The Hydrogen Atom

Probabilities and Probabilistics

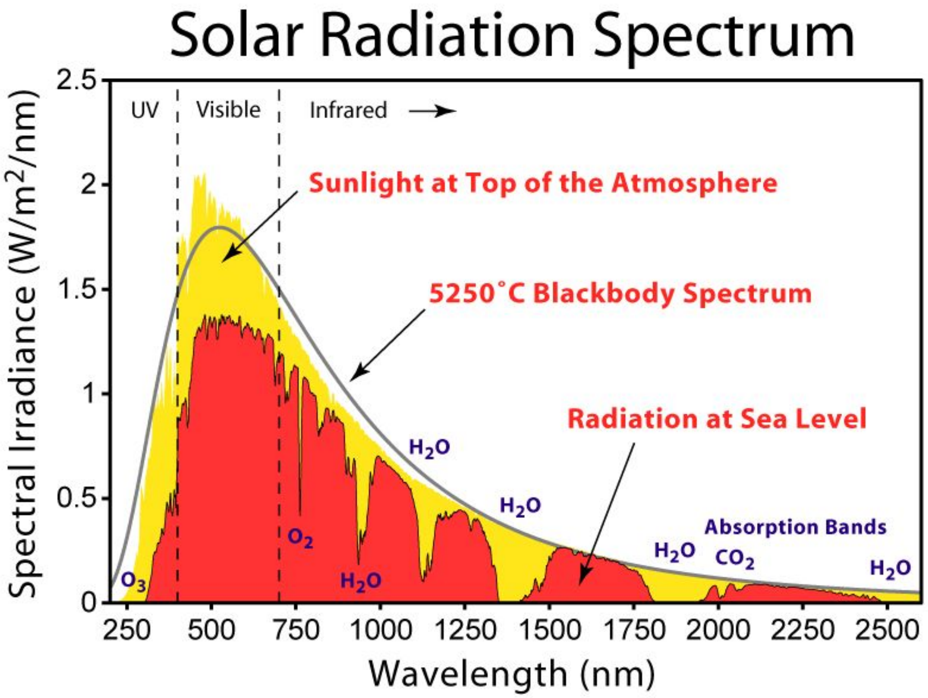
A Catastrophe

Blackbodies

If you shine a light on any object, they can either absorb, reflect, or transmit that light.

Blackbodies are only allowed to absorb and re-emit light.

They pretty accurately model celestial radiation, even for our sun!

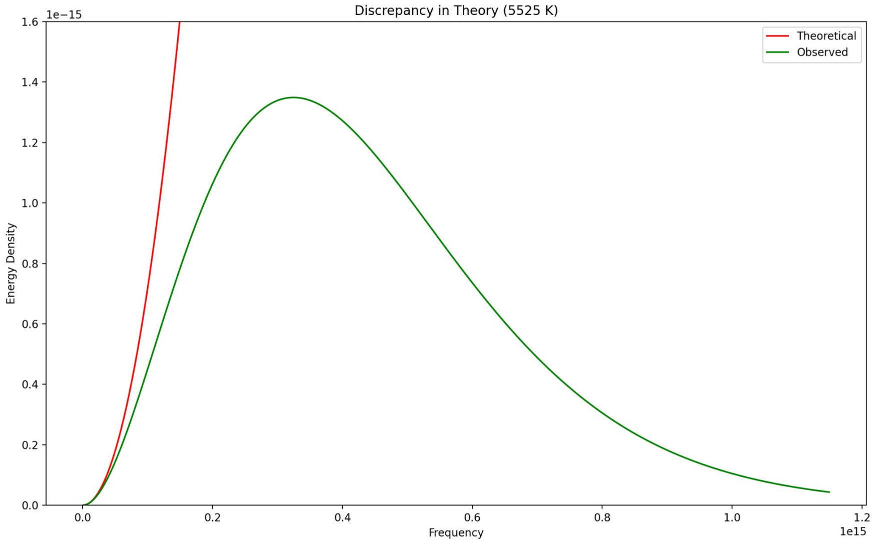


Blackbody Energy

A blackbody gains energy by absorbing light of different frequencies.

How much of the energy is due to light of a specific frequency?

Lord Rayleigh, and later Jeans, came up with an expression that works well for low frequency emissions.



Why does it fail for higher frequencies?

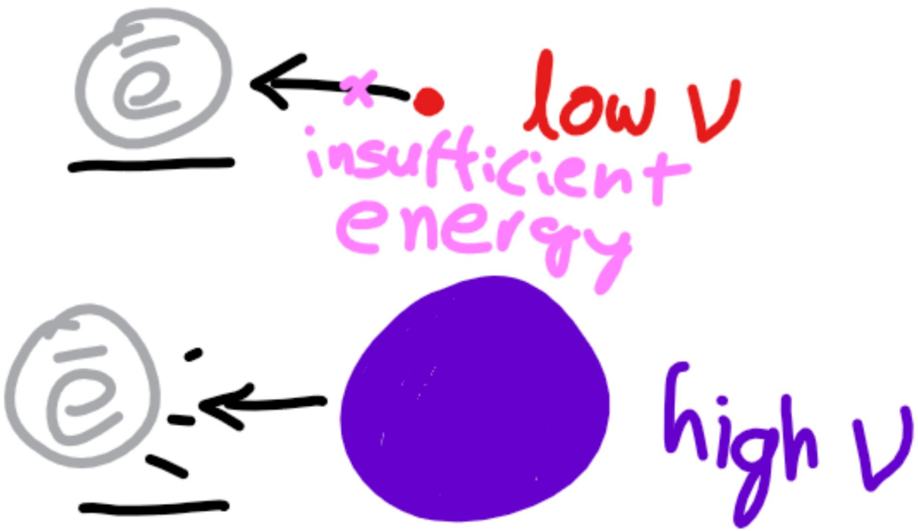
Bite-Sized Pieces

Photoelectric Effect

For decades, people have been using light to blast electrons off of metals.

They noticed higher frequency lights had more success in removing these electrons.

This led to the theory that light was made of particles (photons) whose individual energies were proportional to the frequency of the light.



De Broglie Wavelength

We can compare the photon energy with Einstein's famous equation for massless particles.

A little rearranging gives us the momentum in terms of the frequency.

The product of wavelength and frequency is the speed of the wave, giving us a relation between wavelength and momentum as well.

$$E^2 = p^2c^2 + \cancel{m^2c^4}$$

massless

$$E = h\nu = pc$$

$$\frac{h}{p} = \frac{c}{\nu} = \lambda$$

Coconuts and Castaways

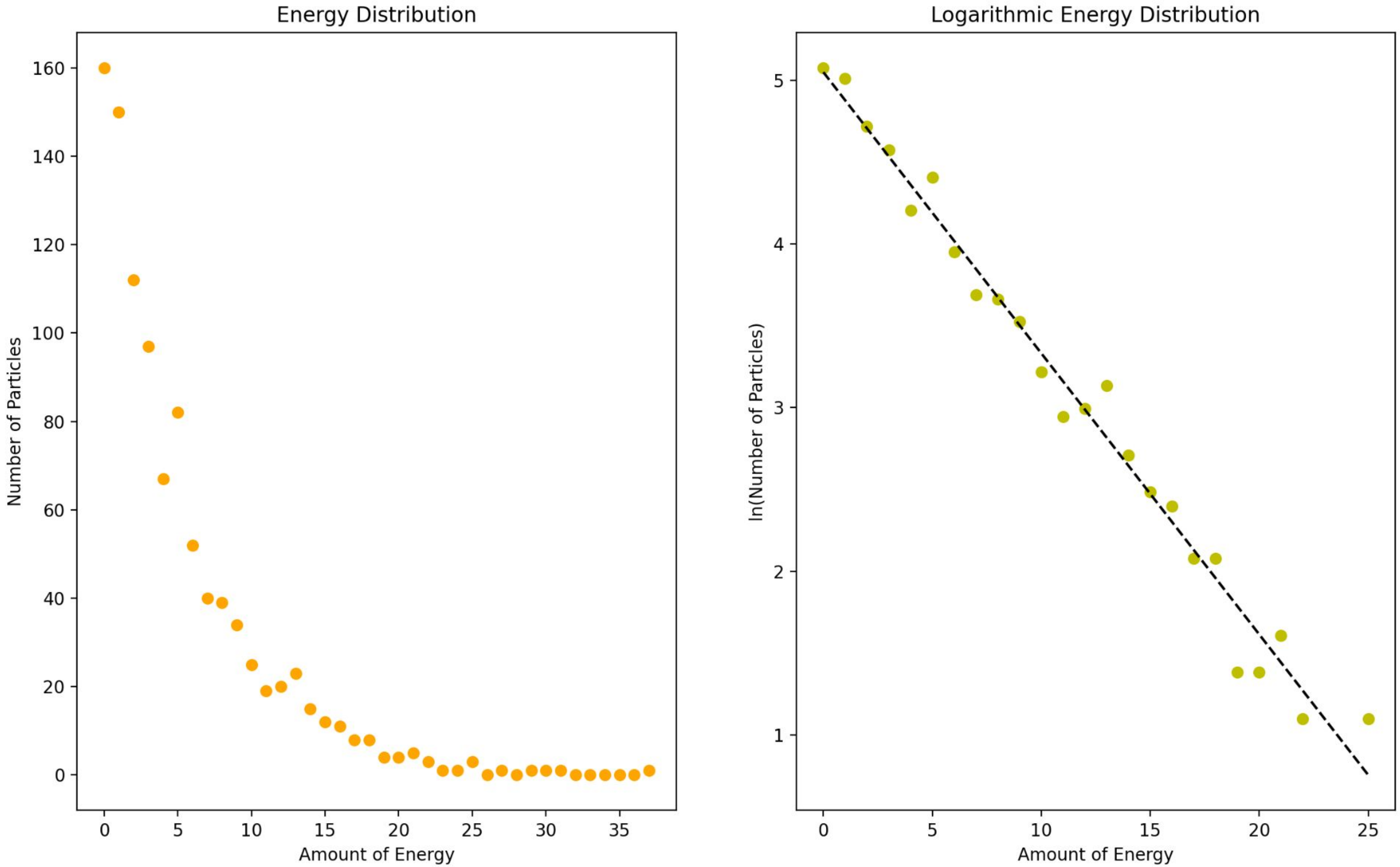
Energy Distribution at Equilibrium

A simple model:

- Consider a system with a 1000 particles.
- Let each particle start with 5 ‘units’ of energy.
- Every time two particles collide with each other, one particle gives the other particle 1 unit of energy.

After a long amount of time, how will the energy be distributed?

- Uniformly?
- Linearly?
- Exponentially?



Energy Distribution
Number of Particles
Amount of Energy
Logarithmic Energy Distribution
ln(Number of Particles)
Amount of Energy

Planck Distribution

Boltzmann derived an exponential decay formula based on energy.

Planck theorized the possible energies were integer multiples of the frequency.

The sum of the probabilities formed an infinite geometric series.

The average thermodynamic energy is related to the derivative of this sum.

Boltzman factor: $e^{-E_n/kT}$

$$E_n = 0h\nu,\ 1h\nu,\ 2h\nu,\ \ldots$$

$$\sum_n e^{-E_n/kT} = \sum_n e^{-nh\nu/kT}$$

$$= \frac{1}{1-e^{-h\nu/kT}}$$

Revised Blackbody Energy

Planck used his distribution to derive a new law for blackbody energy.

$$\text{Planck: } \frac{d}{d\nu}u = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/kT}-1}$$

$$\text{RJ: } \frac{d}{d\nu}u = \frac{8\pi\nu^2 kT}{c^3}$$

Unlike the Rayleigh-Jeans law, his law postulates that at a certain frequency (2.821kT), the energy contributed by higher frequencies begins decreasing since they are less likely to occur.

Total Blackbody Energy

We can actually integrate Planck's law across all frequencies to find the total amount of energy stored in the blackbody.

Integrating the Rayleigh-Jeans law gives an infinite amount of energy in the blackbody, which is obviously false.

$$u = \frac{8\pi k^4 T^4}{h^3 c^3} \int_0^\infty \frac{x^3}{e^x - 1}\,dx$$

$$= \frac{8\pi k^4 T^4}{h^3 c^3} \Gamma(4)\zeta(4)$$

$$= \frac{8\pi^5 k^4 T^4}{15 h^3 c^3}$$

Imaginary Numbers are Real

Wave Equation

All waves can be constructed from combinations of sine waves.

However, sine is not a great function to work with since its derivative, which tells us the velocity of the wave, is another function (cosine).

To make computations easier, we can use an imaginary exponential since the derivative is the same function times some scale factor.

$$\sin\left(\frac{2\pi}{\lambda}x - 2\pi\nu t\right)$$

travelling wave

$$V = \lambda$$

$$e^{i\left(\frac{2\pi}{\lambda}x - 2\pi\nu t\right)}$$

$$= \cos\left(\frac{2\pi}{\lambda}x - 2\pi\nu t\right) + i\sin\left(\frac{2\pi}{\lambda}x - 2\pi\nu t\right)$$

Momentum and Energy

If we differentiate a plane wave with respect to x, we can rearrange the resulting scale factor to be a function of momentum.

Similarly, if we differentiate with respect with t, we can rearrange the resulting scale factor to be a function of energy.

The latter is the time-dependent Schrödinger equation.

$$\psi(x,t) = e^{i\left(\frac{2\pi}{\lambda}x - 2\pi\nu t\right)}$$

$$\frac{\partial}{\partial x}\psi = \frac{2\pi i}{\lambda}\psi = \frac{2\pi \hat{p} i}{h}\psi$$

$$\hat{p}\psi = -i\frac{h}{2\pi}\frac{\partial}{\partial x}\psi$$

$$\frac{\partial}{\partial t}\psi = -2\pi\nu i\psi = -\frac{2\pi \hat{H} i}{h}\psi$$

$$\hat{H}\psi = i\frac{h}{2\pi}\frac{\partial}{\partial t}\psi$$

Commutators

The quantities A and B commute if AB-BA=0. The quantity AB-BA is called the commutator of A and B.

If A and B do not commute, then this means we have a trade-off between measurements of A and B.

The commutator of momentum and position is $i\hbar$, meaning measurements between momentum and position tradeoff (uncertainty principle).

$$[\hat{x},\hat{p}]\psi = (\hat{x}\hat{p} - \hat{p}\hat{x})\psi$$
$$= -i\hbar x\frac{\partial}{\partial x}\psi + i\hbar\frac{\partial}{\partial x}(x\psi)$$
$$= -i\hbar x\frac{\partial}{\partial x}\psi + i\hbar\psi + i\hbar x\frac{\partial}{\partial x}\psi$$
$$= i\hbar\psi$$

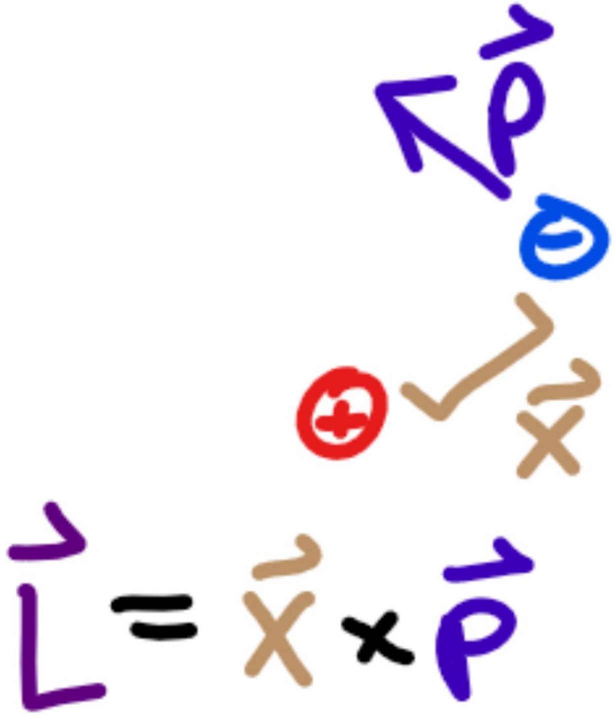
Hydrogen Atom

Angular Momentum

Angular momentum is sort of momentum about an axis of rotation.

For an electron rotating about the nucleus, the value of angular momentum is the (cross) product between position from the nucleus and the momentum of the electron.

We denote the angular momentum L, and angular momentum about the z-axis L_z.



Orbitals and Degeneracies

We can exploit commutators to get relations for L^2 and L_z.

Specifically, we get the L^2 operator is identical to multiplying by $\hbar^2(l^2+l)$ for some positive integer l, and L_z is identical to multiplying by $\hbar m$ for some m. (In position space.)

Since $L_z^2 \leq L^2$ by definition, we have the restriction $m^2 \leq l^2+l$, so $|m| \leq l$.

$$\hat{L}^2\psi = \hbar^2(l^2+l)\psi$$

$$\hat{L}_z^2\psi = \hbar^2 m^2$$

$$m^2 \leq l^2+l$$

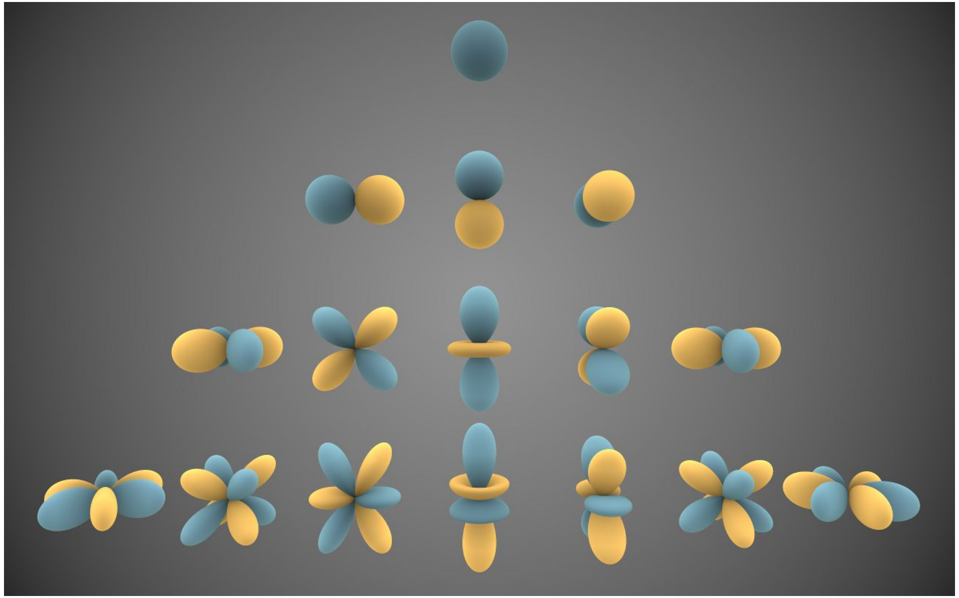
$$m \leq \sqrt{l^2+l}$$

$$\simeq l$$

Spherical Harmonics

We can also use the fact that momentum is $-i\hbar\nabla$ to get solvable equations for the where an electron is likely to be in terms of of l and m.

These solutions are the spherical harmonics, which define the shape of orbitals.



Solving the Radial Equation

We also want to know how energy is related to the other quantities.

The radial equation tells us how the energy due to electron-proton attraction affects the where we find the electron.

Its solution is a sum that needs to be truncated, where the maximum quantity is n=k+l+1 for some natural number k.

$$R(r) = \frac{1}{r}\rho e^{-\rho}\sum_{j=0}^{k} c_j \rho^j$$

$$c_{k+1} = 0 \quad \text{truncate}$$

$$= c_k \frac{2k+2(l+1)-2n}{(k+1)(k+2(l+1))}$$

$$n = k+l+1$$

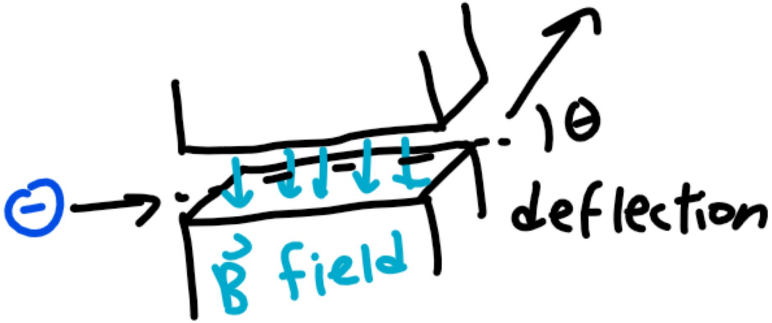
The quantity n is related to the energy and must always be at least one larger than l.

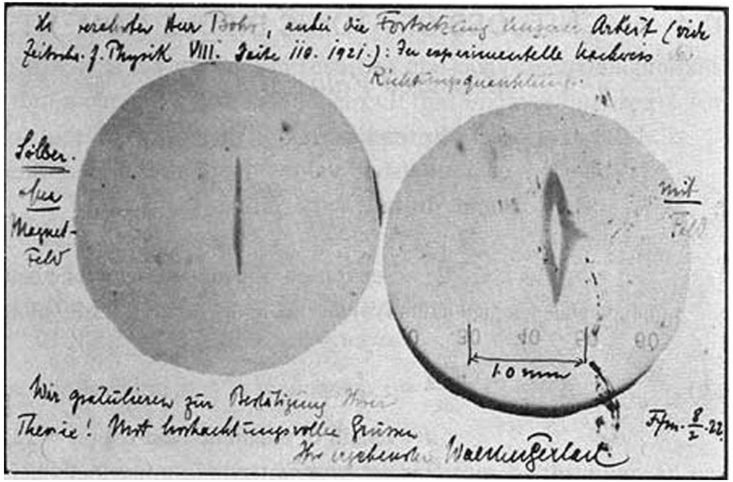
Spin

For a time, it seemed as if n, l, and m fully accounted for the hydrogen atom electron.

Stern-Gerlach revealed electrons had an additional magnetic momentum independent of these quantum numbers.

The spin quantum number, s, was born to account for this.





Rabi Oscillations

We can tune magnetic waves to target the spin of an electron.

Specific frequencies of magnetic waves near an electron will cause them to vibrate intensely.

These Rabi Oscillations are the basis of imaging technology such as magnetic resonance imaging (MRI).