Unconventional Superconductivity: Mechanisms for Time-Reversal Symmetry Breaking

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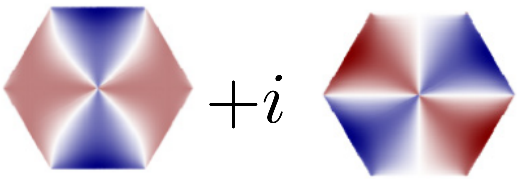
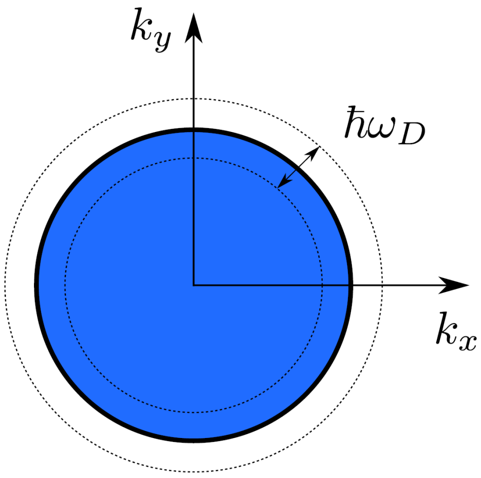


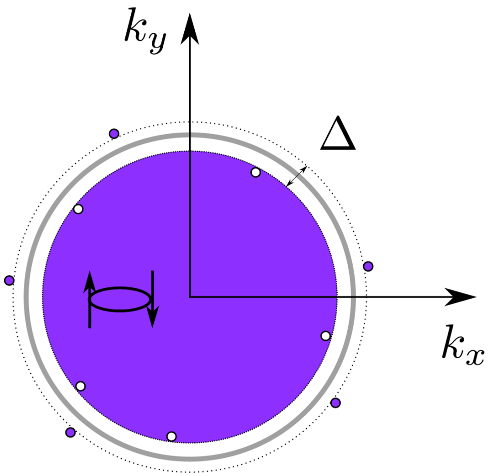
$$\mathrm{d}_{xy} + i d_{x^2-y^2}$$

Superconductivity

- Interactions: Instability of Fermi sea



T>T_c: normal metal, filled Fermi sea



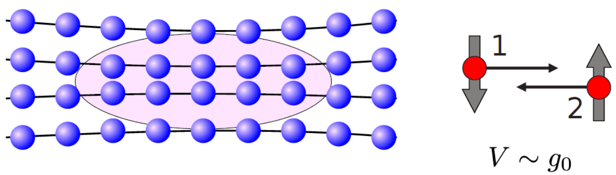
T<T_c gas of Cooper pairs: zero resistivity, Meissner effect, excitation gap

- Order parameter $\Delta_{\mathbf{k}} \sim \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle$ generically complex-valued
- Broken TRSB: complex-valued in any basis

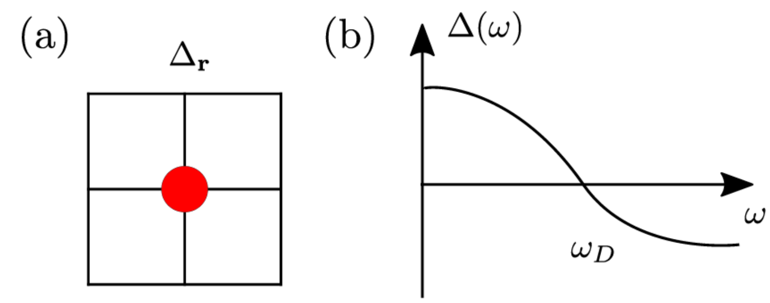
Conventional vs. unconventional superconductivity

- Pairing from phonons

Conventional



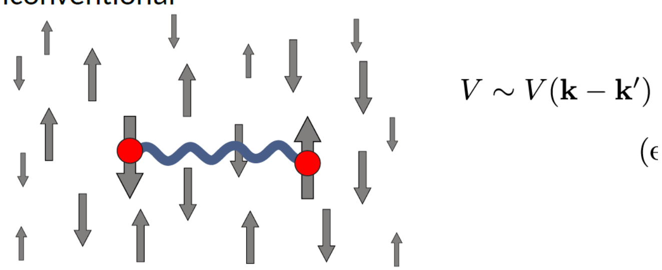
Retarded interaction: electrons avoid repulsive part of Coulomb interaction in time



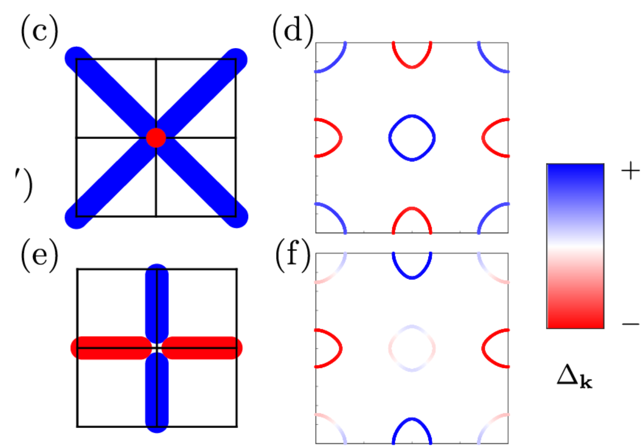
Local order parameter

- Pairing from electronic fluctuations

Unconventional



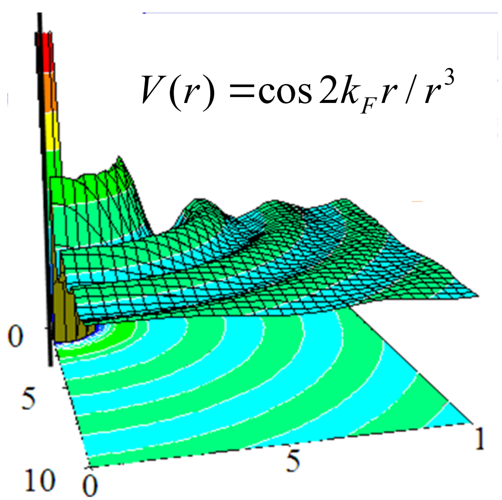
Electrons avoid repulsive part of Coulomb interaction in space rather than time! (Kohn-Luttinger, 1965): Momentum dependent interaction



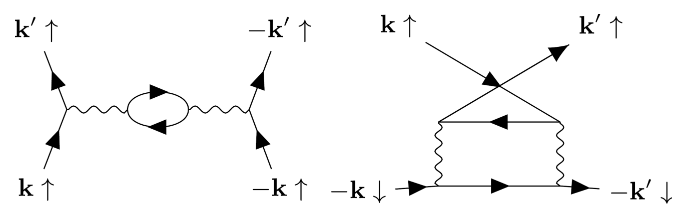
Non-local order parameter: momentum dependent

Pairing from spin fluctuations

- Kohn-Luttinger, 1965



Friedel: Screened interaction



Momentum dependent interaction, repulsive:

$$V(\mathbf{k}-\mathbf{k}') \sim \frac{3}{2}(U + U^2\chi(\mathbf{k}-\mathbf{k}') > 0$$

Spin susceptibility (RPA): peaked at momentum q_0

- BCS gap equation

$$\Delta_{\mathbf{k}}^{s/t} = -\frac{1}{N}\sum_{\mathbf{k}'} V^{s/t}(\mathbf{k},\mathbf{k}')\frac{\Delta_{\mathbf{k}'}^{s/t}}{2E_{\mathbf{k}'}}\tanh\left(\frac{\beta E_{\mathbf{k}'}}{2}\right)$$

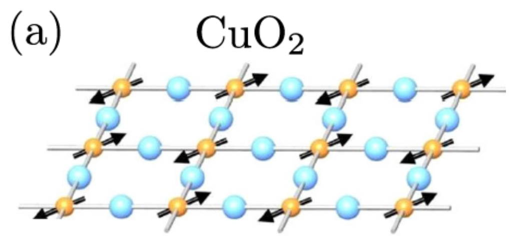
Note: order parameter (matrix) needs to be antisymmetric in all quantum numbers (Pauli principle)

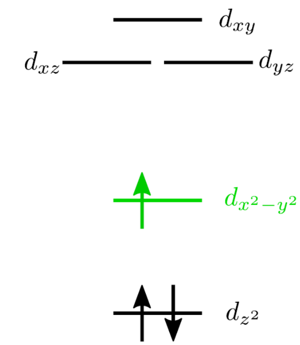
- singlet $\Delta_{\mathbf{k}}^{s} = \Delta_{-\mathbf{k}}^{s}$ $\qquad \chi \sim |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle$
- triplet $\Delta_{\mathbf{k}}^{t} = -\Delta_{-\mathbf{k}}^{t}.$ $\qquad \chi \sim |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle, |\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle$

Rømer, et al., PRB **92**, 104505 (2015)

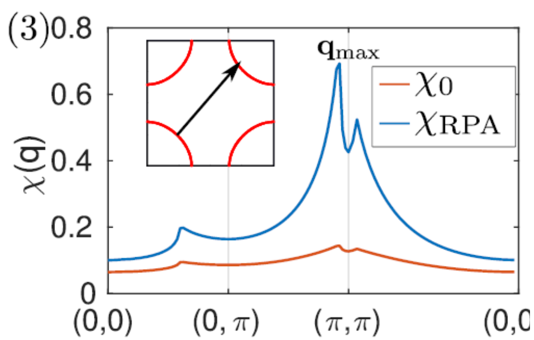
Possible materials (1)

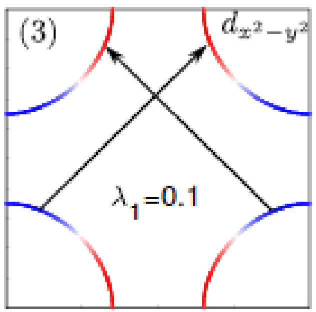
- Cuprates





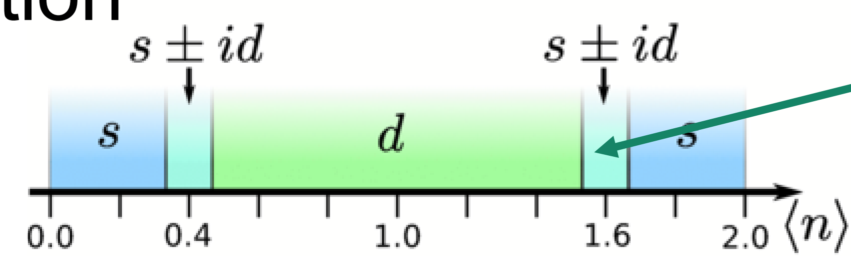
Single band model





single Cu-d orbital

- Phase diagram: Nearest neighbor pairing interaction

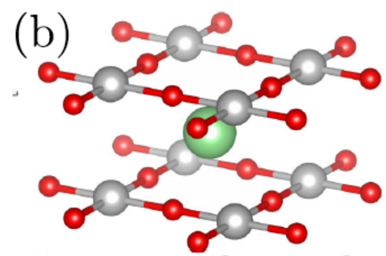


System generically chooses time-reversal symmetry breaking state over nematic state (s+d)

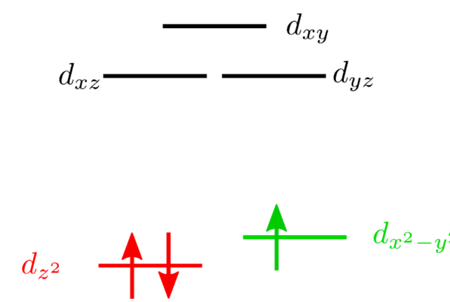
Røising, et al., Phys. Rev. B 109, 054521 (2024)
See also: SHIROKA, Toni, Wednesday

Possible materials (2)

- Nickelates

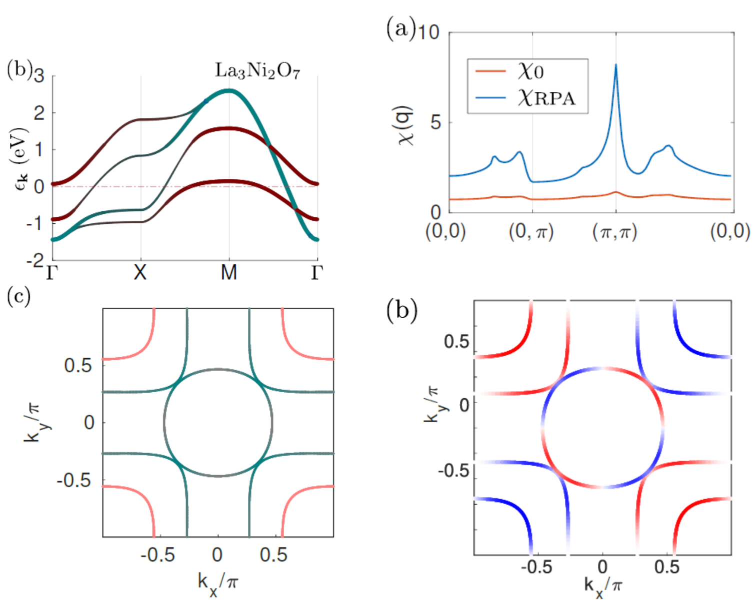


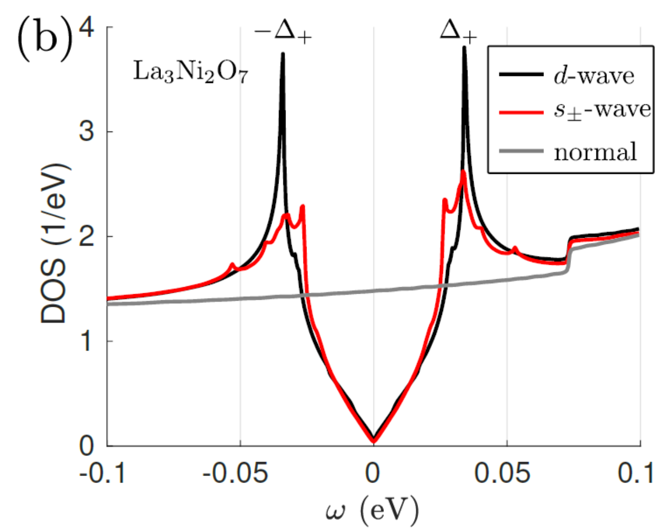
$Nd_{1-x}Sr_xNiO_2$



two Ni d orbitals relevant

Multiband model?!



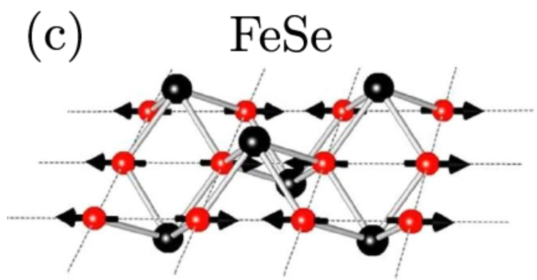


Competing s- and d-wave instabilities
Andreas Kreisel, et al. Phys. Rev. Lett. 129, 077002 (2022)
Frank Lechermann, et al., Phys. Rev. B 108, L201121 (2023)

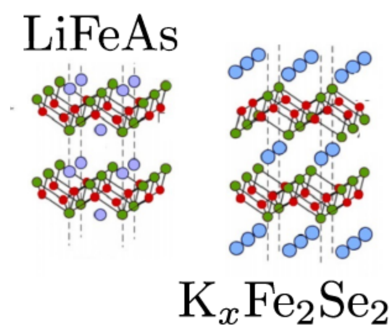
Pairing state cannot be distinguished by spectroscopy / low temperature thermodynamics!

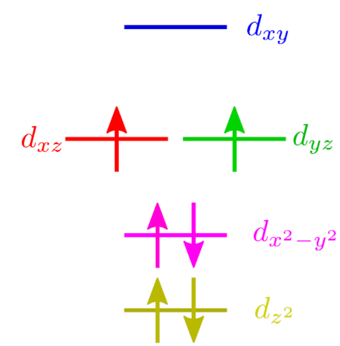
Possible materials (3)

- Fe-based superconductors

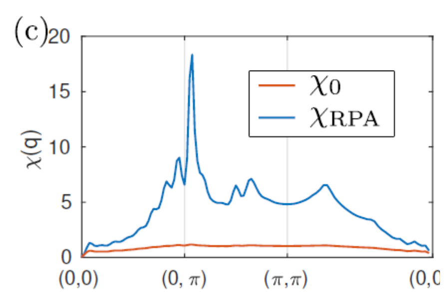


1111, 111, 122, 1122...

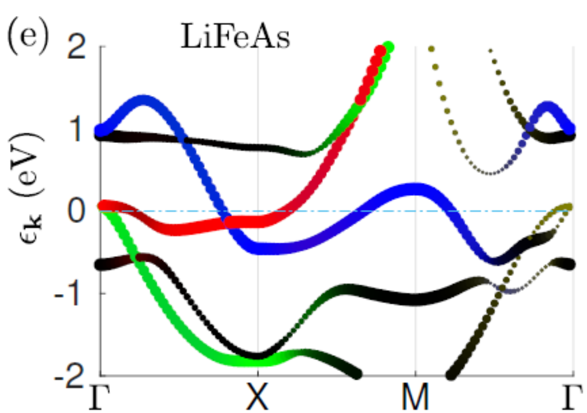




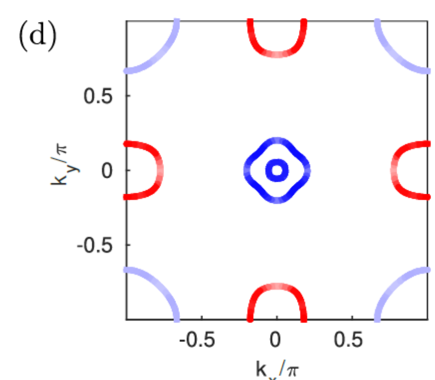
all 5 Fe-d orbitals relevant



Multiband model
+ Hubbard-Kanamouri interaction



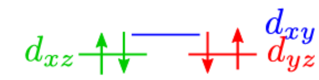
Chi, et al., PRB **94**, 134515 (2016) [LiFeAs]



Dominant instability:
s+/- order parameter

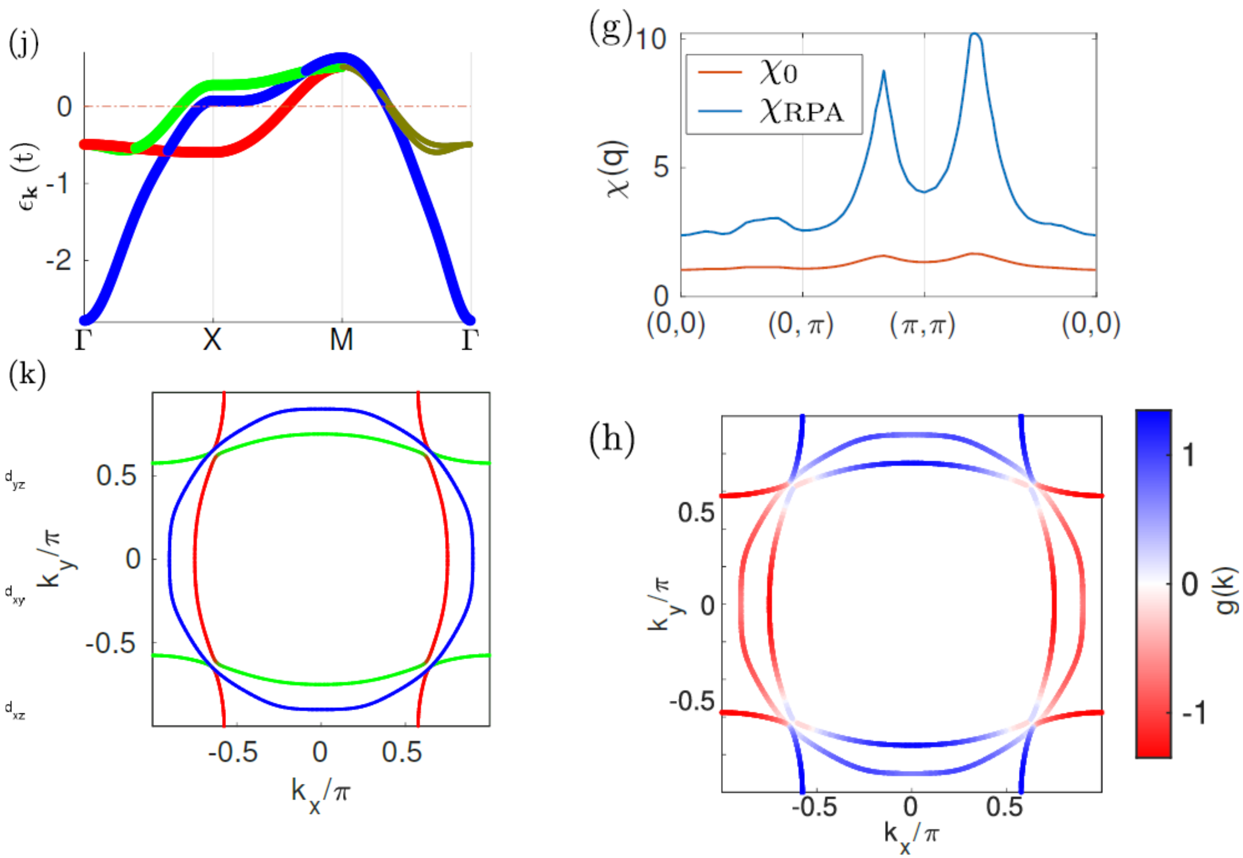
Possible materials (4)

(i) Sr_2RuO_4

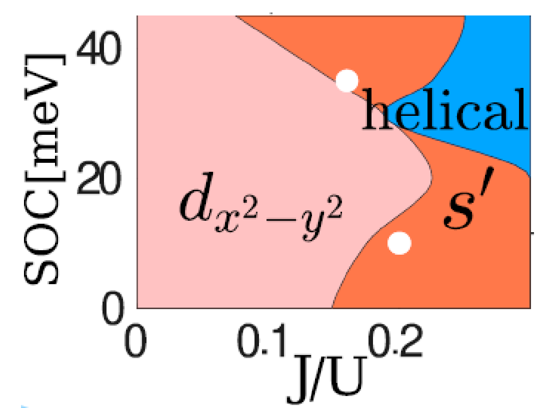


- Sr_2RuO_4

3 Ru-d orbitals relevant



Astrid T. Rømer, et al.,
Phys. Rev. B 102, 054506 (2020)



d-wave instability dominating phase diagram

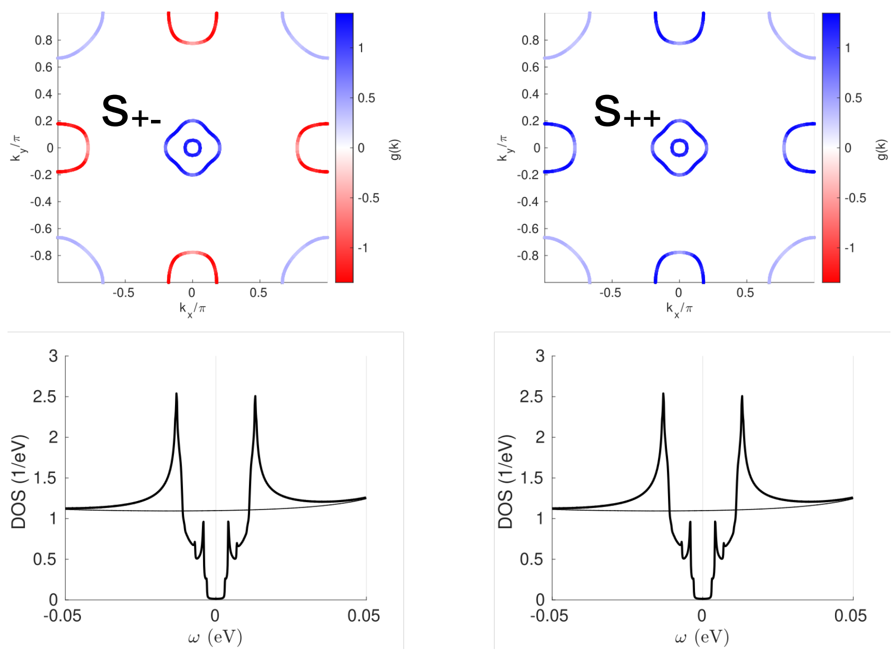
See also: Hans-Henning Klauss

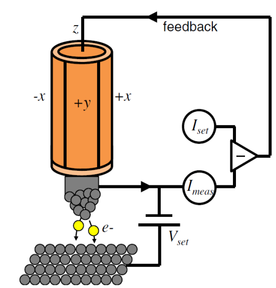
Unconventional superconductivity

- Detecting the nature of the order parameter

$$\Delta_{\mathbf{k}} = |\Delta_{\mathbf{k}}| \exp(i\phi_{\mathbf{k}}) \sim \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle$$

- Phase?





$$E_{\mathbf{k}} = \sqrt{\epsilon_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}}|^2}$$

$$I(V,x,y,z) = -\frac{4\pi e}{\hbar}\rho_t(0)|M|^2 \int_0^{eV} \rho(x,y,z,\epsilon)d\epsilon$$

Same problem: penetration depth, specific heat (T→0 power law)...

Unconventional superconductivity

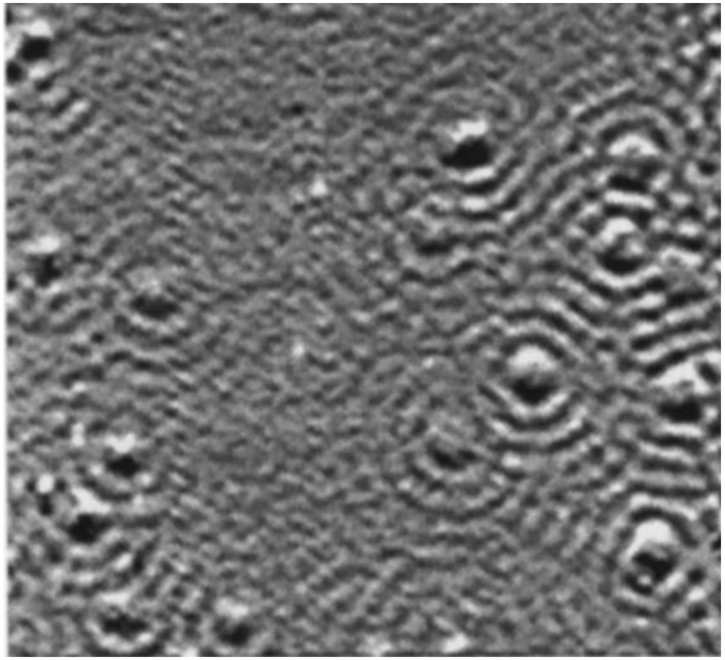
- Detecting the nature of the order parameter

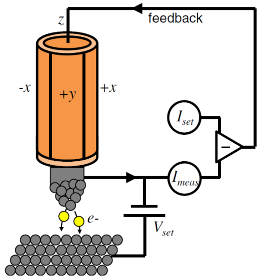
$$\Delta_{\mathbf{k}} = |\Delta_{\mathbf{k}}| \exp(i\phi_{\mathbf{k}}) \sim \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle$$

- Phase?

Interference!
Here: Quasiparticle interference measured in STM

L. Petersen, et al. PRB **57**, R6858(R) (1998)

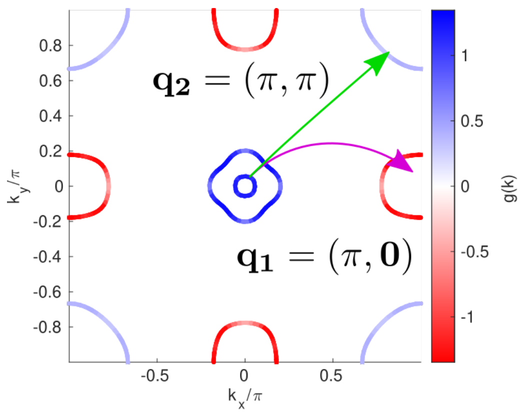


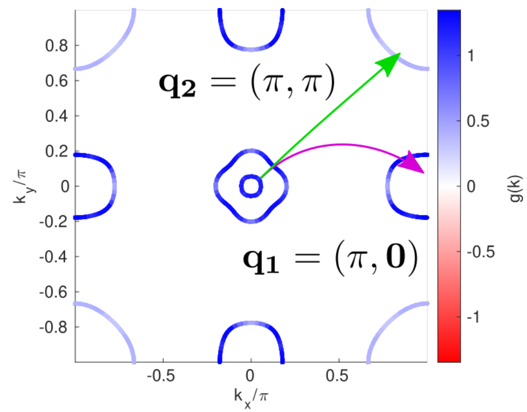


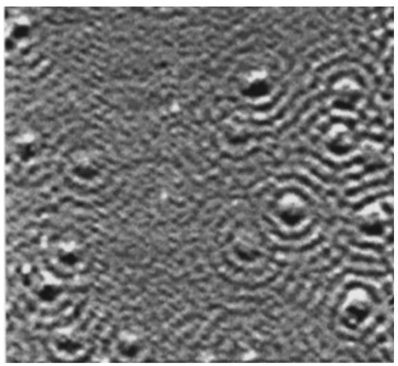
$$I(V,x,y,z) = -\frac{4\pi e}{\hbar}\rho_t(0)|M|^2 \int_0^{eV} \rho(x,y,z,\epsilon)d\epsilon$$

Quasiparticle interference

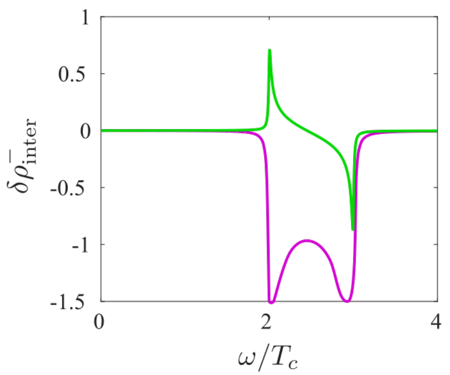
- Sign-change in singlet order parameters

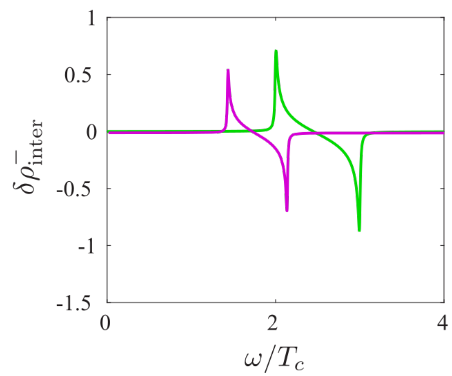






$$\delta\rho^-(\omega) \equiv \delta\rho^{\text{inter}}(\omega) - \delta\rho^{\text{inter}}(-\omega)$$





Relative phase between OP

$$\delta\rho\left(\mathbf{k}_F, \mathbf{q}_i, \omega\right) = -\frac{V_0}{\pi} \operatorname{Im}\left(\frac{(\omega + i\delta)^2 - \Delta_{\mathbf{k}_F}\Delta^*_{\mathbf{k}_F+\mathbf{q}_i}}{\left[(\omega+i\delta)^2 - |\Delta_{\mathbf{k}_F}|^2\right]^2}\right)$$

Hirschfeld, Altenfeld, Eremin, Mazin, Phys. Rev. B **92**, 184513 (2015)
Zengyi Du, et al., Nature Physics 14, 134 (2018).

QPI: Triplet superconductivity

- Role of the d-vector

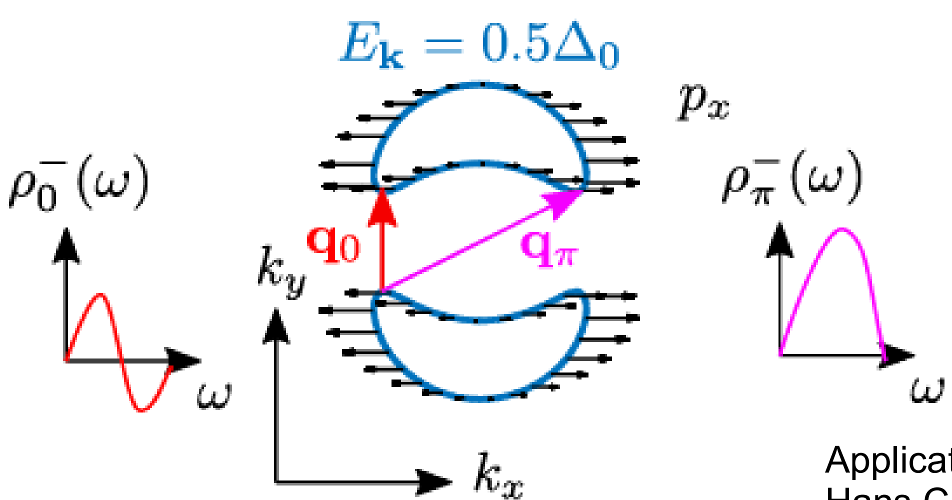
$$\begin{pmatrix} \Delta_{\uparrow\uparrow} & \Delta_{\uparrow\downarrow} \\ \Delta_{\downarrow\uparrow} & \Delta_{\downarrow\downarrow} \end{pmatrix} = \vec{d}_{\mathbf{k}} \cdot \vec{\sigma} i \sigma_y$$

Scalar product between d-vectors

- Calculation of expected QPI signal

$$\delta\rho\left(\mathbf{k}_F, \mathbf{q}_i, \omega\right) = -\frac{2V_0}{\pi} \,\mathrm{Im}\left(\frac{(\omega + i\delta)^2 - \left(\vec{d}_{\mathbf{k_F}} \cdot \vec{d}^{\,*}_{\mathbf{k_F}+\mathbf{q}_i}\right)}{\left[(\omega + i\delta)^2 - \left|\vec{d}_{\mathbf{k_F}}\right|^2\right]^2} \right)$$

"same" direction of d-vector



"opposite" direction of d-vector

Application to UTe_2
Hans Christiansen, et al., arXiv:2505.01404

Other ways to determine order parameter

- Two particle correlation function: susceptibility

$$\chi_0^{+-}(\mathbf{q},\tau) = -\frac{1}{N}\sum_{\mathbf{k}}\left(G^0_{11}(\mathbf{k}+\mathbf{q},-\tau)G^0_{\bar{1}\bar{1}}(\mathbf{k},\tau) + G^0_{\bar{1}1}(\mathbf{k}+\mathbf{q},-\tau)G^0_{1\bar{1}}(\mathbf{k},\tau)\right)$$

- magnitude and sign of order parameter enters

$$\begin{aligned}\chi_0^{+-}(\mathbf{q},\omega) = \frac{1}{N}\sum_{\mathbf{k},E>0}\Bigg[&\left(1-\frac{\epsilon_{\mathbf{k}}\epsilon_{\mathbf{k}+\mathbf{q}}+\Delta^*_{\mathbf{k}+\mathbf{q}}\Delta_{\mathbf{k}}}{E_{\mathbf{k}}E_{\mathbf{k}+\mathbf{q}}}\right)\frac{1-f(E_{\mathbf{k}})-f(E_{\mathbf{k}+\mathbf{q}})}{\omega+E_{\mathbf{k}+\mathbf{q}}+E_{\mathbf{k}}+i\eta}\\
&+\left(1-\frac{\epsilon_{\mathbf{k}}\epsilon_{\mathbf{k}+\mathbf{q}}+\Delta^*_{\mathbf{k}+\mathbf{q}}\Delta_{\mathbf{k}}}{E_{\mathbf{k}}E_{\mathbf{k}+\mathbf{q}}}\right)\frac{f(E_{\mathbf{k}})+f(E_{\mathbf{k}+\mathbf{q}})-1}{\omega-E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}}+i\eta}\\
&+\left(1+\frac{\epsilon_{\mathbf{k}}\epsilon_{\mathbf{k}+\mathbf{q}}+\Delta^*_{\mathbf{k}+\mathbf{q}}\Delta_{\mathbf{k}}}{E_{\mathbf{k}}E_{\mathbf{k}+\mathbf{q}}}\right)\frac{f(E_{\mathbf{k}})-f(E_{\mathbf{k}+\mathbf{q}})}{\omega+E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}}+i\eta}\\
&+\left(1+\frac{\epsilon_{\mathbf{k}}\epsilon_{\mathbf{k}+\mathbf{q}}+\Delta^*_{\mathbf{k}+\mathbf{q}}\Delta_{\mathbf{k}}}{E_{\mathbf{k}}E_{\mathbf{k}+\mathbf{q}}}\right)\frac{f(E_{\mathbf{k}+\mathbf{q}})-f(E_{\mathbf{k}})}{\omega+E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}+i\eta}\Bigg]\end{aligned}$$

same sign
different sign

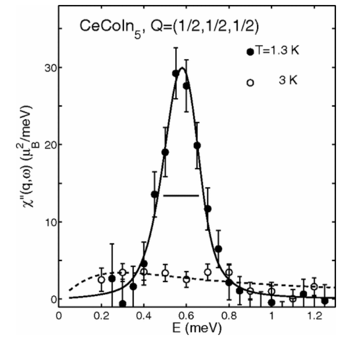
$$\left(1-\frac{\Delta_{\mathbf{k}+\mathbf{q}}\Delta_{\mathbf{k}}}{|\Delta_{\mathbf{k}}||\Delta_{\mathbf{k}+\mathbf{q}}|}\right)\approx\begin{cases}0\\2\end{cases}$$

$$\left(1+\frac{\Delta_{\mathbf{k}+\mathbf{q}}\Delta_{\mathbf{k}}}{|\Delta_{\mathbf{k}}||\Delta_{\mathbf{k}+\mathbf{q}}|}\right)\approx\begin{cases}2\\0\end{cases}$$

Probing susceptibility

- Neutron scattering
  - Enhancement of scattering below $2\Delta \rightarrow$ sign changing OP

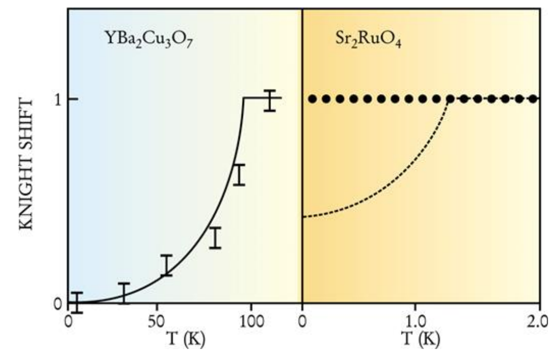
$$\left(1 - \frac{\Delta_{\mathbf{k+q}}\Delta_{\mathbf{k}}}{|\Delta_{\mathbf{k}}||\Delta_{\mathbf{k+q}}|}\right) \approx \begin{cases} {\color{blue}0} \\ {\color{red}2} \end{cases}$$



C. Stock, et al., Phys. Rev. Lett. 100, 087001 (2008)

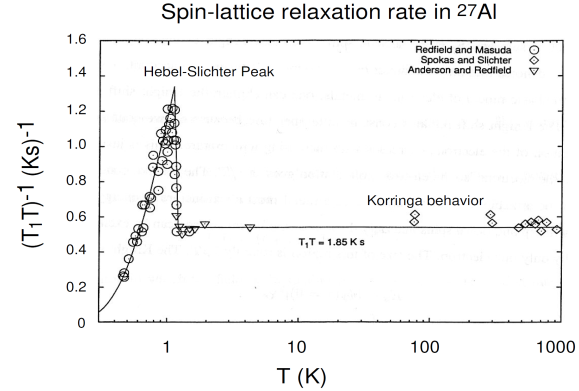
- Nuclear spin resonance (NMR)
  - Screening from external field due to SC (Knight shift)
  - Low energy spin fluctuations (relaxation rate)
  - Peak below T_c $\rightarrow$ non-sign changing OP

$$\left(1 + \frac{\Delta_{\mathbf{k+q}}\Delta_{\mathbf{k}}}{|\Delta_{\mathbf{k}}||\Delta_{\mathbf{k+q}}|}\right) \approx \begin{cases} {\color{blue}2} \\ {\color{red}0} \end{cases}$$



Maeno, Rice, Sigrist Physics Today **54**, 42 (2001)

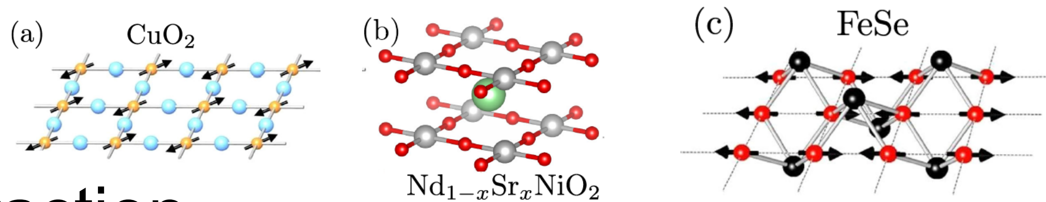
Spin-lattice relaxation rate in 27Al



L. C. Hebel, C. P. Slichter Phys. Rev. **107**, 901 (1957)

Summary (1)

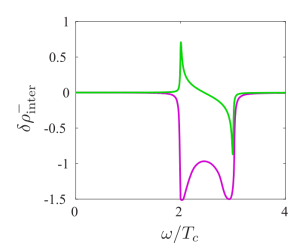
- material candidates for unconventional superconductivity

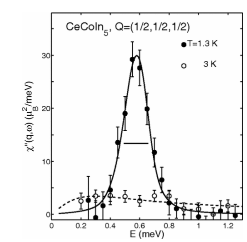


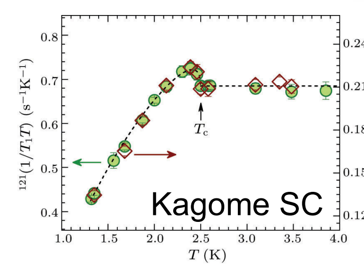
- Momentum dependent interaction
  $\rightarrow$ momentum dependent order parameter/sign change

$$\Delta_{\mathbf{k}} \sim \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle \qquad E_{\mathbf{k}} = \sqrt{\epsilon_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}}|^2}$$

- Experimental probes sensitive to the sign of the order parameter are rare
  - Quasiparticle interference
  - Neutron resonance
  - Hebel-Slichter peak in NMR relaxation rate







Chao Mu, et al., Chinese Phys. Lett. **38** 077402 (2021)

Time reversal symmetry breaking in superconductors

- Triplet: d-vector $\begin{pmatrix} \Delta_{\uparrow\uparrow} & \Delta_{\uparrow\downarrow} \\ \Delta_{\downarrow\uparrow} & \Delta_{\downarrow\downarrow} \end{pmatrix} = \vec{d}_{\mathbf{k}} \cdot \vec{\sigma} i \sigma_y$

$$\vec{q}_{\mathbf{k}} = i\left(\vec{d}_{\mathbf{k}} \times \vec{d}_{\mathbf{k}}^{\,*}\right)$$

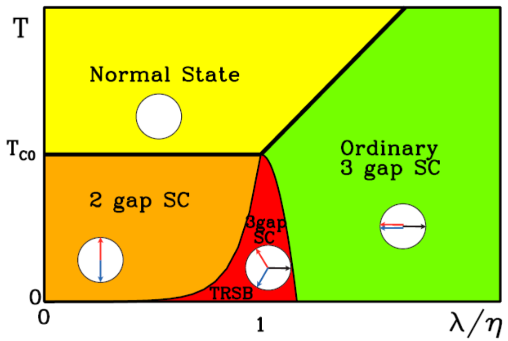
Non-unitary state

Spin momentum of Cooper pair
$\langle \vec{S} \rangle \propto \langle \vec{q}_{\mathbf{k}} \rangle_{\mathrm{FS}}$

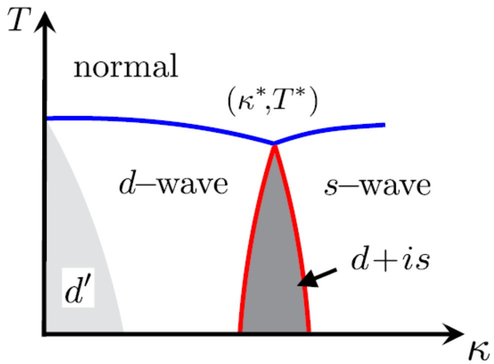
$$\mathrm{E}_{\mathbf{k},\pm} = \sqrt{\epsilon_{\mathbf{k}} + (|\vec{d}_{\mathbf{k}}|^2 \pm \vec{q}_{\mathbf{k}})}$$

"spin-split quasiparticle energies"

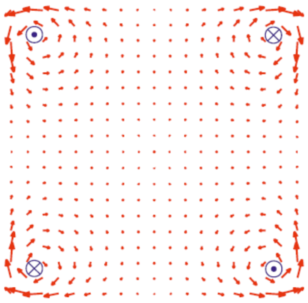
- Singlet
  - Two component / two irrep order parameter



Stanev V, Tešanović Z. Phys Rev B 81,134522 (2010)



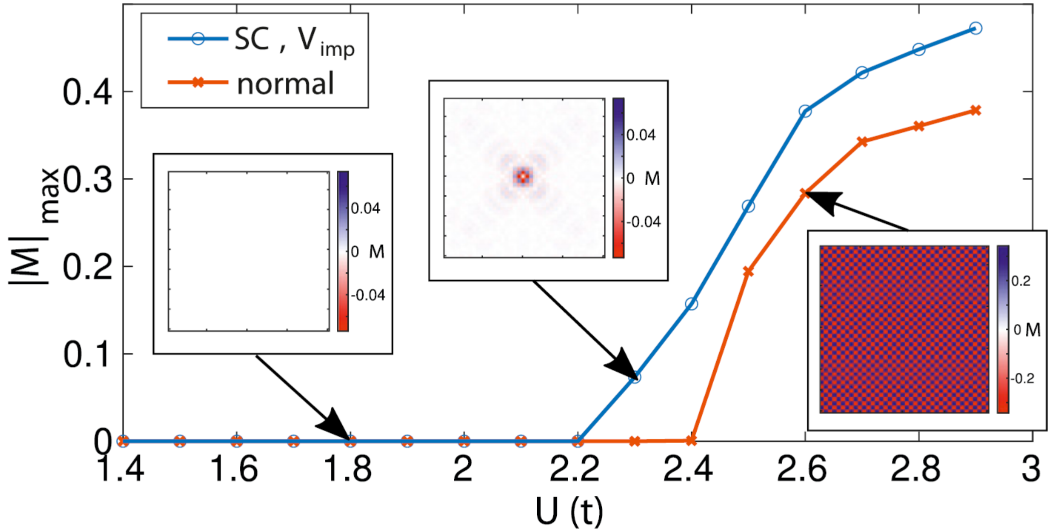
Khodas M, Chubukov AV. Phys Rev Lett 108, 247003 (2012)



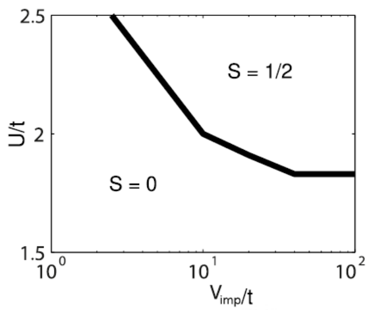
Corner loop currents in d+is state.

Magnetic droplets from impurities

- Nonmagnetic impurity in unconventional SC

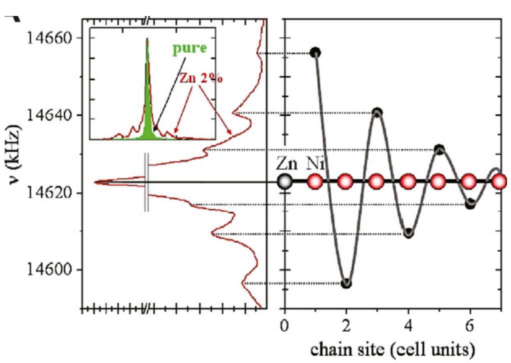


Gap opening promotes local magnetism

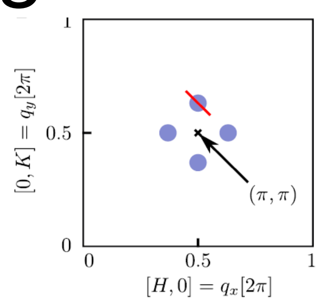


Harter JW, et al., Phys Rev B **75**, 054520 (2007)

- Signatures in NMR, neutron scattering



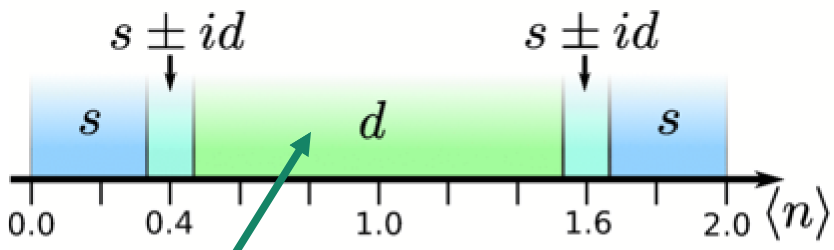
Satellite peaks in NMR: different magnetic environment
Das J, Phys Rev B **69**, 144404 (2004)

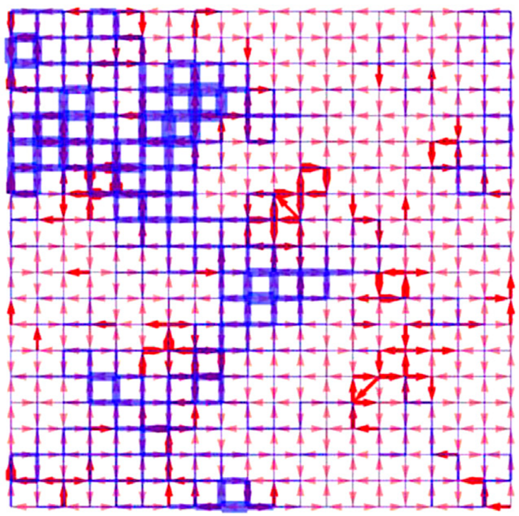


Splitting of neutron diffraction intensity close to (π, π)
Lake B, Nature **415**, 299 (2002)

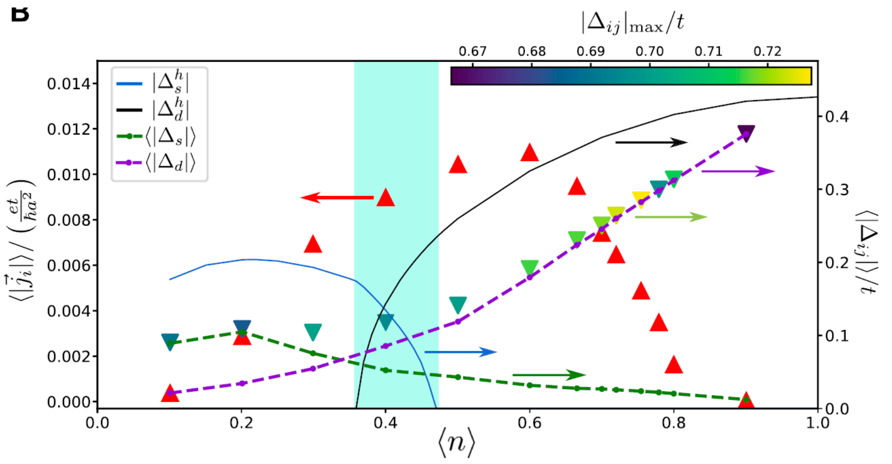
Disorder induced loop currents

- Single band model with nearest neighbour pairing





Loop currents around non-magnetic impurities
Zi-Xiang Li, et al., npj Quantum Materials **6**, 36 (2021)

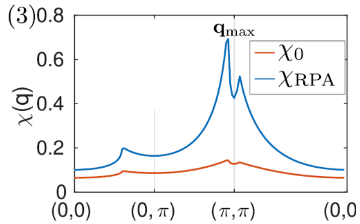


Origin: local s+id regions (with enhanced NN s-wave pairing)

Clara N. Breiø, et al., Phys. Rev. B **105**, 014504 (2022)

Other mechanisms

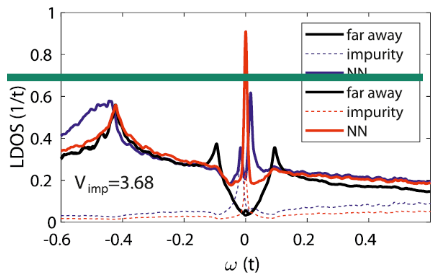
- Slowing down of magnetic fluctuations in SC state
  - System close to, but below magnetic transition



$$\chi \sim \frac{1}{1 - U\rho(0)}$$

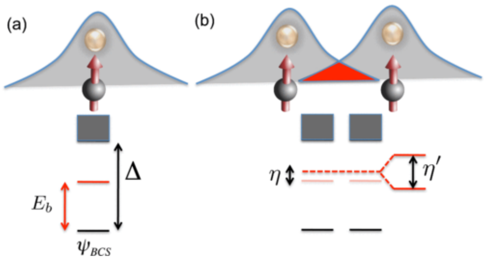
  - Gap opening + disorder enhances DOS locally

$$\frac{1}{U}$$



→ Slow fluctuations or pinned magnetism in SC state

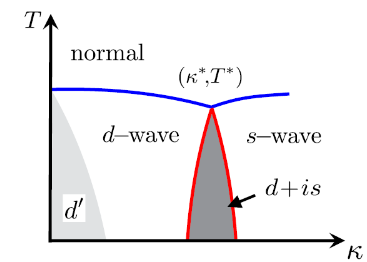
- Enhanced RKKY coupling / exchange coupling
  - YSR states mediate new coupling



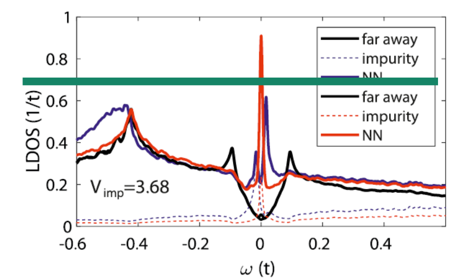
N. Y. Yao, et al., Phys. Rev. Lett. **113**, 087202 (2014)

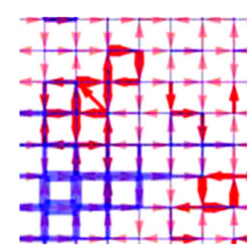
Summary (2)

- Time reversal symmetry breaking in superconductors
- Bulk / local ?
- Mechanisms
  - “frustration” between SC instabilities
  - Correlations lead to local moments
  - Local loop currents



$\frac{1}{U}$

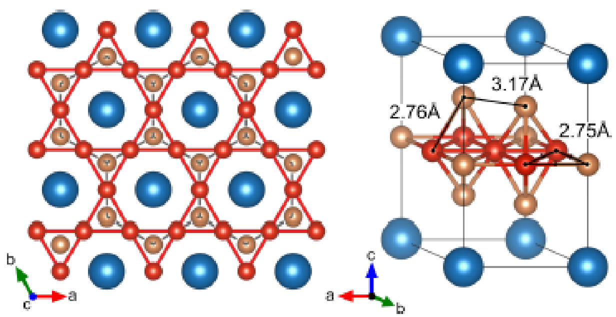




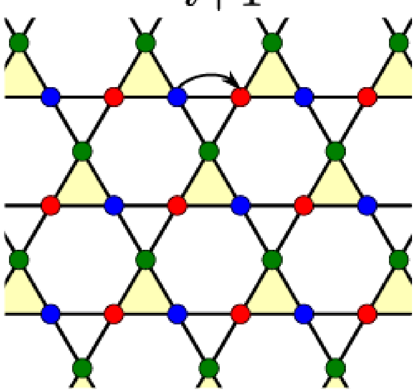
Possible materials (5)

- Kagome superconductors

CsV_3Sb_5

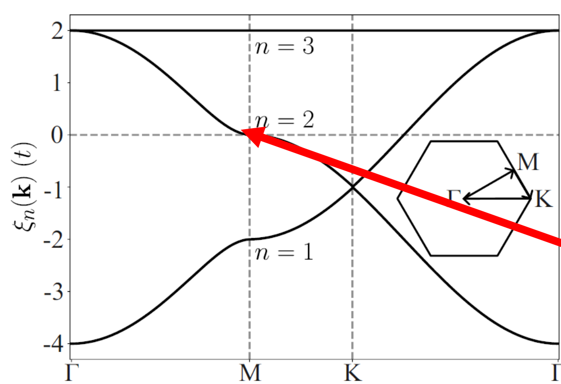


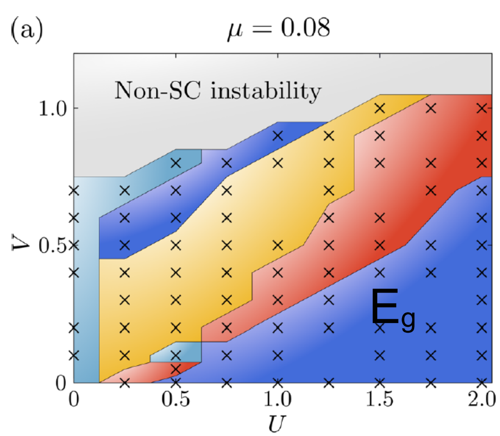
$tc_{i+1}^{\dagger}c_i$

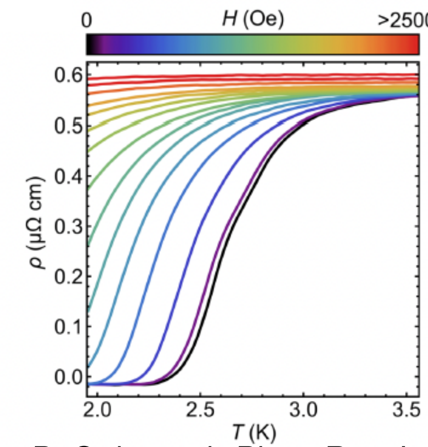


Astrid T. Rømer, et al.,
Phys. Rev. B **106**, 174514 (2022)

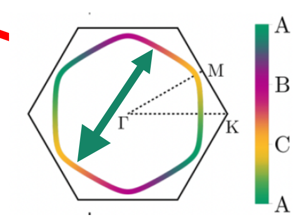
single orbital model: sublattice structure (3 bands)







B. Ortiz *et al.*, Phys. Rev. Lett **125**, 247002 (2020)



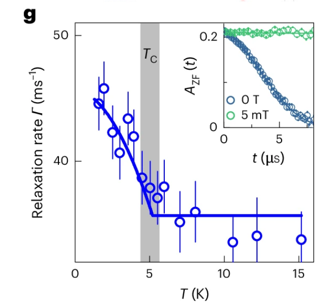
Perfect nesting, but sublattice mismatch

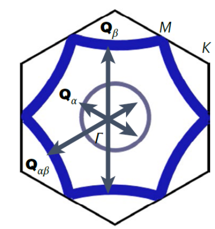
→ competing instabilities, dominating 2D irrep.

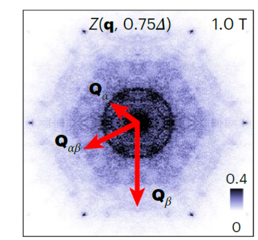
TRSB in Kagome superconductors

- Experimental evidences
  - μSR measurements
  - QPI on $Cs(V, Ta)_3Sb_5$: no CDW
  - TRSB from difference QPI

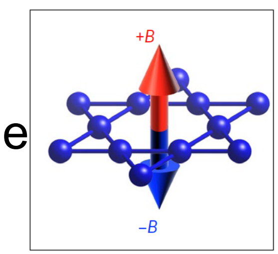
H. Deng, *et al.*,
Nat. Mat. 23, 1639 (2024)

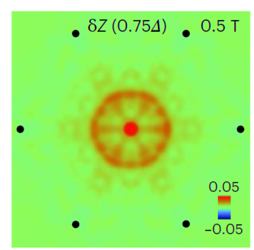


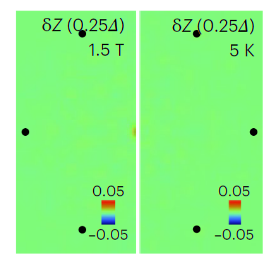




out of plane

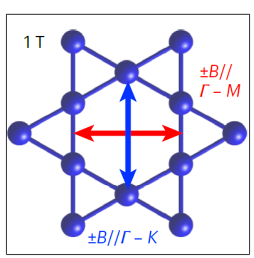


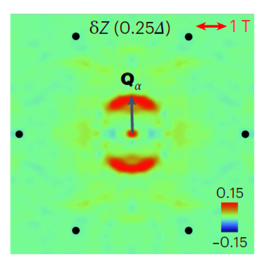


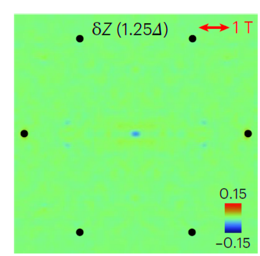


Disappears above T_c and in large field

in plane



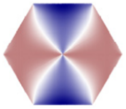
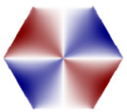




Disappears at E>Δ

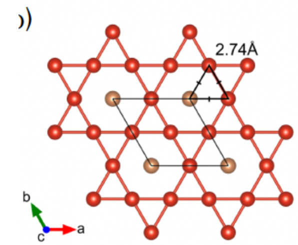
See also: Wang et al., arXiv:2405.12592
(hysteresis of magnetoresistance)
Le, et al, Chinese Phys. B **33,** 107402 (2024)

Is it a d+id state?

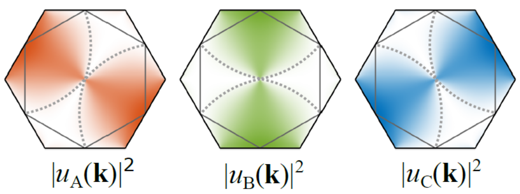
 $+i$ 

$$d_{xy} + i d_{x^2-y^2}$$

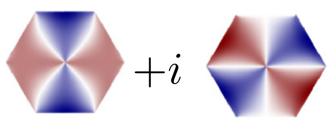
Unconventional SC on Kagome lattice



- Revisit phase sensitive probes for Kagome lattice
- Sublattice interference: eigenstates are polarized

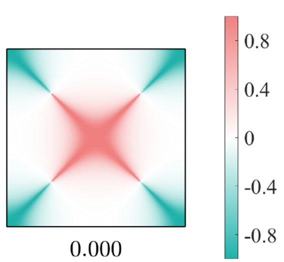


- Sublattice site has lower symmetry than point group

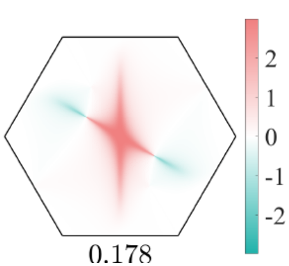


$\mathrm{d}_{xy} + id_{x^2-y^2}$

- product of sublattice weight and order parameter does not average to zero



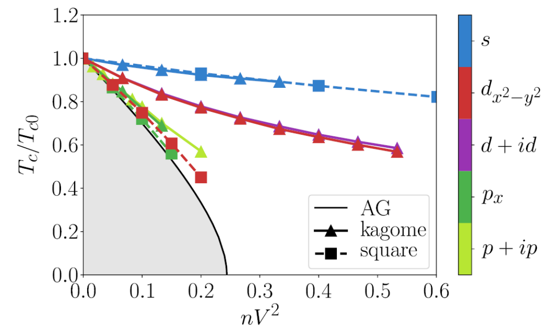
square lattice

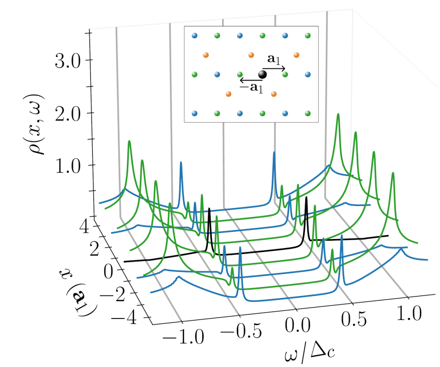


Kagome

Unconventional SC on Kagome lattice

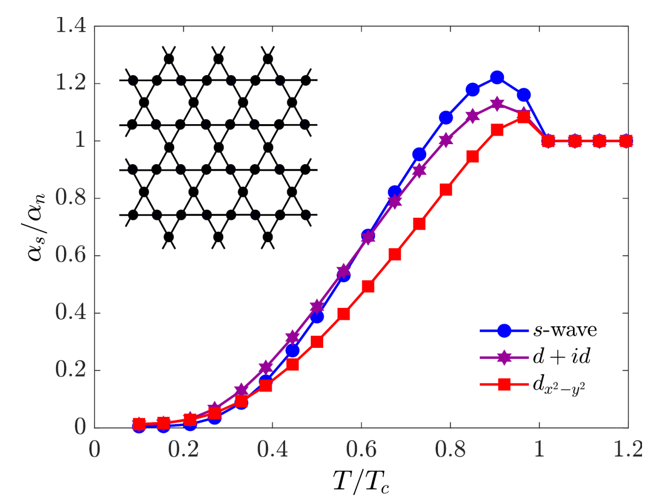
- Robust against disorder
  - Weak T_c suppression
  - No in-gap bound states





Sofie Castro Holbæk, et al., Phys. Rev. B **108**, 144508 (2023)

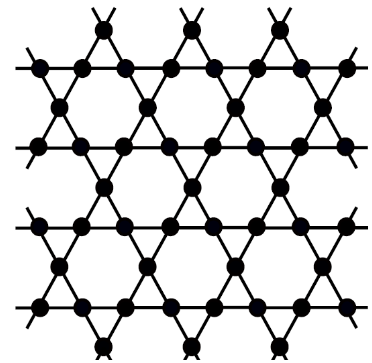
- No expected neutron resonance
- Hebel Slichter peak even for unconventional OP



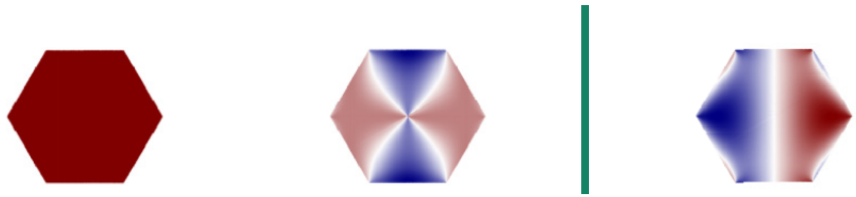
Yi Dai, et al., Phys. Rev. B 110, 144516 (2024)

Summary (3)

- Kagome lattice is different

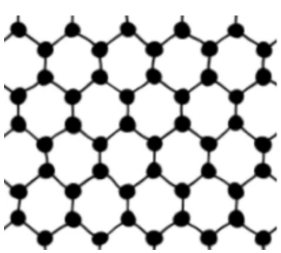


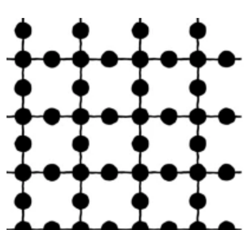
- Sign-changing superconducting states behave as non-sign changing states

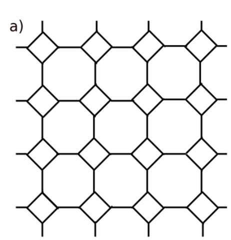


(Odd parity is different)

- Also applies to other lattices!?





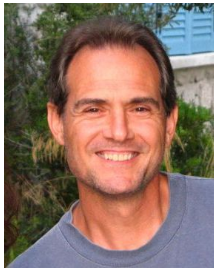


Sofie Castro Holbæk, et al., (in preparation)

Acknowledgements

- Collaborators

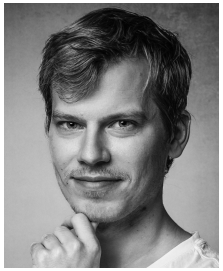
Brian M. Andersen



Peter J. Hirschfeld (U Florida)

Hans **Christiansen**

Sofie Castro Holbæk (U Zürich)



Morten Holm **Christensen**

Yi Dai

Andersen, Kreisel, Hirschfeld, Front. Phys. **12**, 1353425 (2024)

Holbæk, Christensen, Kreisel, Andersen, Phys. Rev. B **108**, 144508 (2023)
Dai, Kreisel, Andersen, Phys. Rev. B **110**, 144516 (2024)
Deng, (…) AK, et al., Nat. Mat. **23**, 1639 (2024)
Christiansen, Andersen, Hirschfeld, Kreisel, arXiv:2505.01404

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