

Quantum Phase Transitions

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Abstract

While classical phase transitions are common phenomena widely understood on a basic level, the subject of quantum phase transitions is much less frequently broached at a pedagogical level. Here, our discussion will start with a basic introduction of the fundamental differences (and similarities) between classical and quantum phase transitions. We will introduce the Ising model as a quantitative model of phase transitions, and major results of the 1D Ising model will be briefly reviewed. Moving into applications of quantum phase transitions using the Ising model, the magnetization phase diagram of LiHoF₄ will be presented, along with some of the electronic structure properties of the compound to demonstrate why it is a suitable example. Electronic structure properties, such as dipole moment, will be calculated in the worksheet using Maple. Overall, students should come away with an appreciation of using the Ising model to understand quantum phase transitions, and how this model can be applied to real systems. This worksheet uses the Maple Quantum Chemistry Toolbox.

Introduction

What is a Phase Transition?

Phase transitions are a very common part of our every day lives. We see the change from ice to liquid water when the snow melts in the Chicago spring, or the hardening of iron into stainless steel with the addition of carbon and other elements. While phase transitions are often visualized as being the intersection of the solid, liquid, and gas phases as a function of temperature and pressure (Figure 1), there are many more distinct types of phase transitions.

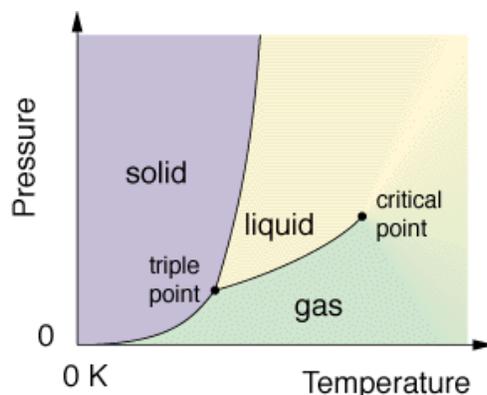


Figure 1: Typical representation of a phase diagram plot, where first order phase transitions occur when crossing over solid lines, and continuous phase transitions occur in the regime past the critical point. This plot, or similar ones with slight variations, are good qualitative descriptors of how phase changes with changes in pressure and temperature. (Source: <http://tl.tkk.fi/research/theory/typicalpt.html>)*

In a first order phase transition, there is a distinct change in the properties of the system, which describes the "phase" of the system. Multiple phases can occur in equilibrium along the boundaries of each phase (see Figure 1), and these boundaries are referred to as coexistence lines. The triple point occurs at the intersection of the coexistence lines, and is where three distinct phases exist in equilibrium with each other.

In a continuous phase transition, the properties of the system vary **continuously**. This behavior can be observed on Figure 1, in the region past the critical point: the transition between liquid and gas can be approached without any jumps or discontinuities in the properties of our system - we can get from the liquid to the gas phase without crossing the coexistence line.

One last observation we can make from the phase diagram in Figure 1 is about the axes, and what they represent. We see that our state is a function of two parameters, temperature and pressure. If we have defined those two, the phase (or phases, if the point falls on a coexistence line) is well defined. The parameters that control the state of our system are referred to as **order parameters**. Other common order parameters observed in quantum phase transitions are composition, strength and orientation of an external field, and even time!

How can we understand Phase Transitions using Statistical Mechanics?

As we move from an ordered phase to a disordered phase, we see a change in the macroscopic order parameter. On the microscopic level, we see a change in the fluctuations of the material, and we can analyze these fluctuations using statistical mechanics. Materials are constantly in motion, even if that motion is on a microscopic scale.

These motions are referred to as fluctuations, and are defined by how far they reach and how long they persist for. The spatial distance that particles remain correlated for is referred to as the **correlation length**, and the duration of time that particles remain correlated for is referred to as the **correlation time**. As both the correlation length and correlation time increase, the system approaches a phase transition - and the increase in correlation lengths and times are a function of order parameter. For most classical transitions, the driving factor for the changes in fluctuations is the thermal energy of the system. In contrast, quantum fluctuations are caused by uncertainty due to the Heisenberg uncertainty principle, because the structure and dynamics (position and momentum) are coupled. There is a transition regime where quantum fluctuations are outweighed by classical fluctuations, as seen in Figure 3 below:

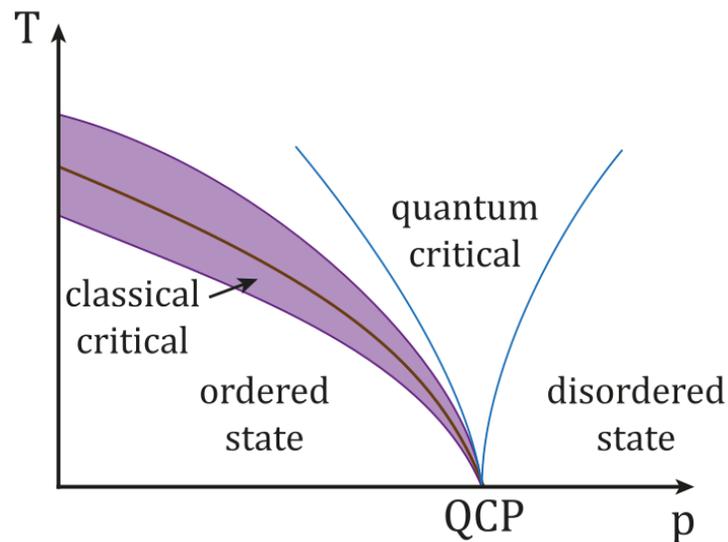


Figure 2: A typical quantum phase diagram. P is a generic order parameter, and T is the temperature of the system. To observe the quantum phase transition from order to disorder the temperature scale must be very close to absolute zero, or else the classical critical regime will be reached first. (Source: <https://commons.wikimedia.org/wiki/File:QuantumPhaseTransition.png>)*

Because of the competing nature of quantum and thermal fluctuations, all quantum phase transitions must take place at very low temperatures. One prevalent behavior that emerges due to quantum phase transitions include superconductivity, and almost all known superconductors operate just a few degrees above absolute zero.

Theory

In the context of statistical mechanics, both classical and quantum phase transitions are understood quantitatively through the Ising model. The Ising model gives us a simple picture to frame our thinking of how we can analytically understand how the interactions between molecules lead to fluctuations and correlated motion.

Ising Model: 1 Dimension

The Ising model starts to analyze correlation lengths by looking just at nearest neighbor interactions. To start, imagine a long line of N spins that can take one of two states: spin up or spin down (Figure 4).



Figure 3: Spins on a one dimensional lattice.**

The spins are in an external magnetic field H , and have a magnetic susceptibility μ . We can set up this system and describe the energy of a particular state a with the following equation:

$$1. \quad E_a = - \sum_{i=1}^N (H \mu s_i) - \sum_{i>j}^N \sum_{j=1}^{N-1} (J s_i s_j)$$

The variable

$s_i = \pm 1$, to designate if the spin is up or down

. The first term simply describes the energy of each individual particle, while the second term describes the pairing between particles with the coupling constant, J . For a positive value of J , we can see that the second term contributes to lowering the energy when the spins are aligned, and introduces an energy penalty for when they are not aligned. The spontaneous magnetization M of the system can be evaluated as:

$$2. \quad M = \sum_{i=1}^N (\mu s_i)$$

Solving for the partition function at zero field (the conditions under which a neat analytical solution can be obtained), we note that the spontaneous magnetization of the system is zero. Introduction of an external magnetic field ($H > 0$), however, introduces the order parameter that controls the behavior of our system and produces continuous changes in the value of our observable M .

Ising Model: 2 Dimensions and More

The one dimensional Ising model can be extended to include pairwise interactions from nearest neighbors in multiple dimensions (Figure 5).

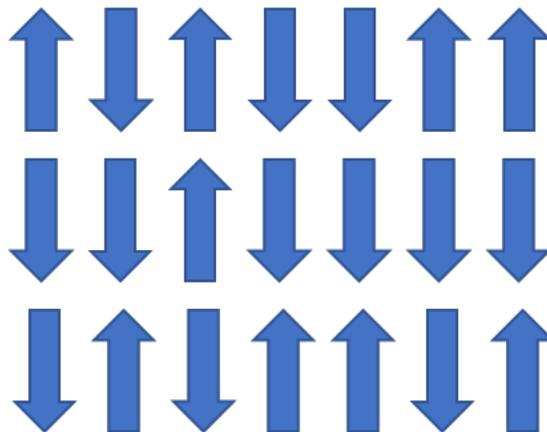


Figure 4: Spins on a two dimensional lattice. **

Generalizing to multiple directions significantly complicates the system, as we are now looking at $2d$ neighbors instead of just 2, where d is the number of dimensions. However, this picture provides a more complete view of how particles interact in space. The equations for the 1-D Ising model can be generalized to give the following result:

$$3. \quad M \sim N \left((T_{crit} - T) \right)^\beta$$

Where T is the observed temperature of the system, T_{crit} is the critical temperature of the system at

which the phase change occurs, and β is the critical coefficient which is equal to 0.125 in two dimensions and roughly equal to 0.313 for three dimensions.

Application: LiHoF4

LiHoF4 is one example of a materials whose magnetic properties change due to a quantum phase transition, and so is well described by the Ising model. After loading the [Quantum Chemistry](#) package, we can visualize LiHoF4 and explore some of these properties using electronic structure methods.

Quantum Chemistry

We set the number of **Digits** to be used in computations to 15 and load the Quantum Chemistry package using Maple's **with** command.

```
> Digits := 10;
Digits := 10 (4.1.1)
```

```
> with(QuantumChemistry);
[AOLabels, ActiveSpaceCI, ActiveSpaceSCF, AtomicData, BondAngles, BondDistances,
Charges, ChargesPlot, CorrelationEnergy, CoupledCluster, DensityFunctional,
DensityPlot3D, Dipole, DipolePlot, Energy, FullCI, GeometryOptimization, HartreeFock,
Interactive, Isotopes, MOCoefficients, MODiagram, MOEnergies, MOIntegrals,
MOOccupations, MOOccupationsPlot, MOSymmetries, MP2, MolecularData,
MolecularGeometry, NuclearEnergy, NuclearGradient, Parametric2RDM, PlotMolecule,
Populations, RDM1, RDM2, ReadXYZ, SaveXYZ, SearchBasisSets, SearchFunctionals,
SkeletalStructure, Thermodynamics, Variational2RDM, VibrationalModeAnimation,
VibrationalModes, Video] (4.1.2)
```

LiHoF4

Lithium holmium (III) fluoride is an excellent example system, as it undergoes a quantum phase transition that can be investigated via the Ising model. The resulting phase diagram is shown in reference 5 with order parameters of temperature and effective field (B_{eff}). When in the ordered state, LiHoF4 is a superconductor, and is one of the prototypical examples for studying superconductivity (5).

Note that many of the properties relevant for phase transitions are based on fluctuations of many molecules, and that LiHoF4 displays these properties when in a crystal lattice. An interactive model of the crystal structure of LiHoF4 is available at https://materials.springer.com/isp/crystallographic/docs/sd_0550732. Notice the arrangement and interconnectivity of each chemical species.

Nevertheless, it is instructive to look at a "molecule" of LiHoF4 using coordinates generated from Avogadro, a molecule building software.

```

> mol := [{"Ho", 1.35262, 0.24058, -0.31919}, {"F", 3.13335,
1.31867, 0.23120}, {"F", -0.23674, -1.03231, -1.01908}, {"Li",
1.99270, -2.45063, 0.92135}, {"F", 1.12078, 2.02964, -1.49465},
{"F", 0.88440, 0.63567, 1.74501}];
mol := [{"Ho", 1.35262000, 0.24058000, -0.31919000}, {"F", 3.13335000, 1.31867000,
0.23120000}, {"F", -0.23674000, -1.03231000, -1.01908000}, {"Li", 1.99270000,
-2.45063000, 0.92135000}, {"F", 1.12078000, 2.02964000, -1.49465000}, {"F",
0.88440000, 0.63567000, 1.74501000}]
> PlotMolecule(mol);

```

(4.2.1)



>

After visualizing the geometry, we can calculate and plot the dipole moment of LiHoF4:

```

> Dipole(mol, method = HartreeFock, basis = "crenbl");

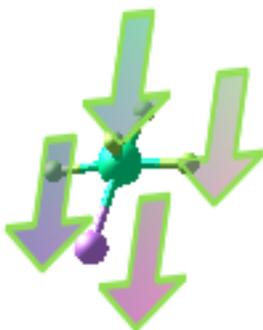
```

"X"	6.16972605		(4.2.2)
"Y"	-13.85126606		
"Z"	3.16209911		

```

> DipolePlot(mol, method = HartreeFock, basis = "crenbl");

```



>

While the above plot is for the electric dipole, it still provides a powerful image for relating the net dipole vector to the Ising model, which relates our hypothetical "spins" to orientations of these vectors within the crystal lattice.

Conclusion

In this review, we have discussed important properties of quantum phase transitions, including their continuous behavior and correlation length and correlation time scales. We discussed the relevance of statistical mechanics, and saw how we can apply the Ising model, a tool from statistical mechanics, to understand the properties of quantum phase transitions. Finally, we used lithium holmium (III) fluoride as an example of a system that has a quantum phase transition, and related the dipole moment direction as an order parameter for a hypothetical Ising model. In general, we could extend this idea to other quantum systems and look at the emergence of unique properties that arise from phase transitions, including superconductivity. Quantum phase transitions are an important field of research, and may yield many surprising and exciting results in the future that build off the basic principles laid out in this worksheet.

References

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