

HOW IS EQUILIBRIUM ESTABLISHED???

Vapor Pressure Movie (15th Grade Version)

Much of the “heat” making the 300 K temperature comes from rotating dipoles of water molecules.

This creates oscillating electric and magnetic fields, some of which is in resonance, $\Delta E = h\nu$.

So there is constantly excitation and de-exciting.

This thermal excitation is slow.

Modern NMR: Series of very strong , short pulses of radiofrequency

Transitions are not instantaneous!

Quantum mechanics says a single spin in resonance will do the following:

$$\Psi_{down} \rightarrow \Psi_{down} + \Psi_{up} \rightarrow \Psi_{up} \rightarrow \Psi_{up} - \Psi_{down} \rightarrow -\Psi_{down}$$

When the pulse comes each spin will start in a different place,

but will go through the sequence.

Wavelength is $\sim \frac{1}{2}$ meter, so:

Entire sample literally feels oscillating magnetic field.

The intense pulse will force the system out of equilibrium and can have EQUAL amounts of up and down and a longer pulse will produce more up than down

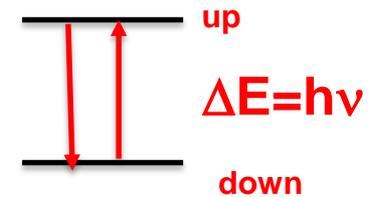
(Boltzmann distribution is INVERTED)

Quantum Concept: Superposition.

A molecule may be “in” more than one state at once!

Although there are two quantum “*energy levels*”: spin up and spin down, there is a continuous mixture.

The spins are all in *superposition* states.



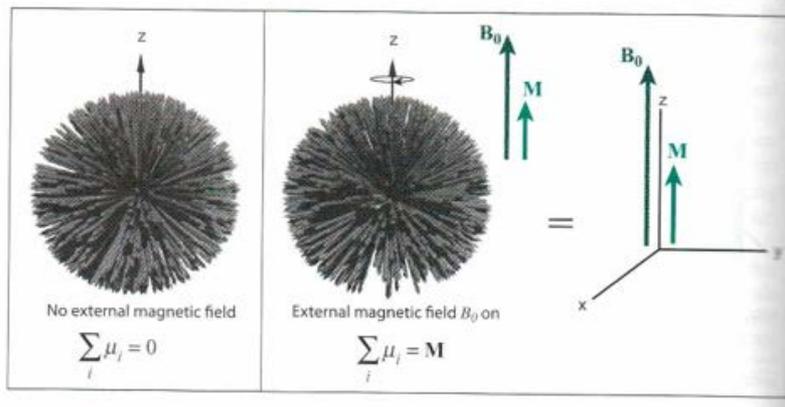
$$\Psi_{total} = c_{up} \Psi_{up} e^{-i \frac{2\pi E_{up} time}{h}} + c_{down} \Psi_{down} e^{-i \frac{2\pi E_{down} time}{h}}$$

Ψ_{up} and Ψ_{down} are “orbitals” i.e., wavefunctions for the nuclear spin.

The **Time Dependent** Schrodinger Equation says that the individual parts **oscillate** at a frequency given by their energy/Plancks constant & cause **PRECESSION**

The **squares** of the coefficients gives probability to observe in the **up or down** state
i.e., **$c_{up}^2 + c_{down}^2 = 1$**

FIGURE 14.3 Visualizing a large number of nuclear magnetic moments of a bulk sample in a bundle. In the absence of any external field (left panel) all nuclear moments μ_i are randomly distributed. In a strong external field along the z-axis (B_0 , right panel), the individual moments are very weakly biased towards the z-axis (the bias is exaggerated 100 fold in the right panel). A vector sum of all of the individual moments reveals the bulk magnetization M parallel to B_0 . As we discuss shortly, the individual nuclear moments rotate around B_0 , a motion termed ‘precession.’

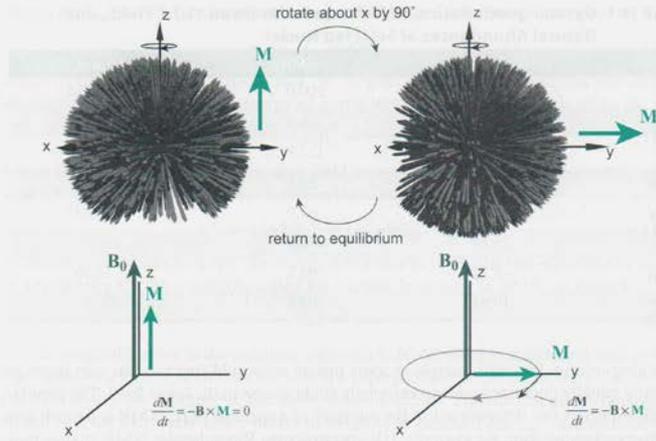


The lines pointing in all directions give an idea of the proportion of spin up and spin down for each of the spins.

The relative signs of c_{up} and c_{down} give **direction**

Result of an very short INTENSE pulse of radio frequency light

FIGURE 14.4 Schematic of the behavior of both individual and bulk magnetic moments that are parallel (left) or perpendicular (right) to the B_0 field. At equilibrium (left) the individual moments precess but M does not. If the nuclei have been perturbed, then both the individual and bulk moments precess (right panel). The dynamics of the bulk magnetization M are always due to the average behavior of a large number of nuclear spins.

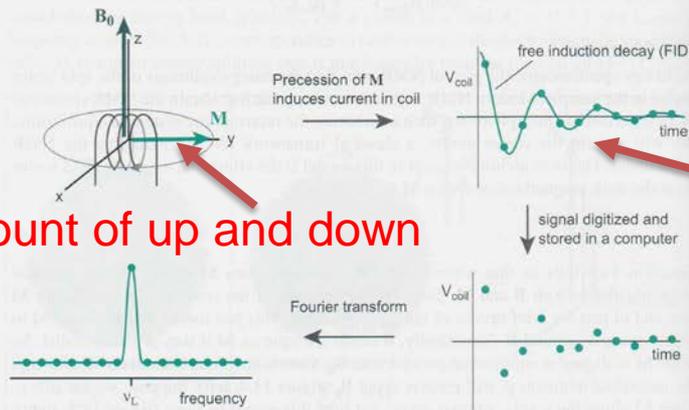


angle between B_0 and M , and so M must rotate around B_0 according to Eq. 14.6. This motion is termed precession, and the frequency of the precession is exactly the Larmor frequency that we wish to know. In order to detect the Larmor precession frequency of M , a coil is placed around the sample along the y -axis (figure 14.5). The coil experiences an oscillating magnetic field due to the linearly oscillating y component of the precessing vector M

$$M_y(t) = M \cos(2\pi\nu t)e^{-t/T_2}, \quad (14.7)$$

where T_2 is a time constant governing the loss of the magnetization in the xy -plane. The vector will precess at the Larmor frequency and will return to be aligned along the positive

FIGURE 14.5 Signal detection in an NMR experiment. The precessing bulk magnetization M induces an oscillating current in the coil which may be detected and digitized using electronic test equipment.



EQUAL amount of up and down

Each spin precessing.

Tipping because the applied pulse can only interact with those individual spins that are in phase with the pulse—a small percentage of the many spins

The whole magnet will tip by an angle proportional to how long the pulse is on.

TWO RELAXATION TIMES, T_1 and T_2 :

Returning to Boltzmann energy equilibrium is T_1

Returning to degeneracy (phase) equilibrium is T_2 .

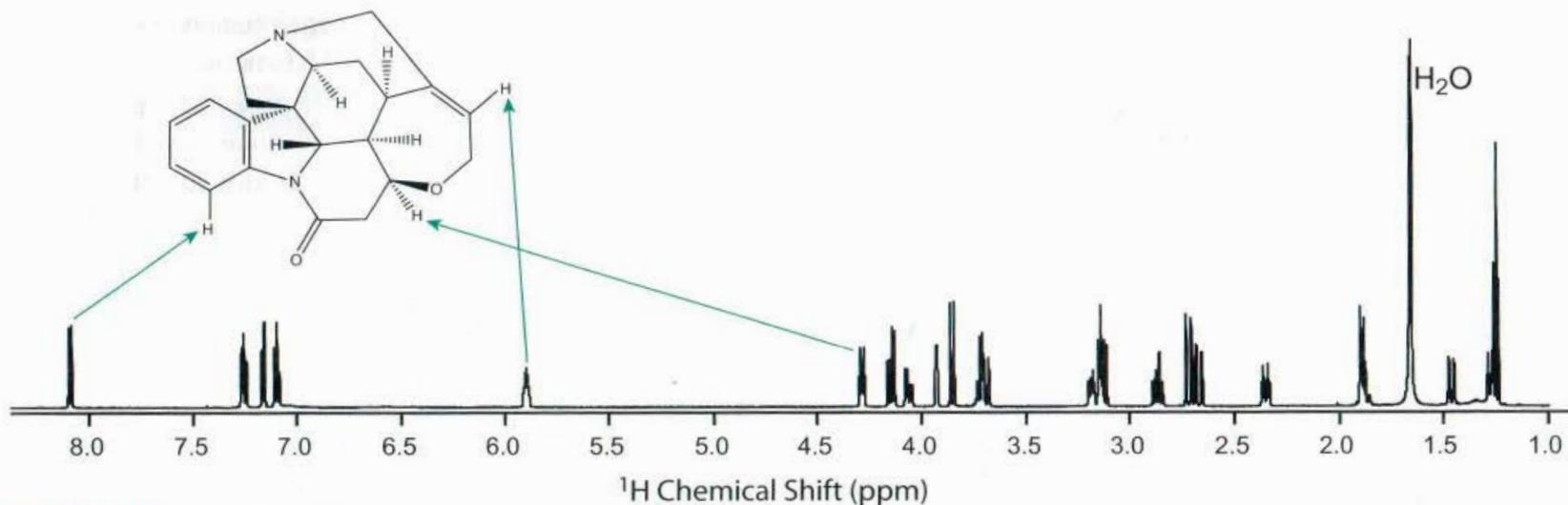


FIGURE 14.1 The ^1H NMR spectrum of strychnine (5 mM, 600 MHz) in deuteriochloroform (CDCl_3) illustrates the ability of NMR to obtain richly detailed information on complex molecules with atomic resolution. Each H atom gives a distinct signal with a characteristic position, splittings and relative intensity that is determined by the structure of the molecule. All signals are assigned, and a few representative assignments are shown on the figure (for clarity, not all H atoms are depicted). Complete assignments are performed with the aid of multidimensional NMR experiments. A residual signal from protonated chloroform (CHCl_3) has been digitally removed, while dissolved H_2O is noted.

very short pulse contains many frequencies

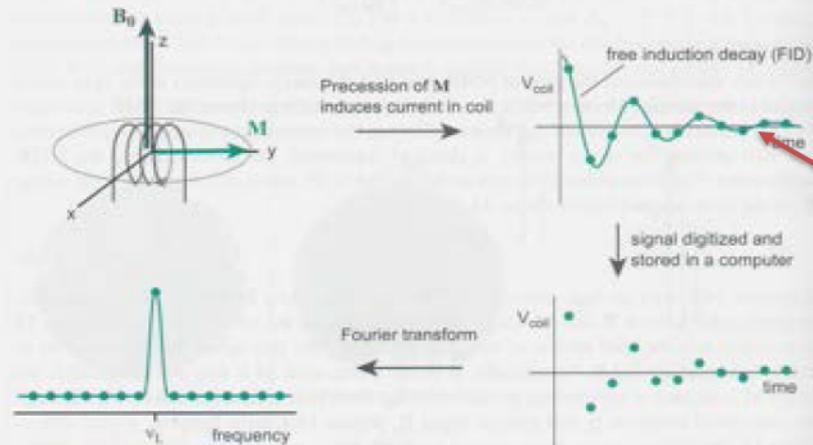
Intense pulse of radio freq. in coil perpendicular changes ratio of up/down from .9999 to 1.0 Causes **coherent motion** of the 0.0001 excess spin up. So sample magnet points horizontally. Creates signal in receiver coil (not shown).

Entropy makes sample return to **most probable state** (Boltzmann distribution). Time to do so is called the **T_1 relaxation time**. (1st order rate constant is $1/T_1$)

$$M_x(t) = M \cos(2\pi\nu t) e^{-t/T_2} \quad (14.7)$$

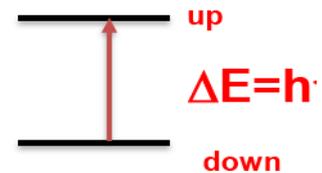
where T_2 is a time constant governing the loss of the magnetization in the xy -plane. The vector will precess at the Larmor frequency and will return to be aligned along the positive

FIGURE 14.5 Signal detection in an NMR experiment. The precessing bulk magnetization \mathbf{M} induces an oscillating current in the coil which may be detected and digitized using electronic test equipment.



Fourier transform of these oscillations give the entire NMR spectrum

Another very important relaxation is the called the T_2 relaxation time which comes from the dephasing of the individual spins due to collisions. The ordering caused by the pulse causing the net dipole of the spins to add up to a vector pointing in the y direction initially, and direction rotating at a frequency given by $(E_{up} - E_{down})/h$ is ruined by the thermal motion. But the energy is not lost so quickly. The phase information is not lost! A second pulse twice as long as the first will reverse the phases and therefore the direction of rotation. Those vectors that lagged behind will be leading the pack, and all will reach the “finish line” simultaneously. Almost all the signal comes back for a brief time. This is called a **“SPIN ECHO”**. Please go to: http://en.wikipedia.org/wiki/Spin_echo for nice visual demos.



T1 is called **“spin lattice relaxation time”**.

This simply means that the thermal motion of solvent creates some oscillating magnetic fields that are in resonance, thus causing transitions.

Another type of relaxation is the T2 relaxation time, called **“spin-spin relaxation”**

http://en.wikipedia.org/wiki/Spin%E2%80%93spin_relaxation

T_2 relaxation generally proceeds more rapidly than T_1 relaxation.

Different samples and different biological tissues have different T_2 .

Fluids have the longest T_2 s (~5000 ms for [protons](#)),

and water based tissues are in the 40–200 [ms](#) range,

while fat based tissues are in the 10–100 ms range.

Amorphous solids have T_2 s in the 1-10 ms range,

crystals have T_2 s around the 0.05 ms range.

What is the pattern?????

http://en.wikipedia.org/wiki/Spin_echo

INTRODUCTION TO QUANTUM MECHANICS

OR

WHY CHEMISTRY IS DIFFICULT TO LEARN

Electrons (and photons) DO NOT behave according to Newton's Laws of Motion

But, Chemistry is all about electrons

Feynman, from *Lectures on Physics III* :

“Quantum Mechanics exactly describes the behavior electrons and light.”

“Electrons and light do not behave like anything we have ever seen.”

“There is one lucky break, however—**electrons behave just like light**”

Understanding Quantum Mechanics?

Richard Feynman lecturing to a lay audience at
Cornell, *circa*. 1965:

“There was a time when the newspapers said that only twelve men understood the theory of relativity.

I do not believe there ever was such a time...

After they read the paper, quite a lot of people understood the theory of relativity... On the other hand, I think it is safe to say that

no one “understands” quantum mechanics...

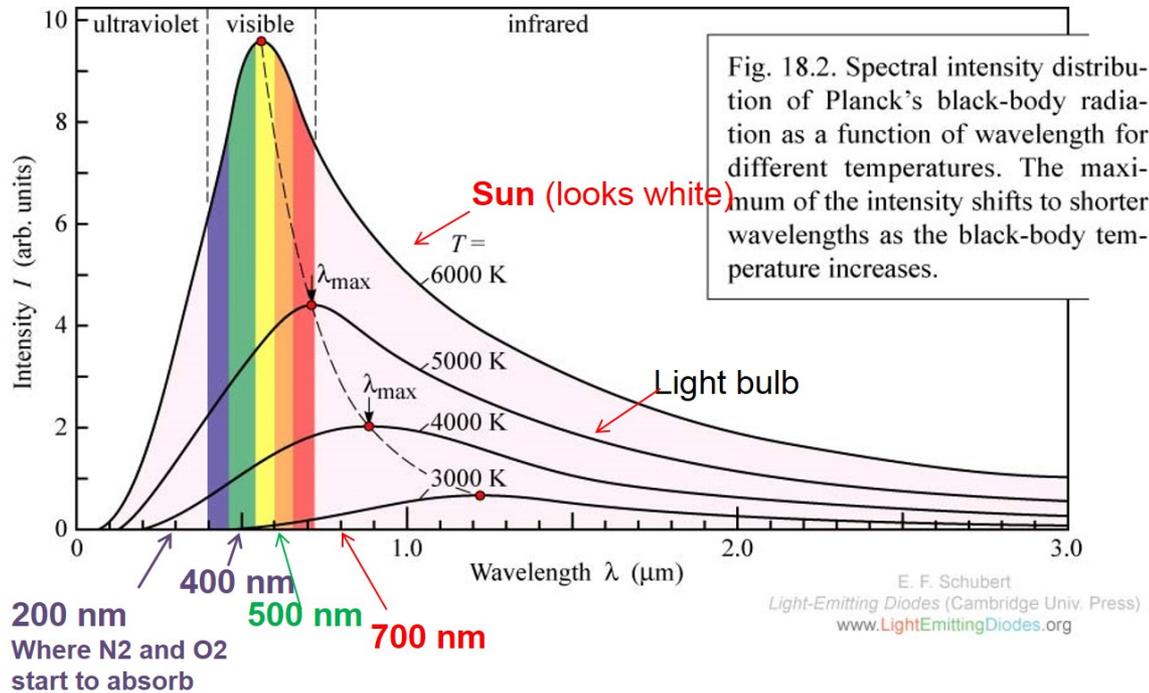
Do not keep saying to your self “But how can it be like that?”, because you will get “down the drain” into a blind alley from which nobody has yet escaped.

NOBODY KNOWS HOW IT CAN BE LIKE THAT. “

--Richard P. Feynman

Chapter 6, *The Character of Physical Law*, 23rd Printing, 1998

Light emitted by all objects not at 0 Kelviin.



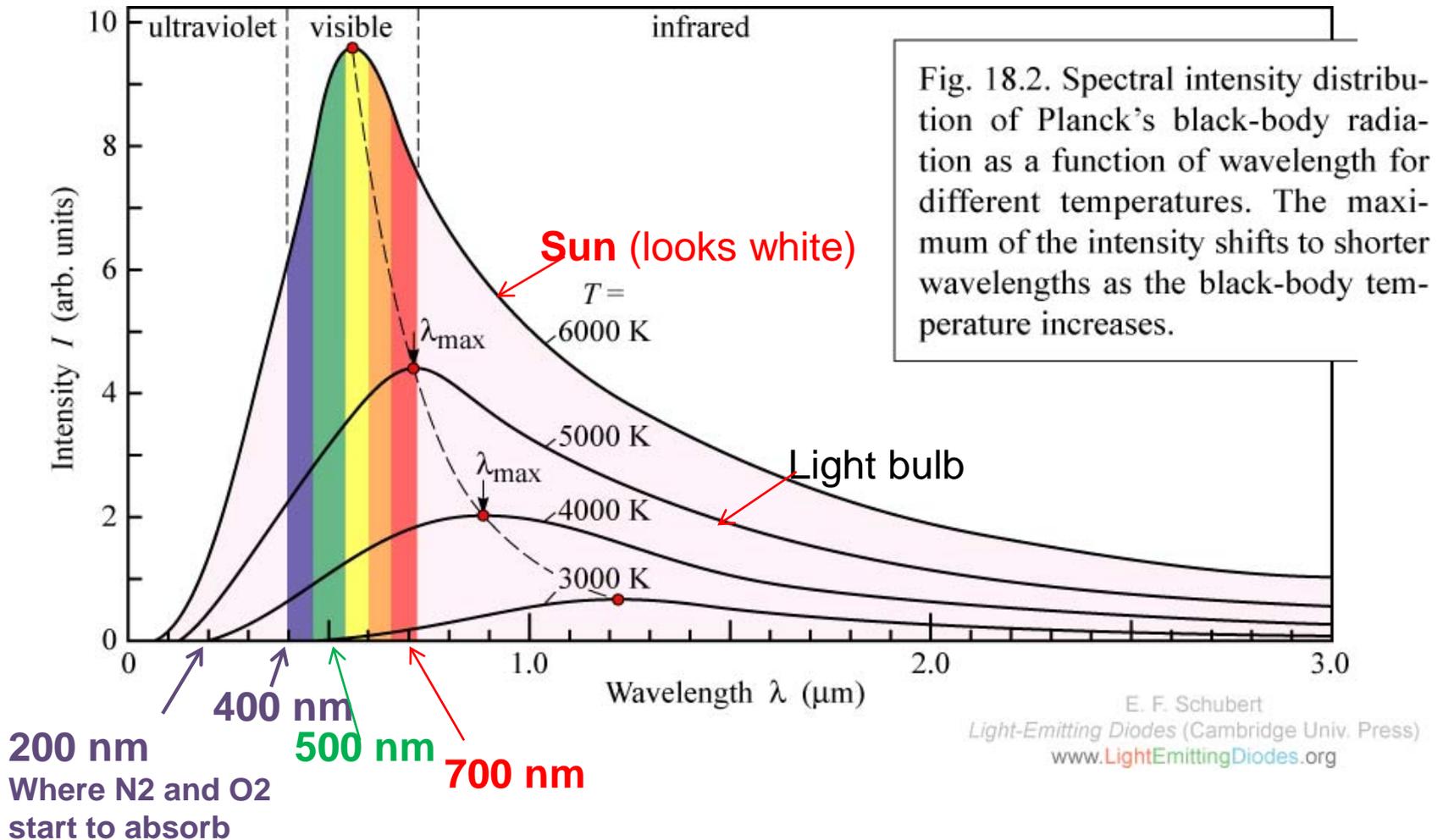
Around **1905**, Max Planck was working hard on trying to understand this behavior. Classical mechanics **worked fine at the LONG** wavelengths but **NOT** at short wavelengths.

Planck found that if energy of matter was quantized so that $\Delta E = h\nu = hc/\lambda$ then classical mechanics predicted the curves perfectly!!!!

Planck varied h and found that 6.62×10^{-34} gave a perfect match to experiment.

In other words, h is an experimentally derived constant.
No theory predicts h

Light emitted by all objects not at 0 Kelvin.



Temperature dependence is from the Boltzmann ratio for probability for the hot matter to be in an excited state:

$$N_{\text{excited}}/N_{\text{ground}} = \exp(\Delta E/k_B T), \text{ where } \Delta E = hc/\lambda$$

So was born the **FIRST QUANTUM CONCEPT:** **Energy is quantized!**

Classical thinking does not work for electrons nor for light. $\Delta E = h\nu$

If the structure of the atom were known in 1905 this would have been much more evident.

The mystery could be stated as a very striking problem obvious to chemists.

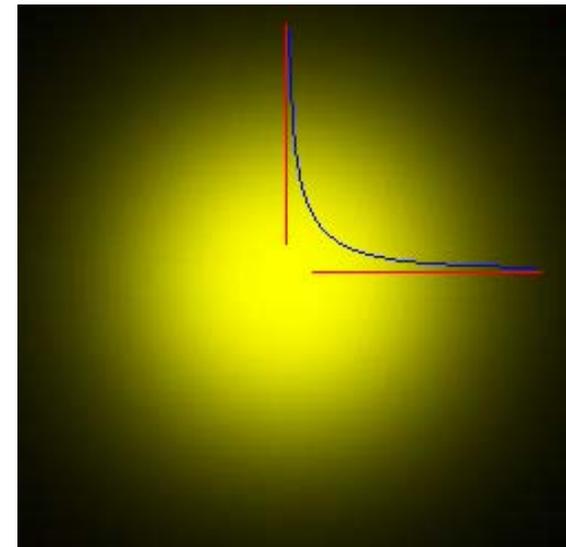
THE ELECTRON WILL NOT FALL TO THE NUCLEUS!!!
despite ENORMOUS Coulomb force.

The *lowest* energy state (1s orbital) of the hydrogen atom.

+ -
proton electron

Probability slice through the 1s orbital. The blue line is the square of the wavefunction (orbital).

Most probable point is AT NUCLEUS.
Most probable DISTANCE is AT Bohr radius



Coulomb's Law Force $\oplus \ominus$
 $\leftarrow 1 \text{ \AA} \rightarrow$

$$\frac{(9 \times 10^9)(1.6 \times 10^{-19})^2}{(1 \times 10^{-10} \text{ m})^2} = 2.3 \times 10^{-8} \text{ N}$$

For 2 elementary charges 1 \AA apart.

at 0.01 \AA $2.3 \times 10^{-4} \text{ N}$

FOR ONE proton & ONE e^-

Equivalent to Gravitational

force of EARTH ON 0.025 gram

But, Experimentally e^- is in the
1S orbital, even at 0 Kelvin!

Striking Example of
Zero point Energy

$$\text{KINETIC } E = 1.3 \times 10^6 \text{ J/mol} \quad U_{\text{rms}} = 2 \times 10^6 \text{ m s}^{-1}$$

YET, IS ABSOLUTELY COLD (& DARK)

Ed Sheeran: “The Shape of You”

https://video.search.yahoo.com/yhs/search?fr=yhs-adk-adk_sbnt&hsimp=yhs-adk_sbnt&hspart=adk&p=ed+sheeran+shape+of+you#id=1&vid=4c2417583a5eddf662b98ab53179450&action=click

a parody of a popular song currently on the radio but the lyrics have been changed to chemistry related topics. It's called **The Molecular Shape of You**.

<https://www.youtube.com/watch?v=f8FAJXPBdOg>