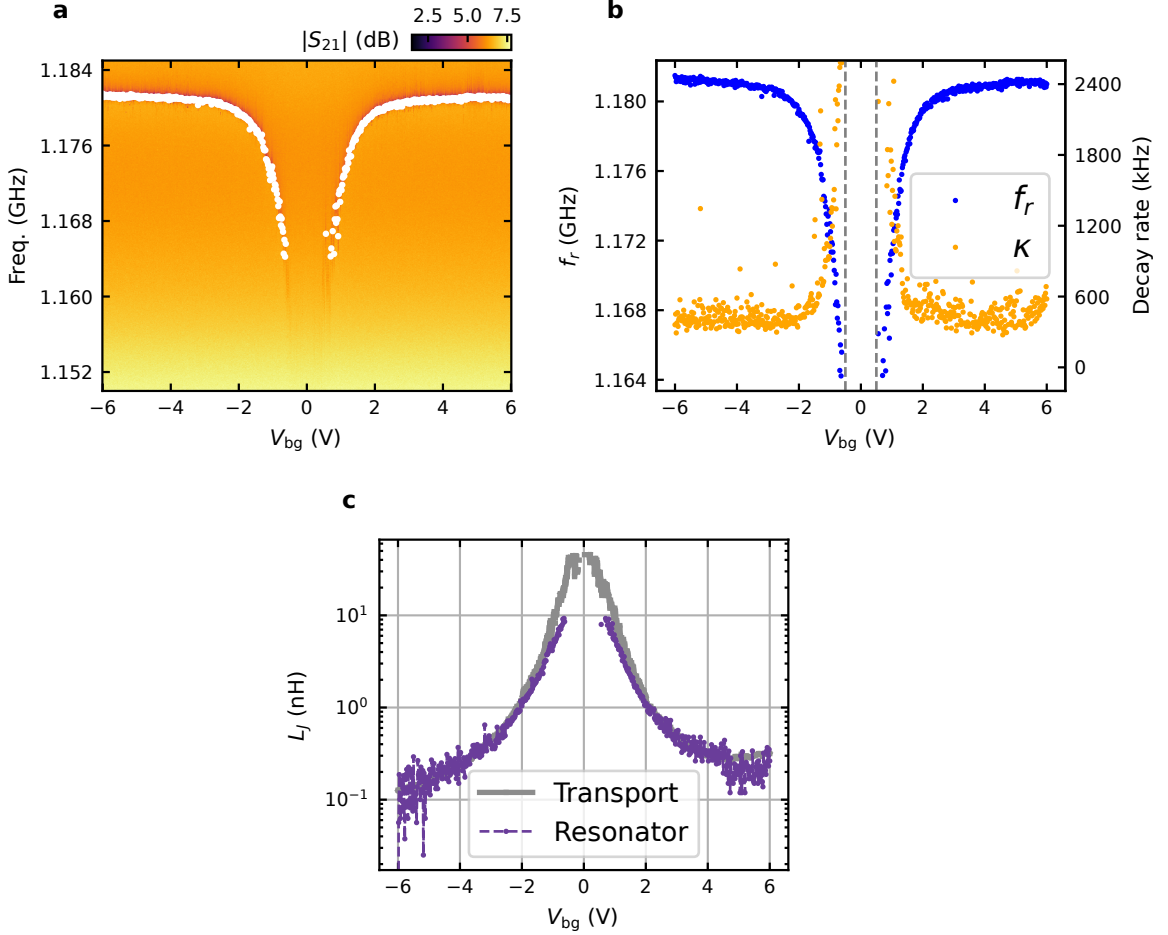
at  $V_{bg} = \pm 5$  V. Fig. 9.3(a) shows  $S_{21}$  as a function of frequency for  $V_{bg} = 0, \pm 5$  V. To clearly separate gate dependent features from background oscillations in  $S_{21}$  as a function of frequency, we plot  $\Delta S_{21} = S_{21}(V_{bg}) - S_{21}(V_{bg} = 0)$  in Fig. 9.3. A clear gate dependent resonance is observed at  $f = 1.179$  GHz. A careful measurement of  $\Delta S_{21}$  over a larger frequency range from 1–6 GHz shows additional modes whose properties are affected by the gate voltage  $V_{bg}$ . Such a systematic process allows us to identify modes which only have a shallow resonance dip or are spread over a large frequency range.

Fig. 9.3 shows the microwave transmission  $S_{21}$  in amplitude and phase over a range of backgate voltages. A large downshift in resonator frequency occurs as the gate voltage approaches the CNP. Since the junction inductance increases significantly near the CNP due to the reduction in the critical current, the additional JJ inductance adds to the resonator inductance and leads to an overall reduction in the resonator frequency. We can now use an impedance model to convert the resonator frequency shift into a value for the Josephson inductance. If we neglect any shunt capacitors associated with the backgate or the source DC line, we get

$$\frac{\Delta\omega_r}{\omega_r} = -\frac{2}{\pi} \tan^{-1} \left( \frac{\omega_r L_J}{Z_r} \right) \quad (9.2)$$

We use  $\omega_r = 2\pi \times 1.179$  GHz as the resonator frequency at  $V_{bg} = -6$  V where the junction impedance

is small and the bare  $\lambda/4$  frequency of the resonator is recovered. Fig. 9.4 shows the extracted junction inductance along with the expected  $L_J$  as described in the previous section. A refined analysis including a shunt capacitor  $C = 50 - 500$  fF shows that these results are not impacted significantly by the presence of the shunt capacitor.



**Figure 9.4: Resonator-based extraction of the Josephson inductance.** (a) Feedline transmission magnitude  $|S_{21}|$  as a function of back-gate voltage  $V_{bg}$  and frequency  $f$ . White points mark the resonance frequency  $f_r$  obtained from hanger fits to each gate trace; near charge neutrality the resonator blends into the background and no fit is reported. (b) Fitted resonance frequency  $f_r$  (blue, left axis) and decay rate  $\kappa = f_r/Q_i$  (orange, right axis) versus  $V_{bg}$ . As the junction approaches charge neutrality (dashed lines at  $V_{bg} = \pm 0.5$  V), the growing Josephson inductance pulls the resonance down by  $\sim 15$  MHz while the decay rate increases sharply, reflecting enhanced losses as the critical current is suppressed. (c) Josephson inductance  $L_J$  extracted from the resonator frequency shift via  $\Delta\omega_r/\omega_r = (2/\pi) \tan^{-1}(\omega_r L_J/Z_r)$  with  $Z_r = 3$  k $\Omega$  (purple), compared with the transport value  $L_J = \hbar/(2eI_c)$  from the measured switching current (grey). The two agree over more than two decades in  $L_J$ ; near charge neutrality the transport estimate exceeds the rf value, consistent with premature switching underestimating the true critical current.

## 9.5 Temperature dependence of resonator response

An additional knob to tune the junction impedance  $L_J$  is the temperature of the junction. At higher temperatures, we expect a reduction in critical current, with the superconducting gap vanishing altogether at temperatures approaching the proximity induced gap in the junction. Fig. 9.5 shows the temperature dependent resonator response at two backgate voltages,  $V_{bg} = -2$  V and  $V_{bg} = -5$  V, from a base temperature of 50 mK to 1100 mK. Above 1100 mK, the resonator dip at  $V_{bg} = -2$  V becomes too shallow and disappears into the background. We therefore restrict the temperature dependent analysis to a maximum temperature of 1100 mK.

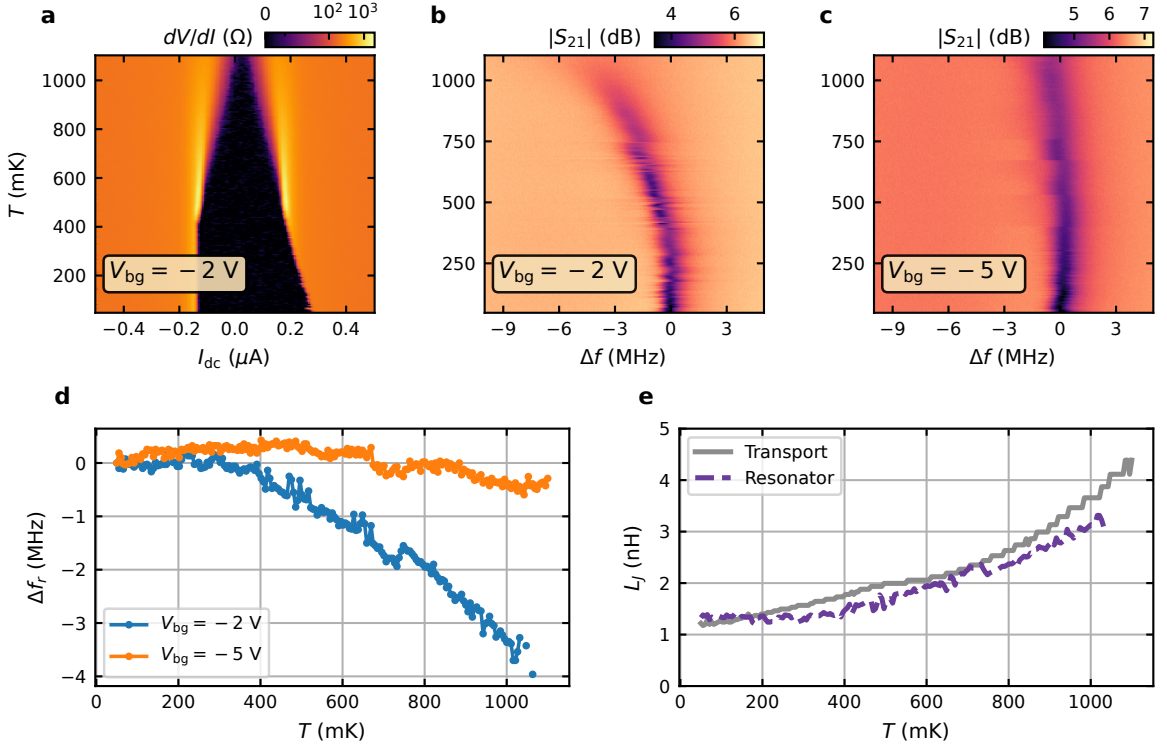


Figure 9.5: **Temperature dependence of the supercurrent and resonator response.** (a) Differential resistance  $dV/dI$  as a function of dc bias current  $I_{dc}$  and temperature  $T$  at  $V_{bg} = -2$  V. The critical current decreases with increasing temperature. (b), (c) Feedline transmission magnitude  $|S_{21}|$  as a function of temperature and frequency detuning  $\Delta f$ , referenced to the base-temperature resonance, at  $V_{bg} = -2$  V (b) and  $-5$  V (c). In (b), the resonance pulls to lower frequency and broadens with increasing temperature, reflecting the growing Josephson inductance and losses as the critical current is suppressed; at  $V_{bg} = -5$  V (c), where the critical current is larger, the resonance shift is much weaker and the dip survives to higher temperatures. (d) Resonance frequency shift  $\Delta f_r$  versus temperature extracted from the maps in (b) and (c). At  $V_{bg} = -2$  V the resonance shifts down by  $\sim 4$  MHz over the measured range, while at  $-5$  V the shift remains below  $\sim 1$  MHz. (e) Josephson inductance at  $V_{bg} = -2$  V extracted independently from the measured switching current via  $L_J = \hbar/(2eI_c)$  (Transport) and from the resonance shift in (d) via the pulling formula with  $Z_r = 3$  k $\Omega$  (Resonator). Both methods show  $L_J$  increasing from  $\approx 1.3$  nH at base temperature to  $\approx 4$  nH at 1.1 K, in good agreement throughout.

## 9.6 DC bias dependence of resonator response

We measure the resonator properties as a function of an applied DC current bias  $I_{dc}$ . We have already encountered  $dV/dI$  measurements as a function of  $I_{dc}$  when extracting the critical current of the junction. When we concurrently measure the resonator  $S_{21}$ , we observe a striking effect in which the resonator dip is minimally affected in the superconducting state, but in the normal state, the resonator dip disappears completely. In Fig. 9.6, the retrapping and critical currents at which the

resonator dip disappears line up exactly with the normal and superconducting states as extracted by  $dV/dI$  measurements. Inside the superconducting state, the DC current dependent inductance is given as follows:

$$L_J(I_{\text{dc}}) = \frac{\Phi_0}{2\pi\sqrt{I_c^2 - I_{\text{dc}}^2}} \quad (9.3)$$

where  $\Phi_0$  is the flux quantum. Note that the above expression is valid in the limit of a  $\sin(\phi)$  current phase relation and is likely an oversimplification for a bilayer graphene JJ with ballistic supercurrent channels. We use this model mainly to illustrate the fact that the junction impedance becomes large as  $|I_{\text{dc}}|$  approaches  $I_c$ , and hence a reduction in resonator frequency is expected. In Fig. 9.6, we observe that the resonator frequency indeed follows a quadratic dependence on  $I_{\text{dc}}$  and is reduced from the zero bias value as  $|I_{\text{dc}}|$  approaches  $I_c$ . We note that the observed dependence of the resonator frequency on  $I_{\text{dc}}$  is weaker than predicted by the square root singularity of Eq. 9.3.

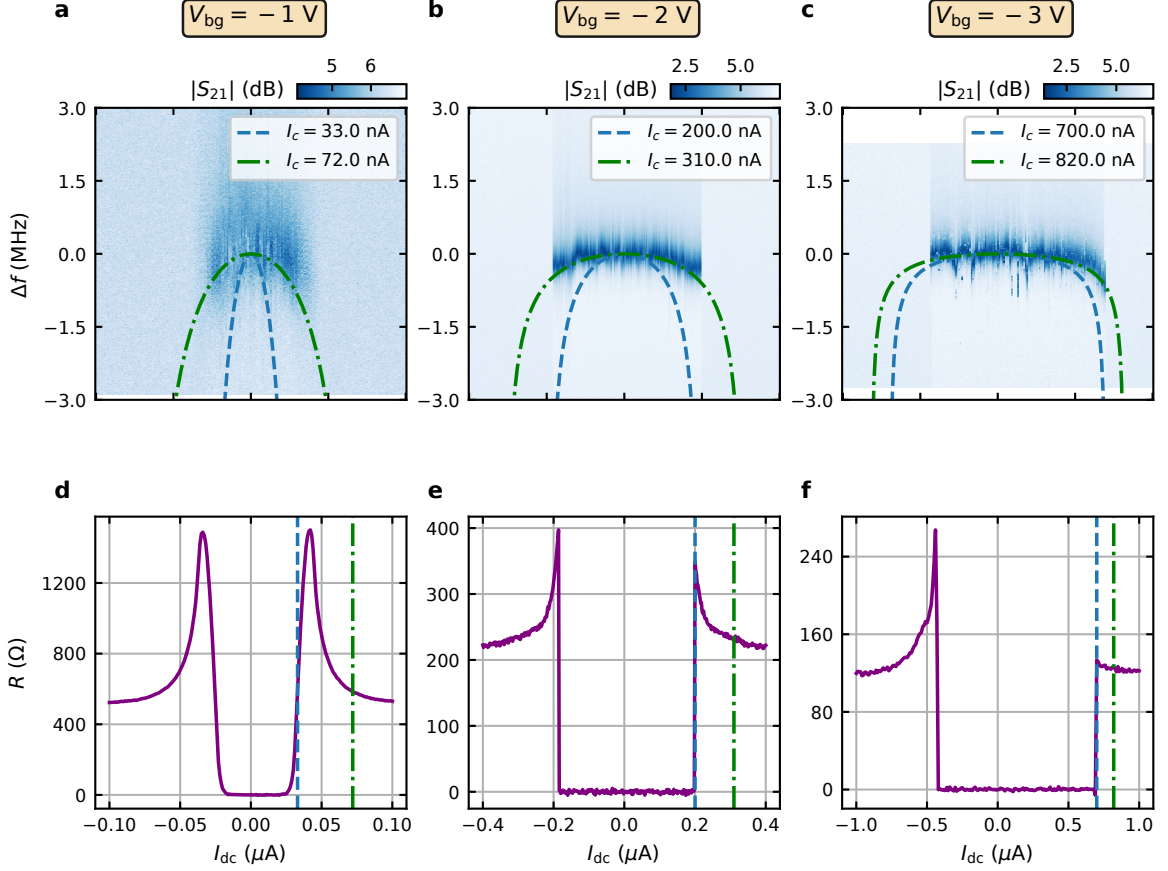


Figure 9.6: **Bias dependence of the resonator response at different gate voltages.** (a–c) Magnitude of the feedline transmission  $|S_{21}|$  as a function of dc bias current  $I_{dc}$  and detuning  $\Delta f$  from the resonance at zero bias, at  $V_{bg} = -1, -2$ , and  $-3$  V. Within the supercurrent branch, the resonance is pulled down as the bias-dependent Josephson inductance  $L_J$  increases toward the critical current  $I_c$ ; beyond  $I_c$ , the junction turns resistive and the resonance disappears from increased dissipation. Curves show the expected frequency shift for a bias-tuned Josephson inductance,  $L_J(I_{dc}) = L_{J0}/\sqrt{1 - (I_{dc}/I_c)^2}$ , using the critical current measured in transport (blue dashed) and a larger critical current (green dash-dotted) chosen to match the observed dispersion. The measured shift is reproduced only with the larger value, indicating that the junction switches before reaching its true critical current. (d–f) Simultaneously measured DC resistance  $R$ , showing the zero-resistance superconducting branch and the switching/re-trapping currents, which increase with more negative  $V_{bg}$  away from charge neutrality. Vertical lines mark the two critical current values used in (a–c).  $I_{dc}$  is swept from negative to positive values.



## 9.7 Resonator frequency as a quantitative probe of junction inductance

In this section we quantify the ability of the resonator to serve as a quantitative probe of the junction inductance. It is qualitatively clear from the preceding sections that the resonator responds in the right direction, with the frequency moving down as the inductance goes up. The stronger claim we want to test is that the frequency can be inverted to recover  $L_J$ , and that the inversion does not depend on how  $L_J$  was tuned. Fig. 9.7 tests this by plotting the junction inductance obtained from the DC switching current against the resonance frequency measured at the same setting, combining the gate dependent and temperature dependent datasets of the previous sections into a single calibration curve.

The two datasets tune  $L_J$  by unrelated physical means, one by changing the carrier density and the transparency of the channel and the other by populating quasiparticle states at finite temperature, and they span the range in opposite directions. That they collapse onto a common curve is the central result of this section. It shows that the resonance frequency is a single valued function of the terminating inductance and carries no memory of which knob produced it, which is what licenses using the frequency as a readout of  $L_J$  in a device where no independent transport measurement is available. The curve is described over more than two decades in  $L_J$  by Eq. 9.2 with  $Z_r = 3 \text{ k}\Omega$  and a bare  $\lambda/4$  frequency of 1.181 GHz, with no further free parameters.

The sensitivity of the measurement follows from differentiating Eq. 9.2. In the regime  $\omega_r L_J \ll Z_r$ , where the junction is a small perturbation on the resonator, the frequency responds linearly to the inductance at a rate

$$\left| \frac{\partial f_r}{\partial L_J} \right| \simeq \frac{4f_r^2}{Z_r}, \quad (9.4)$$

so the smallest resolvable inductance is  $\delta L_J = \delta f_r Z_r / 4f_r^2$ , set by the frequency resolution  $\delta f_r$ . The sensitivity improves as  $f_r^2$ , which is a strong argument for operating at the highest frequency compatible with the gap of the material under study, and it improves as  $Z_r$  is reduced, which runs opposite to the requirement of Chapter 8 that  $Z_r$  exceed the normal state resistance of the channel. The resonator impedance is therefore a design tradeoff rather than a quantity to be maximized. Whereas large  $Z_r$  suppresses the zero-point microwave current and mismatches the resonator to the normal state resistance, it also reduces the sensitivity to small changes in inductance. In our devices, the frequency resolution is not limited by the signal to noise ratio of the hanger fit but by stochastic jumps of  $f_r$  in time, which we attribute to two level fluctuators near the resonator. For  $Z_r = 3 \text{ k}\Omega$  and  $f_r = 1.18 \text{ GHz}$ , Eq. 9.4 gives a resolution of roughly 0.5 pH for every kHz of frequency resolution.

It is useful to ask where a vdW superconductor would sit on this curve, since measuring kinetic inductance of flatband vdW superconductors is the primary goal of the hybrid architecture. The colored markers in Fig. 9.7 show estimated kinetic inductances for several candidate materials, obtained from the band theory expression using carrier density ranges reported in the literature and

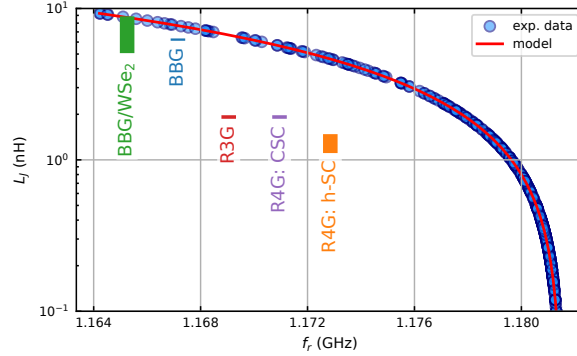


Figure 9.7: **Resonator frequency as a quantitative probe of junction inductance.** Junction inductance  $L_J$  against resonance frequency  $f_r$ , combining the gate dependent and temperature dependent datasets of the previous sections. Blue circles are the measured points, with  $L_J$  obtained from the DC switching current and  $f_r$  from a hanger fit to  $S_{21}$  recorded at the same setting. The red line is the pulling relation of Eq. 9.2 evaluated with  $Z_r = 3 \text{ k}\Omega$  and a bare  $\lambda/4$  frequency of 1.181 GHz, with no further free parameters. Because the two datasets tune  $L_J$  by unrelated means, their collapse onto a single curve establishes that  $f_r$  is a single valued function of  $L_J$  and can be inverted to give the inductance. The colored markers indicate where several candidate vdW superconductors would fall on this curve. Their kinetic inductances are estimated from the band theory expression using carrier density ranges taken from the published literature and setting the effective mass to the bare electron mass  $m_e$ , with the vertical extent of each marker reflecting the spread of reported densities. BBG denotes Bernal bilayer graphene, BBG/WSe<sub>2</sub> the same system proximitized by WSe<sub>2</sub>, and R3G and R4G rhombohedral trilayer and tetralayer graphene, with CSC and h-SC labelling the two distinct superconducting states (candidate chiral superconductor and hole-side superconductor) reported in R4G. These estimates neglect band structure detail and any quantum geometric contribution to the superfluid weight and would be refined by a detailed theoretical calculation. They are included to show that the expected inductances of this class of materials fall on the responsive part of the calibration curve.

taking the effective mass to be the bare electron mass. These estimates are deliberately crude and a proper treatment would require detailed band structure calculations, but they are sufficient to establish the point: the expected inductances of this class of materials all fall in the range of roughly 1 to 10 nH, which is precisely the range over which the resonator has been calibrated in this chapter.

## 9.8 Higher resonator harmonics and other gate-responsive modes

The fundamental is not the only mode that responds to the gate. Fig. 9.8(a) shows a mode near 3.55 GHz that tracks the fundamental closely, moving down and broadening as the junction approaches charge neutrality. Its frequency is very close to  $3f_r$ , identifying it as the third harmonic of the  $\lambda/4$  resonator.

Panels (b) to (d) show further gate-responsive features between 4 and 6 GHz which do not coincide with any harmonic of the resonator. These are associated with the DC lines and their filters, which support their own modes and couple to the junction. What is notable is that several of them show avoided crossings rather than a simple monotonic shift in frequency. A plausible origin is a Josephson plasma mode of the junction itself, formed by  $L_J$  together with the shunt capacitance presented by the back gate and the source DC line, at a frequency  $f_p = 1/2\pi\sqrt{L_J C}$ . Since  $L_J$  grows as the gate approaches charge neutrality,  $f_p$  sweeps downward with gate voltage and hybridizes with each circuit mode it passes through, opening a gap at the crossing. Taking  $L_J \approx 1$  nH near the observed crossings and a shunt capacitance of order 1 pF places  $f_p$  in exactly this frequency window of about 5 GHz. While such modes have been used for engineering gatemon qubits as discussed in the beginning of this chapter, for us, the observed plasmon serves only as a check on our understanding of the electrodynamic environment seen by the resonator at frequencies from 5-6 GHz.

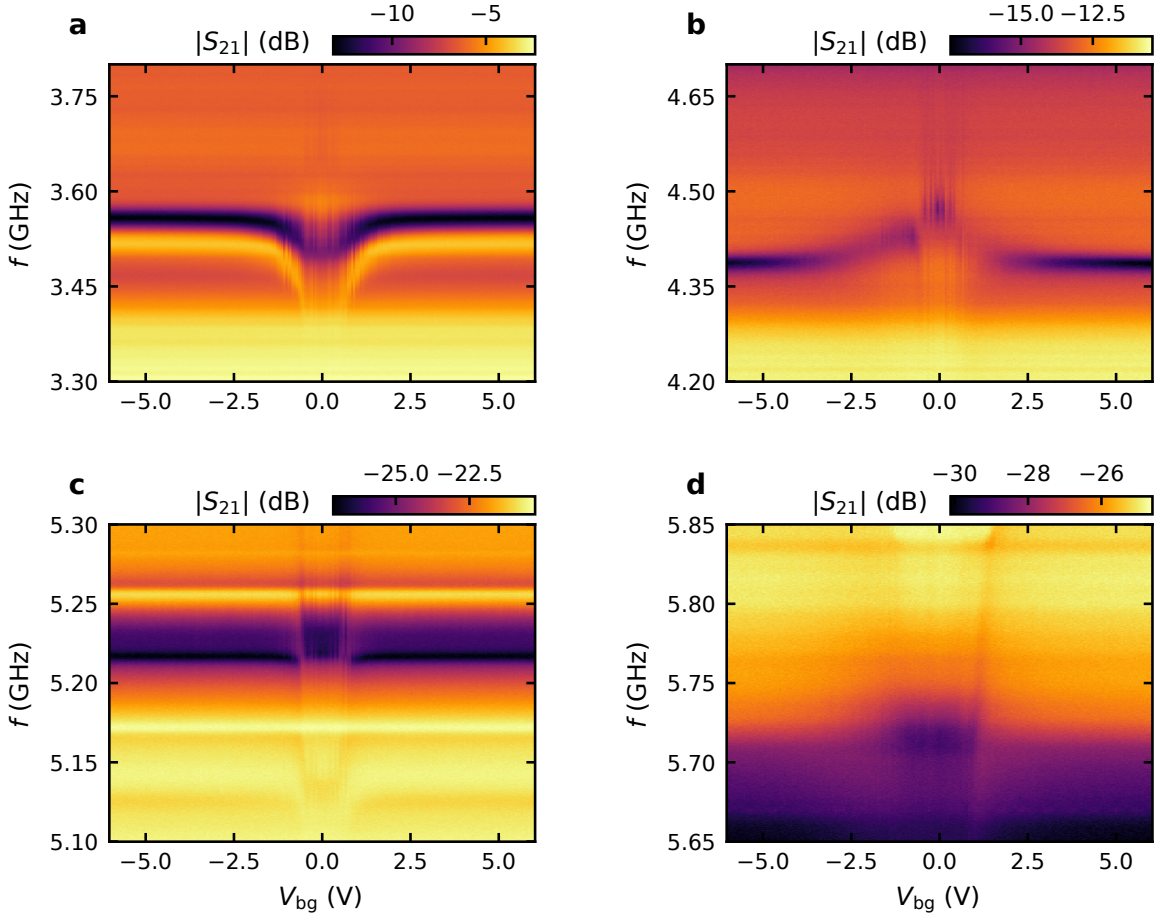


Figure 9.8: **Gate-dependent modes at higher frequencies.** (a–d) Feedline transmission magnitude  $|S_{21}|$  as a function of back-gate voltage  $V_{bg}$  and probe frequency, in four windows above the fundamental resonance. (a) A mode near 3.55 GHz shows the same gate dependence as the fundamental and is consistent with the third harmonic of the  $\lambda/4$  resonator,  $3f_r \approx 3.55$  GHz. (b–d) Additional gate-responsive features near 4.4, 5.2 and 5.7 GHz. These do not match harmonics of the resonator and are associated with modes of the DC lines and their filters, which couple to the junction and therefore acquire a gate dependence. The features in (b–d) show avoided crossings rather than a simple shift in frequency, which we tentatively attribute to a Josephson plasma mode of the junction, formed by  $L_J$  and the shunt capacitance of the gate and source DC line. This mode sweeps down in frequency as  $L_J$  grows toward charge neutrality and hybridizes with each circuit mode in turn. The gate-independent horizontal features are unrelated package or feedline resonances.

## 9.9 Summary

We have used a bilayer graphene Josephson junction as a calibrated test load for the hybrid resonator architecture of Chapter 8. The back gate tunes the critical current over more than two decades,

from 2.5  $\mu\text{A}$  at high hole doping to below 5 nA at charge neutrality, and the corresponding Josephson inductance spans 0.1 to 50 nH. The resonator frequency follows this variation as expected, shifting down by tens of MHz as the junction approaches neutrality. The same behavior is reproduced when the inductance is instead tuned with temperature or with a DC current bias.

The central result is that the gate dependent and temperature dependent datasets collapse onto a single curve of  $L_J$  against  $f_r$ , described by Eq. 9.2 with  $Z_r = 3 \text{ k}\Omega$  and no free parameters. Because the two datasets tune the inductance by different physical means, this collapse establishes that the resonance frequency can be inverted to recover  $L_J$  in a device where no independent transport measurement is available. It also fixes the sensitivity of the technique which scales as  $f_r^2/Z_r$ . The one systematic discrepancy, in which the transport inductance exceeds the microwave value near charge neutrality and in the DC bias data, is consistent with premature switching of the junction and is a shortcoming of the transport estimate rather than of the resonator.

Taken together, these measurements demonstrate that the architecture works as a quantitative inductance probe over precisely the range of 1 to 10 nH expected for the kinetic inductance of flatband vdW superconductors.

## Chapter 10

# Progress towards superfluid stiffness measurements

The previous chapters established a superconducting circuit architecture capable of hosting a van der Waals (vdW) heterostructure, and demonstrated that a Josephson junction embedded in such a circuit can probe the Josephson inductance through its microwave response. In this chapter, we discuss the measurements of the real part of impedance of the vdW heterostructure as seen by the resonator. We develop an impedance model needed to interpret a resistive vdW channel, compare hybrid devices against conventionally fabricated ones, and survey the devices built over the course of this work. Since the overarching goal is superfluid stiffness measurements, we will start by reviewing efforts by other groups in this direction.

### 10.1 Previous work on superfluid stiffness measurements

Two measurements of superfluid stiffness in moiré graphene superconductors appeared in early 2025, and together they define the state of the art that this work builds on.

Banerjee *et al.* [190] measured magic-angle twisted trilayer graphene (TTG) at alternating twist angles of  $\pm 1.55^\circ$ , encapsulated in hBN with graphite gates on both sides and assembled on an insulating silicon substrate to minimize parasitic capacitance. The device was coupled to a lumped-element resonator near 350 MHz and read out in reflection. On entering the superconducting state the resonance moved down by  $\Delta f_r \approx 10\text{--}15$  MHz, from which the kinetic inductance  $L_K$  and hence the stiffness  $\rho_s = (l/w)\hbar^2/(4e^2 L_K)$  were extracted using the aspect ratio  $l/w \approx 5$ . They found a linear temperature dependence of  $\rho_s$  down to 30 mK with no sign of saturation, a nonlinear Meissner response under current bias, and a linear correlation between the zero-temperature stiffness and  $T_c$  across the dome. The first two point to nodes in the gap. The third is reminiscent of the Uemura

relation in cuprates and suggests that  $T_c$  is limited by phase coherence rather than by the pairing amplitude.

Tanaka *et al.* [191] measured magic-angle twisted bilayer graphene (MATBG) using quasi-DC transport combined with microwave circuit QED. They found a stiffness substantially larger than a conventional Fermi liquid estimate and instead consistent with predictions for quantum geometric contributions that become dominant at the magic angle. The temperature dependence follows a power law rather than the exponentially activated form expected for an isotropic BCS gap, again indicating an anisotropic or nodal order parameter.

Both experiments establish that the kinetic inductance route to  $\rho_s$  works on micron-scale vdW samples. These experiments also suggest that the gap is not simple isotropic  $s$ -wave. They also share the limitations discussed in Chapter 8: twist-angle inhomogeneity means the extracted stiffness averages over a spatially varying  $T_c$ , and superconducting contacts mean a proximity contribution to the measured inductance cannot be cleanly separated from the intrinsic response of the channel.

## 10.2 Measurements of a hybrid hallbar resonator device

Every hybrid device measured in this chapter has been resistive across the density-displacement field phase diagram. A resistive channel still loads the resonator, and the frequency and linewidth of the loaded mode encode the channel impedance. Understanding this response quantitatively is a prerequisite for interpreting anything measured below  $T_c$ , because the parasitic elements that dominate the normal state signal do not disappear when the channel condenses into a superconducting state.

The measurement geometry is shown in Fig. 10.1. A dual-gated vdW channel is patterned into a Hall bar at the terminating end of the resonator, with the source contact tying the center pin to the channel so that the microwave mode terminates on the device. Every other contact, and both gates, leaves the chip through an LCL filter, which reflects the microwave mode while passing the quasi-DC bias. The resonator therefore sees the channel in parallel with everything else attached to it.

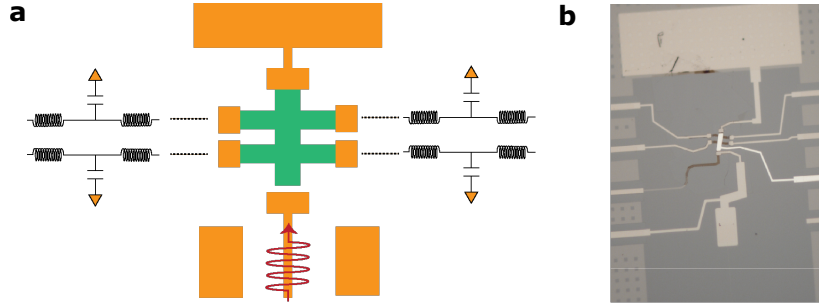


Figure 10.1: **vdW hallbar embedded in hybrid resonator architecture.** (a) Circuit schematic. A dual-gated vdW channel (green) is patterned into a Hall bar and contacted on six sides (orange). The source contact at the bottom connects the channel to the center pin of the  $\lambda/4$  resonator, indicated by the coil, so that the microwave mode terminates on the device. Every remaining contact, together with the top and back gates, leaves the device through an LCL filter consisting of two series nanowire inductors and a shunt capacitor, which reflects microwaves back toward the resonator while passing the quasi-DC frequency signals. The two gates set the carrier density and the displacement field independently. (b) Optical image of a completed device. The vdW stack sits at the center with its superconducting contacts fanning out to the surrounding DC lines and to the resonator.

Because every contact is available at DC, the transport and microwave responses can be acquired simultaneously in the same measurement run. Fig. 10.2 shows the device resistance alongside the resonator frequency shift and decay rate as functions of carrier density and displacement field. Note that this device did not have a working source contact, and we report the device resistance in a 3-terminal configuration. The contact metallization recipe for this device was not a low strain recipe and as a result, we suspect the strain has led to tears in the bilayer graphene rendering certain contacts disconnected at DC. Nevertheless, all three quantities reported in Fig. 10.2 share the same charge neutrality feature, which establishes the basic capability the architecture was built for: the state of the channel can be read out through the microwave port alone, with no quasi-DC configuration required. However, note that microwave maps are not simply copies of the resistance map. In the next section, we build an effective model to quantitatively match these measurements.



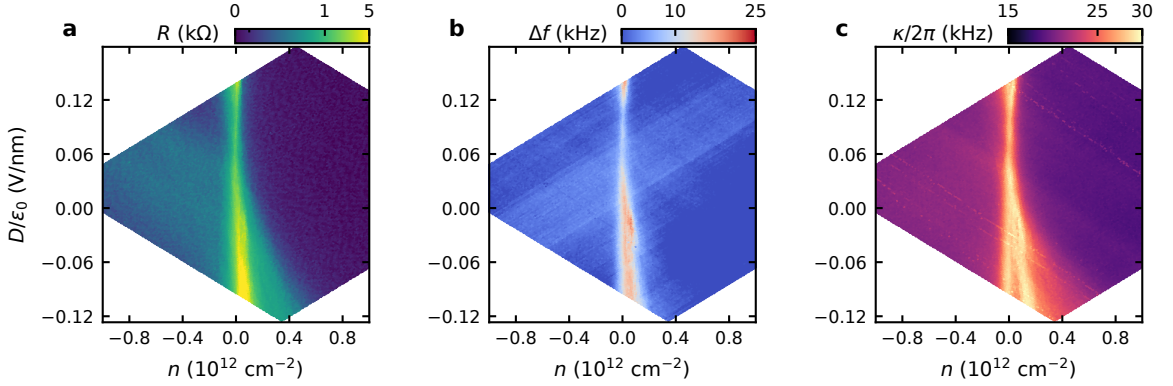


Figure 10.2: **Simultaneous transport and microwave response of a hybrid Hall bar.** (a) Device resistance  $R$  measured in a 3-terminal configuration (b) resonator frequency shift  $\Delta f$  and (c) decay rate  $\kappa/2\pi$ , all measured as functions of carrier density  $n$  and displacement field  $D/\epsilon_0$  in the same cooldown. The resistance peaks along the charge neutrality line near  $n = 0$  and grows as  $|D|$  increases and a gap opens in the bilayer. Both microwave quantities, resonator frequency and decay rate, track this feature, so the channel can be characterized entirely through the microwave measurements. The frequency shifts by at most 25 kHz and the decay rate varies between 15 and 30 kHz, against a resonance frequency of order 1 GHz.

### 10.3 vdW impedance in the normal state

In this section, we build an effective impedance model to connect microwave measurements to quasi-DC transport measurements. It will turn out that shunt parasitic elements which are connected to the resonator need to be incorporated in any quantitative analysis of resonator data.

Chapter 3 showed that an arbitrary complex load  $Z_L$  terminating the line enters only through the complex angle  $\theta = \eta + j\chi = \tanh^{-1}(Z_L/Z_r)$ , and that the resonance frequency and the two quality factors follow from Eqs. 3.66–3.68. Those relations can be inverted. Given a fitted triplet  $(f_r, Q_i, Q_c)$  at each gate voltage,  $\chi$  follows from the frequency shift and  $\eta$  from the internal quality factor, and  $Z_L = Z_r \tanh(\eta + j\chi)$  then gives the load impedance  $Z_L$ .

Fig. 10.3(b) shows the measured frequency shift and decay rate along a back gate sweep, and Fig. 10.3(c) the load impedance obtained from them. The reactance sits at  $\text{Im } Z_L \approx -87 \Omega$  and varies by less than  $0.1 \Omega$  over the entire gate range, while the resistive part never exceeds  $0.05 \Omega$ . The load the resonator sees is capacitive, and its reactance is almost completely insensitive to the state of the channel, even as the channel resistance itself changes by more than an order of magnitude across charge neutrality.

A capacitance that does not respond to the gates cannot be the device, so it must be a parasitic shunt in parallel with it. We show a possible circuit model including the parasitic capacitances in Fig. 10.3(a): a shunt capacitance  $C_p$  to ground in parallel with the series combination of a small coupling capacitance  $C_s$  and the channel impedance  $Z_{\text{vdW}}$ . Writing  $x = C_s/C_p$  and  $y = \omega R C_s$

with  $R = \text{Re } Z_{\text{vdW}}$ , and working in the experimentally relevant limit  $x \ll 1$  and  $y \lesssim 1$ , the load impedance reduces to

$$Z_L \approx -\frac{j}{\omega C_p} + x^2 \left( R + \frac{j}{\omega C_s} \right), \quad (10.1)$$

so that  $\text{Im } Z_L$  is set almost entirely by  $C_p$  and is gate-independent, while  $\text{Re } Z_L = x^2 R$  carries the whole of the device response, attenuated by the square of the capacitance ratio. Fitting this circuit to the measured impedance gives  $C_p = 1.8 \text{ fF}$  and  $C_s = 5.2 \text{ fF}$ . The first is consistent with the observed reactance: at a resonator frequency of order 1 GHz, 1.8 pF corresponds to a reactance close to the  $87 \Omega$  measured in panel (c). The ratio  $x \approx 3 \times 10^{-3}$  gives an attenuation  $x^2 \approx 9 \times 10^{-6}$ , so a channel resistance of order  $10 \text{ k}\Omega$  presents itself to the resonator as a load of a few tens of milliohms. As a result, despite the channel resistance being a few  $\text{k}\Omega$ , we still see a resonance with  $Q_i$  close to 10k.

Equation 10.1 can be inverted to recover the channel resistance, and Fig. 10.3(d) compares the result against DC transport on the same device. The comparison requires one geometric factor: the resonator is connected across a portion of the channel three squares long, so the appropriate transport quantity is  $3R_{\text{DC}}$ , where  $R_{\text{DC}}$  is the 3-terminal resistance reported in the previous section. The two curves agree well at charge neutrality, where both peak near  $10 \text{ k}\Omega$ , which is a non-trivial check given that the microwave value is obtained from a linewidth measurement and the transport value from a lock-in measurement, with no shared calibration. Away from neutrality the microwave value sits systematically above the transport one, by roughly a factor of three in the wings. A contact resistance in series with the channel, which the microwave measurement includes and the four-terminal transport measurement excludes by construction, is the most likely explanation of this discrepancy. We attribute  $C_p$  to a combination of the back gate capacitance and the distributed capacitance of the coplanar waveguide section connecting the DC line to its filter.

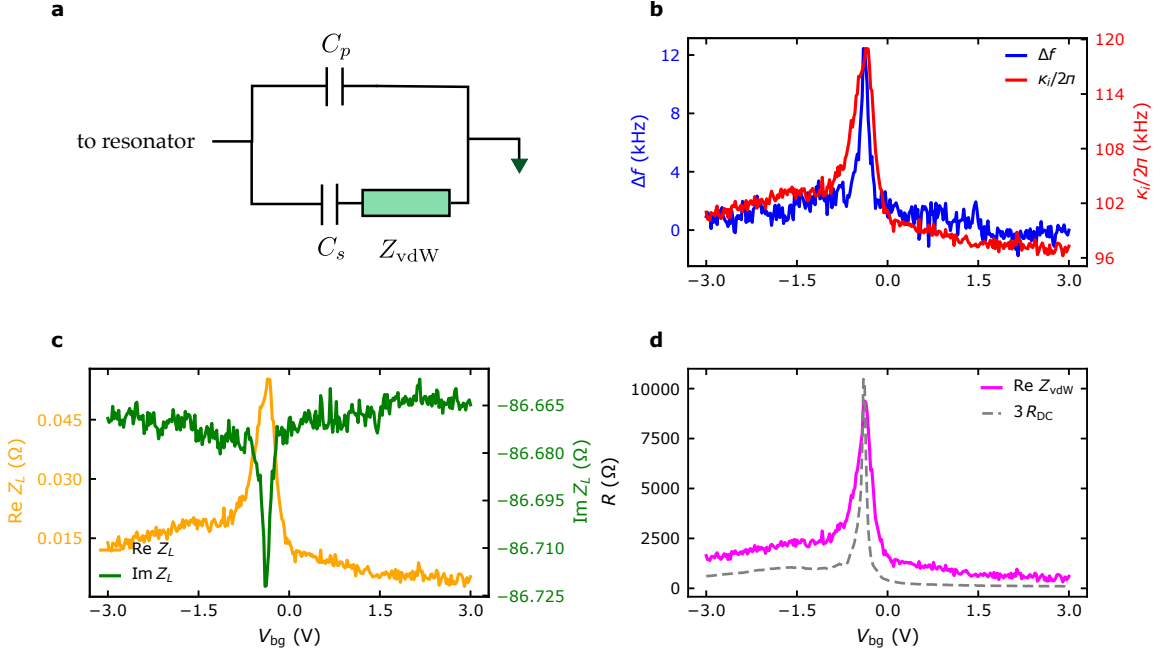


Figure 10.3: **Load impedance presented to the resonator by a hybrid Hall bar.** (a) Circuit model implied by the measurement. The resonator terminates on a parasitic capacitance  $C_p$  shunted to ground, in parallel with the series combination of a small coupling capacitance  $C_s$  and the impedance of the vdW channel  $Z_{\text{vdW}}$ . (b) Measured frequency shift  $\Delta f$  and decay rate  $\kappa_i/2\pi$  as functions of back gate voltage, both peaking sharply at charge neutrality. (c) Real and imaginary parts of the load impedance  $Z_L$ , obtained by inverting Eqs. 3.66–3.68 with no circuit model assumed. Note the scales. The reactance sits at  $\text{Im } Z_L \approx -87 \Omega$  and varies by less than  $0.1 \Omega$  across the full gate range, while  $\text{Re } Z_L$  stays below  $0.05 \Omega$ . The load is capacitive to within three orders of magnitude, and its reactance is essentially independent of the state of the channel, which is what identifies the capacitance as parasitic rather than as part of the device. (d) Channel resistance  $\text{Re } Z_{\text{vdW}}$  recovered from  $\text{Re } Z_L$  using the circuit of (a), compared with the DC resistance scaled by the three squares of channel connected to the resonator,  $3R_{\text{DC}}$ . The two agree at charge neutrality; the excess of the microwave value in the wings is consistent with a series contact resistance, which the microwave measurement includes and the three-terminal transport measurement does not.

## 10.4 Data from an additional device

The device reported in the previous sections had limited gate ranges, and as a result it could not be measured at the high displacement fields ( $\sim 1 \text{ V nm}^{-1}$ ) where the superconducting state has been observed in BBG/WSe<sub>2</sub> devices [157]. In this section we look at measurements of a second device with better hBN dielectrics, where it was indeed possible to gate to high displacement fields. To our surprise, no superconducting state was found in the same region of density and displacement field as previous reports in the literature. We will come back to the missing superconducting state in the next section.

Fig. 10.4 shows the full gate-gate map of this device, with two-terminal and four-terminal resistance alongside the resonator frequency shift and decay rate, all acquired in the same cooldown. The accessible range is much larger than before, reaching  $|D/\epsilon_0| \approx 1.5 \text{ V nm}^{-1}$  and hole densities just beyond  $10^{13} \text{ cm}^{-2}$ . The four-terminal map shows the expected charge neutrality line near  $n = 0$ , which broadens and strengthens as the gap opens with increasing  $|D|$ , together with additional resistive features at higher hole doping. The diagonal streak in panels (a) and (d) does not run along a line of constant  $n$ , but along a line of constant back gate voltage. This is the signature of a region of the stack controlled by only one gate, most plausibly the probe arms extending beyond the top gate.

The frequency shifts by up to 100 kHz rather than 25 kHz, and the decay rate sits between 400 and 500 kHz rather than between 15 and 30 kHz. This device is therefore more than an order of magnitude lossier, which is consistent with the impedance model of Sec. 10.3: a larger  $\text{Re } Z$  follows directly from the larger channel resistance over most of this extended density range.

The region of the phase diagram in which superconductivity is reported now lies well inside the measured window in  $n$ - $D$  space, and there is no zero-resistance state anywhere in either resistance map. Neither microwave map shows the abrupt change in  $\Delta f$  or the collapse of  $\kappa$  that a transition to zero resistance would produce. Agreement between both independent probes makes this conclusion robust. A superconducting patch confined to part of the channel could in principle be missed by a particular four-terminal contact configuration, but it would still affect the microwave current and show up in the resonator response.

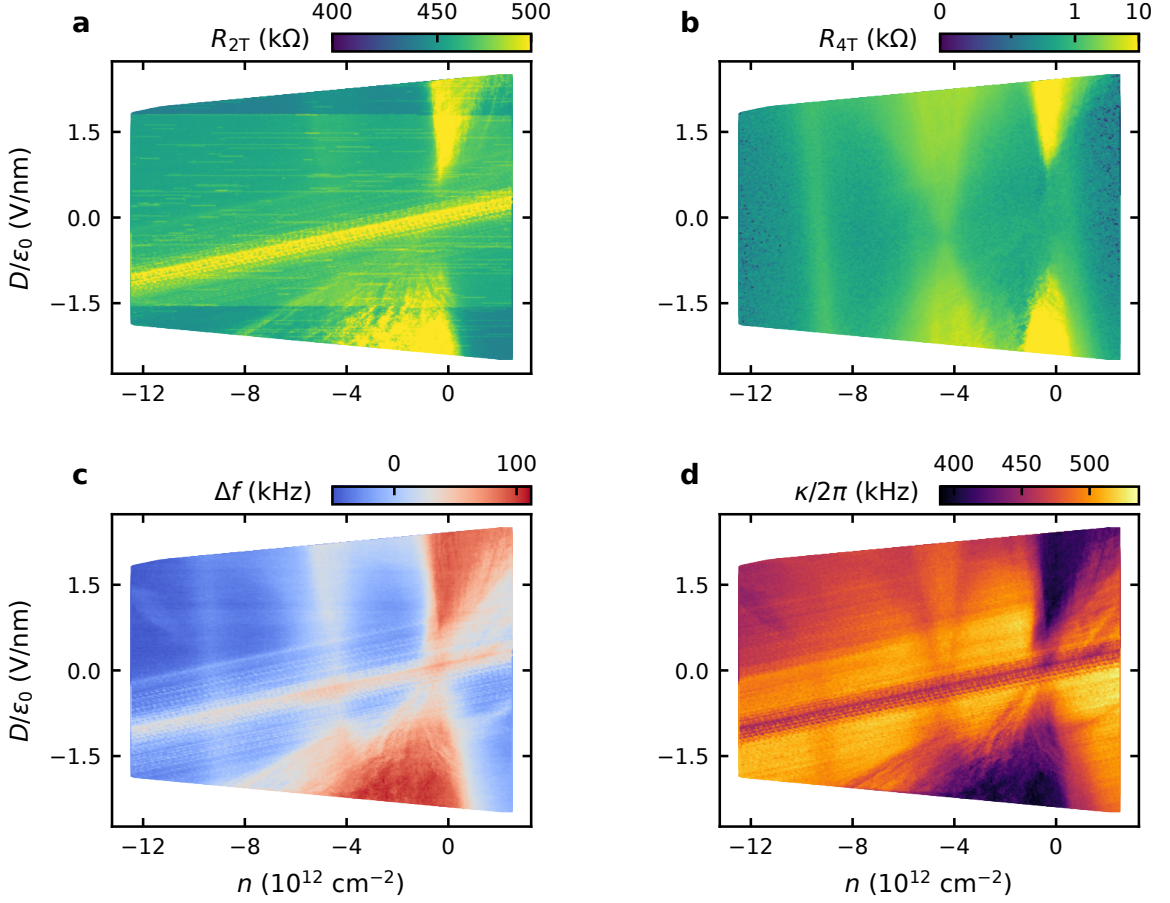


Figure 10.4: **Transport and microwave response of a second hybrid Hall bar over an extended gate range.** Device SF96I3 at base temperature. (a) Two-terminal resistance  $R_{2T}$ , (b) four-terminal resistance  $R_{4T}$ , (c) resonator frequency shift  $\Delta f$  and (d) decay rate  $\kappa/2\pi$ , all as functions of carrier density  $n$  and displacement field  $D/\epsilon_0$  and all acquired in the same cooldown. Thinner hBN ( $\sim 5 - 10$  nm) dielectrics extend the accessible range to  $|D/\epsilon_0| \approx 1.5 \text{ V nm}^{-1}$  and to hole densities beyond  $10^{13} \text{ cm}^{-2}$ , placing the region where superconductivity is reported in BBG/WSe<sub>2</sub> [157] well inside the measured window. Panel (b) shows the charge neutrality line near  $n = 0$ , which strengthens as the gap opens with increasing  $|D|$ , along with further resistive features at higher hole doping. The diagonal streak in (a) and (d) runs along a line of constant back gate voltage rather than constant  $n$ , identifying it as the neutrality point of a region controlled by only one gate, most plausibly the probe arms extending beyond the top gate. Note the scales in (c) and (d): the frequency shifts by up to 100 kHz and the decay rate is 400–500 kHz, more than an order of magnitude larger than in Fig. 10.2, so this device is correspondingly lossier.

## 10.5 Missing superconducting state in BBG/WSe<sub>2</sub> heterostructures

The device of the previous section is not an isolated case. Across every hybrid BBG/WSe<sub>2</sub> Hall bar built for this work, spanning a range of hBN thicknesses, no device has shown a superconducting state. Fig. 10.5 shows this for two devices with the widest accessible range. Both panels show the four-terminal resistance over the full gate-gate plane, with the regions in which superconductivity has been reported for this material marked in red. Superconductivity in BBG/WSe<sub>2</sub> appears at both polarities of displacement field and on both the electron and hole sides of charge neutrality, and in both of our devices those regions lie comfortably inside the measured window. In neither device does the resistance approach zero anywhere within them. The four-terminal resistance in the circled regions is of order 1 k $\Omega$  and there is no suppression of resistance from perhaps a weakly formed superconducting state. The measurements were taken at base temperature of 50 mK, well below the few hundred mK at which the superconducting transition has been reported [157, 158].

The hybrid architecture is common to these two devices: both sit on a superconducting circuit chip, both use superconducting gates, and both are contacted with the stress-optimized Ti/Nb/Al metallization of Chapter 8. Whatever suppresses superconductivity is therefore more likely to be a feature of the platform than an accident of a particular fabrication run.

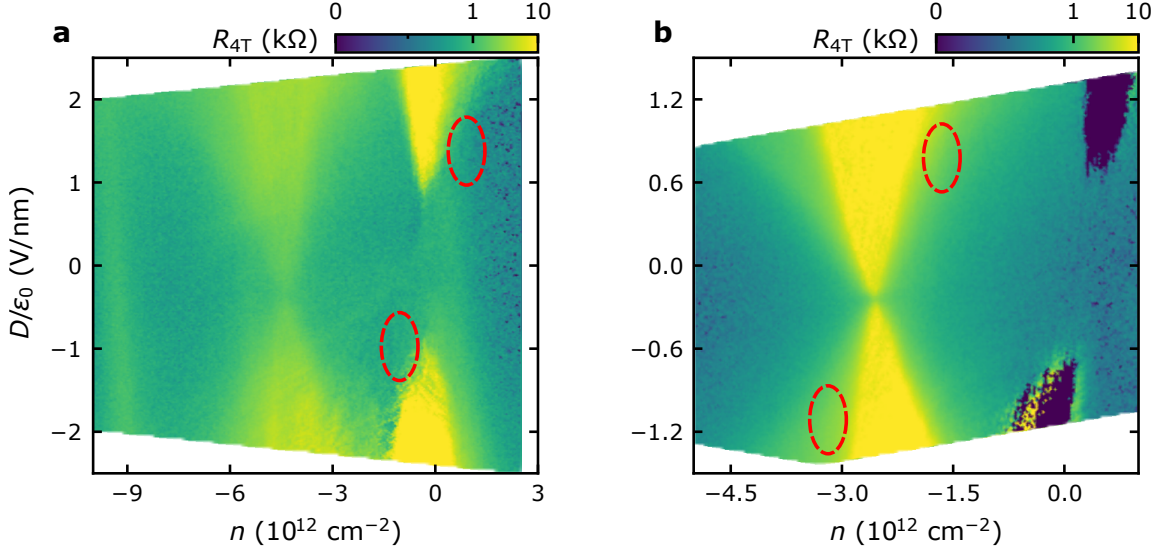


Figure 10.5: **Absence of superconductivity in two hybrid BBG/WSe<sub>2</sub> Hall bars.** Four-terminal resistance  $R_{4T}$  as a function of carrier density  $n$  and displacement field  $D/\epsilon_0$  for devices (a) SF96I3 and (b) SF96K9, both at base temperature. The bright features fanning out with increasing  $|D|$  are the charge neutrality point and the associated gap opening in the bilayer. The red dashed ellipses mark the regions of the phase diagram where superconductivity has been reported in BBG/WSe<sub>2</sub> [157, 158], which occur at both polarities of displacement field and on both the electron and hole sides of neutrality, and which are positioned here relative to the charge neutrality point of each device. In both devices these regions lie well inside the accessible range, and in neither does the resistance drop toward zero within them:  $R_{4T}$  there is of order 1 kΩ, comparable to the surrounding metallic background. Panel (b) shows a noticeably larger offset of charge neutrality from  $n = 0$ , indicating more unintentional doping in that device, but the conclusion is the same in both. The speckled dark region at positive  $n$  and negative  $D$  in (b) is not a low-resistance state. There the sample is so resistive that current cannot be reliably passed through the channel, and the four-terminal voltage is unreliable.

## 10.6 Limitations of current approach to hybrid devices

No hybrid device measured in this work has shown superconductivity. Several explanations remain viable and the present evidence does not decisively select among them.

1. **Charge disorder from the superconducting gates.** Our devices use sputtered NbTiN as the back gate and, in most cases, an evaporated metal as the top gate, whereas the devices reported in the literature use exfoliated graphite gates. Graphite gates are atomically flat and electrostatically homogeneous. We suspect that potential fluctuations from non-graphite gates reduce mobility and suppress correlated phases.
2. **Strain from the superconducting contacts.** The Ti/Nb/Al contacts carry substantial

residual stress, as discussed in Chapter 8, and the same stress that drives spalling will transmit strain into the channel. Strain modifies the BBG band structure and could plausibly suppress a fragile superconducting state. Raman spectroscopy of areas near contact metallization on exfoliated flakes could be used to quantify the strain around these contacts.

3. **Screening by the gates.** Thin hBN dielectrics place metallic gates close to the channel, and strong screening of the Coulomb interaction can suppress interaction-driven phases. Our hBN thicknesses have ranged from about 5 to 23 nm, and superconductivity was absent across that range. This argues against screening as the sole explanation, though it does not exclude a contribution in the thinner devices.
4. **Unintentional doping from contact interfaces.** The selective  $\text{CF}_4$  etch used to expose the graphene edge chemically fluorinates the graphene surface prior to metallization. Unintentional doping near the contacts can also lead to such regions extending into the hallbar channel. The rigid density offset needed to align our maps with the reference devices is consistent with some unintentional doping.

## 10.7 Design principles for future devices

1. **Replace the superconducting gates with graphite.** Graphite gates are the most conspicuous difference between our devices and the devices with a superconducting state reported in literature. A dual-graphite hybrid device has been designed and fabricated, and Fig. 10.6 follows one through the resulting process. Two modifications are required relative to the flow of Chapter 8. The contact etch now has to remove the top graphite before it reaches the top hBN, which is done with a sequence of  $\text{O}_2$  plasma cycles ahead of the selective  $\text{CF}_4$  step, and the superconducting contacts must climb over the edge of the back graphite on their way out to the resonator and the DC lines. The top graphite must then be isolated from those contacts, which is handled by a final  $\text{O}_2$  etch after the mesa step.
2. **Break the path to ground before the device.** The parasitic analysis of Sec. 10.3 shows the shunt is dominated by the DC line and filter attached to the source, not by the device. The remedy is to prevent the source from teeing off to a DC line at all, so that microwave current entering the center pin has no route to ground except through the channel. The dual-graphite design routes the source directly to the resonator with no DC branch.



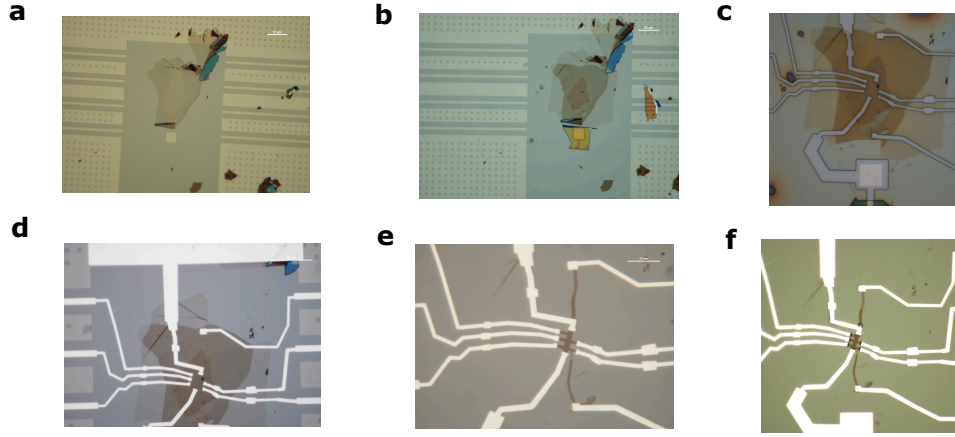
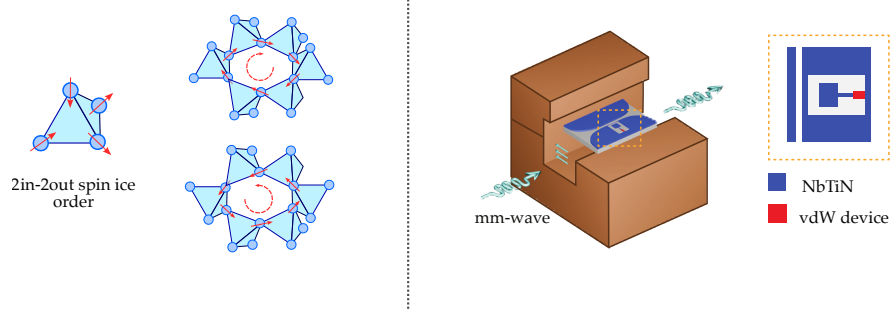


Figure 10.6: **Fabrication of a dual-graphite-gated hybrid device.** Optical images at successive stages of the dual-graphite process. (a) The bottom half of the stack, consisting of the back graphite gate and the bottom hBN, after meltdown onto the circuit chip. (b) The completed stack, with the channel, top hBN and top graphite added. (c) After the contact etch. Because the top graphite now lies above the contact windows, this step is performed in two parts: a sequence of  $\text{O}_2$  plasma cycles removes the top graphite, followed by the selective  $\text{CF}_4$  etch that removes the top hBN and stops on the channel. (d) After deposition and liftoff of the Ti/Nb/Al contacts, which climb over the edge of the back graphite on their way out to the resonator and the DC lines. (e) After the mesa etch, which clears the stack and the back graphite outside the channel so that the surrounding regions are electrically isolated. (f) After a final  $\text{O}_2$  plasma step that liberates the top gate, removing the top graphite where it would otherwise short to the contacts. Full process checklists are given in Appendix F.

# Part IV

## Outlook



## Chapter 11

# Outlook on Future Experiments

The experiments in this thesis rest on a premise: *a superconducting resonator placed in the electromagnetic environment of a quantum material is a sensitive probe of its low-energy response*. The experiments reported here on a few materials only scratch the surface of this premise. In this final outlook chapter, I will sketch out new fruitful directions for such experiments. Fig. 11.1 collects the four directions discussed below.

### 11.1 Microwave resonance in pyrochlore spin ices

Chapter 6 applied the flip-chip platform to  $\text{Gd}_2\text{Ti}_2\text{O}_7$ , which sits at the isotropic end of the pyrochlore titanate family. The titanates  $A_2\text{Ti}_2\text{O}_7$  are valuable because the rare-earth  $A$  site can be varied while the lattice is held fixed, changing the single-ion anisotropy from Heisenberg through Ising to easy-plane [63]. In  $\text{Ho}_2\text{Ti}_2\text{O}_7$  and  $\text{Dy}_2\text{Ti}_2\text{O}_7$  the crystal field forces each moment to point directly into or out of its tetrahedron, and an effectively ferromagnetic coupling selects a two-in-two-out ground state on every tetrahedron (Fig. 11.1(a)). These ice rules leave a macroscopic degeneracy and a residual entropy close to Pauling’s estimate [63]. Flipping a single moment violates the rule on two tetrahedra at once, creating a pair of defects that carry net magnetic charge and can separate at no further energy cost, connected by an unobservable Dirac string [12].

For an ideal Ising doublet the transverse  $g$ -factor vanishes and magnetic-dipole transitions are forbidden; real spin ices retain a small transverse matrix element from crystal-field admixture. At present it is extracted only indirectly, by fitting relaxation data to an assumed mechanism, whereas the method developed in Chapter 5 for the  $\text{Tb}^{3+}$  doublet would access it directly. Holmium offers a second handle:  $^{165}\text{Ho}$  carries  $I = 7/2$  and the largest hyperfine coupling of any rare-earth nucleus, splitting the Ising doublet into eight levels spaced by  $\approx 26\text{ }\mu\text{eV} \approx 6\text{ GHz}$ , which lies inside the band of the resonators used in Part II. Since nuclear-spin-assisted tunneling is known to control the

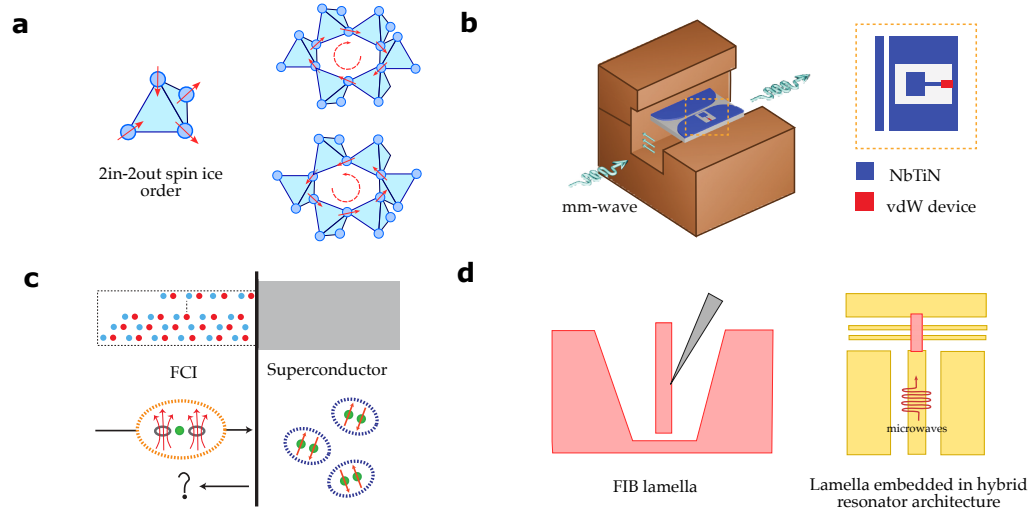


Figure 11.1: **Four directions for future experiments.** (a) Pyrochlore spin ice (Sec. 11.1). Left: a single tetrahedron with  $\langle 111 \rangle$  Ising moments in the two-in-two-out configuration that satisfies the ice rules. Right: two states of a hexagonal plaquette of the pyrochlore lattice, differing in the sense of circulation of the spin loop indicated by the dashed arrows. The ring exchange move connecting them is what generates quantum dynamics within the ice manifold and underlies the emergent photon of a quantum spin ice. (b) Millimeter-wave platform (Sec. 11.3). A waveguide couples mm-wave signals onto a chip carrying a resonator terminated by a van der Waals device, in a geometry adapted from Ref. [214]. The inset shows the chip layout, with the NbTiN circuit layer in blue and the vdW device in red. (c) Interface between a fractional Chern insulator and a superconductor (Sec. 11.4). An electron bound to an even number of flux quanta forms a composite fermion, the emergent quasiparticle of the fractional state. What is reflected when such a quasiparticle is incident on a superconductor, where the available states are Cooper pairs, is the open question marked by the arrow. (d) Focused ion beam route to materials that cannot be exfoliated (Sec. 11.5). Left: a lamella milled from a bulk single crystal and lifted out with a micromanipulator. Right: the same lamella transferred into the hybrid resonator architecture of Chapter 8, where it takes the place of the flake and is probed by the microwave mode of the resonator.

low-temperature monopole dynamics [224], driving these transitions resonantly amounts to a pump-probe experiment on emergent charge carriers. Further afield, quantum spin ice candidates such as  $\text{Ce}_2\text{Zr}_2\text{O}_7$  should support a gapless emergent photon whose bandwidth lies in the same window [225, 226], arising from the ring exchange dynamics sketched in the right half of Fig. 11.1(a), though whether a planar resonator couples to it needs theoretical input first. None of this requires new hardware: the flip-chip platform of Chapter 6 is directly applicable to these proposed experiments.

## 11.2 Superfluid stiffness of rhombohedral graphene superconductors

Recent studies of rhombohedral graphenes ranging from three to six layers have shown a multitude of superconducting states. Out of these, the most surprising is a candidate chiral superconductor (CSC) occurring in four and five layer rhombohedral graphene. Observations of magnetic hysteresis above  $T_c$  and proximity in  $n$ - $D$  space to a quarter metal suggest a time-reversal symmetry broken normal state for the superconductor [168, 169].

Our own transport measurements on rhombohedral tetralayer graphene map this region out in detail [169]. Quantum oscillations, however, show the normal state to be not the simply-connected quarter metal that had been assumed but a more complex multitone state, leaving the pairing channel and the question of chirality open. A stiffness measurement would add additional information about the nature of the candidate chiral superconducting state. The same device offers a natural control. A second superconducting state appears on the hole side of the phase diagram (Sec. S9 and Fig. S19 of Ref. [169]) with  $T_c = 150$  mK. Measuring both in a single cooldown would compare a candidate time-reversal symmetry broken superconductor against a conventional-looking one in the same material, with the same contacts, disorder realization and geometry, so that almost every systematic is common to the two. Both states suit the architecture well: critical temperatures of 150–175 mK sit far below the  $T_c$  of the NbTiN circuit layer, densities of order  $10^{12} \text{ cm}^{-2}$  place the expected kinetic inductance in the range calibrated in Chapter 9, an upper critical field of 0.4 T is modest enough that the field dependence stays well within the usable range of the resonators, and the devices are already dual-graphite gated as recommended in Sec. 10.7.

## 11.3 Hybrid mm-waves probes of the superconducting gap

Superconducting circuits are beginning their own climb in operating frequency, from microwave toward millimeter-wave ( $\sim 100$  GHz), driven by the prospect of faster gates, smaller footprints and relaxed cooling requirements [227, 214]. That climb opens an opportunity for condensed matter physics, and the clearest one concerns the superconducting gap of van der Waals superconductors. Conventional BCS theory predicts  $2\Delta \approx 3.5k_B T_c$ , and elemental superconductors such as Al, Nb and Pb roughly comply, with gap-to- $T_c$  ratios between 3 and 6. Twisted graphenes, by contrast, exhibit ratios as large as 15–25, and recent STM spectroscopy observes a V-shaped gap that deepens the analogy to the cuprates [189]. Part of this discrepancy may be an artifact of the probe, since STM can conflate the superconducting gap with a higher-temperature pseudogap. An independent measurement coupling to the gap directly would help settle the question.

Millimeter-wave circuits operate at exactly the right energy scale: for a van der Waals superconductor with  $T_c \approx 1$  K, BCS theory predicts  $2\Delta \approx 75$  GHz. Fig. 11.1(b) sketches an architecture, in

which a waveguide couples to a millimeter-wave resonator terminated by a van der Waals device. The resonator is patterned from Nb, NbN or NbTiN, whose plasma frequencies are high enough to extend planar circuits into this band and whose sheet inductance allows the impedance to be matched to a van der Waals load, as already exploited in Chapter 8. When the resonator frequency lies above the gap, driving the superconductor normal degrades the quality factor strongly, so tracking  $Q$  from the  $T_c$  of the resonator film down to tens of millikelvin would reveal the temperature at which the gap crosses the resonator frequency. The temperature dependence of that crossing in turn carries information about the pairing mechanism.

## 11.4 Emergent excitations at superconductor-fractional Chern insulator interfaces

Once integer quantum Hall analogues were found at zero magnetic field in materials with a quantized anomalous hall effect [183, 184], the question remained whether an interaction-stabilized fractional phase could exist without a field. That question has now been settled by the discovery of fractional Chern insulators (FCIs) in twisted  $\text{MoTe}_2$  and rhombohedral graphene [163], in which a periodic lattice potential plays the role of the magnetic field. Composite fermions, that is electrons bound to an even number of flux quanta (Fig. 11.1(c)), are believed to be the emergent quasiparticles of a fractional quantum Hall state, but whether the same description applies to FCIs remains open. One way to interrogate the quasiparticles of a novel phase is to look for surprises in interfacial tunneling with a well-understood system: an electron is forbidden from tunneling from a normal metal into an adjacent superconductor except through Andreev reflection, and when the normal electrons are replaced by composite fermions the properties of that interface are largely unexplored. The superconducting contacts developed for the JJ and Hall bar devices in Chapters 9 and 10 is one of the crucial steps to fabricate such tunneling devices for quasi-DC measurements.

Fractionalization and Cooper pairing have historically been mutually exclusive, since fractionalization required strong magnetic fields and such fields are hostile to superconductivity. FCIs remove that obstruction and offer a route to couple fractionalized states to superconductors at zero field. Bias spectroscopy by quasi-DC transport could extract an induced gap at such an interface, and the microwave and millimeter-wave circuits developed in Chapter 8 would allow direct measurement of the many-body gap and, if applicable, of a topological superconducting gap.

## 11.5 Beyond exfoliation: focused-ion-beam microstructures

The architecture of Chapter 8 carries an implicit precondition that the material of interest is a 2D material heterostructure. For a material to enter that architecture, it seems like the material must be a flake and it must cleave to micron lateral extent and tens of nanometers thickness. vdW

materials satisfy all of this because their interlayer bonding is weak; most quantum materials do not. Heavy fermion superconductors, the cuprates, the ruthenates, the kagome metals and  $\text{UTe}_2$  are all three-dimensionally bonded, and all of them present open questions about pairing symmetry that a superfluid stiffness measurement could address. Epitaxy is the alternative, as Chapters 4 and 5 discussed, but growing a complex compound as a film is a research program in its own right.

Focused ion beam (FIB) machining offers a different route: rather than growing or cleaving a thin sample, a FIB carves one out of a bulk single crystal with sub-micron control over shape and orientation, and with no requirement on bonding anisotropy [228]. A recent measurement of chiral boundary states in bismuth illustrates how far the technique has matured [229]. There, lamellae were milled from a bulk crystal with a Xe-plasma FIB, transferred by micromanipulator onto a gold-coated  $\text{SiN}_x$  membrane, contacted by FIB-assisted platinum deposition, and isolated into electrodes by cutting the gold film; because milling is maskless and direct-write, the authors could then return to the same device between cooldowns and add grooves one at a time. If we adapt that fabrication sequence, the workflow is close to the one used in Chapter 8, as sketched in Fig. 11.1(d). The lamella plays the role of the flake, the micromanipulator the role of the polymer stamp, the platinum deposition the role of the edge contact, and the membrane the role of the device substrate. The geometry is then identical to Chapters 8 and 9, and Eqs. 3.66-3.68 translate the measured frequency and quality factors into the complex impedance of the lamella exactly as before.

Certain challenges also exist which we now discuss. FIB-deposited platinum is normal and resistive, and a resistive load comparable to  $Z_r$  in the current path damps the mode entirely (Fig. 3.5(d-f)), so transparent superconducting contact or the capacitive geometry of Chapter 3 would be needed. Xe milling leaves a few nanometers of nanocrystalline material which is a minor perturbation for transport through a micron-thick bar, but a direct dissipation channel for a resonator. And finally, a resonator chip is rigid, whereas Ref. [229] suspends its structures to relieve thermal-mismatch strain. If these can be solved, the hybrid architecture stops being a van der Waals technique and becomes a general one, and the set of materials that can be placed inside a superconducting resonator expands to a wider set of quantum materials.

# Appendices



## Appendix A

# S-parameter analysis using ABCD matrices

### A.1 ABCD Matrices

#### A.1.1 Definition of ABCD matrices

ABCD or transmission matrices are commonly used in microwave circuit design to model a cascaded series of microwave components. The matrix relates the voltage and current on port 1 ( $V_1, I_1$ ) to those on port 2 ( $V_2, I_2$ ). Note the sign convention for the current, which is always defined as flowing from left to right (Fig. A.1(a)). This convention allows us to simply multiply individual ABCD matrices when components are cascaded together (Fig. A.1(b)).

$$\begin{pmatrix} V_1 \\ I_1 \end{pmatrix} = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \begin{pmatrix} V_2 \\ I_2 \end{pmatrix} \quad (\text{A.1})$$

The four elements of the ABCD matrix are defined as follows:

$$A = \left. \frac{V_1}{V_2} \right|_{I_2=0} \quad \text{open circuit voltage ratio} \quad (\text{A.2})$$

$$B = \left. \frac{V_1}{I_2} \right|_{V_2=0} \quad \text{short circuit transfer impedance} \quad (\text{A.3})$$

$$C = \left. \frac{I_1}{V_2} \right|_{I_2=0} \quad \text{open circuit transfer admittance} \quad (\text{A.4})$$

$$D = \left. \frac{I_1}{I_2} \right|_{V_2=0} \quad \text{short circuit current ratio} \quad (\text{A.5})$$

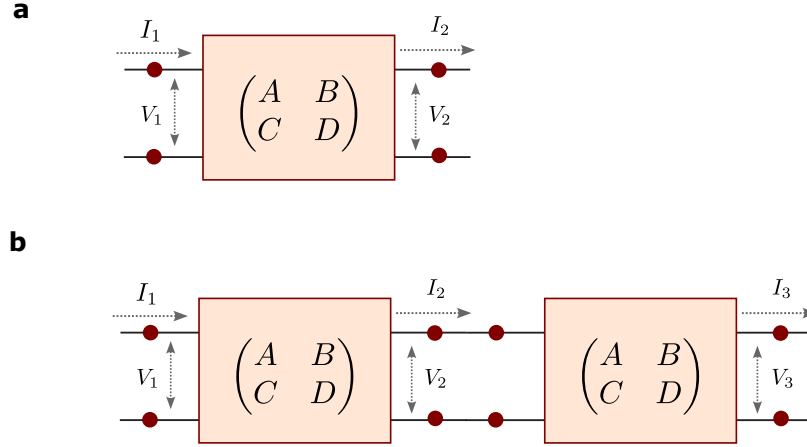


Figure A.1: **Definition and cascading of ABCD matrices.** (a) A two-port network described by an ABCD matrix, which relates the voltage and current at port 1 ( $V_1, I_1$ ) to those at port 2 ( $V_2, I_2$ ). The current is defined as flowing from left to right at both ports, so the current  $I_2$  flowing out of port 2 enters the next network with the same sign convention. (b) Two cascaded networks. With this sign convention, the output variables ( $V_2, I_2$ ) of the first network are the input variables of the second, and the ABCD matrix of the composite network is simply the matrix product of the individual ABCD matrices.

It is useful to remember that the diagonal components  $A$  and  $D$  are unitless ratios quantifying voltage and current ratios respectively.  $B$  has units of impedance while  $C$  has units of admittance. Pozar's book [36] has extensive tables of ABCD matrices for commonly used configurations of microwave circuit elements. As calculations involving ABCD matrices only require simple matrix multiplication, they are also useful for numerically modeling circuits too complicated to solve analytically: metamaterials built from cascaded resonators, Purcell filters, and traveling-wave parametric amplifiers [36, 230, 231]. The same formalism yields the dispersion relation of periodic structures through the eigenvalues of the unit-cell matrix, models non-uniform structures such as impedance tapers by discretization into short segments, and allows de-embedding of known sections of a measurement chain by multiplication with their inverse matrices. Small impedance mismatches in the feedline can likewise be included as additional matrices in the cascade, reproducing the asymmetric (Fano) lineshapes commonly observed in hanger-geometry measurements [40].

Based on their ABCD matrix, networks can be classified into the following categories:

1. **Reciprocal:**  $AD - BC = 1$ . Recall that for a reciprocal network, the S matrix is equal to its transpose, i.e.  $S_{21} = S_{12}$ .
2. **Symmetric:** A network is symmetric if it is reciprocal and  $A = D$ .
3. **Lossless:** A network is lossless if  $A$  and  $D$  (diagonal components) are purely real and  $B$  and  $C$  (off-diagonal components) are purely imaginary.

### A.1.2 ABCD matrices for transmission lines

For a transmission line of length  $l$  with a propagation constant  $\gamma = \alpha + j\beta$ , the ABCD matrix is as follows:

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix} = \begin{pmatrix} \cosh(\gamma l) & Z \sinh(\gamma l) \\ \frac{1}{Z} \sinh(\gamma l) & \cosh(\gamma l) \end{pmatrix} \quad (\text{A.6})$$

Here,  $Z$  is the characteristic impedance of the transmission line and it can be different from  $50\ \Omega$ . Using the definitions from the last section, we can show that a transmission line is reciprocal and symmetric. In addition, when  $\alpha = 0$ , the transmission line is lossless.

### A.1.3 Relation to S parameters

Since S parameters are typically measured in experiments, it is useful to have a conversion between the ABCD matrix of a two-port network and the corresponding S parameters.

$$\begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} = \begin{pmatrix} \frac{A+B/Z-CZ-D}{A+B/Z+CZ+D} & \frac{2(AD-BC)}{A+B/Z+CZ+D} \\ \frac{2}{A+B/Z+CZ+D} & \frac{-A+B/Z-CZ+D}{A+B/Z+CZ+D} \end{pmatrix} \quad (\text{A.7})$$

The above expression assumes that the two ports have the same impedance  $Z$ . The expression for  $S_{21}$ ,

$$S_{21} = \frac{2}{A + B/Z + CZ + D} \quad (\text{A.8})$$

is used in Chapter 3 for analysis and modeling of microwave circuits in the hanger geometry.

### A.1.4 Impedance looking into an ABCD matrix

Assume we have an ABCD matrix describing a microwave circuit between port 1 and port 2. Let port 2 be terminated by a load impedance  $Z_L$ . Often, we are interested in knowing the impedance looking into port 1, which I will refer to as  $Z_{\text{in}}$  (Fig. A.2). Using the defining relations for the ABCD matrix,

$$V_1 = AV_2 + BI_2 \quad (\text{A.9})$$

$$I_1 = CV_2 + DI_2 \quad (\text{A.10})$$

The impedance looking into port 1 is

$$Z_{\text{in}} = \frac{V_1}{I_1} \quad (\text{A.11})$$

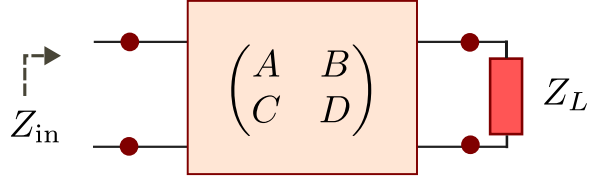


Figure A.2: **ABCD matrix terminated by a load impedance  $Z_L$ .**  $Z_{in}$  is the impedance looking into the ABCD matrix terminated by a load impedance  $Z_L$ . Such a calculation commonly occurs in the analysis of transmission line resonators hanger-coupled to a feedline and terminated by a load impedance  $Z_L$ .

Now, we use the fact that port 2 is terminated by a load  $Z_L$  which leads to  $V_2 = Z_L I_2$ . Using this constraint, we get

$$Z_{in} = \frac{AZ_L + B}{CZ_L + D} \quad (\text{A.12})$$

Two extreme cases arise in practice — open circuit  $Z_L = \infty$  and short circuit  $Z_L = 0$ . In these two cases, the formula for  $Z_{in}$  simplifies to

$$Z_{in} = \frac{A}{C} \quad (\text{open load}) \quad (\text{A.13})$$

and

$$Z_{in} = \frac{B}{D} \quad (\text{short load}). \quad (\text{A.14})$$

## Appendix B

# Derivation of the g-factor $g_J$

We start by defining an effective magnetic moment  $\boldsymbol{\mu}_J = g_J \mathbf{J}$ . We assume that this magnetic moment is the sum of the individual spin and orbital magnetic moments  $\boldsymbol{\mu}_s = g_s \mathbf{S}$  and  $\boldsymbol{\mu}_L = g_L \mathbf{L}$  respectively. We therefore have the following two equations:

$$g_J \mathbf{J} = g_s \mathbf{S} + g_L \mathbf{L} \quad (\text{B.1})$$

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad (\text{B.2})$$

Our goal here is to find  $g_J$  in terms of  $g_s$ ,  $g_L$  and the angular momentum quantum numbers  $S$ ,  $L$  and  $J$ . We multiply both sides of the top equation by  $J$ .

$$g_J \mathbf{J} \cdot \mathbf{J} = g_s \mathbf{S} \cdot \mathbf{J} + g_L \mathbf{L} \cdot \mathbf{J} \quad (\text{B.3})$$

The expectation value for  $\langle \mathbf{J} \cdot \mathbf{J} \rangle = J(J+1)$ . In order to solve for  $g_J$ , we need to determine the expectation value for  $\mathbf{S} \cdot \mathbf{J}$  and  $\mathbf{L} \cdot \mathbf{J}$ . To do so, we can rewrite the defining equation for  $\mathbf{J}$  as:

$$\mathbf{S} = \mathbf{J} - \mathbf{L} \quad (\text{B.4})$$

Squaring both sides,

$$\mathbf{S} \cdot \mathbf{S} = \mathbf{J} \cdot \mathbf{J} + \mathbf{L} \cdot \mathbf{L} - 2\mathbf{L} \cdot \mathbf{J} \quad (\text{B.5})$$

Taking expectation values, we get,

$$\langle \mathbf{L} \cdot \mathbf{J} \rangle = \frac{1}{2} [J(J+1) + L(L+1) - S(S+1)] \quad (\text{B.6})$$

Similarly, we can show,

$$\langle \mathbf{S} \cdot \mathbf{J} \rangle = \frac{1}{2} [J(J+1) + S(S+1) - L(L+1)] \quad (\text{B.7})$$

Substituting these expectation values in Eq., we get a closed form expression for  $g_J$ .

$$g_J = g_s \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} + g_L \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} \quad (\text{B.8})$$

The theory of atomic structure predicts that  $g_s \approx 2$  (with small correlations  $O(\alpha)$ , where  $\alpha \approx 1/137$  is the fine structure constant, originating from quantum electrodynamics) and  $g_L = 1$ . We can simplify the above expression to the following:

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \quad (\text{B.9})$$

## Appendix C

# Wafer Scale Marker Chips

In order to speed up nano-fabrication of vdW devices, I deposited Ti/Pt markers on full 4-inch wafers which were subsequently diced into  $5 \times 5$  mm chips. In this short chapter, I will describe the marker alignment pattern that I have developed for standard SiO<sub>2</sub>/Si wafers as well as NbTiN/Si wafers for hybrid superconducting devices. All chips use Ti/Pt markers instead of Ti/Au markers to support high-temperature annealing (e.g. 500 °C), as Ti/Au markers tend to form intermetallics at high temperatures and ruin the clear sharp boundaries of the marker. 10  $\mu$ m square markers are used as they are preferred by the EBPg software.

### C.1 SiO<sub>2</sub>/Si wafers

Each  $5 \times 5$  mm chip has a grid of 10  $\mu$ m square markers at a spacing of 100  $\mu$ m in both x and y directions (Fig. C.1). Alternate markers in a row and column have text labeling their location in units of 100  $\mu$ m. For example, the marker  $(-14, -14)$  denotes the position  $(-1400 \mu\text{m}, -1400 \mu\text{m})$  from the center of the chip. To mark the bottom left corner of the chip, I put a large L shape which can be seen with the naked eye.

#### C.1.1 Fabrication recipe

- ☐ Clean a 4-inch wafer in a large beaker of acetone for 5 min. Sonicate at power setting = 5 in the cleanroom.
- ☐ Clean the wafer in a large beaker of isopropanol for 5 min. Sonicate at power setting = 5 in the cleanroom.
- ☐ Blow dry aggressively with the N<sub>2</sub> gun. Make sure to dry off any solvent from the backside of the wafer.

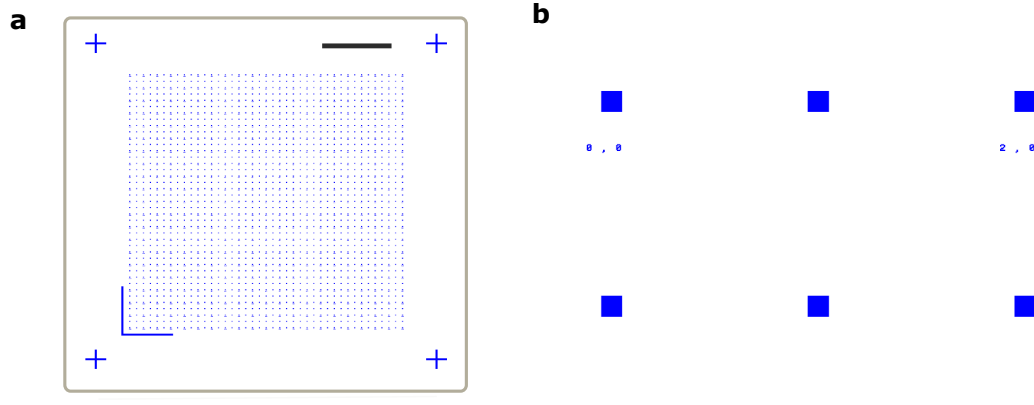


Figure C.1: **Wafer-scale marker pattern for  $\text{SiO}_2/\text{Si}$  chips.** (a) CAD design of the marker pattern for  $\text{SiO}_2/\text{Si}$  chips. The black scale bar denotes 1 mm. A grid of  $10\text{ }\mu\text{m}$  square markers for optical alignment of vdW heterostructures to marker positions is fabricated using a Ti/Pt liftoff process. The grid of crosses near the edge is used as markers during dicing. (b) Zoom-in of the marker grid. Alternate markers in both rows and columns have a label denoting their location from the center of the chip in units of  $100\text{ }\mu\text{m}$ .

- ☐ Spin CSAR 62.09 at 5000 RPM.
- ☐ 5 min bake at  $150\text{ }^\circ\text{C}$ .
- ☐ E-beam write in the EBPG at dose =  $450\text{ }\mu\text{C cm}^{-2}$  and 150 nA current. The entire write will take about 90 min.
- ☐ Develop in o-xylene for 1 min and stop development in isopropanol.
- ☐ Do a 30-second  $\text{O}_2$  descum in the NPC Oxford RIE.
- ☐ Load in the KJL evaporator. Deposit 5 nm Ti/45 nm Pt.
- ☐ Liftoff in Remover PG at  $80\text{ }^\circ\text{C}$  for 1–2 h. Sonicate to remove large flakes. The liftoff tends to leave long “wires” on the wafer. I have found that flipping the wafer and putting it upside down in a beaker of isopropanol helps to remove these Pt wires. Sonicating in the upside down position helps with the liftoff process.
- ☐ Spin PMMA 950 A11 for protection during the dicing process.
- ☐ Dice into  $5 \times 5\text{ mm}$  pieces using a hub blade (SC42ED0-DK). Feed speed =  $3\text{ mm/s}$ .



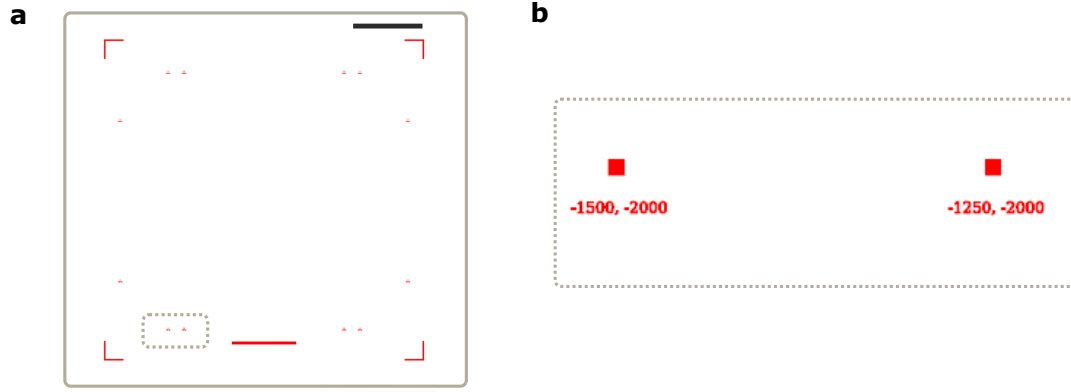


Figure C.2: **Marker pattern for hybrid device wafers.** (a) CAD design of the marker pattern for hybrid resonator chips. The black scale bar denotes 1 mm. The L shapes near the edge are used as markers during dicing. (b) Zoom-in of the markers denoted by the dashed rectangle in (a). Each marker is a  $10\text{ }\mu\text{m}$  square.

## C.2 Hybrid device wafers

These wafers consist of NbTiN deposited on high resistivity silicon. The marker pattern consists of three independent sets of four markers (Fig. C.2). Any of these three sets can be used for alignment. Each marker is a  $10\text{ }\mu\text{m}$  square and its location is printed below the marker. To mark the orientation of the chip, a horizontal bar is located on the bottom edge of the chip. The fabrication process for these markers is identical to the  $\text{SiO}_2/\text{Si}$  marker chips described in the previous section. The only difference is that I dice these hybrid device wafers not into  $5 \times 5\text{ mm}$  pieces but into  $15 \times 15\text{ mm}$  chips. These  $15 \times 15\text{ mm}$  “mother chips” are first processed as a grid of nine  $5 \times 5\text{ mm}$  daughter chips through a superconducting circuit patterning lithography and etch. After the superconducting circuit has been defined, the mother chip is diced into  $5 \times 5\text{ mm}$  daughter chips. The process for dicing the  $15 \times 15\text{ mm}$  chips involves gluing the mother chip (GE varnish + PMMA glue, bake at  $50^\circ\text{C}$  for 5 min) on a carrier wafer. I have found that other mounting methods are not sufficiently rigid to hold the daughter chips in place during the dicing process. I also use a different hub blade (SC42ED0-JK) than the one used in the previous section. This blade has a larger exposure and can handle dicing both the mother chip and the carrier wafer.

## Appendix D

# Stacking SOPs

### D.1 Exfoliation

1. Start by cleaving a wafer into  $10 \times 25$  mm pieces. The size of the pieces is not crucial, but it needs to be small enough that it fits in the slots of the clear polycarbonate boxes.
2. I like to use 2–4 such pieces in one round of exfoliation. Sonicate the chips in acetone for 2 min.
3. Sonicate in isopropanol for 2 min.
4. Blow dry aggressively with the N<sub>2</sub> gun.
5. Put the chips back in the box. Take the box to the plasma cleaner. Run a 75 W, 20 sccm O<sub>2</sub> recipe for a given period of time. For hBN, I do 10 minutes of plasma cleaning. For graphene, 2 min is usually good enough. I have observed that long plasma cleaning recipes, especially for graphene, can lead to extremely large ( $\sim 500 \mu\text{m}$ ) flakes. However, these flakes are often strongly adhered to the substrate and are hard to pick up. 2 min is a compromise between cleanliness and the ability to pick up graphene flakes.
6. While the plasma cleaning is happening, prepare the tape. For graphene, I use Flaggy XL graphite flakes. For hBN, I use crystals from NIMS in Japan.
  - Peel off a 5–6 inch long piece of tape. Prepare handles on the ends of the tape by gluing part of the tape to itself.
  - Spread a large piece of graphite or crystals of hBN on one end of the tape.
  - Press and peel parts of the tape 5–6 times so that the exfoliated crystals are spread evenly across the tape.
  - Using two new pieces of tape, glue this mother tape on top of the lab bench.

- Prepare a daughter tape identical in length to the mother tape. Press the daughter tape on the mother tape. The idea behind preparing a daughter tape is to ensure that when the tape is pressed on the chip, the bottom surface of the flake is freshly cleaved and has never encountered tape. Since the bottom surface of hBN flakes sees the graphene and is one of the crucial interfaces in a stack, we ensure the cleanliness of that interface.
7. After plasma cleaning, bring the chips back to the fume hood. Turn on the hot plate to 90 °C.
  8. Peel off the daughter tape slowly from the mother tape. I peel slowly at almost a 180° angle from the mother tape.
  9. Inside the fume hood, press the daughter tape on the Si pieces. I use my fingers and an aluminum block to press the tape on the chips.
  10. Press the tape along with the chips on the hot plate. Make sure to press the tape on the hot plate to ensure that the chips are in direct contact with the hot plate.
  11. Heat the chips for 2 min. After 2 min, let the chips cool down on the metallic surface of the fume hood for another 2 min.
  12. Peel off the tape slowly while holding the chip down with tweezers.
  13. Make a scratch mark at the bottom left corner with a diamond scribe. You can blow dry any dust created by the scribing process. This mark will help us align the chip in subsequent stacking processes.
  14. The chips are now ready for searching.

## D.2 Searching for flakes

I use the automated search algorithm implemented in the flake finder software developed by Zack Gomez, building on earlier work by Jan-Lucas Uslu. The search algorithm runs on the Leica automated microscope.

## D.3 Stacking

I use PC stamps on PDMS domes developed by Albert Nazeeri or PC pillars developed by Steven Tran, Marisa Hocking, and others.

1. Set the stage temperature to 70 °C. For pillar stamps, the pickup temperature is often higher, closer to 95 °C. (If you see hBN picking up partially in the subsequent steps, increase the

temperature. Partial pickup at colder temperatures often leads to wrinkling or cracking of flakes.) Place the chip containing the top hBN on the stage and turn on the chip vacuum. Use the microscope to locate the flake on the chip.

2. Place the stamp on the transfer station and turn on the stamp vacuum. Adjust the position of the stamp so that the “circle of light” defined by the PDMS dome is roughly centered on the flake of interest.
3. Lower the stamp until the surface of the dome is a few hundred  $\mu\text{m}$  from the surface of the flake. You can also set the stamp stage height directly to 9 mm, at which point the stamp is close enough to the chip to begin a slow downward descent.
4. Approach the flake in steps of 1  $\mu\text{m}$ . Around 8.4–8.6 mm stage height, you should see interference fringes. At this point, we start a thermal roll-on. Check the PID settings and ensure the max output is limited to 20 %. This is to ensure that the temperature setpoint is reached slowly without significant overshoots. Set the temperature to about 5 °C above the current chip temperature.
5. Retract in steps of 100 nm. If the stamp adhesion to the flake is good enough to peel the flake off the substrate, the flake is picked up and it loses its characteristic color set by the  $\text{SiO}_2$  substrate. If the flake does not pick up, you can try raising the stage temperature in steps of 5 °C.

### D.3.1 Design principles for good hybrid stacks

1. Ideally, choose the sizes of the flakes so that top hBN > bottom hBN > graphene >  $\text{WSe}_2$ . The general principle is to pick up each subsequent flake after the top hBN using only flakes, instead of a combination of flake and stamp. The differential adhesion between picking up with the stamp and picking up with the flake on the stamp often leads to cracks and wrinkles.
2. When routing traces over wrinkles, increase the width of the trace to over 3  $\mu\text{m}$ . Avoid any nearby sharp corners when going over wrinkles. Otherwise, the deposited Nb layer will spall independent of the thickness of the wrinkle.
3. Round the corners of liftoff patterns. For fine patterns, set the radius to 0.5  $\mu\text{m}$ . For intermediate traces, set the radius to 1  $\mu\text{m}$ . For larger patterns, the rounding is optional, but you can set it to 5  $\mu\text{m}$ . For all traces over a vdW flake, rounding is important. It is not important in regions where the trace is directly on the Si substrate.
4. Add a 50 nm bias to the mesa pattern when preparing the CAD file in BEAMER. This will ensure that there are no single-gated regions beyond the actual outline of the top gate.

5. When blow drying solvents using the N<sub>2</sub> gun, keep the N<sub>2</sub> flow perpendicular to the chip. Avoid blowing from the side, as the stack can occasionally wrinkle or contacts can delaminate.
6. Use isolated flakes on the exfoliation chip. If you are going to use non-isolated flakes, use a cleanup stamp to pick up the unwanted flakes first. Non-isolated flakes in proximity to the main stack can often interfere with the meltdown process and might cause cracks or wrinkling in the stack of interest.

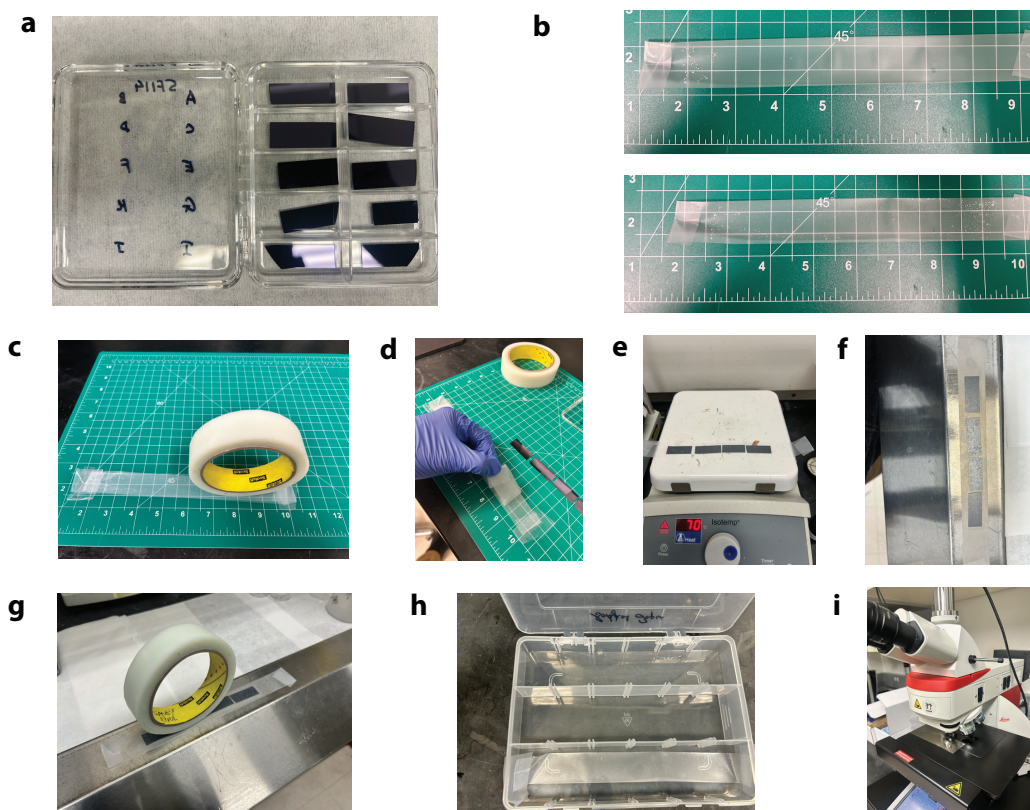


Figure D.1: **Process flow for flake exfoliation.** (a) 90 nm SiO<sub>2</sub> chips diced from a fresh wafer. I use 12-compartment boxes from Ted Pella to store diced chips. (b) Top panel shows hBN crystals put on the left side of the tape. Bottom panel shows hBN crystals now exfoliated across the tape after 5–6 join and peel operations. (c) Daughter tape pressed on the mother tape using a tape roll. (d) Daughter tape being peeled from the mother tape. I peel the tape slowly ( $\sim$ cm per second) at an obtuse angle. (e) Daughter tape pressed on freshly plasma cleaned chips and put on the hot plate at 90°C. (f) Daughter tape cooling down with the chips on the metallic part of the fume hood frame. (g) Using a roll of tape to press down the daughter tape on the chips after the cooling process in the previous step. (h) hBN mother tape stored in a plastic box for future use. The mother tape can be reused for another 2–3 exfoliations. (i) Chips with exfoliated flakes set up for scanning on the automated Leica microscope.

## Appendix E

# Nanofabrication Recipes

In this appendix, I list common nanofabrication recipes that I have optimized on tools in the shared facilities of nano@stanford.

### E.1 Etching

#### E.1.1 O<sub>2</sub> etch for graphite

**Tool:** *NPC Oxford RIE*

Table [E.1](#) shows the parameters for a weak oxygen etch recipe with a variable number of cycles (denoted as  $N$  in the table). Each cycle consists of a 30-second pure O<sub>2</sub> etch followed by a 60-second cooldown. When used with  $N = 1$ , the same recipe can be used for descumming post development, typically prior to a deposition step. Fig. [E.1](#) shows the effect of this etch on a multilayer graphene flake after one cycle. The etch rate is  $\approx 1.5$  nm, or about 5 layers, per cycle.

Table E.1: **Plasma etch recipe: O<sub>2</sub> descum with cooldown step.**

| Parameter              | O <sub>2</sub> descum | Cooldown |
|------------------------|-----------------------|----------|
| Strike pressure        | 100 mTorr             | —        |
| DC bias min            | 20 V                  | —        |
| Ramp rate              | 10                    | —        |
| Pressure               | 10 mTorr              | —        |
| O <sub>2</sub> flow    | 40 sccm               | —        |
| CHF <sub>3</sub> flow  | 0 sccm                | —        |
| RF power               | 20 W                  | —        |
| Time                   | 30 s                  | 60 s     |
| Repeat                 | $N$ cycles            | —        |
| DC bias (measured)     | 118 V                 | —        |
| Valve angle (measured) | 23°                   | —        |

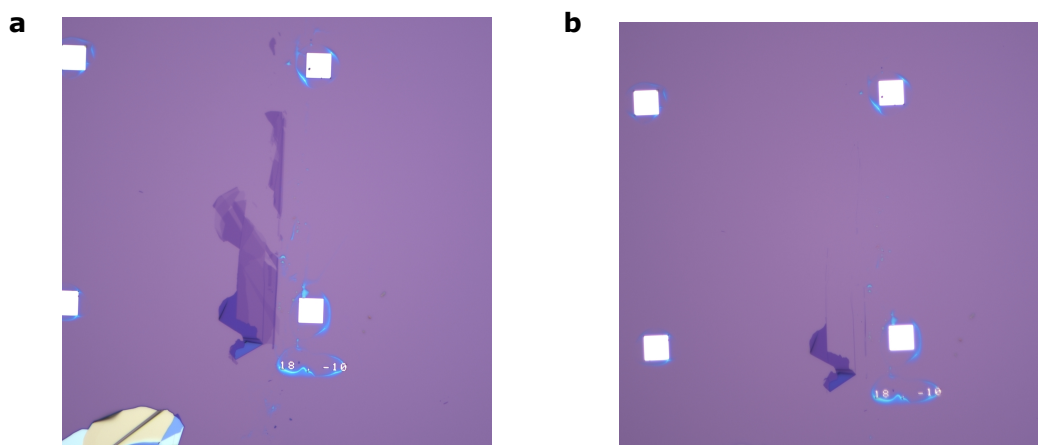


Figure E.1: **Effect of the O<sub>2</sub> etch on multilayer graphene.** (a) A multilayer graphene flake prior to the O<sub>2</sub> etch. (b) The same flake exposed to one cycle of the O<sub>2</sub> etch. A minimum of 5 layers of graphene ( $\approx 1.5$  nm) are etched.

### E.1.2 CHF<sub>3</sub>/O<sub>2</sub> mesa and edge contact etch

**Tool:** NPC Oxford RIE

Table E.2 shows the parameters for the CHF<sub>3</sub>/O<sub>2</sub> recipe with a variable number of cycles (denoted as  $N$  in the table), typically used for mesa etching. The first descum is used for cleaning resist residue



after development, while the last descum does an overall cleanup and removes any fluorinated resist. When using this recipe prior to contact deposition, do only the O<sub>2</sub> descum and one cycle of CHF<sub>3</sub>/O<sub>2</sub>, and do not do any final descum. Skipping the last O<sub>2</sub> descum step is critical, as depositing metal on fluorinated graphene edges from the CHF<sub>3</sub>/O<sub>2</sub> etch gives much lower contact resistances than those terminated by the O<sub>2</sub> descum step. The hBN etch rate for the CHF<sub>3</sub>/O<sub>2</sub> recipe is about 8–9 nm per cycle. The graphite etch rate is very slow, about 1–2 monolayers per cycle.

Table E.2: **Plasma etch recipe: O<sub>2</sub> descum, cycled CHF<sub>3</sub> etch with cooldown, and final O<sub>2</sub> descum.**

| Parameter             | O <sub>2</sub> descum | CHF <sub>3</sub> /O <sub>2</sub> etch | Cooldown           | O <sub>2</sub> descum |
|-----------------------|-----------------------|---------------------------------------|--------------------|-----------------------|
| Strike pressure       | 100 mTorr             | 150 mTorr                             | —                  | 100 mTorr             |
| DC bias min           | 20 V                  | 20 V                                  | —                  | 20 V                  |
| Ramp rate             | 10                    | 10                                    | —                  | 10                    |
| Pressure              | 10 mTorr              | 150 mTorr                             | —                  | 10 mTorr              |
| O <sub>2</sub> flow   | 40 sccm               | 5 sccm                                | —                  | 40 sccm               |
| CHF <sub>3</sub> flow | 0 sccm                | 40 sccm                               | —                  | 0 sccm                |
| RF power              | 20 W                  | 50 W                                  | —                  | 20 W                  |
| Time                  | 30 s                  | 30 s                                  | 60 s               | 30 s                  |
| Repeat                | no                    | yes ( $\times N$ )                    | yes ( $\times N$ ) | no                    |
| DC bias (measured)    | 119 V                 | 136 V                                 | —                  | —                     |

### E.1.3 CF<sub>4</sub> selective etch

**Tool:** *NPC Oxford RIE*

The CF<sub>4</sub> recipe etches hBN very quickly ( $\sim 3 \text{ nm s}^{-1}$ ) but stops completely on graphene. Note that this recipe can also fluorinate the resist, which can fall back onto the chip when dissolved in acetone/IPA. Therefore, except for making contacts, this recipe is not good for etching mesas unless combined with explicit O<sub>2</sub> descums, which can potentially etch the fluorinated resist.

Table E.3: **Plasma etch recipe: CF<sub>4</sub> etch with cooldown step.**

| Parameter              | CF <sub>4</sub>    | Cooldown |
|------------------------|--------------------|----------|
| Strike pressure        | 150 mTorr          | —        |
| DC bias min            | 20 V               | —        |
| Ramp rate              | 10                 | —        |
| Pressure               | 150 mTorr          | —        |
| O <sub>2</sub> flow    | 0 sccm             | —        |
| CF <sub>4</sub> flow   | 40 sccm            | —        |
| RF power               | 15 W               | —        |
| Time                   | 30 s               | 60 s     |
| Repeat                 | yes ( $\times 1$ ) | —        |
| DC bias (measured)     | 50 V               | —        |
| Valve angle (measured) | 11°                | —        |

**E.1.4 XeF<sub>2</sub> hBN etch****Tool:** *Xactix etcher in SNF*

XeF<sub>2</sub> etches both Si and hBN very aggressively. One cycle of the following recipe can easily etch 25–30 nm of hBN.

Table E.4: **XeF<sub>2</sub> etch recipe.**

| Parameter  | Value  |
|------------|--------|
| Pressure   | 3 Torr |
| Time/cycle | 30 s   |
| # cycles   | 3      |

**E.1.5 NbTiN etch — fluorine chemistry****Tool:** *NPC Oxford-RIE*

Table E.5: **ICP plasma etch recipe: O<sub>2</sub> descum, CF<sub>4</sub>/O<sub>2</sub>/Ar etch, and final O<sub>2</sub> descum, with cooldown steps.**

| Parameter              | O <sub>2</sub> descum | Cooldown | CF <sub>4</sub> /O <sub>2</sub> /Ar etch | Cooldown | O <sub>2</sub> descum |
|------------------------|-----------------------|----------|------------------------------------------|----------|-----------------------|
| Strike pressure        | 100 mTorr             | —        | 100 mTorr                                | —        | 100 mTorr             |
| DC bias min            | 20 V                  | —        | 20 V                                     | —        | 20 V                  |
| Ramp rate              | 10                    | —        | 10                                       | —        | 10                    |
| Pressure               | 100 mTorr             | —        | 5 mTorr                                  | —        | 100 mTorr             |
| O <sub>2</sub> flow    | 50 sccm               | —        | 5 sccm                                   | —        | 50 sccm               |
| Ar flow                | 0 sccm                | —        | 10 sccm                                  | —        | 0 sccm                |
| CF <sub>4</sub> flow   | 0 sccm                | —        | 50 sccm                                  | —        | 0 sccm                |
| Power                  | 20 W                  | —        | 20 W                                     | —        | 20 W                  |
| Time                   | 60 s                  | 60 s     | 160 s                                    | 60 s     | 60 s                  |
| Repeat                 | No                    | —        | —                                        | —        | No                    |
| DC bias (measured)     | 96 V                  | —        | 125 V                                    | —        | 93 V                  |
| Valve angle (measured) | 12°                   | —        | 42°                                      | —        | 13°                   |

### E.1.6 NbTiN etch — chlorine chemistry

**Tool:** *Ox-gen in SNF*

The following recipe etches about 30 nm of NbTiN/Si, where the NbTiN thickness is about 10 nm.

Table E.6: **ICP plasma etch recipe: O<sub>2</sub> descum, Cl<sub>2</sub>/BCl<sub>3</sub> etch, and final O<sub>2</sub> descum, with cooldown steps.**

| Parameter                              | O <sub>2</sub> descum | Cooldown | Cl <sub>2</sub> /BCl <sub>3</sub> etch | Cooldown | O <sub>2</sub> descum |
|----------------------------------------|-----------------------|----------|----------------------------------------|----------|-----------------------|
| Pressure                               | 10 mTorr              | —        | 4 mTorr                                | —        | 10 mTorr              |
| O <sub>2</sub> flow                    | 40 sccm               | —        | 0 sccm                                 | —        | 40 sccm               |
| Cl <sub>2</sub> /BCl <sub>3</sub> flow | 0 sccm                | —        | 20/5 sccm                              | —        | 0 sccm                |
| ICP power                              | 100 W                 | —        | 100 W                                  | —        | 100 W                 |
| RF power                               | 10 W                  | —        | 20 W                                   | —        | 10 W                  |
| Time                                   | 30 s                  | 60 s     | 120 s                                  | 60 s     | 30 s                  |
| DC bias (measured)                     | 0 (ICP-only)          | —        | 150–160 V <sup>a</sup>                 | —        | 0 (ICP-only)          |

<sup>a</sup>Oscillating; tuned to ~200 V during the last 30–40 s.

## E.2 Deposition

### E.2.1 Cr/Au normal contacts

**Tool:** *KJL evaporator*

Table E.7: **Electron-beam evaporation log: Cr/Au (5/75 nm) on the KJL evaporator.**

| Parameter            | Value                      |
|----------------------|----------------------------|
| Pressure (pre-load)  | $2.4 \times 10^{-7}$ Torr  |
| LL pressure at load  | $9.7 \times 10^{-5}$ Torr  |
| Pressure (post-load) | $3.0 \times 10^{-7}$ Torr  |
| Ti clean             | 100 nm at 1 Å/s            |
| Pressure after clean | $1.5 \times 10^{-7}$ Torr  |
| Metal 1              | Cr                         |
| Rate                 | 1 Å/s                      |
| Thickness            | 5 nm                       |
| Deposition current   | 69.4 mA                    |
| Wait?                | no                         |
| Pressure             | $2.4 \times 10^{-7}$ Torr  |
| Metal 2              | Au                         |
| Rate                 | 3 Å/s                      |
| Thickness            | 75 nm                      |
| Deposition current   | 114 mA                     |
| Wait?                | no                         |
| Pressure             | —                          |
| Liftoff              | acetone 15 min, spray, IPA |

### E.2.2 NbTiN sputtering

**Tool:** *Lesker2 in SNF*

The following recipe deposits 10.8 nm of NbTiN.

Table E.8: **Reactive magnetron sputter deposition recipe for NbTiN.**

| Parameter                  | Chamber conditioning      | Deposition                |
|----------------------------|---------------------------|---------------------------|
| LL pressure at load        | —                         | $1 \times 10^{-5}$ Torr   |
| Chamber pressure post load | $1.7 \times 10^{-7}$ Torr | $1.7 \times 10^{-7}$ Torr |
| Ignition pressure          | 15 mTorr                  | 15 mTorr                  |
| Power/voltage (Ti)         | 150 W / 356 V             | 150 W / 356 V             |
| Power/voltage (Nb)         | 200 W / 321 V             | 200 W / 322 V             |
| Deposition pressure        | 15 mTorr                  | 15 mTorr                  |
| Burn-in                    | 120 s                     | 120 s                     |
| Deposit                    | 300 s                     | 250 s                     |
| MFC ratio                  | 11 %                      | 11 %                      |
| Ar flow                    | —                         | 94.5 sccm                 |
| N <sub>2</sub> flow        | —                         | 10.4 sccm                 |
| Substrate bias             | 100 W / 520 V             | 525 V                     |

### E.2.3 Ti/Nb/Al superconducting contacts

**Tool:** *KJL2 evaporator*

Table E.9: **E-beam deposition recipe: Ti/Nb/Al trilayer with static oxidation.** Source chamber/sample chamber pressures given as PC2/PC1 in Torr.

| Parameter                 | Value                                       |
|---------------------------|---------------------------------------------|
| Holder                    | flat, Kapton on all 4 sides                 |
| Pump-down time            | overnight                                   |
| PC2/PC1                   | $1.3 \times 10^{-7}$ / $7.7 \times 10^{-8}$ |
| Ti getter                 | yes, 1 kÅ at 2 Å/s                          |
| PC2/PC1 (pre-dep)         | $6.3 \times 10^{-8}$ / $2.9 \times 10^{-8}$ |
| Ti thickness/rate/current | 3 nm, 1 Å/s, 49.3 mA                        |
| PC2/PC1 pressure          | $6.4 \times 10^{-8}$ / $3 \times 10^{-8}$   |
| Nb thickness/rate/current | 7 nm (9.2 nm), 10 Å/s, 260 mA               |
| Nb shutter delay          | 30 s                                        |
| PC2/PC1 pressure          | $6.2 \times 10^{-8}$ / $3.6 \times 10^{-8}$ |
| Al thickness/rate/current | 40 nm, 1 Å/s, 34 mA                         |
| PC2/PC1 pressure          | $1.2 \times 10^{-7}$ / $8.3 \times 10^{-8}$ |
| Static oxidation          | 1000 mTorr, 180 s                           |

## Appendix F

# Fabrication Checklists

### F.1 Superconducting resonator fab for frustrated magnet devices

#### Superconductor deposition

**Tool:** *Lesker2 in SNF*

- ☐ Clean chip in acetone with weak sonication for 1 min
- ☐ Clean chip in isopropanol with weak sonication for 1 min
- ☐ Blow dry using N<sub>2</sub>
- ☐ Deposit NbTiN using Lesker2

#### Resonator patterning using direct-write photolithography

**Tool:** *ML3*

- ☐ Clean chip in acetone with weak sonication for 1 min
- ☐ Clean chip in isopropanol with weak sonication for 1 min
- ☐ Blow dry using N<sub>2</sub>
- ☐ Spin AZ1512 at 5000 RPM for 1 min
- ☐ 5 min bake at 110 °C

- ☐ Write using ML3 at  $0.6\text{ }\mu\text{m}$  resolution and  $120\text{ mJ cm}^{-2}$  dose. Use real-time focus=ON using DLP, quality=Super, real-time focus correction=Best, reduce stage speed=ON. Total write takes about 22 min.
- ☐ Develop for 1 min in MF-319 and stop development with a double DI water rinse
- ☐ Inspect under optical microscope and save images

**NbTiN etch****Tool:** *NPC Oxford RIE*

- ☐ Chamber clean using  $\text{SF}_6/\text{O}_2$  recipe for 5 min
- ☐ Etch using  $\text{O}_2$  descum +  $\text{SF}_6/\text{Ar}$  etch recipe (300 W, 30 sccm  $\text{SF}_6$ , 3 sccm Ar, 10 mTorr, 90 s); note down DC bias and valve angle
- ☐ Inspect under optical microscope and save images
- ☐ Remove resist in acetone for 3 min followed by isopropanol for 2 min

**F.2 Superconducting fab for hybrid devices: superconducting circuit layers**

I have diced the Si wafer with the NbTiN superconductor into mother chips of size  $15 \times 15\text{ mm}$ . These chips already have Ti/Pt markers corresponding to  $5 \times 5\text{ mm}$  chips. Each  $5 \times 5\text{ mm}$  chip is then used to fabricate a single hybrid device. In order to speed up the fabrication process, I process the entire mother chip at the same time and write the superconducting circuit layer as a  $3 \times 3$  grid of  $5 \times 5\text{ mm}$  chips.

**Resonator definition write****Tool:** *Raith EBPG*

- ☐ Remove resist from the marker step by soaking the mother chip in Remover PG overnight at  $90^\circ\text{C}$
- ☐ Sonicate at medium power (dial position = 5, NPC cleanroom) in a large beaker of acetone for 2–3 min
- ☐ Sonicate at medium power (dial position = 5, NPC cleanroom) in a large beaker of IPA for 2–3 min
- ☐ Spin CSAR 62.09 at 5000 RPM



- ☐ 5 min bake at 150 °C
- ☐ Prepare GPF file with BEAMER: 20 nA for resonator pattern and 50 nA for DC lines and vortex traps, dose =  $470 \mu\text{C cm}^{-2}$ , beam step size = 10 nm for resonator, beam step size = 15 nm for DC lines and vortex traps, 200  $\mu\text{m}$  write field for resonator, 500  $\mu\text{m}$  write field for DC lines and vortex traps
- ☐ Develop with cold (0 °C) o-xylene for 60 s and stop development in IPA for 30 s
- ☐ Inspect under optical microscope and save images

**Etch****Tool:** *Ox-gen in SNF*

- ☐ Chamber clean using  $\text{BCl}_3/\text{SF}_6/\text{O}_2$  recipe for 6 min
- ☐ Etch using  $\text{Cl}_2/\text{BCl}_3$  recipe for 2 min
- ☐ Inspect under optical microscope and save images
- ☐ Spin resist (typically the thickest version of PMMA you can spin) for protection

**Dice****Tool:** *DISCO wafer saw*

- ☐ Glue the mother chip on a carrier wafer with a combination of GE varnish and PMMA glue; I bake the chip for 2–3 min at 50 °C. Good adhesion to the carrier wafer is critical as the small  $5 \times 5 \text{ mm}$  chips tend to fly away during the dicing operation
- ☐ Dice using the wafer saw with a pitch of 5 mm. Blade diameter = 55.58 mm, width and exposure as shown on the blade box; feed speed = 2 mm/s
- ☐ Detach diced chips from the carrier wafer and soak in Remover PG overnight at 90 °C
- ☐ Do a final clean on individual chips by sonicating in acetone and IPA sequentially for 2–3 min each

**F.3 Hybrid JJ devices**

Hybrid JJ devices consist of an SNS JJ with monolayer or multilayer graphene proximitized by superconducting contacts, along with a galvanic connection to a superconducting resonator.

**Contact write****Tool:** *Raith EBPG*

- ☐ Spin EL6 at 5000 RPM
- ☐ 2 min bake at 180 °C, cooldown for 10–20 s
- ☐ Spin 950 A3 at 5000 RPM
- ☐ 2 min bake at 180 °C
- ☐ Prepare GPF file with BEAMER: beam step size = 1 nm; PEC is on, short-range correction is on, write field = 1040  $\mu\text{m}$
- ☐ Write pattern at 0.5 nA (fine contacts) and 10 nA (filters), dose = 1400  $\mu\text{C cm}^{-2}$
- ☐ Develop with cold (5 °C) 1:3 water:IPA for 60 s
- ☐ Inspect under optical microscope and save images

**Contact etch****Tool:** *NPC Oxford RIE*

- ☐ Chamber clean using  $\text{SF}_6/\text{O}_2$  recipe for 5 min
- ☐ Etch using  $\text{O}_2$  descum +  $\text{CF}_4$  etch recipe; note down DC bias and valve angle
- ☐ Inspect under optical microscope and save images

**Contact deposition****Tool:** *KJL2*

- ☐ Mount the sample using Kapton tape on all 4 sides on the flat sample holder
- ☐ Load the sample holder and let it pump overnight
- ☐ Record PC2/PC1 pressure
- ☐ Run a Ti getter recipe (1 kÅ, 2 Å/s)
- ☐ Record PC2/PC1 pressure
- ☐ Run a Ti deposition (3 nm, 1 Å/s)
- ☐ Record PC2/PC1 pressure

- ☐ Run a Nb deposition (20 nm, 10 Å/s) with extended shutter delay of 30 s
- ☐ Record PC2/PC1 pressure
- ☐ Run an Al deposition (40 nm, 1 Å/s)
- ☐ Record PC2/PC1 pressure
- ☐ Run a static oxidation recipe (1 Torr, 180 s)
- ☐ Vent
- ☐ Inspect under optical microscope and save images
- ☐ Liftoff in acetone for 60 min, followed by IPA rinse. Blow dry gently and only in a vertical direction
- ☐ Inspect under optical microscope and save images

**Mesa write**

**Tool:** *Raith EBPG*

- ☐ Spin 950 A6 at 5000 RPM
- ☐ 5 min bake at 180 °C
- ☐ Prepare GPF file with BEAMER: beam step size = 1 nm; PEC is on, short-range correction is on, write field = 1040  $\mu\text{m}$
- ☐ Write pattern at 1 nA, dose = 1600  $\mu\text{C cm}^{-2}$
- ☐ Develop with cold (5 °C) 1:3 water:IPA for 60 s
- ☐ Inspect under optical microscope and save images

**Mesa etch**

**Tool:** *NPC Oxford RIE*

- ☐ Chamber clean using  $\text{SF}_6/\text{O}_2$  recipe for 5 min
- ☐ Etch using  $\text{O}_2$  descum +  $\text{CHF}_3/\text{O}_2$  etch recipe; note down DC bias and valve angle. I run over 10 cycles of the  $\text{CHF}_3/\text{O}_2$  etch step to fully etch the stack and also the superconducting back gate
- ☐ Inspect under optical microscope and save images

- ☐ Remove resist with 3 min acetone and 1 min IPA
- ☐ Inspect under optical microscope and save final images

## F.4 vdW fab for hybrid devices with superconducting gates

### Contact write

**Tool:** *Raith EBPG*

- ☐ Spin EL6 at 5000 RPM
- ☐ 2 min bake at 180 °C, cooldown for 10–20 s
- ☐ Spin 950 A3 at 5000 RPM
- ☐ 2 min bake at 180 °C
- ☐ Prepare GPF file with BEAMER: beam step size = 1 nm; PEC is on, short-range correction is on, write field = 1040  $\mu\text{m}$
- ☐ Write pattern at 0.5 nA (fine contacts) and 10 nA (filters), dose = 1400  $\mu\text{C cm}^{-2}$
- ☐ Develop with cold (5 °C) 1:3 water:IPA for 60 s
- ☐ Inspect under optical microscope and save images

### Contact etch

**Tool:** *NPC Oxford RIE*

- ☐ Chamber clean using  $\text{SF}_6/\text{O}_2$  recipe for 5 min
- ☐ Etch using  $\text{O}_2$  descum +  $\text{CF}_4$  etch recipe; note down DC bias and valve angle
- ☐ Inspect under optical microscope and save images

### Contact deposition

**Tool:** *KJL2*

- ☐ Mount the sample using Kapton tape on all 4 sides on the flat sample holder
- ☐ Load the sample holder and let it pump overnight
- ☐ Record PC2/PC1 pressure
- ☐ Run a Ti getter recipe (1 kÅ, 2 Å/s)

- ☐ Record PC2/PC1 pressure
- ☐ Run a Ti deposition (3 nm, 1 Å/s)
- ☐ Record PC2/PC1 pressure
- ☐ Run a Nb deposition (10 nm, 10 Å/s) with extended shutter delay of 30 s
- ☐ Record PC2/PC1 pressure
- ☐ Run an Al deposition (30 nm, 1 Å/s)
- ☐ Record PC2/PC1 pressure
- ☐ Run a static oxidation recipe (1 Torr, 180 s)
- ☐ Vent
- ☐ Inspect under optical microscope and save images
- ☐ Liftoff in acetone for 60 min, followed by IPA rinse. Blow dry gently and only in a vertical direction
- ☐ Inspect under optical microscope and save images

### Top gate write

**Tool:** *Raith EBPG*

- ☐ Spin EL6 at 5000 RPM
- ☐ 2 min bake at 180 °C, cooldown for 10–20 s
- ☐ Spin 950 A3 at 5000 RPM
- ☐ 2 min bake at 180 °C
- ☐ Prepare GPF file with BEAMER: beam step size = 1 nm; PEC is on, short-range correction is on, write field = 1040 μm
- ☐ Write pattern at 0.5 nA (fine features) and 10 nA (coarse features), dose = 1400 μC cm<sup>-2</sup>
- ☐ Develop with cold (5 °C) 1:3 water:IPA for 60 s
- ☐ Inspect under optical microscope and save images

**Top gate descum****Tool:** *NPC Oxford RIE*

- ☐ Chamber clean using  $\text{SF}_6/\text{O}_2$  recipe for 5 min
- ☐ Etch using  $\text{O}_2$  descum; note down DC bias and valve angle
- ☐ Inspect under optical microscope and save images

**Top gate deposition****Tool:** *KJL2*

- ☐ Mount the sample using Kapton tape on all 4 sides on the flat sample holder
- ☐ Load the sample holder and let it pump overnight
- ☐ Record PC2/PC1 pressure
- ☐ Run a Ti getter recipe (1 kÅ, 2 Å/s)
- ☐ Record PC2/PC1 pressure
- ☐ Run a Ti deposition (3 nm, 1 Å/s)
- ☐ Record PC2/PC1 pressure
- ☐ Run a Nb deposition (10 nm, 10 Å/s) with extended shutter delay of 30 s
- ☐ Record PC2/PC1 pressure
- ☐ Run an Al deposition (30 nm, 1 Å/s)
- ☐ Record PC2/PC1 pressure
- ☐ Run a static oxidation recipe (1 Torr, 180 s)
- ☐ Vent
- ☐ Inspect under optical microscope and save images
- ☐ Liftoff in acetone for 60 min, followed by IPA rinse. Blow dry gently and only in a vertical direction
- ☐ Inspect under optical microscope and save images

**Mesa write****Tool:** *Raith EBPG*

- ☐ Spin 950 A6 at 5000 RPM
- ☐ 5 min bake at 180 °C
- ☐ Prepare GPF file with BEAMER: beam step size = 1 nm; PEC is on, short-range correction is on, write field = 1040  $\mu\text{m}$
- ☐ Write pattern at 1 nA, dose = 1600  $\mu\text{C cm}^{-2}$
- ☐ Develop with cold (5 °C) 1:3 water:IPA for 60 s
- ☐ Inspect under optical microscope and save images

**Mesa etch****Tool:** *NPC Oxford RIE*

- ☐ Chamber clean using  $\text{SF}_6/\text{O}_2$  recipe for 5 min
- ☐ Etch using  $\text{O}_2$  descum +  $\text{CHF}_3/\text{O}_2$  etch recipe; note down DC bias and valve angle. I run over 10 cycles of the  $\text{CHF}_3/\text{O}_2$  etch step to fully etch the stack and also the superconducting back gate
- ☐ Inspect under optical microscope and save images
- ☐ Remove resist with 3 min acetone and 1 min IPA
- ☐ Inspect under optical microscope and save final images

**F.5 vdW fab for hybrid devices with dual-graphite gates****Contact write****Tool:** *Raith EBPG*

- ☐ Spin EL6 at 5000 RPM
- ☐ 2 min bake at 180 °C, cooldown for 10–20 s
- ☐ Spin 950 A6 at 5000 RPM
- ☐ 2 min bake at 180 °C

- ☐ Prepare GPF file with BEAMER: beam step size = 1 nm; PEC is on, short-range correction is on, write field = 1040  $\mu\text{m}$
- ☐ Write pattern at 0.5 nA (fine contacts) and 10 nA (filters), dose = 1400  $\mu\text{C cm}^{-2}$
- ☐ Develop with cold (5 °C) 1:3 water:IPA for 60 s
- ☐ Inspect under optical microscope and save images

**Contact etch**

**Tool:** *NPC Oxford RIE*

- ☐ Chamber clean using SF<sub>6</sub>/O<sub>2</sub> recipe for 5 min
- ☐ Etch top graphite using O<sub>2</sub> descum. Choose an appropriate number of cycles to completely etch the top graphite
- ☐ Etch top hBN using O<sub>2</sub> descum + CF<sub>4</sub> etch recipe; note down DC bias and valve angle
- ☐ Inspect under optical microscope and save images

**Contact deposition**

**Tool:** *KJL2*

- ☐ Mount the sample using Kapton tape on all 4 sides on the flat sample holder
- ☐ Load the sample holder and let it pump overnight
- ☐ Record PC2/PC1 pressure
- ☐ Run a Ti getter recipe (1 kÅ, 2 Å/s)
- ☐ Record PC2/PC1 pressure
- ☐ Run a Ti deposition (3 nm, 1 Å/s)
- ☐ Record PC2/PC1 pressure
- ☐ Run a Nb deposition (7 nm, 10 Å/s) with extended shutter delay of 30 s
- ☐ Record PC2/PC1 pressure
- ☐ Run an Al deposition (40 nm, 1 Å/s)
- ☐ Record PC2/PC1 pressure
- ☐ Run a static oxidation recipe (1 Torr, 180 s)



- ☐ Vent
- ☐ Inspect under optical microscope and save images
- ☐ Liftoff in acetone for 60 min, followed by IPA rinse. Blow dry gently and only in a vertical direction
- ☐ Inspect under optical microscope and save images

**Mesa write****Tool:** *Raith EBPG*

- ☐ Spin 950 A6 at 5000 RPM
- ☐ 5 min bake at 180 °C
- ☐ Prepare GPF file with BEAMER: beam step size = 1 nm; PEC is on, short-range correction is on, write field = 1040  $\mu\text{m}$
- ☐ Write pattern at 1 nA, dose = 1600  $\mu\text{C cm}^{-2}$
- ☐ Develop with cold (5 °C) 1:3 water:IPA for 60 s
- ☐ Inspect under optical microscope and save images

**Mesa etch****Tool:** *NPC Oxford RIE*

- ☐ Chamber clean using  $\text{SF}_6/\text{O}_2$  recipe for 5 min
- ☐ Etch using  $\text{O}_2$  descum +  $\text{CHF}_3/\text{O}_2$  etch recipe; note down DC bias and valve angle. I run over 10 cycles of the  $\text{CHF}_3/\text{O}_2$  etch step to fully etch the stack and also the back gate
- ☐ Inspect under optical microscope and save images
- ☐ Remove resist with 3 min acetone and 1 min IPA
- ☐ Inspect under optical microscope and save final images

**Top gate liberation write****Tool:** *Raith EBPG*

- ☐ Spin EL6 at 5000 RPM
- ☐ 2 min bake at 180 °C, cooldown for 10–20 s

- ☐ Spin 950 A3 at 5000 RPM
- ☐ 2 min bake at 180 °C
- ☐ Prepare GPF file with BEAMER: beam step size = 1 nm; PEC is on, short-range correction is on, write field = 1040  $\mu\text{m}$
- ☐ Write pattern at 1 nA, dose = 1400  $\mu\text{C cm}^{-2}$
- ☐ Develop with cold (5 °C) 1:3 water:IPA for 60 s
- ☐ Inspect under optical microscope and save images

**Top gate liberation**

**Tool:** *NPC Oxford RIE*

- ☐ Chamber clean using  $\text{SF}_6/\text{O}_2$  recipe for 5 min
- ☐ Etch using appropriate number of  $\text{O}_2$  descum cycles; note down DC bias and valve angle
- ☐ Inspect under optical microscope and save images

## Appendix G

# Microwave probe for VTI

The factory-made cryogenic probe for the variable temperature insert (VTI) in the lab had a few pitfalls: the entire probe was structurally weak as it consisted of a single long stainless steel tube which buckled under very little force; the dc wiring was unfiltered and limited to 32 lines; no high-frequency lines were installed; and the sample thermometer and heater were not coupled through a single copper block, which made precise temperature-dependent measurements unreliable. In order to resolve these issues, I decided to build a new cryogenic probe with the following requirements:

1. Maintain structural integrity during sample loading and unloading
2. Carry microwave coaxial cables with K connectors to enable experiments up to 40 GHz
3. Couple the sample heater and thermometer strongly to each other on a single Cu block
4. Allow mounting of custom PCBs with microwave connectors and on-chip filters

### G.1 Structural design

The main drawback of the old VTI probe was its structural weakness. The old probe consisted of a single hollow stainless steel tube which, being nearly 2 m long, could buckle and bend considerably during sample loading and unloading. To give the probe a stiff structure, I switched to using four stainless steel tubes (1/4", SS316, McMaster-Carr) located near the periphery of the probe. Spacer plates placed at approximately equal spacings along the length of the probe hold these four rods in place. Fig. [G.1\(b\)](#) shows these spacer plates. A set of four set screws on each of these spacer plates clamps the plate onto the steel rods. These spacer plates are machined from 6061 Al alloy and contain four threaded holes on the circumference for #2-56 UNC set screws. These set screws bite into the stainless steel rods and hold the assembly together. I used six of these spacers to hold the probe together. They also act as radiation baffles which block room-temperature radiation

from reaching the lower, i.e. colder, parts of the probe. These spacers also contain slots near the circumference to pass both the dc and microwave wiring. I wrapped Kapton tape on the sides of the baffles to prevent these wires from slipping out and also to serve as a buffer between the wires and the bore of the VTI when the probe is loaded.

The top of the probe is a KF50-to-KF25 reducer cross (P102658, Ideal Vacuum). One KF25 port carries a tee with two Fischer connectors for dc measurements. Another port has a 9-pin feedthrough on an NW25 KF flange (9C-K25, Accu-Glass Products, Inc.). Internal wiring to the thermometer was done with Lake Shore Quad-Twist 32 AWG phosphor-bronze cryogenic wire, soldered onto the thermometer leads and connected to the back side of the 9C-K25 feedthrough with 26–30 AWG T1 gold contacts from Accu-Glass.

The stainless steel rods terminate on a Cu fixture at the cold end of the probe (Figs. G.1(d) and (e)). A Lake Shore heater cartridge (HTR-25-100) is placed into a cylindrical cavity in this fixture. A Cu cold finger is screwed to the bottom part of the Cu fixture and contains several through holes for mounting thermometers and sample carriers.

## G.2 Microwave hardware

2.92 mm hermetic connectors (x4, C7093 from Centric RF) are attached to the top flange of the KF50 cross. This flange was machined from 6061 Al and has specially designed D-shaped holes to hold the hermetic connectors in place. Bulkhead adapters (x8, C7088 2.92 mm bulkhead from Centric RF) were used at the Al spacer plates to connect cryogenic attenuators (XMA Corp.) for thermalization of the microwave cables (Fig. G.1(c)). For the actual microwave cables, we used 2.92 mm male to 2.92 mm male cable assemblies made from 0.086" semi-rigid stainless steel coax cable from Flexi RF. To connect the bulkhead connectors to the mini-SMP connectors on the sample PCBs, we use 2.92 mm to mini-SMP cable assemblies from Centric RF. These cables have a plastic outer jacket which, to our knowledge, has not degraded in cryogenic conditions.

## G.3 Microwave-only PCB

Fig. G.1(d) shows a microwave-only PCB attached to the cold finger of the probe. This PCB is attached to a Cu block and screwed onto the end of the cold finger. The Cu block has two slots such that it can be loaded in two orientations, with the magnetic field in-plane or out-of-plane of the sample. The PCB has four mini-SMP connectors (18S141-40ML5, Rosenberger) connected to on-chip waveguides terminated by bondpads for bonding to samples. A Cu lid with mouse-hole ports can optionally be used to block out any low-frequency cavity modes [227]. The PCB was designed using KiCad software and manufactured by OSH Park. We took special care to make sure the waveguides on the PCB have an impedance close to  $50\,\Omega$  and placed fencing vias on the ground

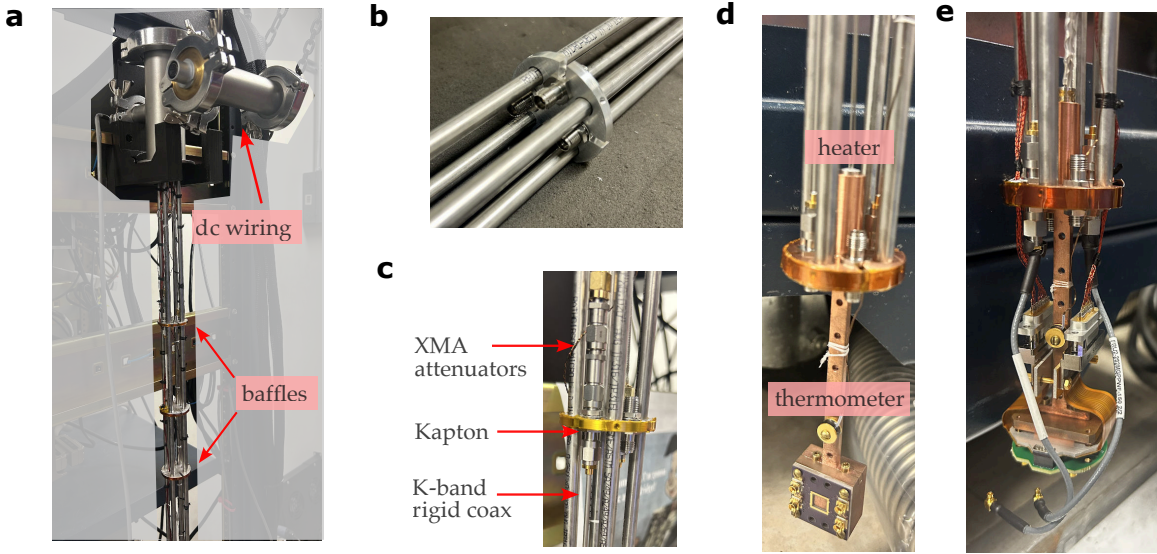


Figure G.1: **Custom microwave probe for the VTI.** (a) Overview of the assembled probe. The four stainless steel support rods carry the dc wiring and coaxial lines down to the sample stage; radiation baffles along the length reduce the heat load from room temperature. (b) Spacer plate holding the four peripheral support rods. A set screw at each rod clamps the plate in place, giving the probe its stiffness against buckling during loading and unloading. (c) Microwave lines: K-band semi-rigid coax with XMA cryogenic attenuators. The spacer plates are wrapped in Kapton tape to prevent the wiring from scratching the inside of the VTI bore. (d) RF sample carrier. The heater and thermometer are mounted on a single copper block connected directly to the sample mount, ensuring the measured temperature closely tracks the sample temperature. (e) DC + RF sample carrier with a custom PCB installed.

plane to prevent cross-talk between microwave lines.

## G.4 Cryogenic dc wiring and PCB

A hybrid PCB capable of both dc and RF measurements has been designed and optimized by my colleagues Karna Morey and Bingcheng Suo. Refer to their notes for further details (Fig. G.1(e)). There are 48 dc lines soldered from the top of the probe to 25-pin micro-D connectors usually placed near the bottom Cu fixture. These micro-D connectors plug onto an equivalent set of micro-D connectors soldered onto a Kapton flexible PCB. The Kapton PCB acts as the motherboard for the sample carrier and a separate daughterboard is used for individual samples.

## G.5 Hardware summary

Table G.1 lists the hardware used to construct the probe, with part numbers and suppliers where applicable.

Table G.1: **Hardware used in the VTI probe.** Custom parts were machined by the SLAC machine shop from the indicated material. OFHC stands for oxygen free high conductivity.

| Component                                                                    | Part number      | Supplier      | Qty. |
|------------------------------------------------------------------------------|------------------|---------------|------|
| <i>Structural and vacuum</i>                                                 |                  |               |      |
| KF50 to KF25 reducer cross                                                   | P102658          | Ideal Vacuum  | 1    |
| Top flange with 2.92 mm connector holes                                      | custom (6061 Al) | machine shop  | 1    |
| Thin-wall 1/4" SS316 rods                                                    | —                | McMaster-Carr | 4    |
| Top breakout plate                                                           | custom (6061 Al) | machine shop  | 1    |
| Spacer plates / radiation baffles                                            | custom (6061 Al) | machine shop  | 6    |
| Bottom breakout plate                                                        | custom (OFHC Cu) | machine shop  | 1    |
| Cold finger                                                                  | custom (OFHC Cu) | machine shop  | 1    |
| Sample holder                                                                | custom (OFHC Cu) | machine shop  | 1    |
| Sample lid                                                                   | custom (OFHC Cu) | machine shop  | 1    |
| #2 set screws, 1/8" and 3/8" (brass, SS316)                                  | —                | McMaster-Carr | —    |
| <i>Microwave</i>                                                             |                  |               |      |
| 2.92 mm hermetic connector                                                   | C7093            | Centric RF    | 4    |
| 2.92 mm bulkhead adapter (F-F)                                               | C7088            | Centric RF    | 8    |
| Cryogenic attenuator                                                         | —                | XMA Corp.     | 4    |
| 0.086" semi-rigid SS coax assembly,<br>2.92 mm (M) to 2.92 mm (M), dc–40 GHz | —                | Flexi RF      | 4    |
| 2.92 mm to mini-SMP cable assembly                                           | —                | Centric RF    | 4    |
| Mini-SMP PCB connector                                                       | 18S141-40ML5     | Rosenberger   | 4    |
| Microwave-only PCB                                                           | custom           | OSH Park      | 1    |
| <i>Thermometry and dc wiring</i>                                             |                  |               |      |
| Heater cartridge (100 W, 25 $\Omega$ )                                       | HTR-25-100       | Lake Shore    | 1    |
| Cernox thermometer                                                           | —                | Lake Shore    | 1    |
| Quad-Twist 32 AWG phosphor-bronze wire                                       | WQT-32           | Lake Shore    | —    |
| 9-pin feedthrough on NW25 KF flange                                          | 9C-K25 (100016)  | Accu-Glass    | 1    |
| 9-pin air-side cable assembly                                                | 100020           | Accu-Glass    | 1    |
| Gold contacts, female, 26–30 AWG T1                                          | 100181           | Accu-Glass    | 1    |
| 10-pin circular receptacle                                                   | MSW01A12-10P-SR  | Milspecwest   | 1    |
| Micro-D 25-pin connectors                                                    | —                | —             | 2    |

# Appendix H

## Pink Fridge

This chapter captures useful information about one of the dilution fridges in the lab, known as the Pink Fridge. It is a cryogen-free system (CF-CS81-1600M) built by Leiden Cryogenics. See Praveen Sriram’s thesis from the Goldhaber-Gordon group for an extended discussion of the DC probe wiring, filtering, and sample holders used in this fridge [232].

### H.1 Grounding

The fridge is grounded at a single point to the shielded room wall using a copper braid. When this copper braid is removed, the fridge should be electrically isolated from the shielded room wall. When debugging ground loops, start by checking if the fridge is isolated from the wall with the copper braid removed. The usual culprits for creating ground loops in this fridge are the fridge/probe heaters. Other electrical connections such as thermometry, vacuum gauges, the probe motor, the OVC mini turbo, the OVC gauge, and the probe control laptop do not pass ground to the fridge. Vacuum bellows which touch the top plate of the fridge can also cause a ground loop. Strategically placed foam and painters’ tape prevent the vacuum bellows from touching the fridge frame. The active vibration isolation also creates a ground loop when the top surface of the isolators touches the Al plate from which the fridge is suspended. We have placed cleanroom wipes at this isolator–top-plate interface to prevent this particular ground loop. A Megger ground current detector can be placed around the grounding strap to monitor the drain current. Typically, a drain current of 20  $\mu\text{A}$  is seen in the known best grounding configuration of the fridge.

### H.2 Electron Thermometry

I have used mesoscopic Cr/Au wires (meso-wires) fabricated by my colleague Bingcheng Suo for calibrating the electron temperature in this fridge. Josh Folk’s group gave us valuable guidance on

using these wires for electron thermometry. The basic idea is to rely on the effect of electron–electron interactions on the resistance of a diffusive quasi-1D wire. The change in resistance  $\Delta R(T)$  at mK temperatures for these wires is given by

$$\frac{\Delta R(T)}{R} \approx 3.126 \frac{R}{R_q} \frac{L_T}{L} = \frac{C}{\sqrt{T}} \quad (\text{H.1})$$

where  $L$  is the length of the wire,  $L_T = \sqrt{\frac{\hbar D}{k_B T}}$  is the thermal length with  $D$  the diffusion constant, and  $R_q = \frac{h}{e^2}$  [233]. Quantitatively, the fractional change in resistance from 500 mK to 50 mK is about 0.1–0.5 %.

The meso-wires were fabricated by e-beam lithography and e-beam deposition of Cr/Au (8 nm/4 nm) on a SiO<sub>2</sub>/Si substrate. Al wire was used for wire-bonding from the chip to the PCB. Anecdotaly, wire-bonding with Au wires leads to even better thermalization of the meso-wire, but since wire-bonding with Au wires typically requires elevated temperatures during the bonding process to make strong bonds, I have not used Au wires for bonding. Meso-wires typically have a resistance of about 30 k $\Omega$  at cryogenic temperatures when measured in a 4-terminal configuration. To extract the small changes in resistance, we use a lock-in amplifier set to a long time constant (10 s) to current bias the meso-wire and measure the voltage difference. The bias current is set to 100–200 pA so that the excitation energy  $eV$  across the meso-wire does not substantially exceed  $k_B T$  at the lowest temperature of the fridge.

Fig. H.1(a) shows the measured change in the meso-wire resistance as a function of  $T_{MC}^{-1/2}$  from 400 mK down to a base temperature of about 50 mK, where  $T_{MC}$  is the temperature of the RuO<sub>x</sub> mixing chamber thermometer on the probe. A weighted linear fit to this data provides the thermometer calibration, which is inverted in Fig. H.1(b) to extract the electron temperature  $T_e$ .



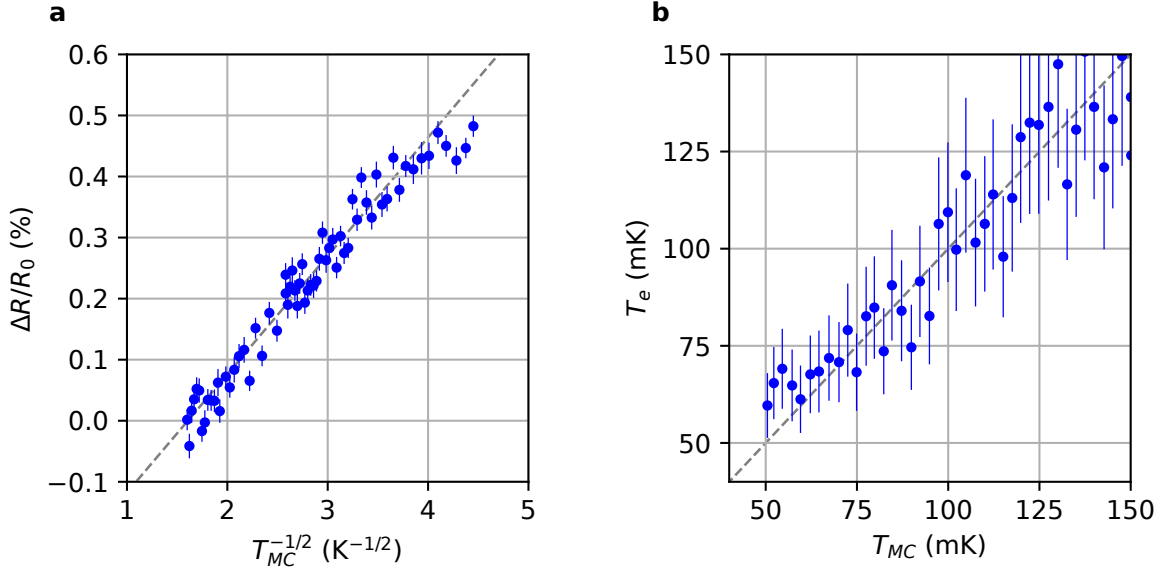


Figure H.1: **Electron thermometry from meso-wire resistance.** (a) Relative change of the meso-wire resistance  $\Delta R/R_0$  as a function of  $T_{MC}^{-1/2}$ , where  $T_{MC}$  is the mixing-chamber temperature. The resistance follows the  $T^{-1/2}$  dependence expected from electron–electron interaction corrections; the dashed line is a weighted linear fit, which serves as the thermometer calibration. (b) Electron temperature  $T_e$  extracted by inverting the calibration in (a), plotted against  $T_{MC}$ . The dashed line marks  $T_e = T_{MC}$ . The electron temperature tracks the mixing-chamber temperature closely down to  $\sim 60$  mK with some saturation from 60 mK to 50 mK, indicating good thermalization of the electrons. Error bars combine the measurement uncertainty of  $\Delta R/R_0$  with the fit-parameter uncertainties.

### H.3 Cryogenic microwave wiring

The cryogenic probe has a click-in plate with SMP connectors at the bottom of the probe. When the probe is inserted into the fridge, the click-in plate connects to SMP connectors inside the fridge located on the mixing chamber plate. The microwave wiring inside this fridge is anchored directly to the fridge plates and is accessible using a breakout on top of the fridge. At the time of writing this thesis, eight cryogenic coax cables are in use. Fig. H.2 shows the wiring diagram for these eight lines, including the attenuation at each temperature stage and the location of the cryogenic amplifiers. Each coax cable inside the fridge has both inner and outer conductors made from a CuNi alloy and was installed by Leiden Cryogenics. The lines typically used for sending microwave signals down are thermalized by varying levels of attenuation anchored at various stages inside the cryostat. Currently, we use two lines as output lines. Line 7 is used primarily for the measurements described in this thesis. It consists of a microwave isolator (Quinstar, 4–8 GHz) at the mixing chamber along with a cryogenic amplifier (Cosmic Microwave, CITLF3) mounted on the lower side of the 4 K plate.

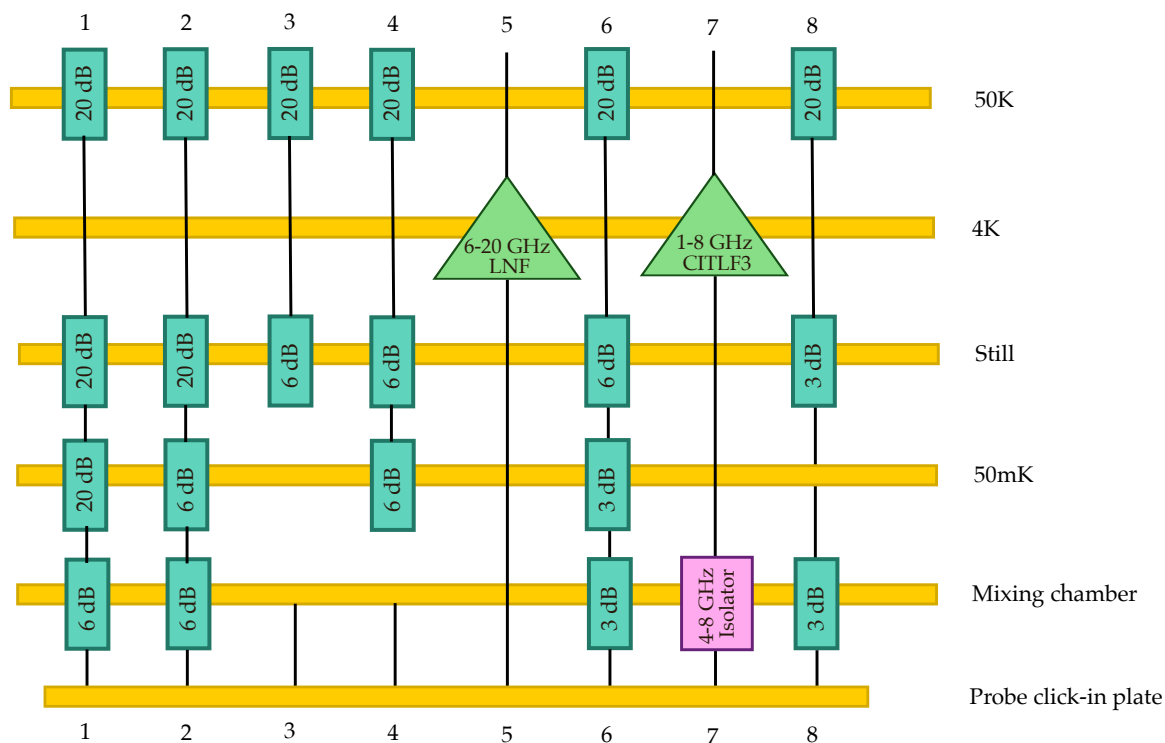


Figure H.2: **Cryogenic microwave wiring.** Wiring diagram of microwave lines 1–8 inside the dilution refrigerator, from the room-temperature feedthroughs down to the probe click-in plate. Input lines (1–4, 6, 8) are attenuated at each temperature stage (XMA cryogenic attenuators, total attenuation distributed as shown) to thermalize the inner conductor and suppress room-temperature noise. Lines 5 and 7 are output lines: line 5 carries a 6–20 GHz low-noise amplifier (Low Noise Factory, LNF-LNC6.20D) at the 4 K stage, and line 7 carries a 1–8 GHz CITLF3 amplifier (Cosmic Microwave Technology) at 4 K with a 4–8 GHz isolator (Quinstar) at the mixing chamber. Lines 2–3 were designed to hold a directional coupler at the mixing-chamber stage, which has since been removed. All coax lines are CuNi or stainless steel. The dc power lines for the amplifiers are not shown.

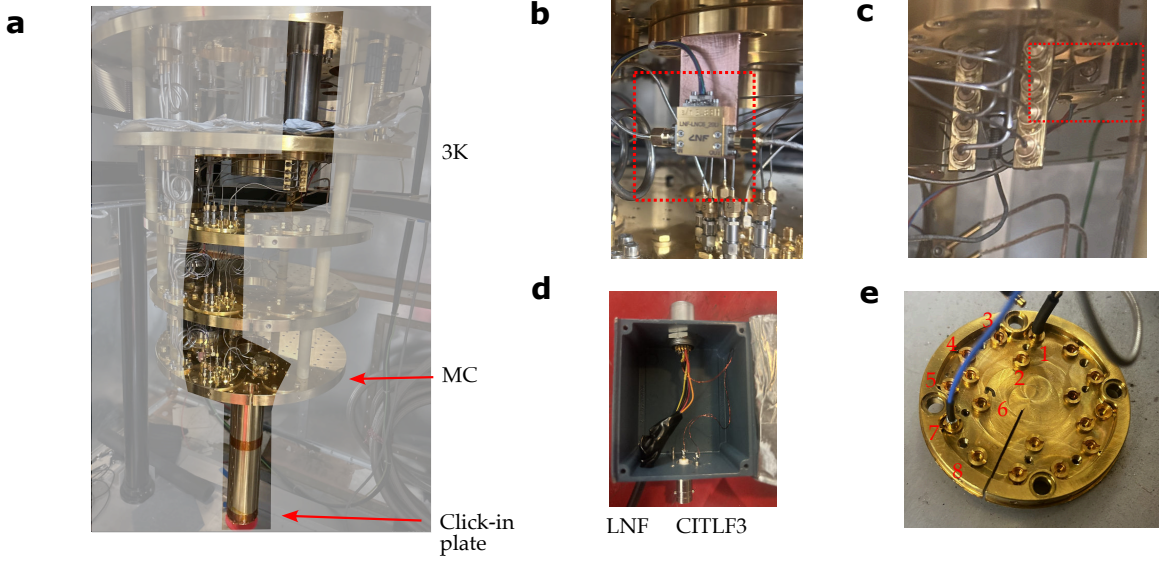


Figure H.3: **Microwave wiring inside the fridge.** (a) Photograph of the fridge with the microwave wiring highlighted, from the 4K stage down to the mixing chamber (MC) and the probe click-in plate. (b) LNF low-noise amplifier (dashed box) mounted at the 4K stage. (c) CITLF3 amplifier (dashed box), also mounted at the 4K stage. (d) Pomona box used to power the two cryogenic amplifiers, with separate connectors for the LNF and CITLF3. (e) Probe click-in plate with microwave lines 1–8 labeled; in this photograph, cables are connected to lines 1 and 7.

The amplifier is powered using a DC breakout located at the 4K plate and is connected through a Fischer connector on top of the fridge (near the fridge thermometry Fischer connector). The CITLF3 takes in 2–3 V of bias voltage and typically draws 15–20 mA. I use a Yokogawa DC source (GS200) to power this amplifier and monitor the drawn current.

The second output line (line 5) carries a Low Noise Factory cryogenic amplifier (LNF-LNC6\_20D), also mounted at the 4K plate, capable of amplifying signals from 6 to 20 GHz (usable down to about 3 GHz before the performance degrades). To power this amplifier, we have power supplies LNF-PS3b and LNF-PBA from Low Noise Factory. The power lines for both amplifiers are connected to the wires inside the fridge through a Pomona box attached via a Fischer connector. In case of any amplifier power-up issues, check the soldering inside the box. Fig. H.3 shows photographs of the microwave wiring inside the fridge, the mounting locations of both cryogenic amplifiers, the Pomona power box, and the probe click-in plate.

## H.4 Room temperature microwave setup

Fig. H.4 shows various parts of the room temperature microwave setup. First, a breakout plate with SMA bulkhead flange adapters (Centric RF, C3125B), connected on one side to the fridge with

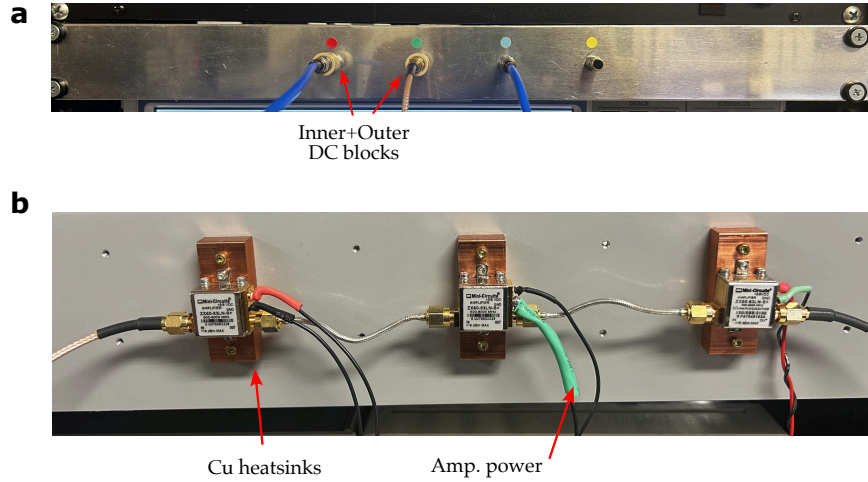


Figure H.4: **Room-temperature microwave electronics.** (a) Breakout panel on the measurement rack. The microwave lines are color-coded, and inner+outer DC blocks (CD9519, Centric RF; 0.01–18 GHz, 0.5 dB insertion loss) are installed at the panel to break ground loops between the fridge and the room-temperature electronics. (b) Room-temperature amplification chain on the output line: three Mini-Circuits ZX60-83LN-S+ low-noise amplifiers (0.5–8 GHz) in series, each mounted on a Cu heatsink for thermal management, with dc power supplied through the labeled wiring.

SMA coax cables (Mini-Circuits, ULC-10FT-SMSM+), is mounted on a standard 19" rack. Since this breakout plate is made out of aluminum, we used plastic mounting screws to isolate the shield of the coax cables from the rack. In order to isolate the DC ground potential carried by the shield of the coax cable from instrumentation such as the VNA or microwave sources, we use inner and outer DC blocks (Centric RF, CD9519) mounted on the breakout plate for each of the SMA connectors. While most scientists working on mesoscopic physics are careful about eliminating ground loops associated with low-frequency transport equipment, we had the additional challenge of isolating high-frequency equipment for the hybrid experiments on vdW heterostructures described in this thesis. These inner and outer DC blocks came in quite handy and keep us from forming unnecessary ground loops.

For  $S_{21}$  measurements, one of the SMA connectors on the breakout is connected to the VNA output. The output line from the fridge goes through a series of three room temperature amplifiers (Mini-Circuits, ZX60-83LN-S+). These amplifiers are mounted on copper blocks (acting as heat sinks) which are screwed onto an aluminum plate attached to the rack. The amplifiers are powered by a low-noise DC power supply from HP with a nominal voltage of 5 V. The output of the amplifier chain is connected back to the input port of the VNA.

For two-tone spectroscopy measurements, an additional power splitter (Mini-Circuits, ZFRSC-123-S+) is attached to the input line. I use a second tunable microwave source, either a second Rohde & Schwarz VNA (ZNL) or an SMB100A microwave signal generator.

## H.5 Hardware summary

Table H.1 lists the microwave and measurement hardware discussed in this chapter, with part numbers and suppliers where applicable.

Table H.1: **Hardware used in the Pink Fridge microwave setup.**

| Component                             | Part number        | Supplier                    |
|---------------------------------------|--------------------|-----------------------------|
| <i>Cryogenic</i>                      |                    |                             |
| CuNi coax lines (installed by Leiden) | —                  | Leiden Cryogenics           |
| Cryogenic attenuators (3/6/20 dB)     | —                  | XMA Corp.                   |
| Low-noise amplifier, 6–20 GHz         | LNF-LNC6_20D       | Low Noise Factory           |
| Low-noise amplifier, 1–8 GHz          | CITLF3             | Cosmic Microwave Technology |
| Isolator, 4–8 GHz                     | —                  | Quinstar                    |
| <i>Amplifier power</i>                |                    |                             |
| LNF power supply                      | LNF-PS3b + LNF-PBA | Low Noise Factory           |
| DC source for CITLF3                  | GS200              | Yokogawa                    |
| Pomona box with Fischer connector     | custom             | —                           |
| <i>Room temperature</i>               |                    |                             |
| SMA bulkhead flange adapter           | C3125B             | Centric RF                  |
| SMA coax cables, fridge to rack       | ULC-10FT-SMSM+     | Mini-Circuits               |
| Inner+outer DC block, 0.01–18 GHz     | CD9519             | Centric RF                  |
| Low-noise amplifier, 0.5–8 GHz        | ZX60-83LN-S+       | Mini-Circuits               |
| Power splitter                        | ZFRSC-123-S+       | Mini-Circuits               |
| Low-noise DC power supply             | —                  | HP                          |
| VNA                                   | ZNL, ZNB8          | Rohde & Schwarz             |
| Microwave signal generator            | SMB100A            | Rohde & Schwarz             |

# Appendix I

## Miscellaneous Fabrications

### I.1 Coax straightening tool

For the new RF VTI probe, I had decided to use stainless steel semi-rigid coax cables of length 1.2 m. Unfortunately, the vendor decided to use packaging which caused the cables to acquire a curved shape. Together with Aaron Sharpe, I made a tool which utilizes five bearings to straighten out the cable, shown in Fig. I.1. The cable is clamped in a 3D-printed vise and drawn through the bearings, which removes the curvature (Fig. I.1(b)). All parts except the actual bearings were 3D printed, and the drawings for these parts are located at 00 - Misc/3d printed coax straightener/ (path is relative to my google drive folder).

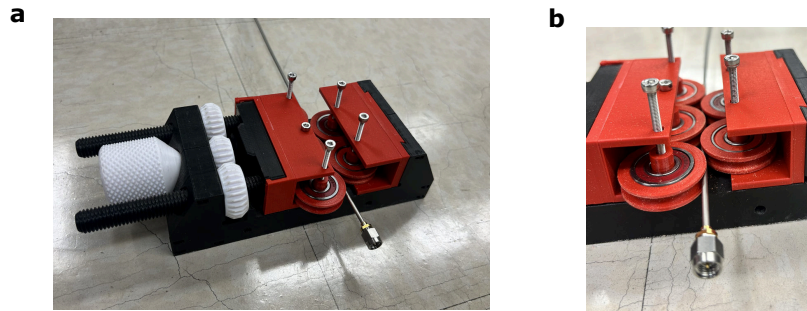


Figure I.1: **3D-printed coax straightening tool.** (a) Overview of the tool. The semi-rigid coax cable is clamped in the 3D-printed vise (white) and fed through a series of five bearings mounted on the 3D-printed frame. (b) Close-up of the bearings. The cable passes through the grooves of the bearings, which are arranged in two offset rows; drawing the cable through the bearings removes the curvature acquired during shipping. All parts except the bearings were 3D printed.

## I.2 LN<sub>2</sub> trap holder for baking

Most dilution fridges include a carbon powder trap which needs to be baked every few months to release adsorbed impurity gases (nitrogen, water vapor, hydrocarbon oils). These traps consist of closed cylinders with hollow tubes soldered on top, which can be attached to vacuum bellows through KF flanges. The aspect ratio of these traps is often such that they cannot stand vertically upright on their own, and groups typically rest them against a wall while cleaning the traps. The traps are heated with a heat gun while being pumped on with a vacuum pump. While this process works fine, I used to be annoyed at placing the traps precariously against a wall while using a hot air gun on them. Using a hot air gun also meant that the process needed constant supervision. I therefore designed a trap holder, shown in Fig. I.2, which consists of steel tubes soldered onto a thick steel plate. The tubes keep the traps upright. For heating, heater tape is wrapped around the steel tubes, and a thermocouple is used along with the heater tape to maintain a constant temperature during the process of cleaning the traps.

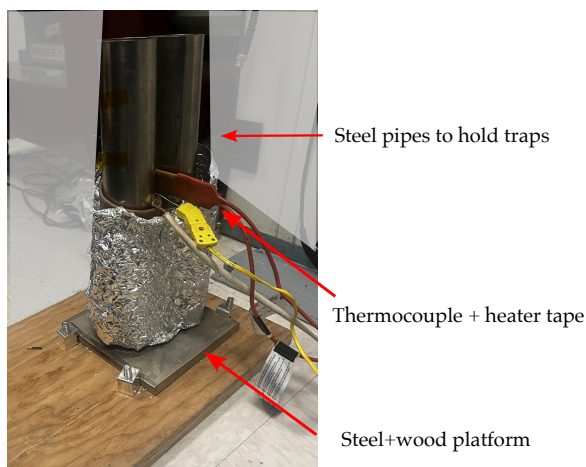


Figure I.2: **Trap holder for baking carbon powder traps.** The traps sit inside steel pipes soldered onto a steel plate, which rests on a wooden platform, keeping the traps vertically upright during baking. Heater tape is wrapped around the steel pipes and covered with aluminum foil; a thermocouple placed under the tape is used with a temperature controller to maintain a constant temperature, so the bake can run without constant supervision.

## Appendix J

# Matplotlib rcParams

I use Python and matplotlib extensively to prepare figures for presentations and papers. I have found myself reinventing the wheel and adjusting minor things like font sizes, line widths, etc. to make publication and presentation quality figures every time I started working on a new project. To save time in the future, the following matplotlib rcParams can be loaded to make presentation-ready and publication-ready figures. Listing [J.1](#) is for presentation figures, with larger fonts and thicker lines suitable for slides. Listing [J.2](#) is for publication figures, with font sizes matched to the typical column width of a journal article.



Listing J.1: matplotlib rcParams for presentation figures

```
rc_params = {
    'xtick.direction': 'in',
    'xtick.top': True,
    'ytick.direction': 'in',
    'ytick.right': True,
    'axes.edgecolor': 'k',
    'axes.labelcolor': 'k',
    'xtick.color': 'k',
    'ytick.color': 'k',
    'figure.facecolor': 'white',
    'font.size': 16,
    'axes.labelsize': 16,
    'legend.title_fontsize': 16,
    'axes.linewidth': 1.5,
    'xtick.major.size': 5,
    'xtick.major.width': 1.5,
    'xtick.minor.size': 2.5,
    'xtick.minor.width': 1.5,
    'ytick.major.size': 5,
    'ytick.major.width': 1.5,
    'ytick.minor.size': 2.5,
    'ytick.minor.width': 1.5,
    'lines.linewidth': 2.5,
    'pdf.fonttype': 42,
    'ps.fonttype': 42,
    'figure.figsize': [3*1.618, 3]
}
plt.rcParams.update(rc_params)
```

Listing J.2: matplotlib rcParams for publication figures

```
scale = 0.56
rc_params = {
    # Font and font sizes
    'font.family': 'sans-serif',
    'font.size': 9,
    'axes.labelsize': 8,
    'axes.titlesize': 8,
    'legend.title_fontsize': 7,
    'legend.fontsize': 7,
    'xtick.labelsize': 7,
    'ytick.labelsize': 7,
    # Ticks
    'xtick.direction': 'in',
    'xtick.top': True,
    'ytick.direction': 'in',
    'ytick.right': True,
    'xtick.major.size': 5*scale,
    'xtick.major.width': 1.5*scale,
    'xtick.minor.size': 2.5*scale,
    'xtick.minor.width': 1.5*scale,
    'ytick.major.size': 5*scale,
    'ytick.major.width': 1.5*scale,
    'ytick.minor.size': 2.5*scale,
    'ytick.minor.width': 1.5*scale,
    # Linewidths
    'axes.linewidth': 1.5*scale,
    'lines.linewidth': 2.5*scale,
    # Font embedding for PDF/PS output
    'pdf.fonttype': 42,
    'ps.fonttype': 42,
}
plt.rcParams.update(rc_params)
```

## Appendix K

# Commonly Used Physical Constants in Uncommon Units

All values have been rounded for quick mental estimates and are good to  $\sim 10\%$ .

| Quantity                                                      | Expression                    | Value                                                   |
|---------------------------------------------------------------|-------------------------------|---------------------------------------------------------|
| <i>Energy and temperature conversions</i>                     |                               |                                                         |
| Thermal energy at 1 K                                         | $k_B \cdot 1 \text{ K}$       | $\sim 86 \text{ } \mu\text{eV}$                         |
| Thermal frequency at 1 K                                      | $k_B \cdot 1 \text{ K}/h$     | $\sim 20 \text{ GHz}$                                   |
| Temperature to Photon Frequency                               | $k_B \cdot 50 \text{ mK}/h$   | $\sim 1 \text{ GHz}$                                    |
| Photon energy at 1 GHz                                        | $h \cdot 1 \text{ GHz}$       | $\sim 4 \text{ } \mu\text{eV}$                          |
| Energy of 1 $\mu\text{eV}$                                    | $1 \text{ } \mu\text{eV}/k_B$ | $\sim 10 \text{ mK}$                                    |
| Room temperature                                              | $k_B \cdot 300 \text{ K}$     | $\sim 26 \text{ meV}$                                   |
| BCS gap for $T_c = 1 \text{ K}$                               | $3.5 k_B T_c$                 | $\sim 300 \text{ } \mu\text{eV} \approx 75 \text{ GHz}$ |
| <i>Magnetic field and flux</i>                                |                               |                                                         |
| Zeeman splitting for $g = 2$                                  | $g\mu_B B$                    | $\sim 120 \text{ } \mu\text{eV}/\text{T}$               |
| Zeeman frequency for $g = 2$                                  | $g\mu_B B/h$                  | $\sim 28 \text{ GHz}/\text{T}$                          |
| Superconducting flux quantum                                  | $\Phi_0 = h/2e$               | $\sim 2 \text{ mT } \mu\text{m}^2$                      |
| Field at $\nu = 1$ for $n = 1 \times 10^{11} \text{ cm}^{-2}$ | $nh/e$                        | $\sim 4 \text{ T}$                                      |
| Magnetic length                                               | $\ell_B = \sqrt{\hbar/eB}$    | $\sim 25 \text{ nm}/\sqrt{B [\text{T}]}$                |
| <i>Transport and Josephson relations</i>                      |                               |                                                         |
| Resistance quantum                                            | $h/e^2$                       | $\sim 26 \text{ k}\Omega$                               |
| Conductance quantum                                           | $e^2/h$                       | $\sim 40 \text{ } \mu\text{S}$                          |
| Josephson voltage–frequency relation                          | $h/2e$                        | $\sim 2 \text{ } \mu\text{V}/\text{GHz}$                |

Table K.1: **Commonly used physical constants in uncommon units.**

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