

Modern Physics (PHY 3305) Lecture Notes

Think Big: Statistical Mechanics I (Ch. 9.1, 9.3, and Appendix J-8)

Steve Sekula, 16 March 2010 (created 16 March 2010)

Review

no tags

Let's begin with a post-Spring Break refresher on spin. I want to spend a little extra time on this because it's an important concept going forward and I want things fresh in your mind.

The Atom

A discussion of the atom, in lieu of non-relativistic quantum mechanics and the SWE, revealed that for each dimension in which the problem is studied (e.g. 3 dimensions of space), we obtain a new quantized thing - a new QUANTIZATION CONDITION. From the atom, with its spherical symmetric Coulomb Potential, we obtained:

- Principal Quantum Number, n , from the radial coordinate (r)
- Total Angular Momentum (L) Quantum Number, ℓ , from the polar angle (angle of the electron from the z axis)
- Z-component of Angular Momentum (L_z) Quantum Number, m_ℓ , from the azimuthal angle (angle around the z -axis in the x - y plane)

The rules for relating quantum numbers to quantities were:

- Total energy is related to n , just as in our square well considerations
- Total angular momentum is given by $L = \sqrt{\ell(\ell+1)}\hbar$, where $\ell = 0, 1, 2, \dots, n-1$
- L_z is given by $L_z = m_\ell \hbar$, where $m_\ell = -\ell, -\ell+1, \dots, \ell-1, \ell$

We also observed that $L_z < L$, and that this is because of the uncertainty principle (if $L_z = L$, we know the total momentum in the z -direction is exactly zero and we know the wave function is entirely confined to the x - y plane ($z=0$), and this is not possible).

Testing Angular Momentum Quantization

We then discussed how you look for angular momentum quantization, and we talked about the *Stern-Gerlach* experiment. We predicted that putting hydrogen atoms into this experiment, prepared in a state of $L = 0$, would lead to no deflection of the hydrogen atoms by the non-linear magnetic field. However, in reality there is a bifurcation (a splitting in two) of the beam, even when $L = 0$! We attribute this to an INTERNAL ANGULAR MOMENTUM QUANTITY intrinsically carried by the electron, proton, etc, called "SPIN".

Spin

Spin has no classical analog. As your homework #6 illustrates, it DOES NOT correspond to the actual rotation of the electron. It is a name for a thing for which we have no equivalent, but which behaves AS IF the electron were a top that cannot be stopped or sped up.

Spin is just like orbital angular momentum, L :

- $S = \sqrt{s(s+1)}\hbar, s = 0, \pm\frac{1}{2}, \pm 1, \dots$
- $S_z = m_s\hbar, m_s = -s, -s+1, \dots, s-1, s$

Wave Functions in Lieu of Spin

We then re-thought the wave function and realized that spin has to be incorporated into it. We wrote:

- *Missing close brace*

Experimentally, we know that the spin of the electron (and many other particles) is $s = \frac{1}{2}$, which means that an electron by itself already has two possible states of S_z : spin-up, or $S_z = +\frac{1}{2}\hbar$, and spin-down, or $S_z = -\frac{1}{2}\hbar$. So all other things being equal in an atom (two electrons in the same orbital position in an atom, for instance), there are still two possible internal quantum states the electrons can occupy. This fact gives RICH structure to the atom, and is in fact the basis of chemistry.

Identical Particles

We then confronted a problem that is also unique to quantum mechanics:

identical particles. Since we can use a Sharpie to mark which electron is which, all electrons are essentially indistinguishable. For instance, if I tell you there are two electrons in an otherwise empty box, separated into different halves of the box by a partition, and then I ask you to close your eyes and open them later, is there an experiment you can conduct to figure out whether I swapped the electrons?

The answer is "no," and this has consequences.

Since two electrons are IDENTICAL, we have to assert that the laws of nature cannot depend on whether Electron A is doing something that Electron B could be doing, or vice versa. Nature should be "democratic" in this way. But if we try to write a two-particle wave function describing two electrons as

$$\psi(x_1, x_2) = \psi_n(x_1)\psi_{n'}(x_2)$$

where 1 and 2 label the electrons, we get into trouble, since there is no guaranteed that:

$$P(x_1, x_2) = P(x_2, x_1)$$

That is, that the outcome of a measurement is independent of which electron (1 or 2) is where. The example is to consider two electrons in an infinite well, one in the ground state and another in the first excited state. Try swapping them and see if the above is invariant under that exchange.

Instead, we have to construct multi-particle wave functions that satisfy:

$$P(x_1, x_2) = P(x_2, x_1)$$

Or nature will "know the difference" when two electrons swap roles. We constructed two kinds of wave functions, based on this requirement:

$$\psi_S(1, 2) = \psi_n(1)\psi_{n'}(2) + \psi_{n'}(1)\psi_n(2)$$

(the symmetric wave function) and

$$\psi_A(1,2) = \psi_n(1)\psi_{n'}(2) - \psi_{n'}(1)\psi_n(2)$$

(the anti-symmetric wave function).

We observed that symmetric wave functions allow two particles to occupy the same quantum state ($n = n'$) with non-zero probability, but the same is NOT true for anti-symmetric multi-particle wave functions.

Spin and *Multi-Particle* Systems

it has been shown theoretically, and demonstrated experimentally, that when a multi-particle system consists entirely of identical half-integer-spin particles (FERMIONS), the total wave function is ANTISYMMETRIC. Likewise, it has been shown theoretically and experimentally that when a multi-particle system consists entirely of identical integer-spin particles (BOSONS), like photons, the total wave function is SYMMETRIC.

This leads to the idea of the Pauli Exclusion Principle: identical fermions cannot occupy the same quantum state. It's not that they repel one another - it's that their wave functions must configure in such a way as to give zero-probability of being in the same state where they DO overlap. This leads to higher-curvature wave functions (functions with implicitly higher frequencies and shorter wavelengths), and this fermion systems tend to have more internal energy than bosonic systems. This same idea is behind the idea of a *Bose-Einstein* condensate, where a large number of identical bosons all enter into the same quantum state and behave as one, single wave function in a single state.

Describing *Multi-Particles* Systems - Statistical Mechanics

We are surrounded by a vast number of particles. As physicists, we are concerned with making predictions about the properties and behavior of systems where the NUMBER OF PARTICLES IS LARGE, typically Avagadro's Number (6.022×10^{23}).

- We want to make STATISTICAL predictions based on the laws of MECHANICS

We will see that quantum ideas, such as spin, will play important roles in

the behavior of large systems. But first, we need to develop a language for describing and studying such systems. That language is statistics and probability.

Coin Flips

We begin with the simplest example of probability. Imagine a perfect coin, where the chance of landing heads or tails is exactly 50%. What is the chance that the coin will land heads up if 5 flips are performed?

ANSWER: $P = p^n$ where p is the probability of heads and n is the number of flips. Each flip is independent (doesn't depend on the outcome of the previous flip), and so the probability just multiplies. $P = 3.1\%$.

Fun example of the maddening coin toss: the film "Rosencrantz and Guildenstern Are Dead" depicts a coin which, when flipped, each time lands heads - 92 times in a row. I always took this to mean that they are thinly aware that they are not acting outside of the force of the author (Shakespeare), who has a path set for them (death) from which, despite their actions, they cannot deviate - chance plays no role in their fate.

Building on Coin Flips - Parking Cars

Let's park some cars. Imagine we have N cars and N spaces in which to stick them. How many unique arrangements of the cars are there?

- ANSWER: we can put any of N cars in the first space, $N-1$ in the second, etc. Parking just TWO cars already has $N(N-1)$ possibilities! The total number of possibilities is $N(N-1)(N-2)\dots 3 \cdot 2 \cdot 1 \equiv N!$ Factorials are part of the language of probability, and will play a leading role in our discussions. It is critical to build comfort with them.

Let's make the problem slightly harder, shall we? What if we designate N_i of the N spaces as some kind of special zone - like, cars that park there get coupons on their windshield, or something like that? For a given arrangement of all cars in the parking spaces, there will be N_i cars in those spots. But it doesn't matter what ORDER those three cars park in the N_i spots - they're going to get coupons, so long as they park in those three spots. So now we can ask: how many arrangements of those N_i cars are there such that the remaining $N - N_i$ cars are unaffected?

ANSWER: $N_i!$.

Let's go one step further. How many arrangements of the N cars are there result in a unique group of people getting the coupons? Well, there are $N!$ arrangements of the N cars in N spaces, for each there are $N_i!$ arrangements of cars in the N_i spaces that leave the rest unchanged (those same three cars will all get coupons regardless of how they are arranged in the spaces).

ANSWER: $N!/N_i!$ Work an example of 4 cars to demonstrate this.

Now, imagine that two different establishments run coupon deals, and each designate different groups of N_i and N_j spaces for their rewards. How many arrangements of N cars will result in unique people getting the coupons?

ANSWER: $N!/(N_i!N_j!)$

In general, if you have N things that can be arranged into M groups:

$$W = N! / \prod_{i=1}^M N_i!$$

A typical case is $M=2$ - a two-state system - where we define the number of objects in one state as n and the number in the other state as $N - n$, yielding:

$$W = \frac{N!}{n!(N - n)!}$$

This is called the BINOMIAL COEFFICIENT of such a state, and is the number of ways that state can be achieved. It is often written using the notation:

$$W = \binom{N}{n}$$

A *Two-State* Multi-particle System

Let's go back to thinking about particles. We have some language now that we can use to discuss the number of unique ways that a given state is possible. By "state", I mean a specific way of arranging particles into a set of "boxes" (e.g. energy levels, positions in space, etc).

Consider a gas that is trapped in a box. Imagine drawing a line down the center of the box and partitioning the gas into two halves. You can then ask questions like, "What is the chance that half the gas molecules are on the left side or the right side of the box?" or "What is the chance that all gas molecules are on the right side?"

Let's define N as the number of molecules in a gas, and N_R the number of those molecules present on the right-hand side of the box. Let's consider a gas of just four molecules, and answer some of these basic questions:

- What is the number of ways that all particles can be on the left-hand side of the box?
 - ANSWER: $W_{N_R}^N = \binom{N}{N_R}$ for our problem, and we are interested in $N = 4$ and $N_R = 0$. Thus: $W_0^4 = 4!/0!(4-0)! = 1$. There is ONE way of obtaining this case
- What is the number of ways that 1 particle can be on the right-hand side?
 - ANSWER: $W_1^4 = 4!/1!(4-1)! = 4$. There are four ways this can happen.
- What is the number of ways that half of the particles can be on the right-hand side?
 - ANSWER: $W_2^4 = 4!/2!2! = 6$. There are six ways this can happen.

What do we observe?

ANSWER: The more uniformly distributed the system, the more chances there are to be in that state. This observation extends to even larger number of particles, but is nicely illustrated here.

In fact, the more particles, the less likely you are to wind up in extreme cases where all gas molecules are on just one side of the room. We can know properties much better as the number of participants increases.

Statistical Mechanics: Definitions

We have seen how increasing the number of objects to a large number

(we'll be concerned with Avagadro's number, typically), makes it easier to make predictions about the state of the system. Let us make some definitions:

- A THERMODYNAMIC SYSTEM is one in which the number of particles is large enough that predictions become precise
 - properties under consideration are macroscopic properties, such as temperature, pressure, and density.
 - STATISTICAL MECHANICS is an area of research that informs many other areas, but is it's own study in physics. We will need it going forward to discuss solids and gases, so we'll pause from quantum mechanics for a bit to learn this tool.
- Our concerns: energy distributions
 - generally, the higher the energy of a state, the fewer the number of particles occupying that state.
- States:

Reliable Predictions: Example

See slides for demonstration of the reliability of predictions for large numbers of weakly/non-interacting particles (systems where particle states are not correlated).

Micro-states and Macro-states

Each "way" of obtaining a distribution in which (as above) $N_R = \frac{1}{2}N$ is a "micro-state." Think about the parked cars (see slides).

- The micro-state is the state of the system given complete microscopic knowledge of the individual particles. In the two-sided room, each particle is either a left-side or a right-side particle.

Can we know the micro-state of a gas?

ANSWER: not realistically. We know what limits quantum mechanics places on exact knowledge about each individual particle.

We therefore are more interested in the "macro-state" of the system - the number, or concentration, of particles on each side of the room, for instance.

- The macro-state describes an overall condition of being, achieved by

many possible micro-states. To know the macro-state is to know properties that don't depend on the exact microscopic states of individual particles: number, energy, volume, average pressure, average temperature, particle density.

Let's think about our four gas molecules again. The macrostate $N_R = 2$ has the most corresponding micro-states that achieve it, while the case $N_R = 0$ has the fewest micro-states that achieve it (there is 1).

The macro-state that corresponds to the most micro-states, where each micro-state is equally probably, is the mostly likely macro-state of the system. It's the most probable state of the system. This is called the EQUILIBRIUM STATE.

Equilibrium

If left alone (no external forces), a thermodynamic system eventually comes to EQUILIBRIUM, the state where its properties (pressure, temperature, density) do not change with time.

DISCUSS what happens if you prepare the room such that all particles start on one side.

- later, left unaffected by external forces, the particles will end up on a micro-state that yields the most probably macro-state - that's simply because there are more micro-states available to that macro-state, and it's highly unlikely to end up back in the state where all gas is on one side of the room again.

This defines equilibrium.

The same argument applies to energy states. If we prepare a system of atoms such that half are in their ground state and the other half are in their 37th energy level, eventually they will all wind up in whatever the most-probable state is for the system.

Our next study will focus on EQUILIBRIUM ENERGY STATES.

Next Time

- The Boltzmann Distribution

- Classical averages - average speeds and densities, without regard to the indistinguishability of particles
- Quantum distributions - how do indistinguishability and quantized properties affect nature?

Reminder

Choose your in-class presentation topic by Friday!