Symmetry and Order in Quantum Materials

John Harter
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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:

\[
\mathbf{r} \rightarrow \{R|\mathbf{T}\}\mathbf{r} = R\mathbf{r} + \mathbf{T}
\]

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

\[
R = \begin{bmatrix}
0 & -1 & 0 \\
1 & 0 & 0 \\
0 & 0 & 1
\end{bmatrix}, \quad \mathbf{T} = \begin{bmatrix}
0 \\
0 \\
\frac{c}{4}
\end{bmatrix}
\]
What is symmetry?

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

\[ U^\dagger \mathcal{H} U = \mathcal{H} \]

\[ \Rightarrow \mathcal{H} U = U \mathcal{H} \]

\[ \Rightarrow [\mathcal{H}, U] = 0 \]

\[ \Rightarrow \text{can simultaneously diagonalize } \mathcal{H} \text{ and } U \]

\[ \Rightarrow \text{wavefunctions are eigenfunctions of } U \]

• Example: an isolated atom
  • \( \mathcal{H} \) is invariant under spatial inversion (\( \vec{r} \rightarrow -\vec{r} \))
  • 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

• Symmetry has many useful implications
  • Indicates what wavefunctions **must** 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 \([t \rightarrow -t]\)
  • Permutation symmetry \([\hat{P}\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1)]\)
  • Enables classification of elementary particles:
    • Eigenvalue = +1: “Bosons”
    • Eigenvalue = −1: “Fermions”
    • Eigenvalue = \(e^{i\theta}\): “Anyons” (only allowed in 2D)
  • Gauge symmetry \([\psi(\vec{r}, t) \rightarrow e^{i\theta(\vec{r}, t)}\psi(\vec{r}, t)]\)
  • Requires simultaneous transformation of potential functions: \(V \rightarrow V + \hbar \frac{\partial \theta}{\partial t}, \vec{A} \rightarrow \vec{A} - (\frac{\hbar}{e}) \vec{V} \theta\)
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$_3$

$$Pm\overline{3}m \rightarrow I4/mcm$$

Loetzsch (2010)
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 $\mathcal{H}$: $\sigma_i \rightarrow -\sigma_i$ ($\mathbb{Z}_2$ 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):

\[
F = \left(\frac{zJ}{2}\right) \langle \sigma \rangle^2 - k_B T \ln\left(e^{+zJ\langle \sigma \rangle/k_B T} + e^{-zJ\langle \sigma \rangle/k_B T}\right)
\]

depends on \(T\) — entropic

\[
\langle \sigma \rangle_{\text{min}}: \begin{cases} 
1.2 \\
1.1 \\
1.0 \\
0.9 \\
0.8
\end{cases}
\]

PM: \(\langle \sigma \rangle = 0\)

FM: \(\langle \sigma \rangle \neq 0\)

\(Z_2\) sym. broken
Symmetry Breaking in the Ising Model

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

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

PM: \( \langle \sigma \rangle = 0 \)

FM: \( \langle \sigma \rangle \neq 0 \) (sym. broken)

PM: quantum critical point (QCP): ground state changes symmetry, not related to entropy

FM: classical (i.e. thermal) Ising critical point, entropy-driven
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 \quad \rightarrow \quad \text{OP} = \phi
```

{Atom 1: $\Delta \vec{r} = \begin{bmatrix} \phi \\ 0 \end{bmatrix}$, Atom 2: $\Delta \vec{r} = \begin{bmatrix} 0 \\ -\phi \end{bmatrix}$, ...}
Magnetic Order Parameters

- The fundamental symmetry broken by magnetic order is time reversal symmetry ($t \rightarrow -t$)
  - Spins are odd under time reversal ($\vec{S}_i \rightarrow -\vec{S}_i$)
    - 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

![Diagram of FeGe with magnetic phases]
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 $\rightarrow$ 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)

\[ \eta = \sum_k \hat{k} \cdot s(k) \]

**Ferroelectric** (vector)

\[ P = \sum \hat{k} \times s(k) \]

**Multipolar Nematic** (rank-2 pseudotensor)

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

\[ P \parallel \hat{z} \]

\[ Q_{xy} \neq 0 \]
Superconducting Order

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

- OP is the Cooper pair wavefunction:
  $$\psi_{-k}^{\alpha \beta} = \left\langle \hat{c}_{-k \alpha} \hat{c}_{-k \beta} \right\rangle \quad \alpha, \beta = \uparrow, \downarrow$$

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

\[
\begin{align*}
\text{Hg, Nb, Pb, etc.} & \quad \psi(\vec{k}) \propto 1 \\
& \quad (\text{singlet, } s\text{-wave}) \\
\text{cuprates} & \quad \psi(\vec{k}) \propto (k_x^2 - k_y^2) \\
& \quad (\text{singlet, } d\text{-wave}) \\
\text{Sr}_2\text{RuO}_4 & \quad \tilde{\psi}(\vec{k}) \propto \hat{z}(k_x \pm i k_y) \\
& \quad (\text{triplet, } p\text{-wave})
\end{align*}
\]
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) $\rightarrow$ acoustic phonons
  Ferromagnetism (spin rotation sym. broken) $\rightarrow$ 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

\[
F = \frac{zJ}{2} \langle \sigma \rangle^2 - k_B T \ln (e^{+zJ\langle \sigma \rangle/k_B T} + e^{-zJ\langle \sigma \rangle/k_B T})
\]
\[
= F_0 + a \langle \sigma \rangle^2 + b \langle \sigma \rangle^4 + \ldots
\]

\[
F_0 = -k_B T \ln 2
\]
\[
a = \frac{zJ}{2} \left( 1 - \frac{T_c}{T} \right)
\]
\[
b = \frac{z^4 J^4}{12 k_B^3 T^3}
\]

Due to \( Z_2 \) symmetry (\( \sigma \rightarrow -\sigma \)), only even powers allowed

reverses sign when \( T = T_c \)

always positive
Landau Theory

- Classic second-order (continuous) phase transition with OP $\phi$:

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

**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.

![Diagram](image_url)
Landau Theory

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

\[ F(\phi) = F_0 + a \left( \frac{T}{T_c} - 1 \right) \phi^2 - b\phi^3 + c\phi^4 \]
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$_2$Si$_2$

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

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