Symmetry and Order in Quantum Materials

John Harter

Quantum Science Summer School

July 26, 2022

UC SANTA BARBARA Quantum | Foundry

DMR-1906325

What is symmetry?

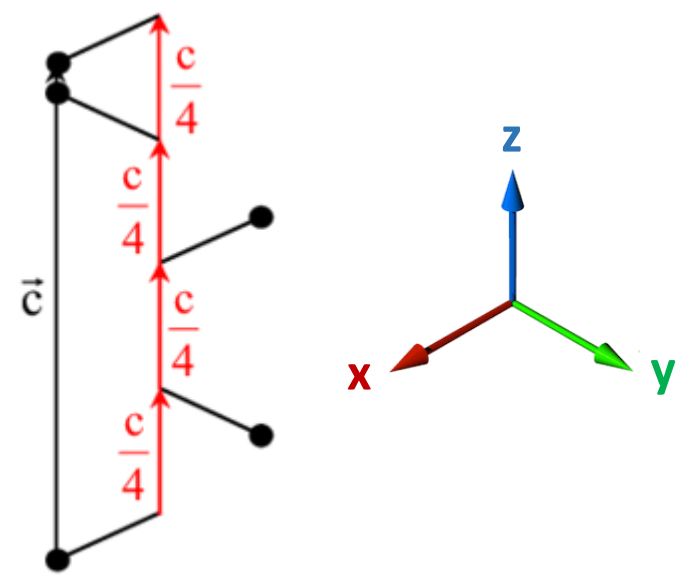
- A symmetry is a physical transformation that leaves a system (i.e. a material) invariant

- Symmetries in condensed matter systems often take the form of spatial rotations, translations, or combinations of the two:

$$\vec{r} \longrightarrow \{R|\vec{T}\}\vec{r} = R\vec{r} + \vec{T}$$

- **Example:** a 4_1 screw axis in a crystal

$$R = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \ \vec{T} = \begin{bmatrix} 0 \\ 0 \\ \frac{c}{4} \end{bmatrix}$$



What is symmetry?

- In quantum mechanics, a symmetry is a unitary transformation that leaves the Hamiltonian invariant:

$$U^\dagger \mathcal{H} U = \mathcal{H}$$
$$\Longrightarrow \mathcal{H} U = U \mathcal{H}$$
$$\Longrightarrow [\mathcal{H}, U] = 0$$

$\Longrightarrow$ can simultaneously diagonalize $\mathcal{H}$ and U

$\Longrightarrow$ wavefunctions are eigenfunctions of U

- **Example:** an isolated atom
  - $\mathcal{H}$ is invariant under spatial inversion ($\vec{r} \longrightarrow -\vec{r}$)
  - All wavefunctions (orbitals) are eigenfunctions of inversion:
    - Eigenvalue = +1: "Even" orbitals {*s*, *d*}
    - Eigenvalue = −1: "Odd" orbitals {*p*, *f*}

Why is symmetry so useful?

- Symmetry is constant—it can only change at a phase transition
  - We classify phases of matter by the symmetries that are broken by that phase

Gas

Liquid

Solid

- Symmetry has many useful implications
  - Indicates what wavefunctions <u>must</u> be degenerate
  - Determines quantities that are conserved

- Enables the powerful mathematical machinery of **group theory**
  - The set of all symmetries of a system forms a group

Intrinsic Symmetries

- Unlike spatial symmetries, which can be though of as coordinate transformations, **intrinsic** symmetries do not depend on the geometry of the system

- **Examples:**
  - Time reversal symmetry $[t \longrightarrow -t]$
  - Permutation symmetry $[\hat{\mathcal{P}}\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1)]$
    - Enables classification of elementary particles:
      - Eigenvalue = +1: "Bosons"
      - Eigenvalue = –1: "Fermions"
      - Eigenvalue = $e^{i\theta}$: "Anyons" (only allowed in 2D)
  - Gauge symmetry $[\psi(\vec{r}, t) \longrightarrow e^{i\theta(\vec{r},t)}\psi(\vec{r}, t)]$
    - Requires simultaneous transformation of potential functions: $V \longrightarrow V + \hbar\frac{\partial\theta}{\partial t}, \vec{A} \longrightarrow \vec{A} - \left(\frac{\hbar}{e}\right)\vec{\nabla}\theta$

Crystallographic Symmetries

- Most quantum materials are crystalline: they break *continuous* translational symmetry but still possess **periodic** translational symmetry ($\vec{T} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3, n_i \in \mathbb{Z}$)

- Crystal momentum $\vec{k}$, appearing in Bloch's theorem, is the conserved quantity arising from periodic translational symmetry
  - $e^{i\vec{k}\cdot\vec{T}}$ is the eigenvalue of the translation operators:

$$\{I|\vec{T}\}\psi(\vec{r}) = \psi(\vec{r} + \vec{T}) = e^{i\vec{k}\cdot\vec{T}}\psi(\vec{r})$$

- Consistent with periodic translational symmetry, there are:
  - **230** space groups
  - **32** point groups (space groups minus all translations)

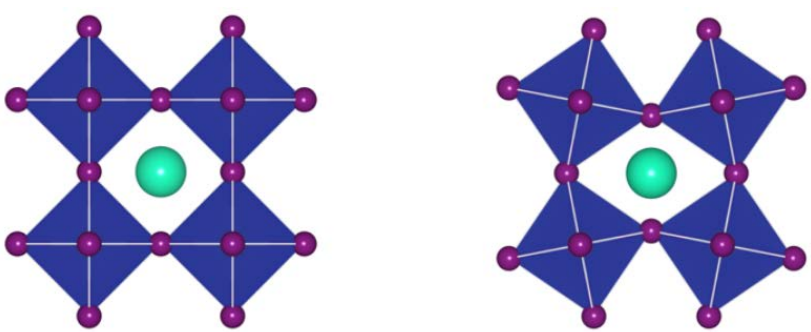
Spontaneous Symmetry Breaking

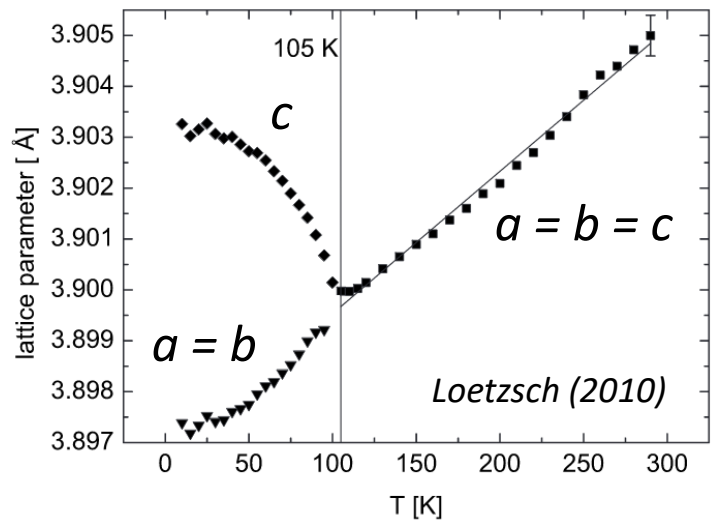
- Some of the most interesting phenomena in quantum materials occur through **spontaneous** symmetry breaking
  - One or more symmetries of a system are spontaneously broken as an external parameter (e.g. temperature, pressure, magnetic field) is tuned across a critical value

- For thermal phase transitions, this is mainly due to a competition between internal energy and entropy in free energy: $F = U - TS$

- **Example:** structural transition in $SrTiO_3$

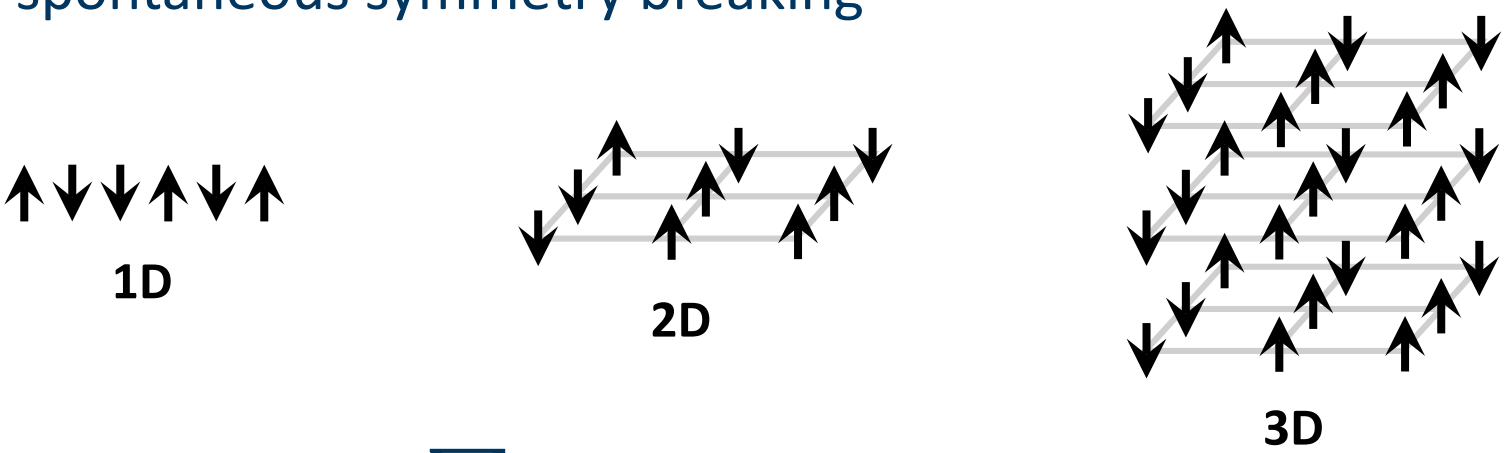
$$Pm\bar{3}m \longrightarrow I4/mcm$$





Symmetry Breaking in the Ising Model

- The Ising model (interacting spins on a lattice) is a simple model of spontaneous symmetry breaking



$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j$$

exchange interaction strength

sum over nearest neighbors

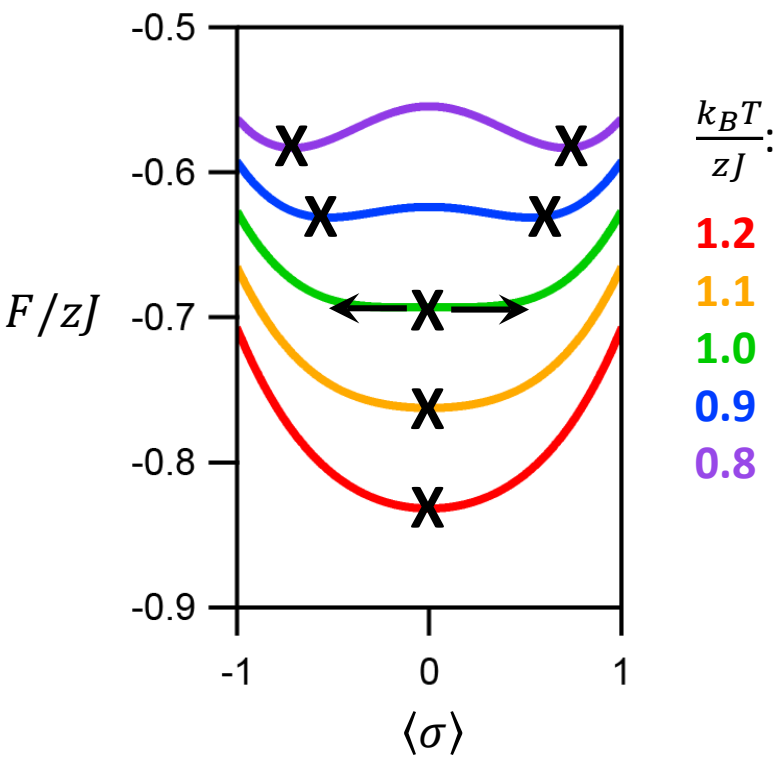
Ising spin: $\sigma_i = \pm 1$

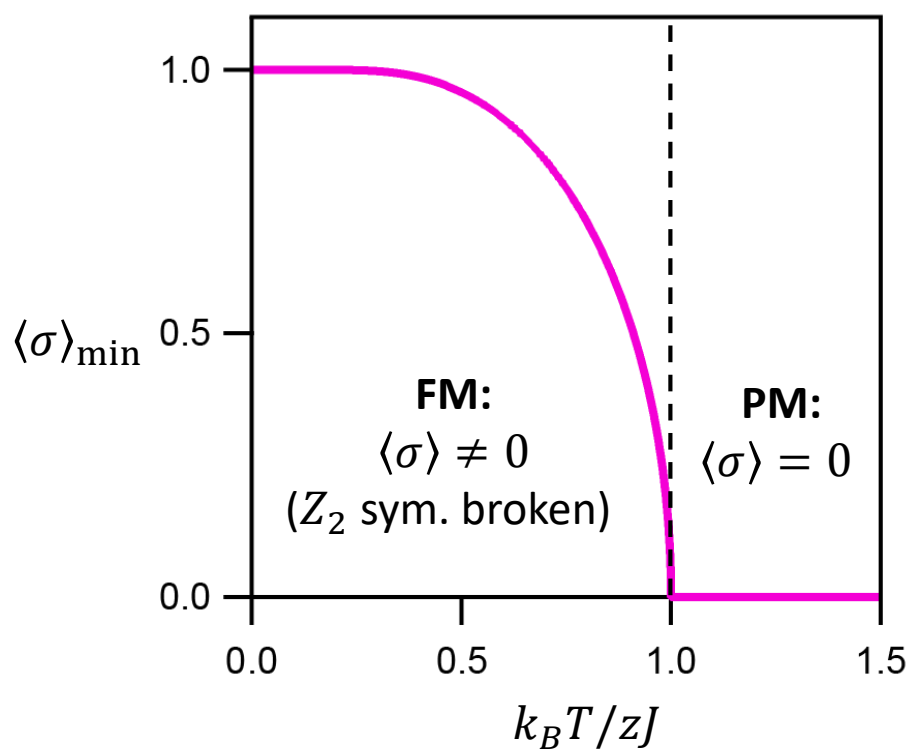
Symmetry of $\mathcal{H}$: $\sigma_i \longrightarrow -\sigma_i$ (Z_2 symmetry)

Symmetry Breaking in the Ising Model

- Within mean field theory (treating the spin–spin interactions in an "average" way), can compute the free energy (per spin):

$$F = \left(\frac{zJ}{2}\right)\langle\sigma\rangle^2 - \underbrace{k_B T \ln\left(e^{+zJ\langle\sigma\rangle/k_B T} + e^{-zJ\langle\sigma\rangle/k_B T}\right)}_{\text{depends on } T\text{—entropic}}$$



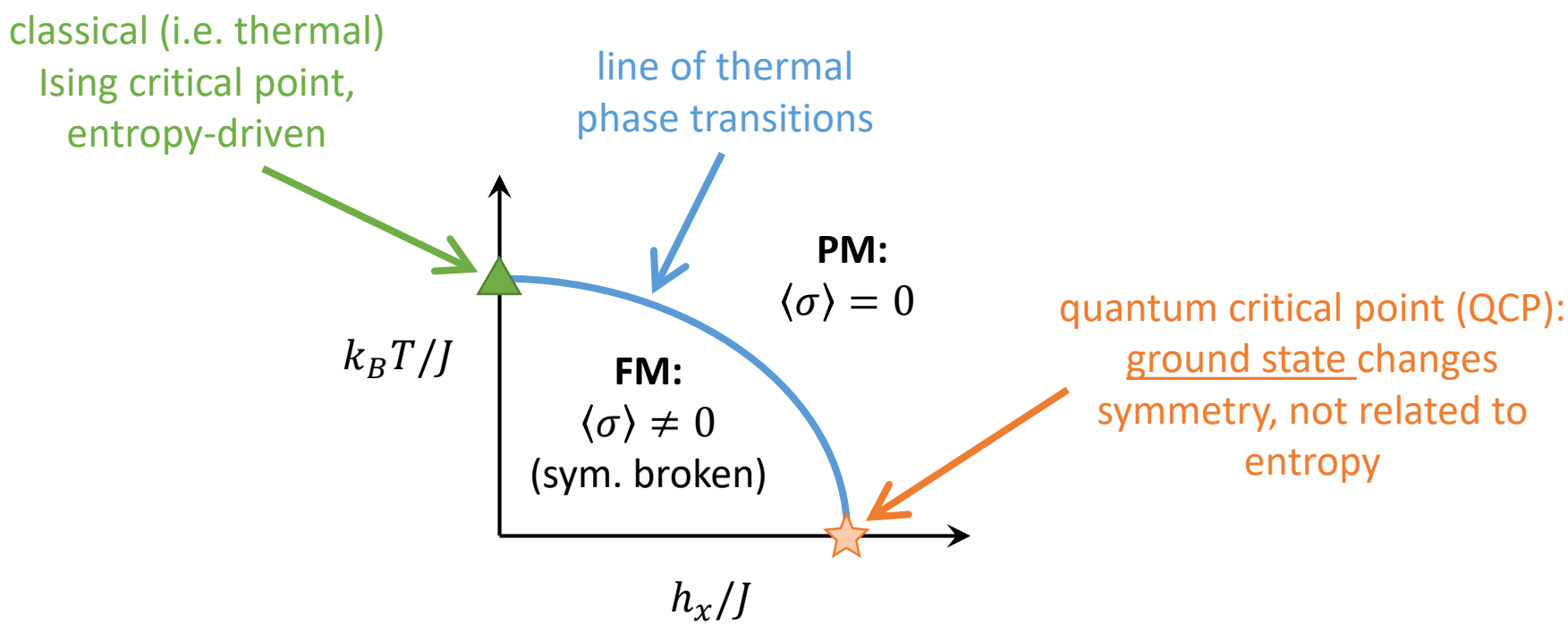


Symmetry Breaking in the Ising Model

- The transverse-field Ising model shows a **"quantum" phase transition:**

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \sigma_i^z \sigma_j^z - h_x \sum_i \sigma_i^x$$

magnetic field



Order Parameters

- In the Ising model, the value of the average spin $\langle\sigma\rangle$ determined if any symmetries of the Hamiltonian (e.g. Z_2) were broken
  - Enabled classification of the paramagnetic $[\langle\sigma\rangle = 0]$ and ferromagnetic $[\langle\sigma\rangle \neq 0]$ phases

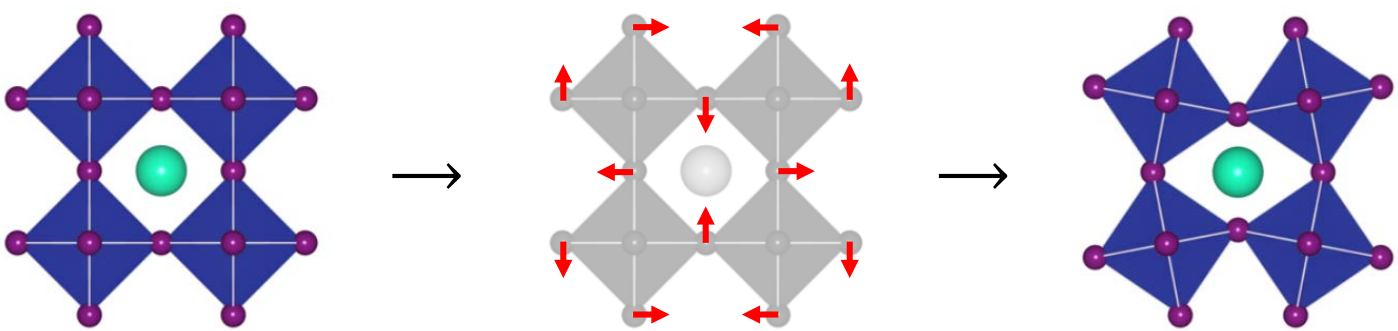
- $\langle\sigma\rangle$ is an example of an "**order parameter**," which is a number that parameterizes a specific physical configuration of a system
  - OPs break specific symmetries of the Hamiltonian
    - Example: $\langle\sigma\rangle$ breaks Z_2 symmetry
  - An OP is zero in the symmetric phase and becomes nonzero at a phase transition to a broken symmetry phase
  - In the language of group theory, an OP must transform like an **irreducible representation** of the symmetry group

Structural Order Parameters

- For structural phase transitions, where the atom locations within a crystal's unit cell rearrange themselves, the OP is the set of displacement vectors of the atoms

- **Example:** structural transition in $SrTiO_3$

$Pm\bar{3}m$ $\qquad\qquad\qquad\qquad$ $I4/mcm$



OP = ϕ

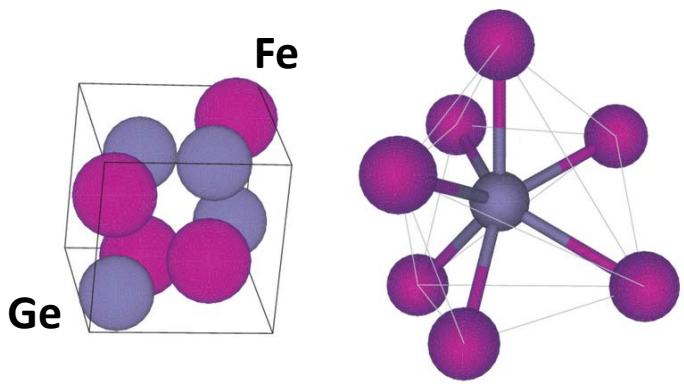
$$\{\text{Atom 1: } \overrightarrow{\Delta r} = \begin{bmatrix} \phi \\ 0 \\ 0 \end{bmatrix}, \text{Atom 2: } \overrightarrow{\Delta r} = \begin{bmatrix} 0 \\ -\phi \\ 0 \end{bmatrix}, \ldots\}$$

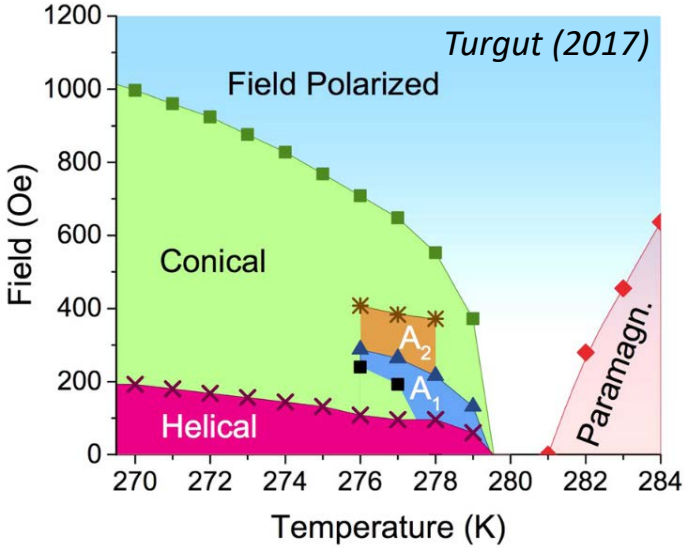
Magnetic Order Parameters

- The fundamental symmetry broken by magnetic order is time reversal symmetry ($t \longrightarrow -t$)
  - Spins are odd under time reversal ($\vec{S}_i \longrightarrow -\vec{S}_i$)
    - Why? Magnetic moments = circulating current
  - Any ordering of magnetic moments breaks TR symmetry

- There are 1651 **magnetic space groups** (symmetry groups that include both spatial symmetries and time reversal symmetry)

- **Example:** cubic B20 FeGe



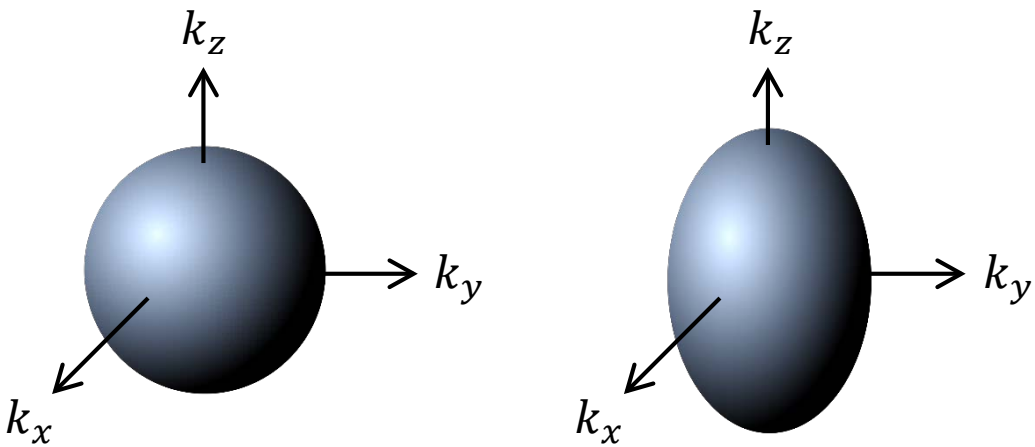


Electronic Order Parameters

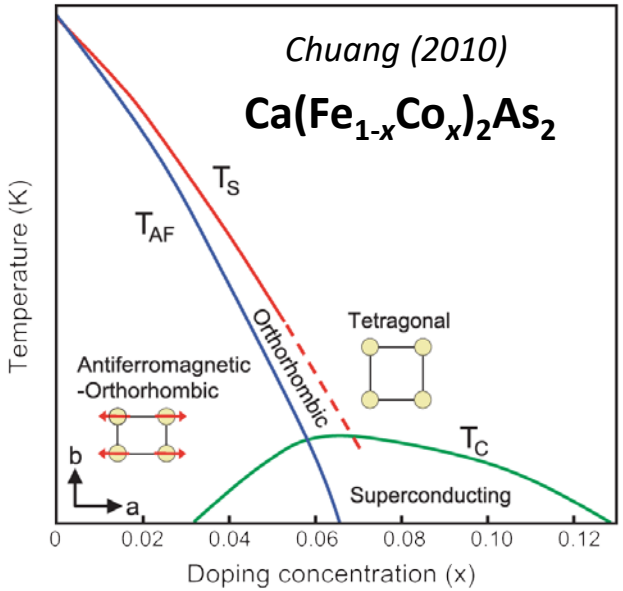
- In itinerant electron systems (i.e. metals), the electrons can drive symmetry breaking (independent of structure)

- Called a **"Pomeranchuck instability"**
  - Involves a distortion of the Fermi surface shape

- **Example:** electron nematicity



Symmetric FS ⟶ **Distorted FS "nematic"**

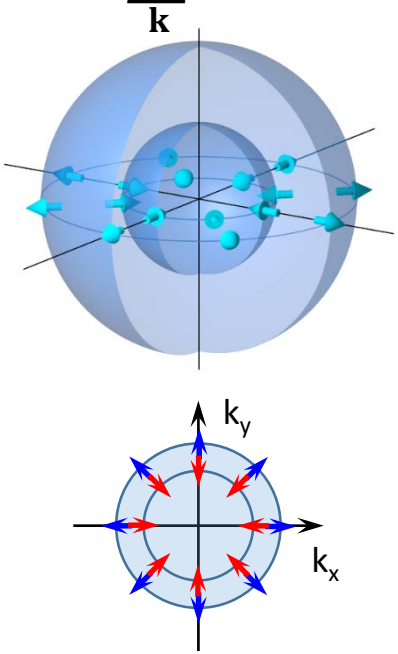


Electronic Order Parameters

- If strong spin-orbit coupling is included, more exotic Pomeranchuk instabilities can appear
- **Example:** odd-parity Fermi liquid instabilities [*Fu (2015)*]

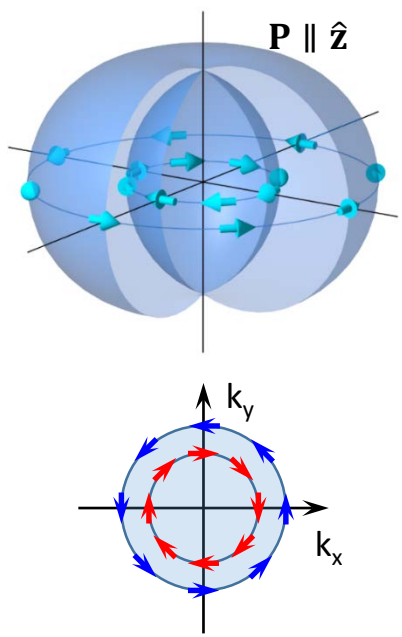
Gyrotropic
(pseudoscalar)

$$\eta = \sum_{\mathbf{k}} \hat{\mathbf{k}} \cdot \mathbf{s}(\mathbf{k})$$



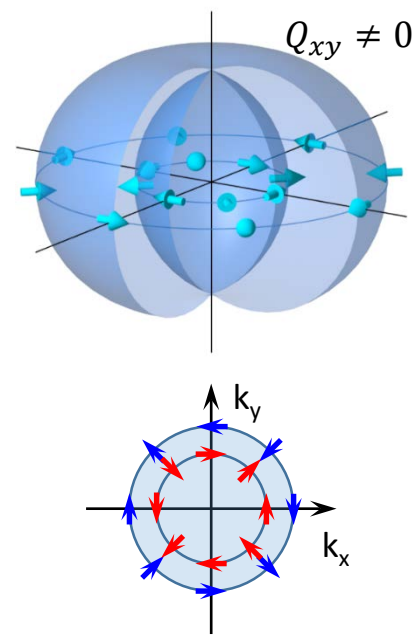
Ferroelectric
(vector)

$$\mathbf{P} = \sum \hat{\mathbf{k}} \times \mathbf{s}(\mathbf{k})$$



Multipolar Nematic
(rank-2 pseudotensor)

$$Q_{ij} = \sum \hat{k}_i s_j(\mathbf{k}) + \hat{k}_j s_i(\mathbf{k})$$



Superconducting Order

- Superconductivity breaks gauge symmetry
  - OP is a complex number with a well-defined <u>phase</u>
  - Broken gauge symmetry implies the photon "gains mass" via the Anderson-Higgs mechanism
    - Origin of the Meissner Effect
  - Gauge symmetry $\longleftrightarrow$ charge conservation, so charge is not conserved in a superconductor
    - Uncertainty relation: $\Delta\theta\Delta N \geq 1$

- OP is the Cooper pair wavefunction:

$$\psi_{\vec{k}}^{\alpha\beta} = \left\langle \hat{c}_{\vec{k}\alpha}\hat{c}_{-\vec{k}\beta} \right\rangle \qquad \alpha, \beta = \uparrow, \downarrow$$

singlet pairing: $\psi_{\vec{k}}^{\alpha\beta} = \psi(\vec{k})|\uparrow\downarrow - \downarrow\uparrow\rangle$

triplet pairing: $\psi_{\vec{k}}^{\alpha\beta} = \vec{\psi}(\vec{k}) \cdot [|\uparrow\uparrow\rangle \quad |\uparrow\downarrow + \downarrow\uparrow\rangle \quad |\downarrow\downarrow\rangle]^T$

Superconducting Order

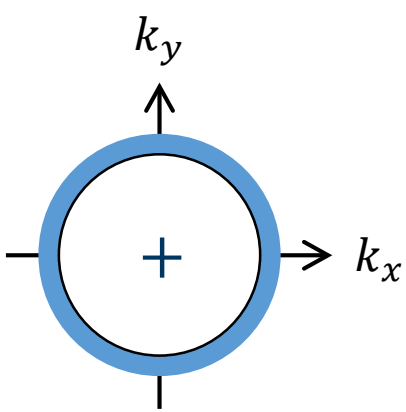
- The orbital part of the pair wavefunction, $\psi(\vec{k})$, can also be classified by symmetry (e.g. angular momentum)
  - s-wave ($L = 0$), p-wave ($L = 1$), d-wave ($L = 2$), etc.

- **Example:** pairing symmetries of some superconductors

Hg, Nb, Pb, etc.

$\psi(\vec{k}) \propto 1$

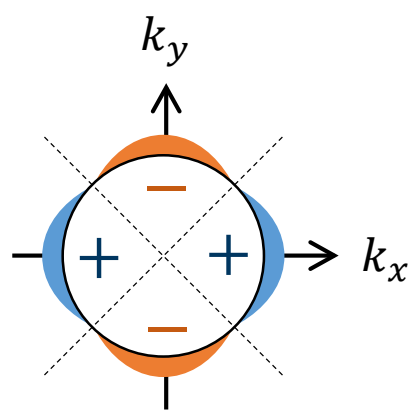
(singlet, s-wave)



cuprates

$\psi(\vec{k}) \propto (k_x^2 - k_y^2)$

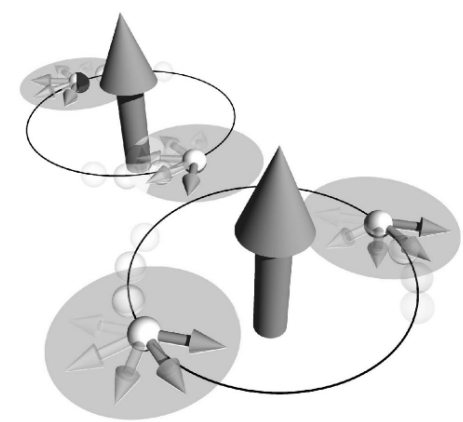
(singlet, d-wave)



Sr_2RuO_4

~~$\vec{\psi}(\vec{k}) \propto \vec{z}(k_x \pm ik_y)$~~

~~(triplet, p-wave)~~

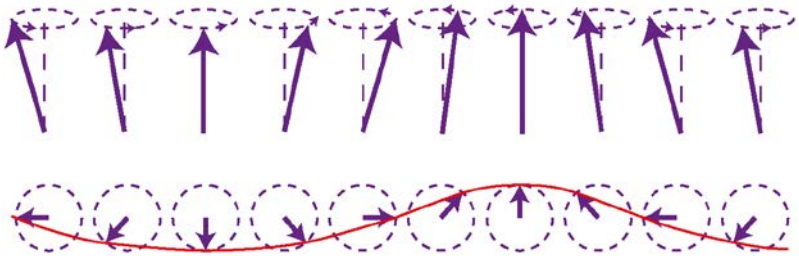


Mackenzie (2003)

Goldstone Modes

- **Goldstone Theorem:** Whenever a *continuous* symmetry is broken, gapless modes (i.e. excitations costing infinitesimal energy) appear
  - Long-wavelength fluctuations of the order parameter

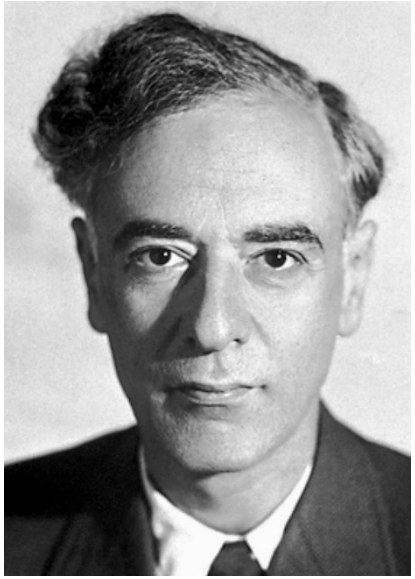
- **Examples:**
  Crystallization (translation sym. broken) ⟶ acoustic phonons
  Ferromagnetism (spin rotation sym. broken) ⟶ magnons



- **Mermin-Wagner Theorem**: Thermal fluctuations of Goldstone modes in 1D and 2D will completely destroy long-range order
  - No breaking of continuous symmetries in 1D and 2D!

Landau Theory

- Basic idea: Expand the free energy of a system as a Taylor series polynomial in the OP(s)
  - Each term in the polynomial must be invariant under all symmetry operations



- To get phase transitions, make coefficients in the polynomial temperature dependent

- **Example:** the Ising model

$$F = \left(\frac{zJ}{2}\right)\langle\sigma\rangle^2 - k_B T \ln\left(e^{+zJ\langle\sigma\rangle/k_B T} + e^{-zJ\langle\sigma\rangle/k_B T}\right)$$
$$= F_0 + a\langle\sigma\rangle^2 + b\langle\sigma\rangle^4 + \cdots$$

Due to Z_2 symmetry ($\sigma \longrightarrow -\sigma$), only <u>even</u> powers allowed

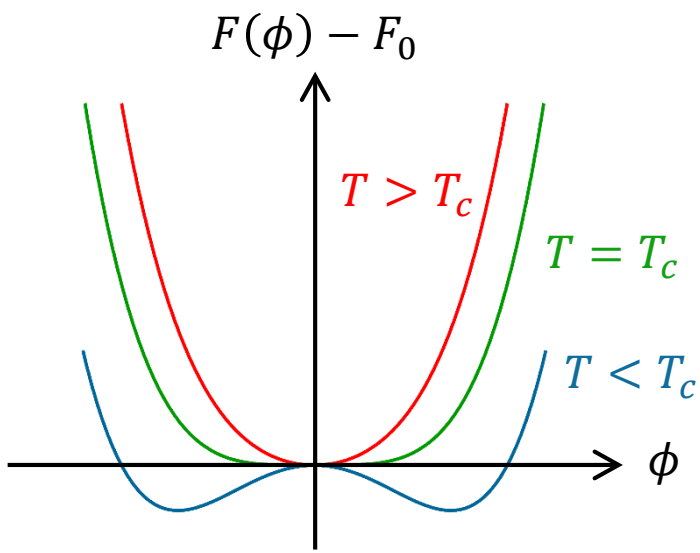
$$F_0 = -k_B T \ln 2 \qquad a = \underbrace{\frac{zJ}{2}\left(1 - \frac{T_c}{T}\right)}_{\text{reverses sign when } T = T_c} \qquad b = \underbrace{\frac{z^4 J^4}{12 k_B^3 T^3}}_{\text{always positive}}$$

Landau Theory

- Classic second-order (continuous) phase transition with OP ϕ:

$$F(\phi) = F_0 - C\phi + a\left(\frac{T}{T_c} - 1\right)\phi^2 + b\phi^4$$

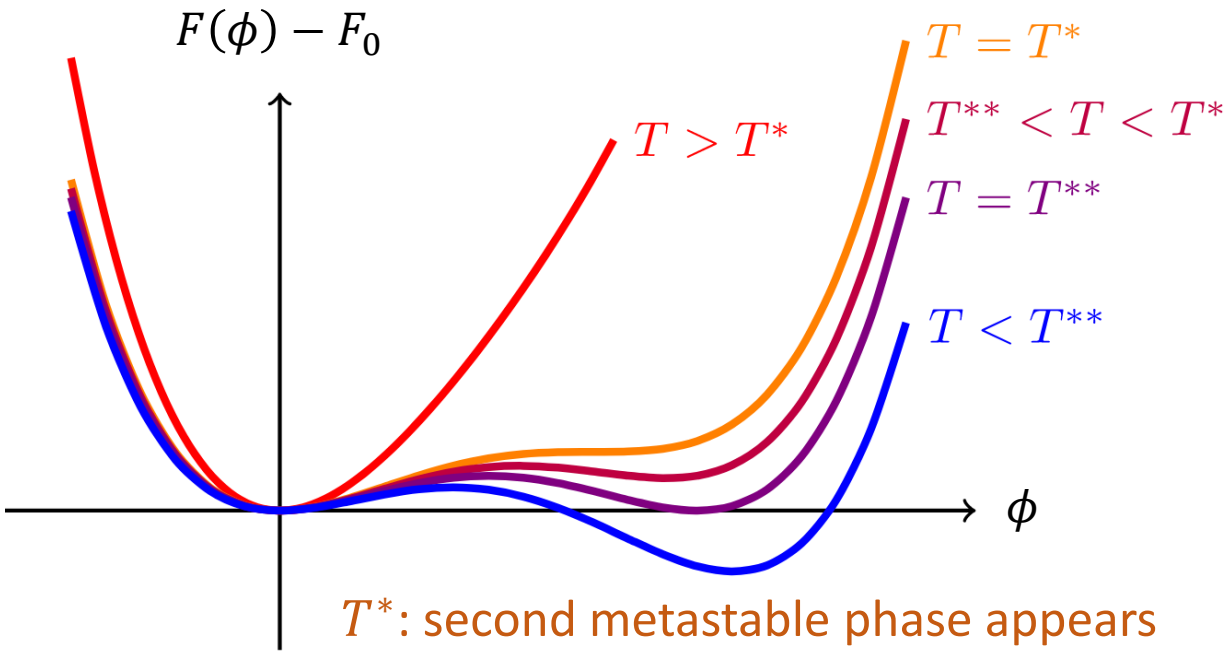
Conjugate Field: external field that couples linearly to the OP (e.g. ferromagnetism: magnetic field, ferroelectricity: electric field, structural distortion: strain). Must have same symmetry (irrep) as the OP it couples to.

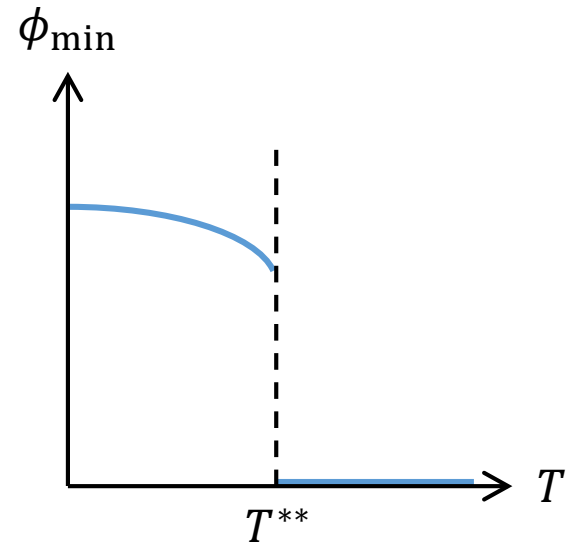


Landau Theory

- Landau theory can also describe first-order phase transitions
  - Requires an invariant <u>cubic</u> term in the free energy

$$F(\phi) = F_0 + a\left(\frac{T}{T_c} - 1\right)\phi^2 - b\phi^3 + c\phi^4$$





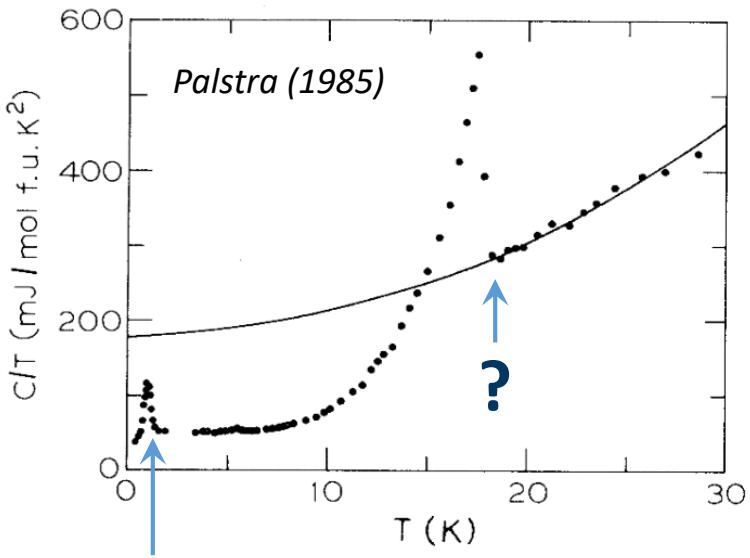
T^*: second metastable phase appears

T^{**}: phase coexistence

Hidden Order

- "Hidden Order": when there are thermodynamic signatures of a phase transition (e.g. heat capacity) but no other evidence
  - No apparent conjugate field
    - Could arise from a higher-order symmetry breaking (e.g. multipolar order)

- **Example:** URu_2Si_2



superconductivity

Mydosh (2014)

Table 2. Summary of analytic theories and models proposed to explain the HO, with an emphasis on the recent contributions.

Barzykin and Gorkov (1995)	three-spin correlations [45]
Kasuya (1997)	uranium dimerisation [46]
Ikeda and Ohashi (1998)	*d*-spin density wave [47]
Okuno and Miyake (1998)	CEF and quantum fluctuations [48]
Chandra et al. (2002)	orbital currents [49]
Viroszek et al. (2002)	unconv. spin density wave [50]
Mineev and Zhitomirsky (2005)	staggered spin density wave [51]
Varma and Zhu (2006)	helicity (Pomeranchuk) order [52]
Elgazzar et al. (2009)	dynamical symmetry breaking [53]
Kotetes et al. (2010)	chiral *d*-density wave [54]
Dubi and Balatsky (2011)	hybridization wave [55]
Pepin et al. (2011)	modulated spin liquid [56]
Fujimoto (2011)	spin nematic order [57]
Riseborough et al. (2012)	unconv. spin-orbital density wave [58]
Das (2012)	spin-orbital density wave [59]
Chandra et al. (2013)	hastatic order [60]
Hsu and Chakravarty (2013)	singlet-triplet *d*-density wave [61]