1.021, 3.021, 10.333, 22.00 : Introduction to Modeling and Simulation : Spring 2012

Part II – Quantum Mechanical Methods : Lecture 2

Quantum Mechanics: Practice Makes Perfect

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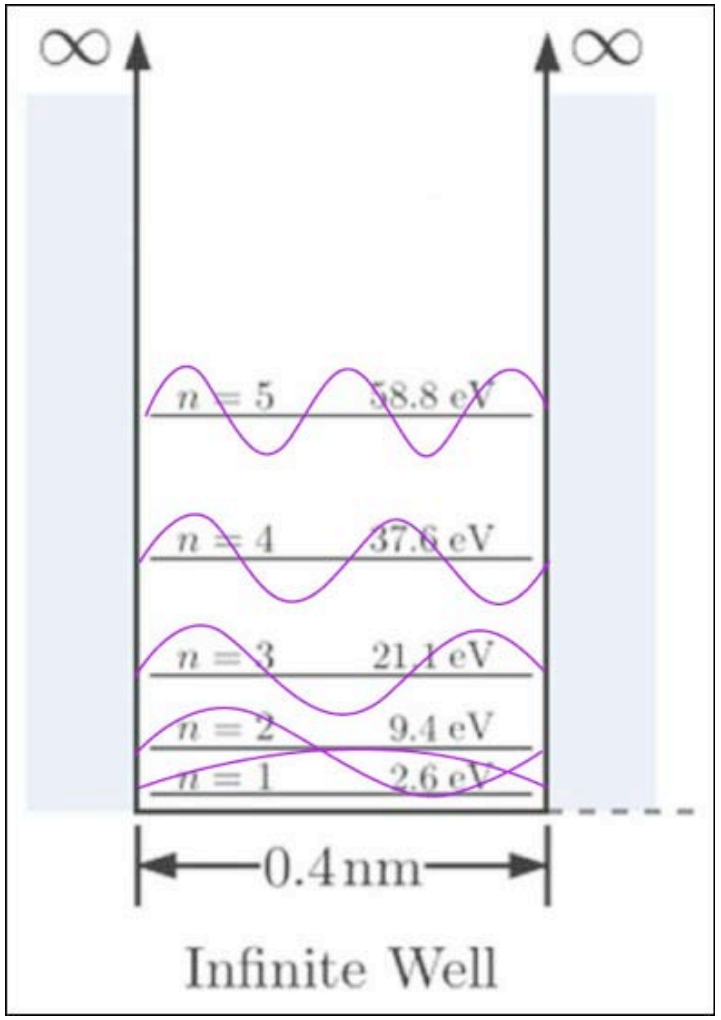
Part II Topics

1. It's a Quantum World: The Theory of Quantum Mechanics
2. Quantum Mechanics: Practice Makes Perfect
3. From Many-Body to Single-Particle; Quantum Modeling of Molecules
4. Application of Quantum Modeling of Molecules: Solar Thermal Fuels
5. Application of Quantum Modeling of Molecules: Hydrogen Storage
6. From Atoms to Solids
7. Quantum Modeling of Solids: Basic Properties
8. Advanced Prop. of Materials: What else can we do?
9. Application of Quantum Modeling of Solids: Solar Cells Part I
10. Application of Quantum Modeling of Solids: Solar Cells Part II
11. Application of Quantum Modeling of Solids: Nanotechnology

Motivation

electron in box



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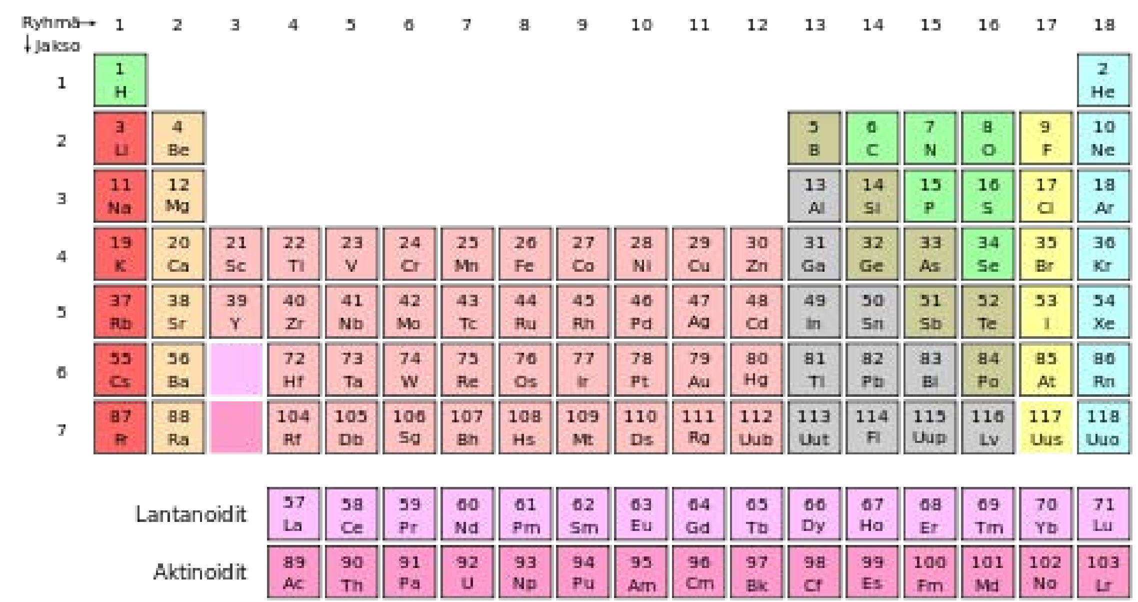
Lesson outline

- Review
- A real world example
- Everything is spinning
- Pauli's exclusion
- Periodic table of elements



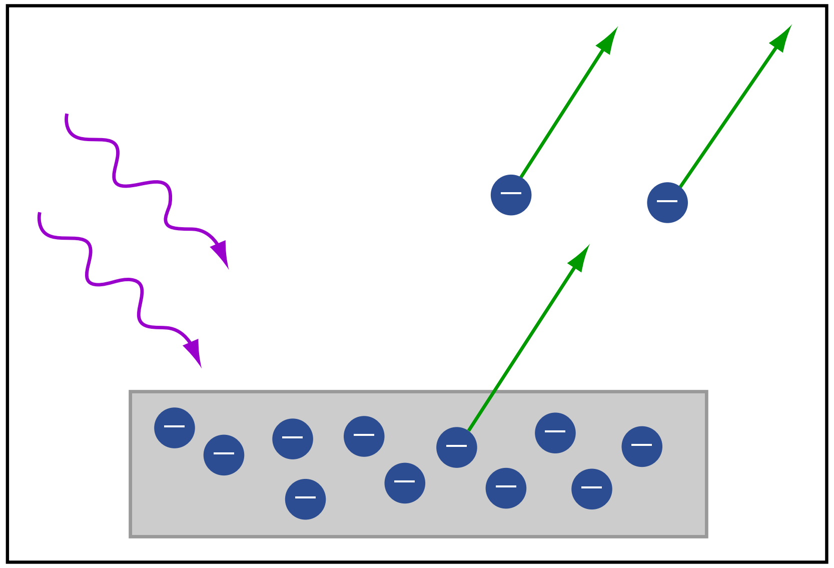
Review: Why QM?

Problems in classical physics that led to quantum mechanics:

- "classical atom"
- quantization of properties
- wave aspect of matter
- (black-body radiation), ...

Review: Quantization

photoelectric effect



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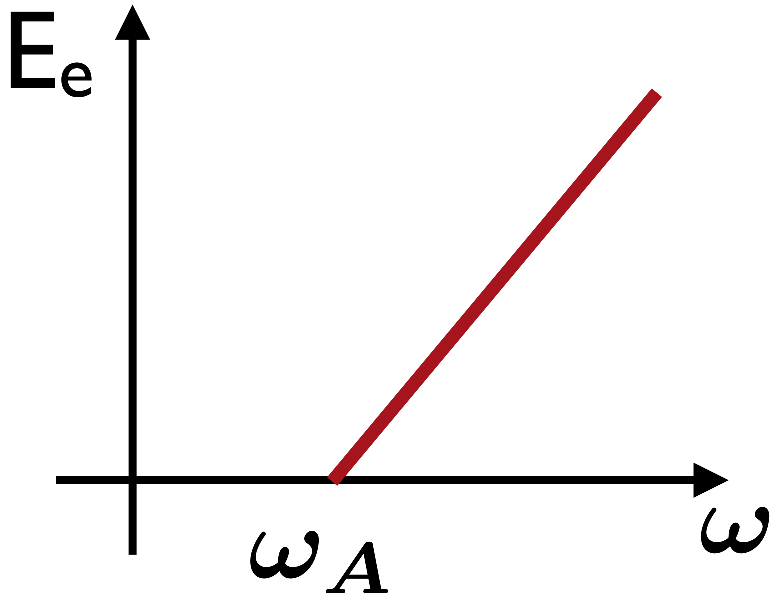
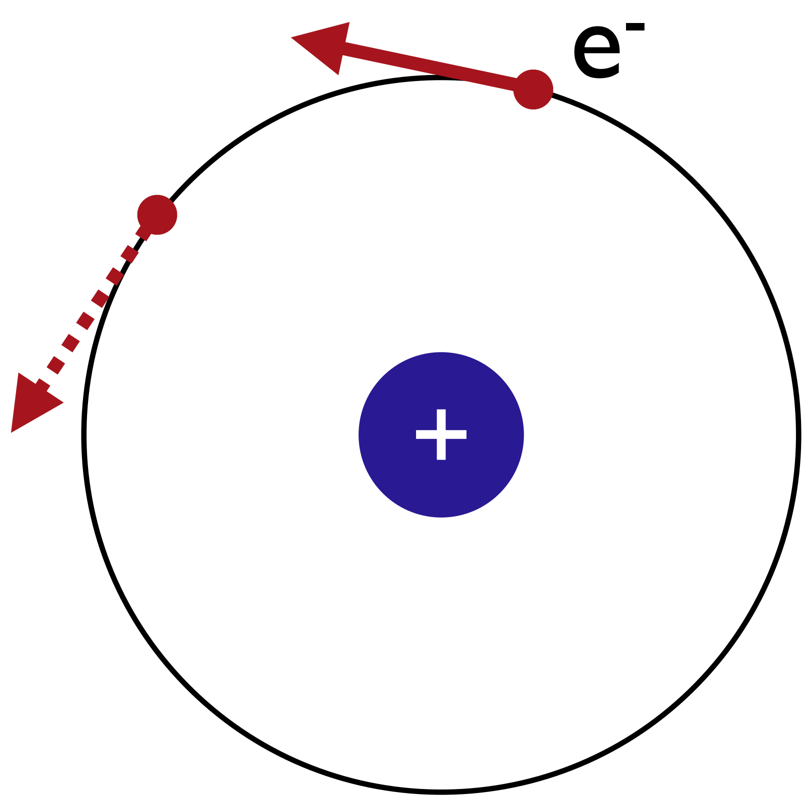


$$E = \hbar(\omega - \omega_A) = h(\nu - \nu_A)$$

$$h = 2\pi\hbar = 6.6 \cdot 10^{-34} \text{ Wattsec.}^2$$

Einstein: photon $E = \hbar\omega$

“Classical atoms”



hydrogen atom

problem:
accelerated charge causes radiation, atom not stable!

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Liénard–Wiechert potential

From Wikipedia, the free encyclopedia

Liénard-Wiechert potentials describe the classical electromagnetic effect of a moving electric point charge in terms of a vector potential and a scalar potential. Built directly from Maxwell's equations, these potentials describe the complete, relativistically correct, time-varying electromagnetic field for a point charge in arbitrary motion, but are not corrected for quantum-mechanical effects. Electromagnetic radiation in the form of waves can be obtained from these potentials.

These expressions were developed in part by Alfred-Marie Liénard in 1898 and independently by Emil Wiechert in 1900[1] and continued into the early 1900s.

The **Liénard-Wiechert potentials** can be generalized according to gauge theory.

The explicit expressions for potentials related to moving dipoles and quadrupoles in the same way as the **Liénard-Wiechert potentials** are related to a point charge were computed by Ribarič and Šušteršič in 1995.[2]

Implications [edit]

The study of classical electrodynamics was instrumental in Einstein's development of the theory of relativity. Analysis of the motion and propagation of electromagnetic waves led to the special relativity description of space and time. The Liénard–Wiechert formulation is an important launchpad into more complex analysis of relativistic moving particles.

The Liénard–Wiechert description is accurate for a large, independent moving particle, but breaks down at the quantum level.

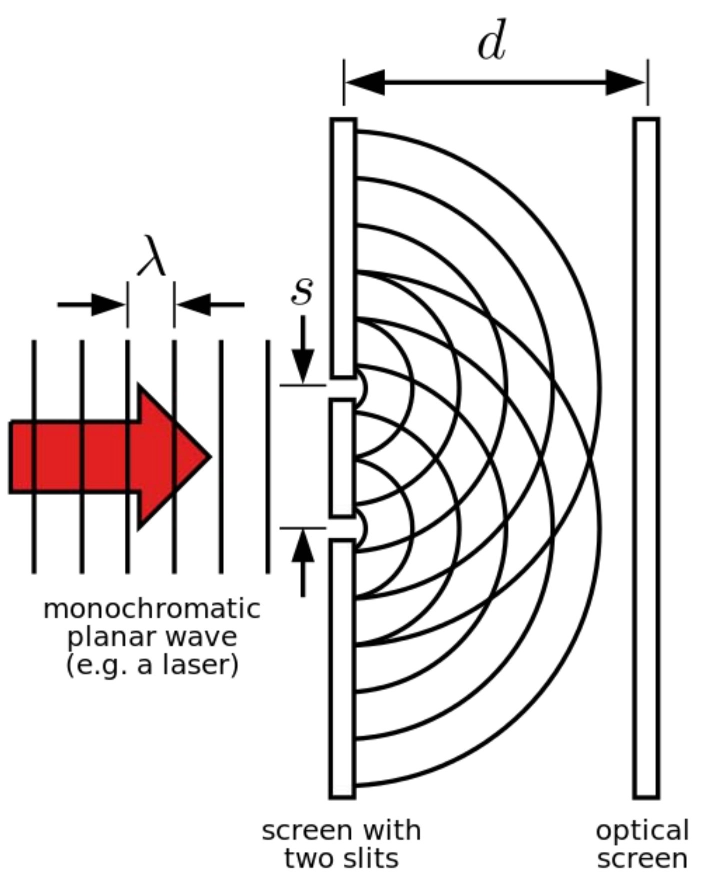
Quantum mechanics sets important constraints on the ability of a particle to emit radiation. The classical formulation, as laboriously described by these equations, expressly violates experimentally observed phenomena. For example, an electron around an atom does not emit radiation in the pattern predicted by these classical equations. Instead, it is governed by quantized principles regarding its energy state. In the later decades of the twentieth century, quantum electrodynamics helped bring together the radiative behavior with the quantum constraints.

Review: Wave aspect

light
matter

wave character

particle character



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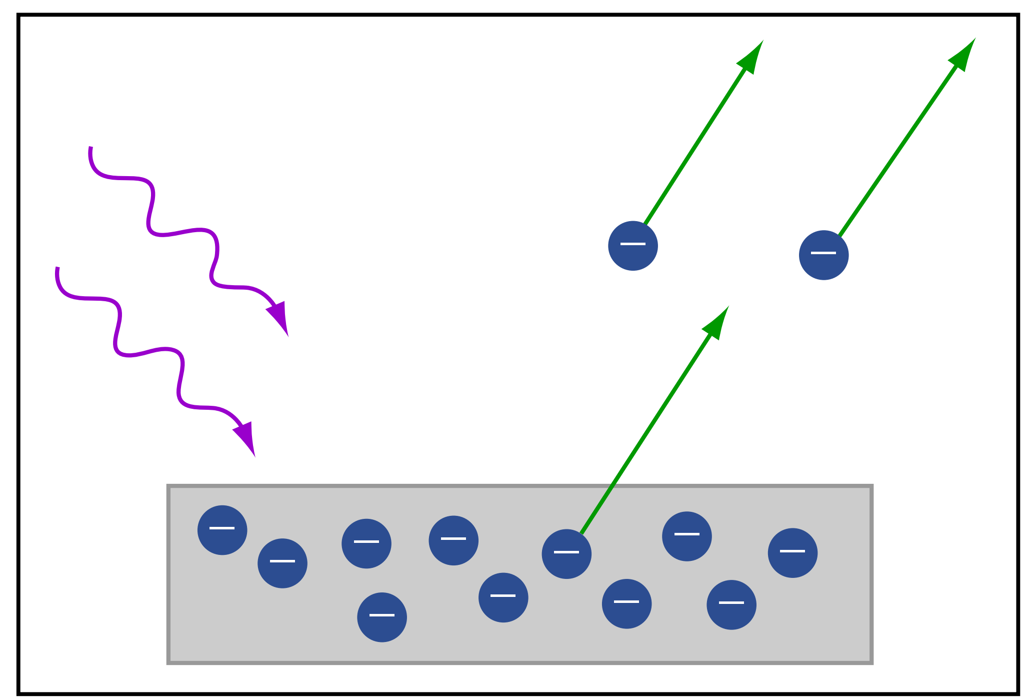

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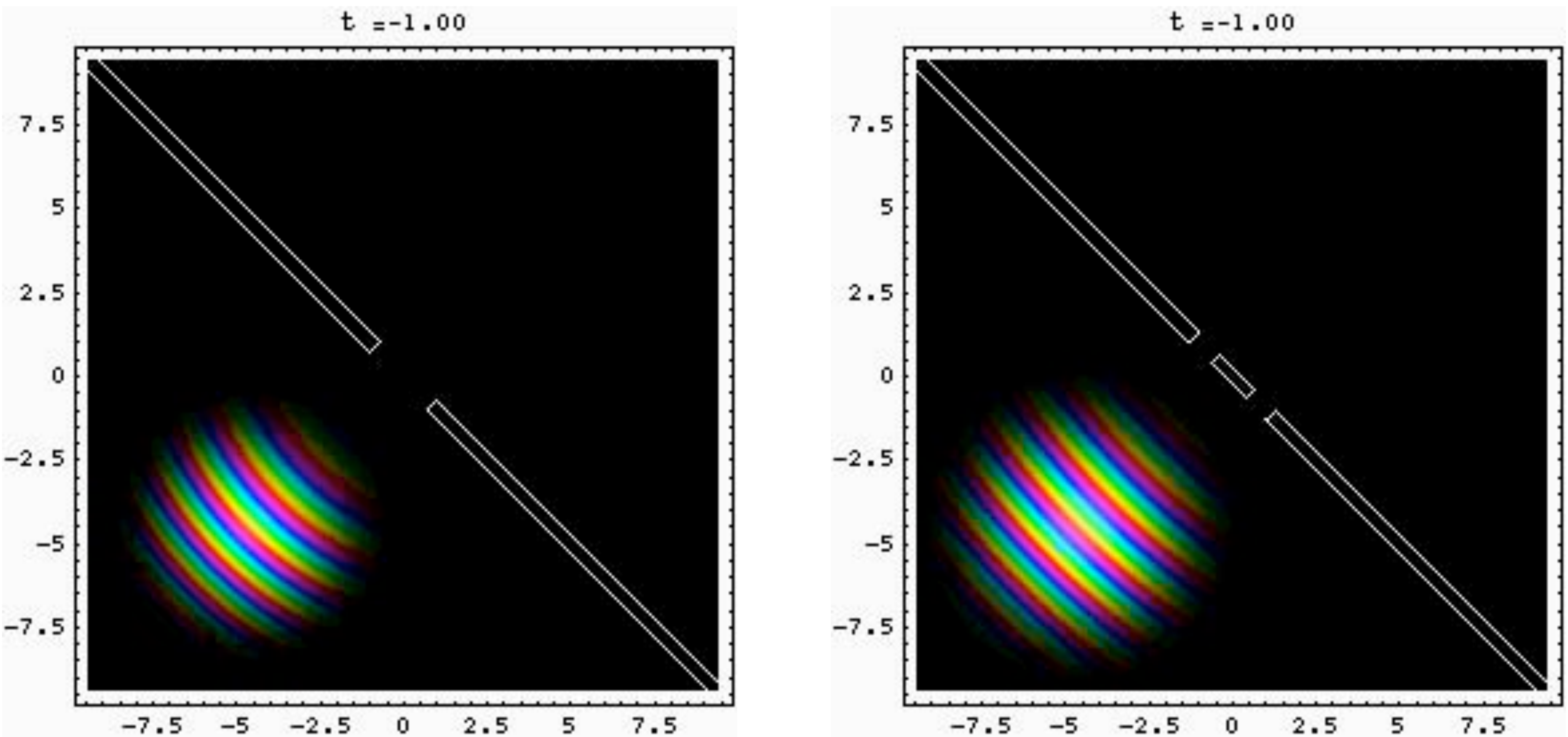
Double-Slit



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Review: Wave aspect

particle: E and momentum $\vec{p}$

wave: frequency ν and wavevector $\vec{k}$

$$E = h\nu = \hbar\omega$$

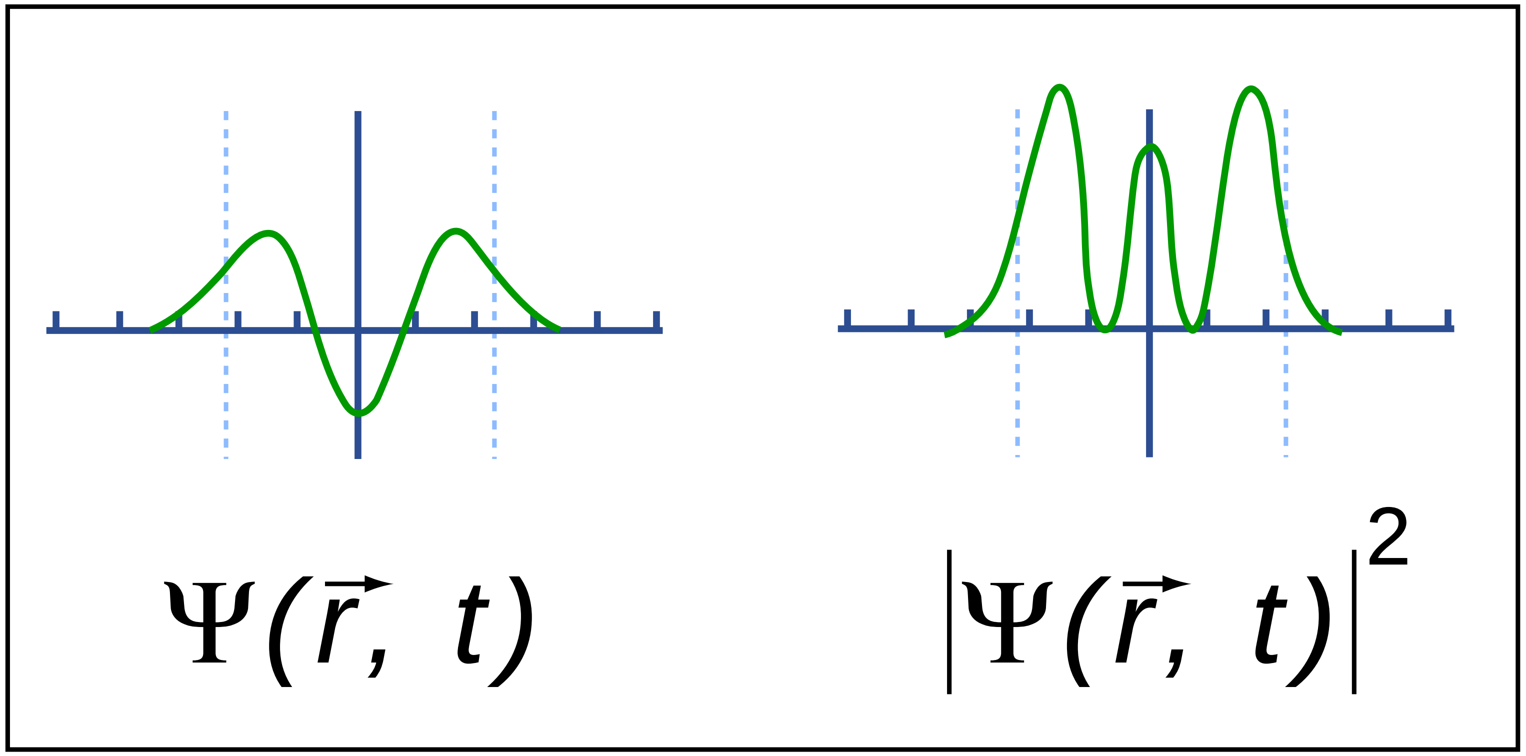
$$\vec{p} = \hbar\vec{k} = \frac{h}{\lambda}\frac{\vec{k}}{|\vec{k}|}$$

de Broglie: free particle can be described a as planewave $\psi(\vec{r},t) = Ae^{i(\vec{k}\cdot\vec{r}-\omega t)}$ with $\lambda = \frac{h}{mv}$

Review: Interpretation of QM

$\psi(\vec{r}, t)$ → wave function (complex)

$|\psi|^2 = \psi\psi^*$ → interpretation as probability to find particle!



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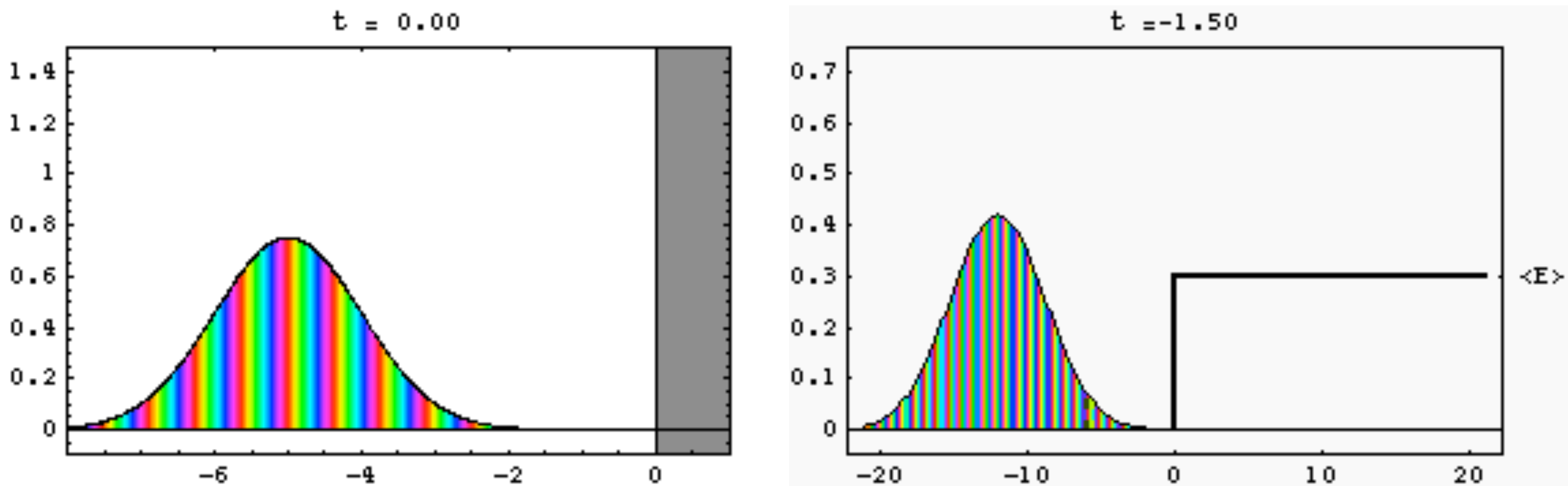
$$\int_{-\infty}^{\infty} \psi\psi^* dV = 1$$

Wave Particles Hitting a Wall



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Electron Wave/Particle Video

Courtesy of cassiopeiaproject.com.

Source: YouTube (cassiopeiaproject)

Review: Schrödinger equation

a wave equation:

second derivative in space
first derivative in time

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r,t)\right]\psi(r,t) = i\hbar\frac{\partial}{\partial t}\psi(r,t)$$

Hamiltonian

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r,t) =$$
$$= \frac{p^2}{2m} + V = T + V$$

$$\vec{p} = -i\hbar\nabla$$

Schrödinger...

Following up on these ideas, Schrödinger decided to find a proper wave equation for the electron. He was guided by William R. Hamilton's analogy between mechanics and optics, encoded in the observation that the zero-wavelength limit of optics resembles a mechanical system—the trajectories of light rays become sharp tracks which obey Fermat's principle, an analog of the principle of least action.[6] A modern version of his reasoning is reproduced in the next section. The equation he found is:

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\nabla^2\Psi(x,t) + V(x)\Psi(x,t).$$

Using this equation, Schrödinger computed the Hydrogen spectral series by treating a hydrogen atom's electron as a wave $\Psi(x, t)$, moving in a potential well V, created by the proton. This computation accurately reproduced the energy levels of the Bohr model.

However, by that time, Arnold Sommerfeld had refined the Bohr model with relativistic corrections.[7][8] Schrödinger used the relativistic energy momentum relation to find what is now known as the Klein–Gordon equation in a Coulomb potential (in natural units):

$$\left(E + \frac{e^2}{r}\right)^2 \psi(x) = -\nabla^2\psi(x) + m^2\psi(x).$$

He found the standing waves of this relativistic equation, but the relativistic corrections disagreed with Sommerfeld's formula. Discouraged, he put away his calculations and secluded himself in an isolated mountain cabin with a lover.[9]

While at the cabin, Schrödinger decided that his earlier non-relativistic calculations were novel enough to publish, and decided to leave off the problem of relativistic corrections for the future. He put together his wave equation and the spectral analysis of hydrogen in a paper in 1926.[10] The paper was enthusiastically endorsed by Einstein, who saw the matter-waves as an intuitive depiction of nature, as opposed to Heisenberg's matrix mechanics, which he considered overly formal.[11]

Review: Schrödinger equation

H time independent: $$\psi(\vec{r},t) = \psi(\vec{r}) \cdot f(t)$$

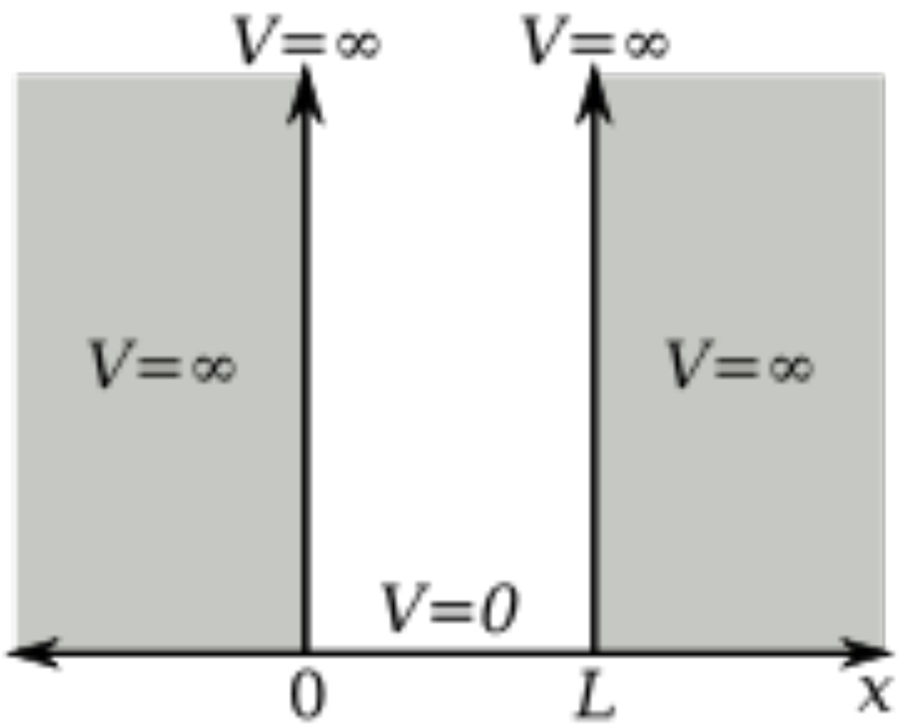
$$i\hbar \frac{\dot{f}(t)}{f(t)} = \frac{H\psi(\vec{r})}{\psi(\vec{r})} = \text{const.} = E$$

$$H\psi(\vec{r}) = E\psi(\vec{r})$$

time independent Schrödinger equation
stationary Schrödinger equation

$$\psi(\vec{r},t) = \psi(\vec{r}) \cdot e^{-\frac{i}{\hbar}Et}$$

Particle in a box



Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x)\psi(x) = E\psi(x) \quad (1)$$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} = E\psi(x) \quad (2)$$

boundary conditions

$$\psi(0) = \psi(L) = 0 \quad (4)$$

$$\psi(x) = A\sin(kx) \quad (5)$$

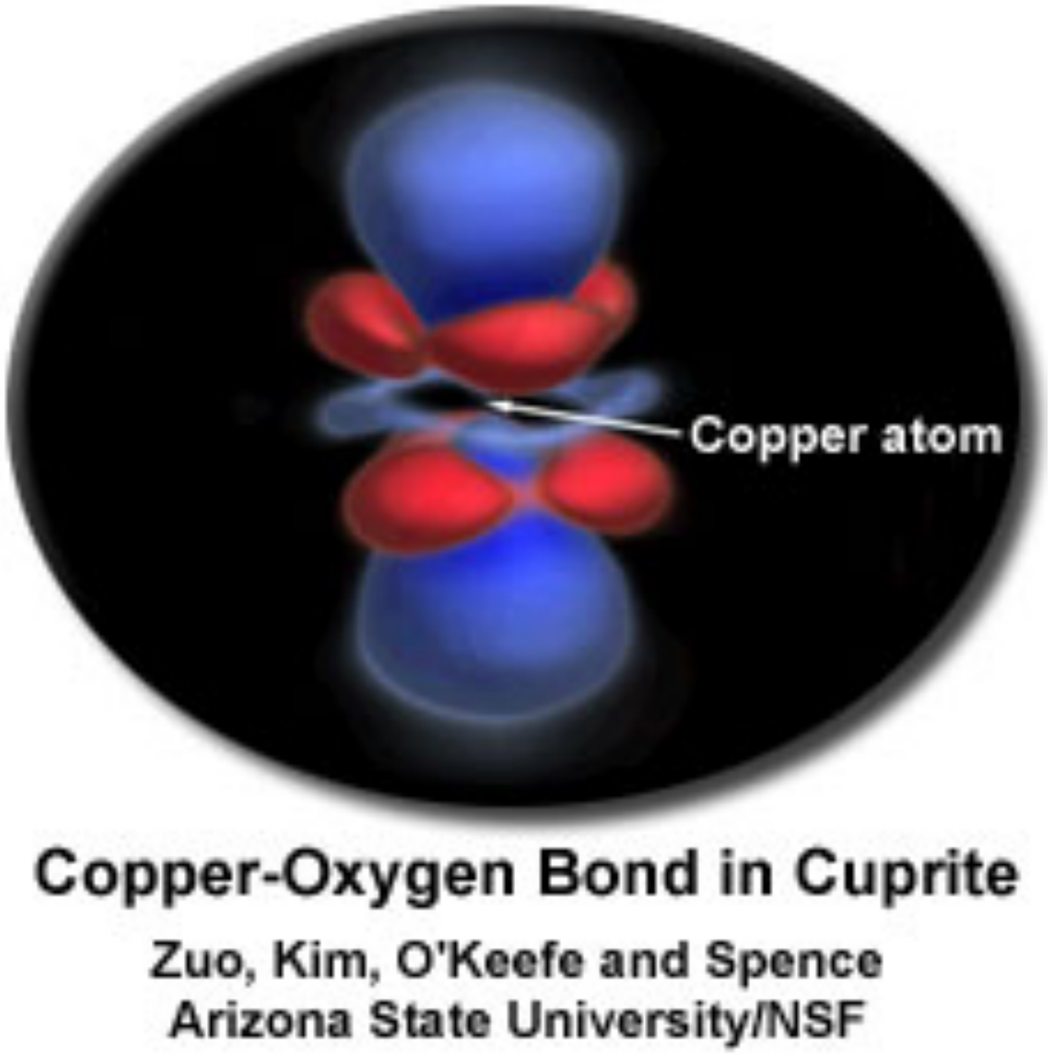
$$\psi(L) = A\sin(kL) = 0 \quad (6)$$

general solution

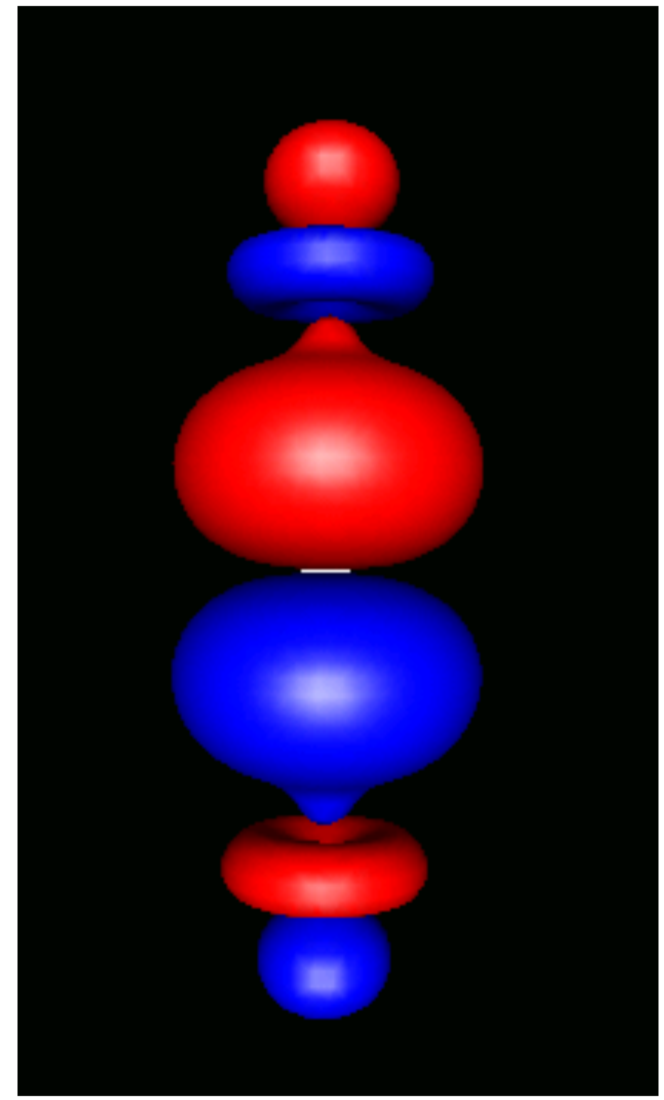
$$\psi(x) = A\sin(kx) + B\cos(kx)$$

$$E = \frac{k^2\hbar^2}{2m} \quad (3)$$

It's real!



Cu-O Bond
(experiment)



Ti-O Bond
(theory)

Screenshot of Scientific American article "Observing Orbitals" removed due to copyright restrictions; read the article online.

What's this good for?

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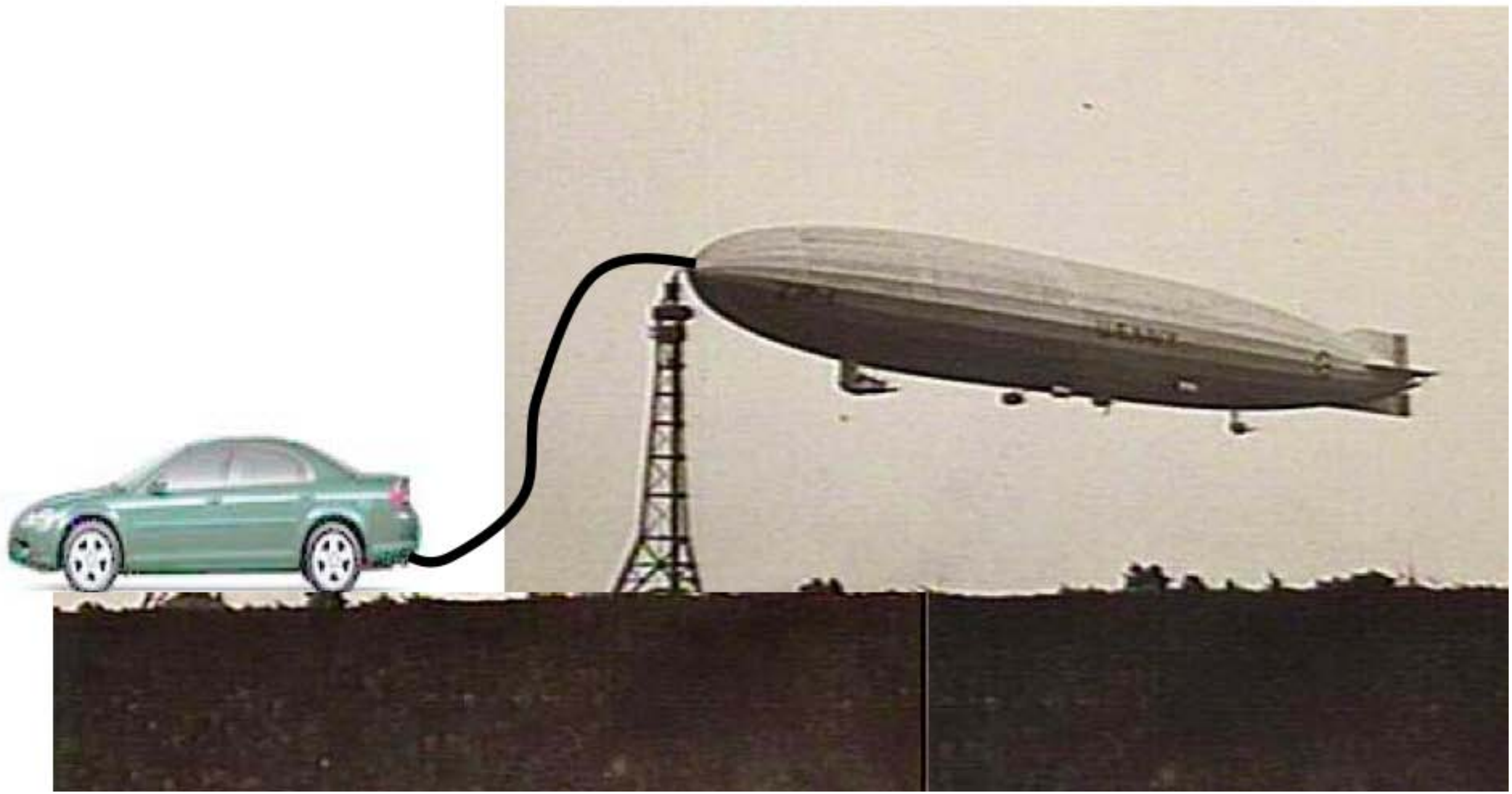
Hydrogen:
a real world
example.

The Hydrogen Future?



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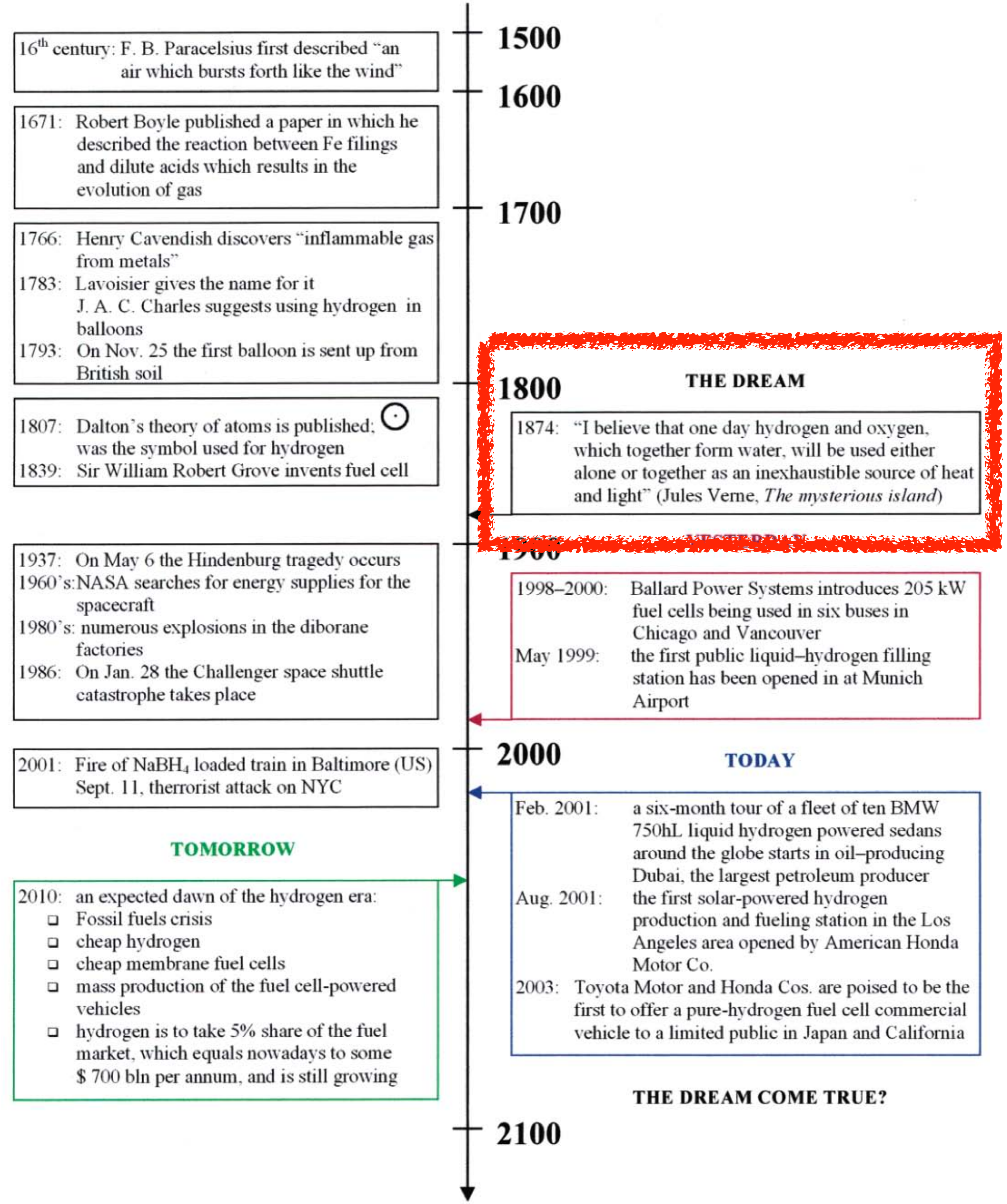
History of Hydrogen



How large of a gas tank do we want?

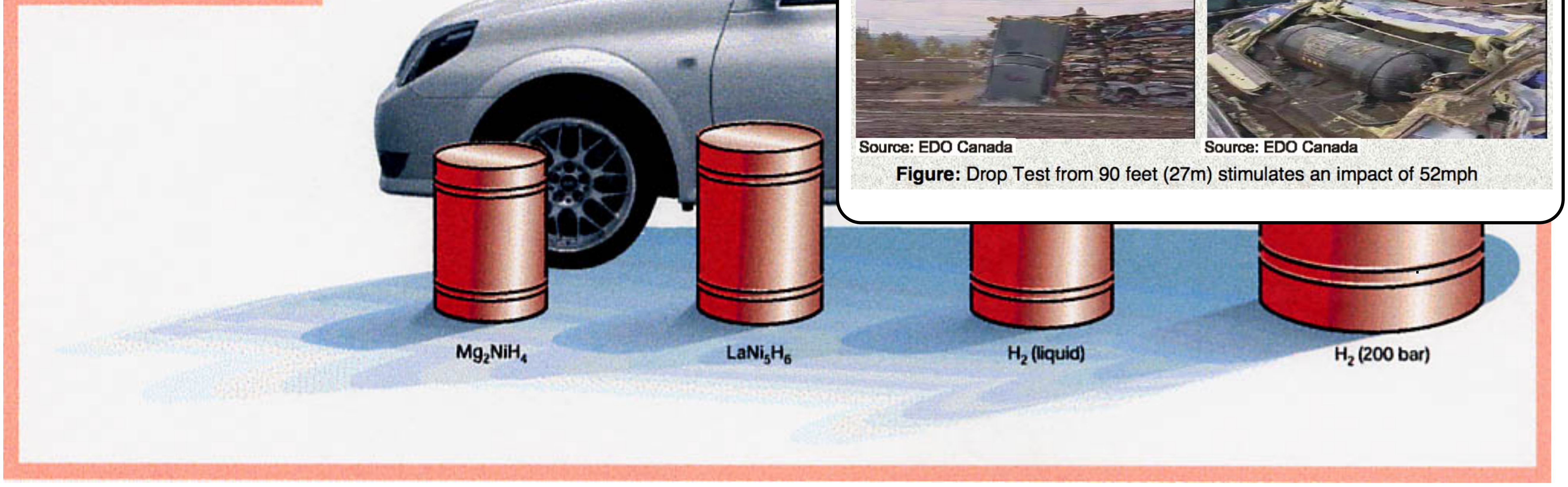
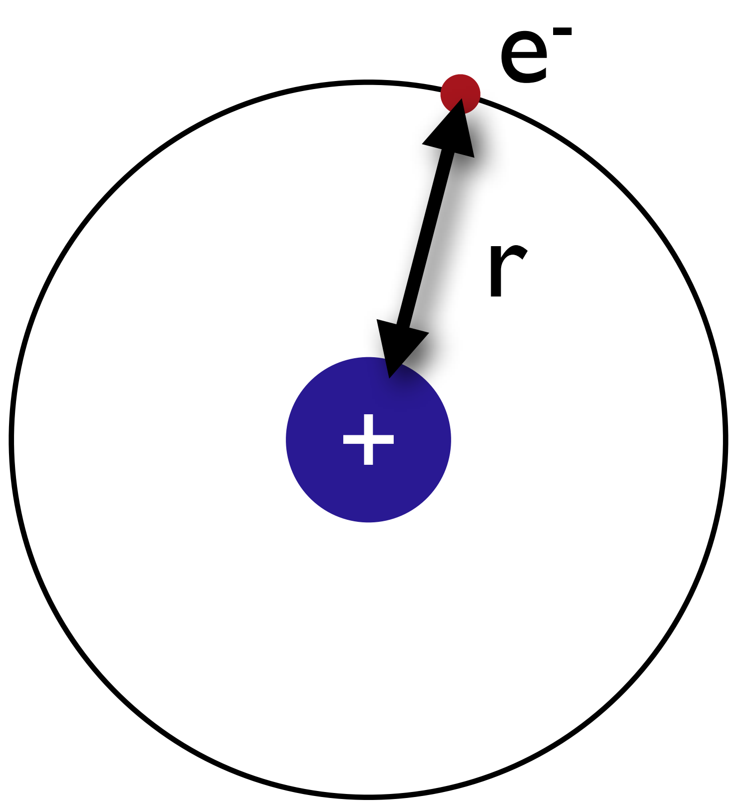


Figure 1 Volume of 4 kg of hydrogen compacted in different ways, with size relative to the size of a car. (Image of car courtesy of Toyota press information, 33rd Tokyo Motor Show, 1999.)

The "Drop Test"

Figure: Drop Test from 90 feet (27m) stimulates an impact of 52mph

The hydrogen atom



electrostatics:
Coulomb potential

stationary
Schrödinger equation

wave functions
possible energies

The hydrogen atom

stationary
Schrödinger equation

$$H\psi = E\psi$$

$$\left[\, T + V \,\right]\psi = E\psi$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]\psi(\vec{r}) = E\psi(\vec{r})$$

just solve ☺

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}\right]\psi(\vec{r}) = E\psi(\vec{r})$$

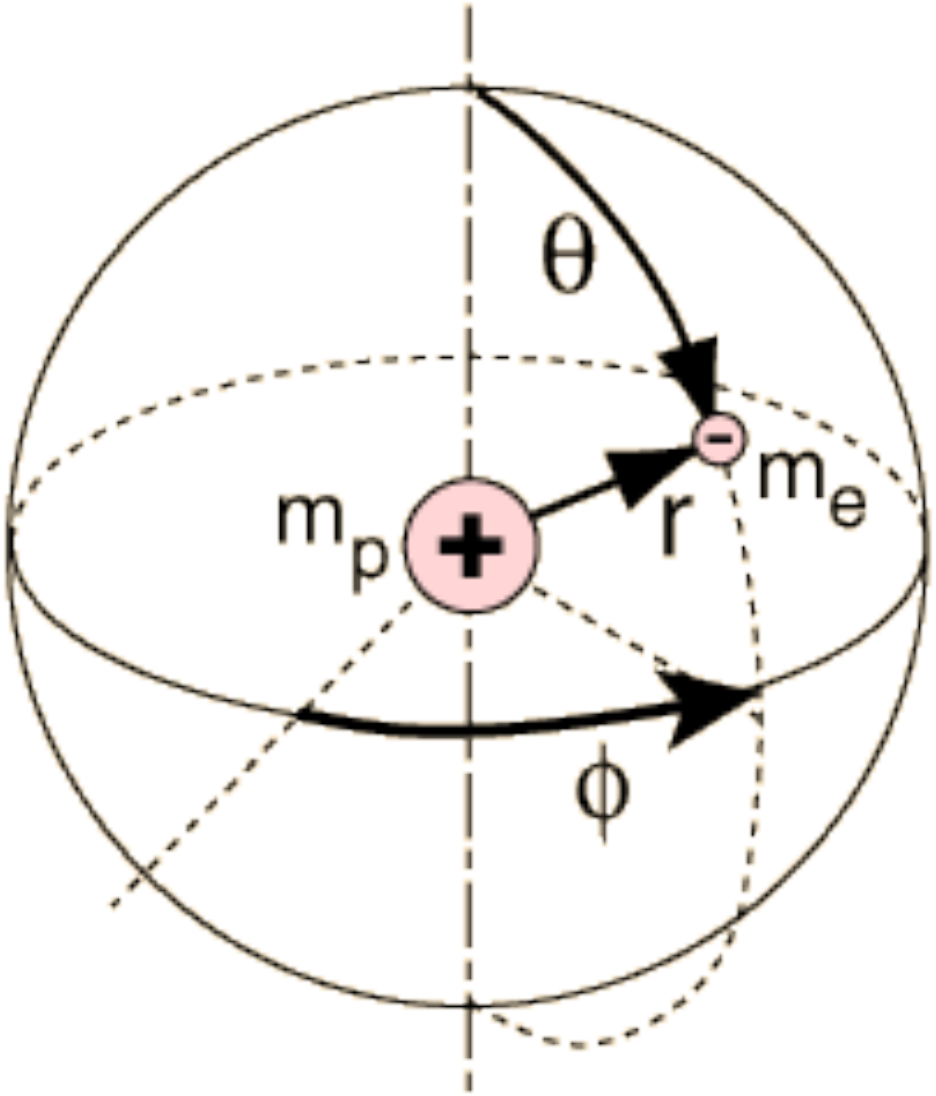
The hydrogen atom

choose a more suitable coordinate system:

spherical coordinates

$$\psi(\vec{r}) = \psi(x, y, z)$$

$$= \psi(r, \theta, \phi)$$

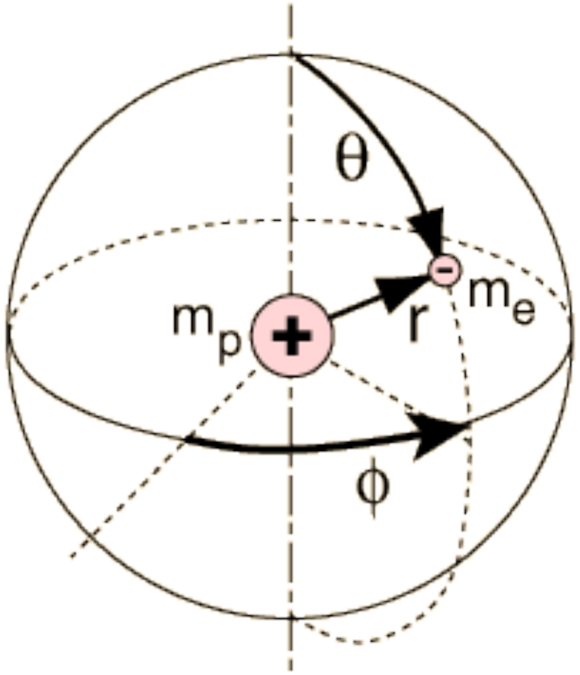


The hydrogen atom

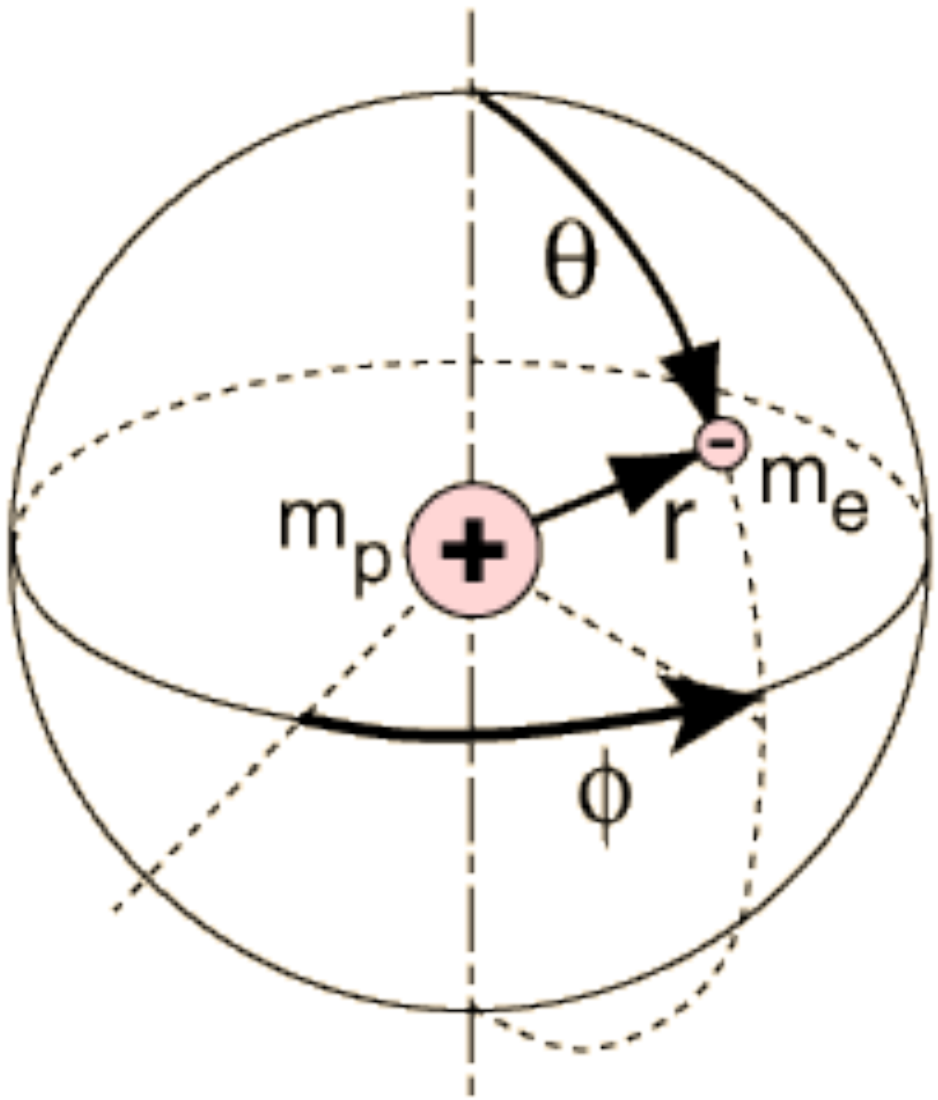
Schrödinger equation in spherical coordinates:

$$\frac{-\hbar^2}{2\mu}\frac{1}{r^2\sin\theta}\left[\sin\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{\sin\theta}\frac{\partial^2\Psi}{\partial\phi^2}\right]$$

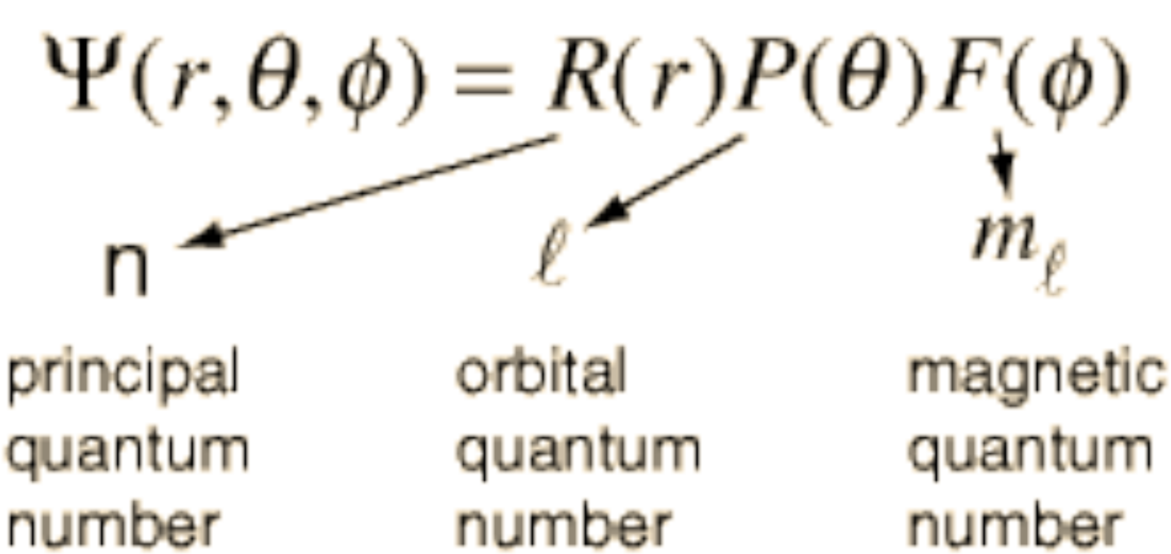
$$+U(r)\Psi(r,\theta,\phi)=E\,\Psi(r,\theta,\phi)$$



The hydrogen atom



solve by separation of variables:



The hydrogen atom

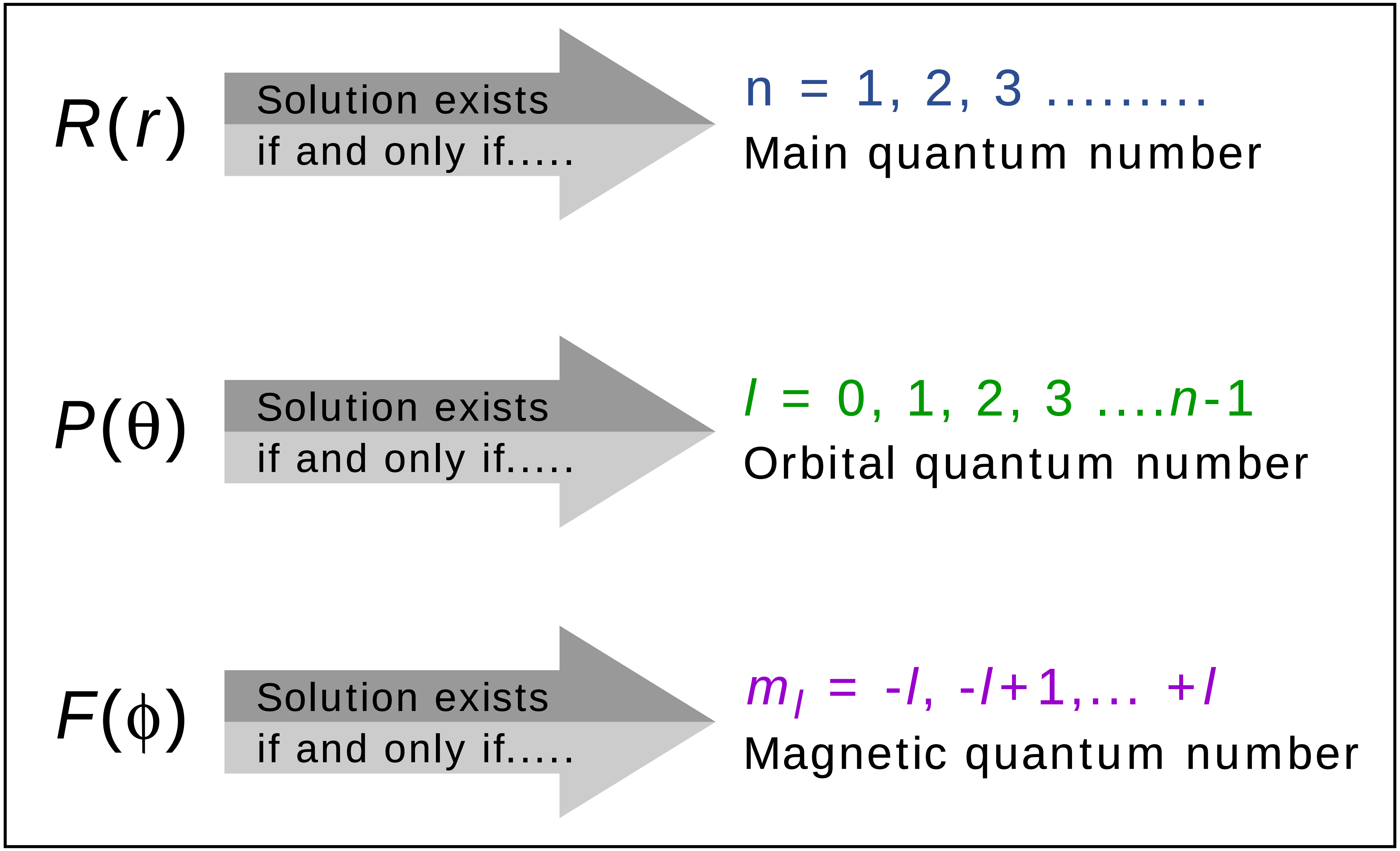
separation of variables

$$\frac{1}{R}\frac{d}{dr}\left[r^2\frac{dR}{dr}\right]+\frac{2\mu}{\hbar^2}(Er^2+ke^2r)=l(l+1)$$

$$\frac{\sin\theta}{P}\frac{d}{d\theta}\left[\sin\theta\frac{dP}{d\theta}\right]+C_r\sin^2\theta=-C_\phi$$

$$\frac{1}{F}\frac{d^2F}{d\phi^2}=C_\phi$$

The hydrogen atom



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The hydrogen atom

quantum numbers

n	l	m_l	$F(\phi)$	$P(\theta)$	$R(r)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}\, a_0^{3/2}} \left[2 - \frac{r}{a_0}\right] e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$
2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$

The hydrogen atom

standard notation for states:

"Sharp"	*s*	$l = 0$	*For example, if $n = 2$, $l = 1$, the state is designated 2p*
"Principal"	*p*	$l = 1$	
"Diffuse"	*d*	$l = 2$	
"Fundamental"	*f*	$l = 3$	

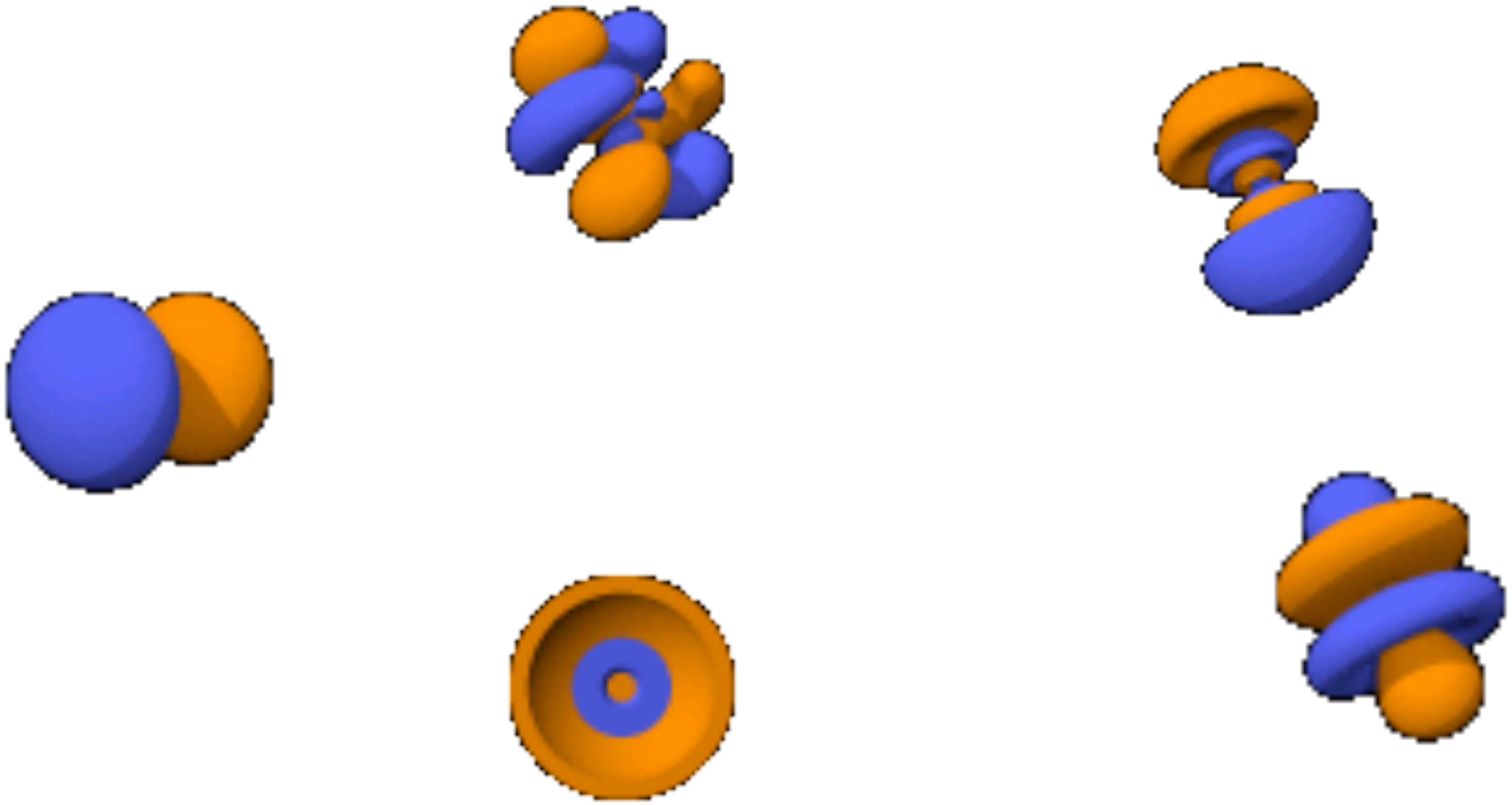
The hydrogen atom

quantum numbers

n	l	m_l	$F(\phi)$	$P(\theta)$	$R(r)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}\, a_0^{3/2}} \left[2 - \frac{r}{a_0}\right] e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$
2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$

The hydrogen atom

http://www.orbitals.com/orb/orbtable.htm



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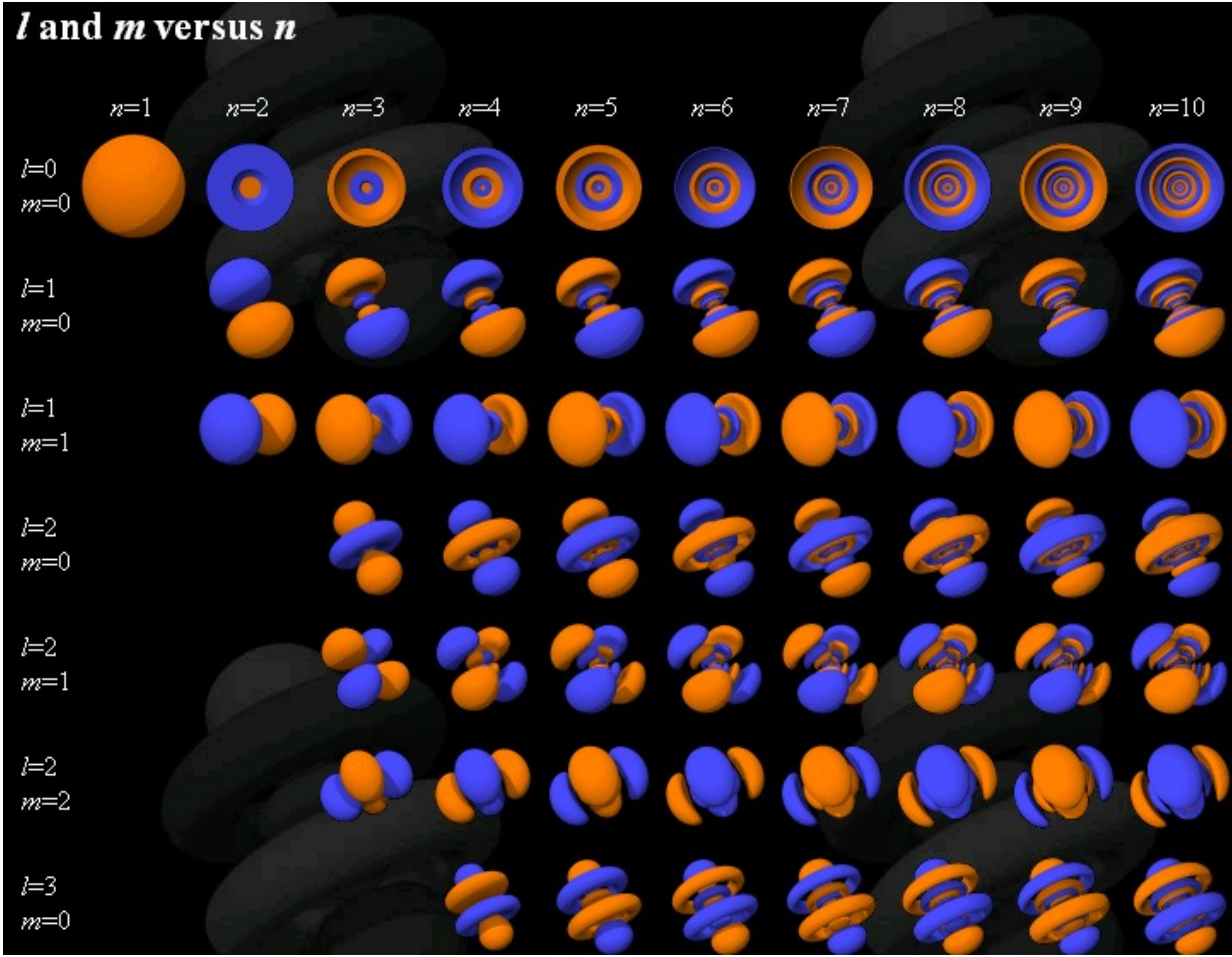
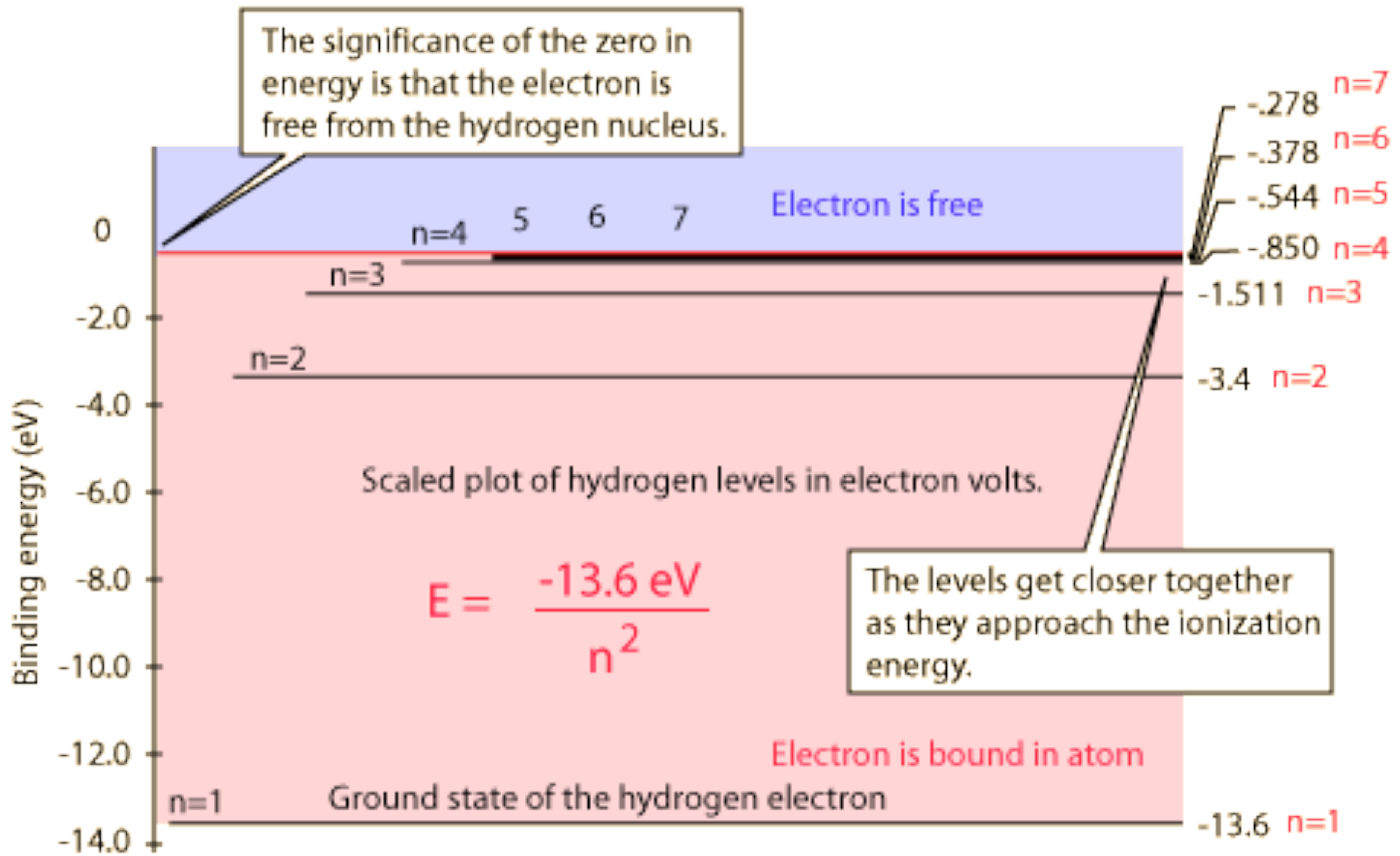
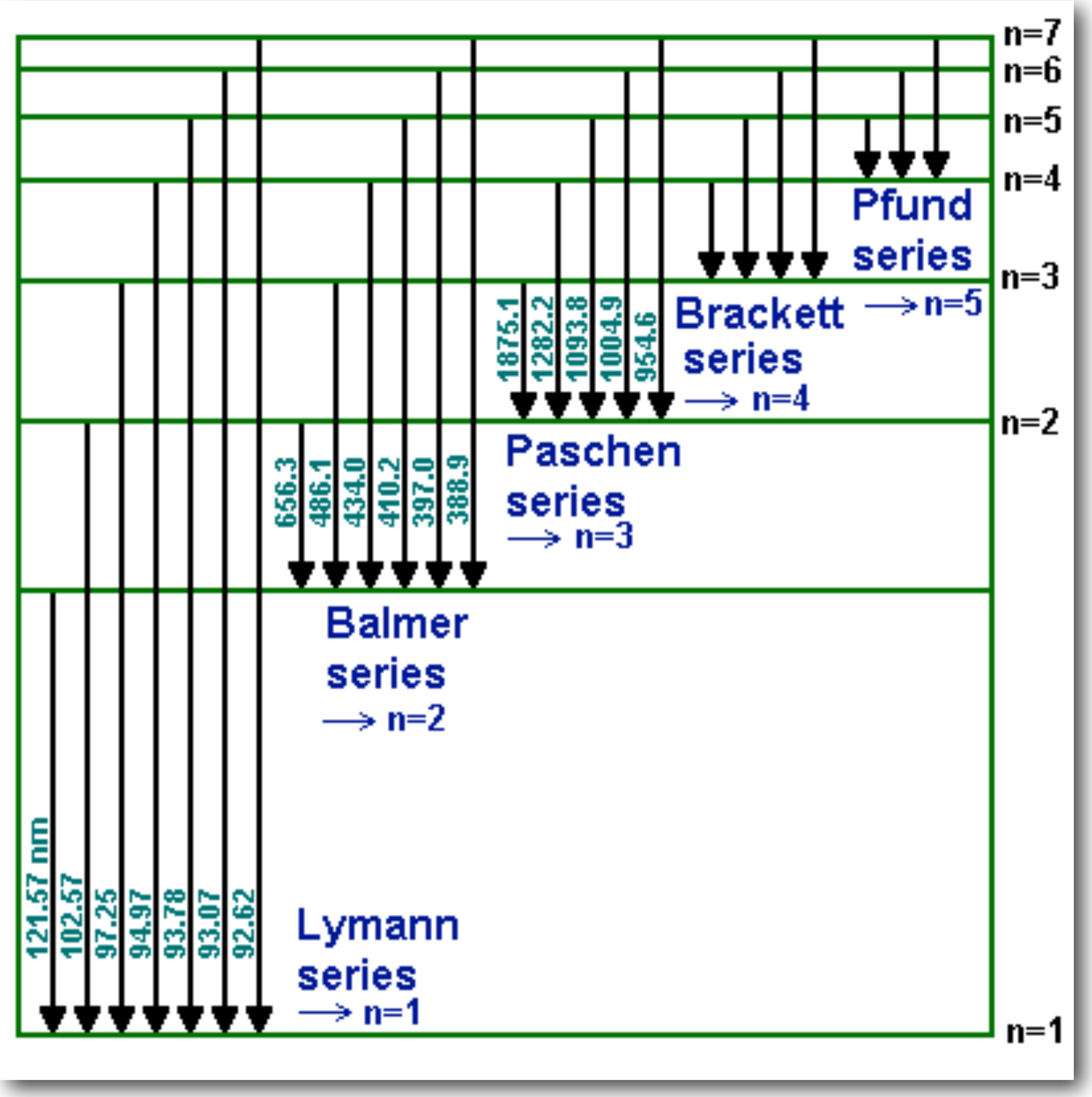

l and m versus n
n=1
n=2
n=3
n=4
n=5
n=6
n=7
n=8
n=9
n=10
l=0 m=0
l=1 m=0
l=1 m=1
l=2 m=0
l=2 m=1
l=2 m=2
l=3 m=0

The hydrogen atom

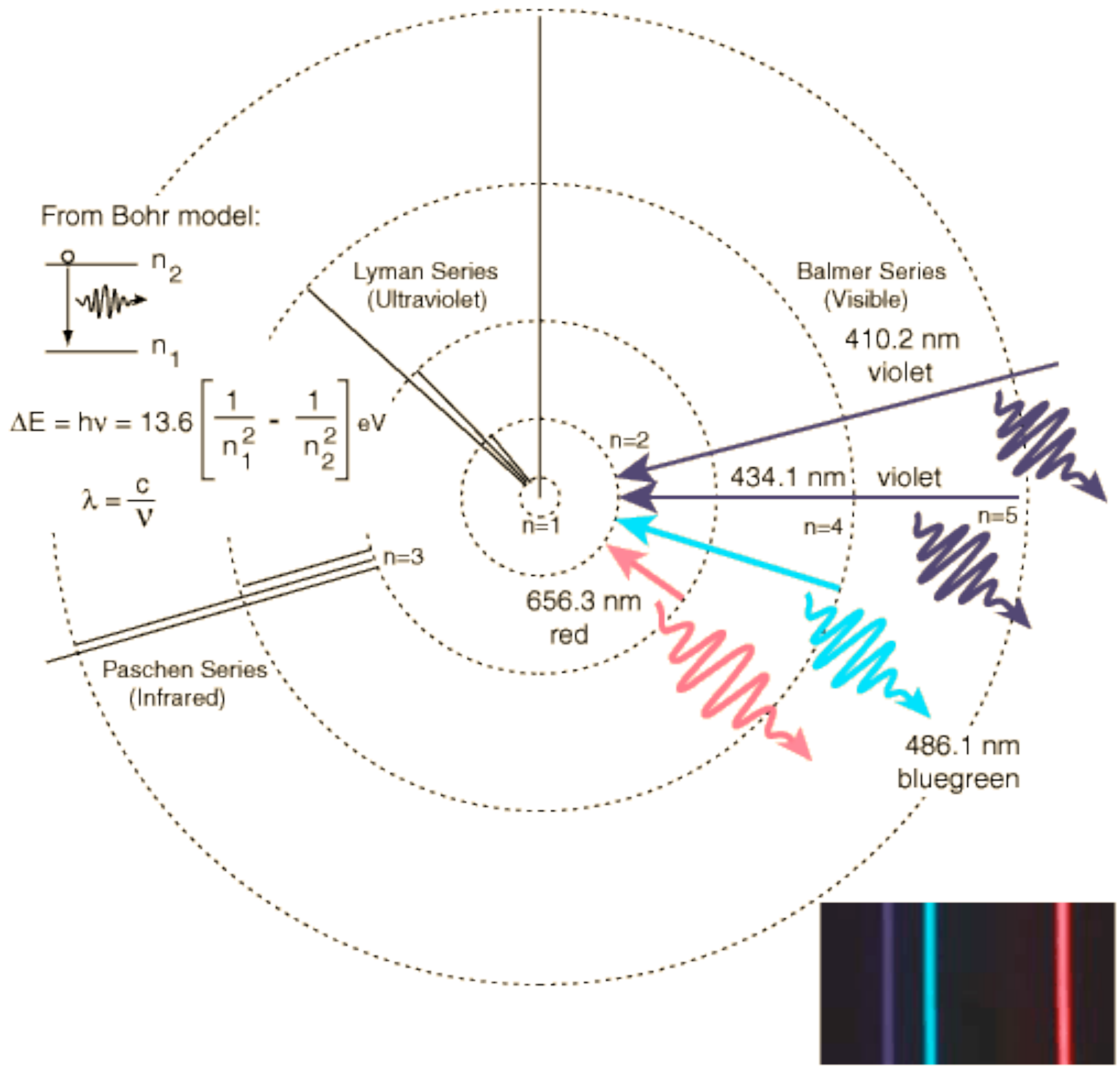
Energies: $$E_n = \frac{-me^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} = \frac{-13.6eV}{n^2} \qquad n = 1,2,3,\ldots$$



The hydrogen atom



The hydrogen atom



Atomic units

1 eV = 1.6021765^{-19} J

1 Rydberg = 13.605692 eV = 2.1798719^{-18} J

1 Hartree = 2 Rydberg

1 Bohr =5.2917721^{-11} m

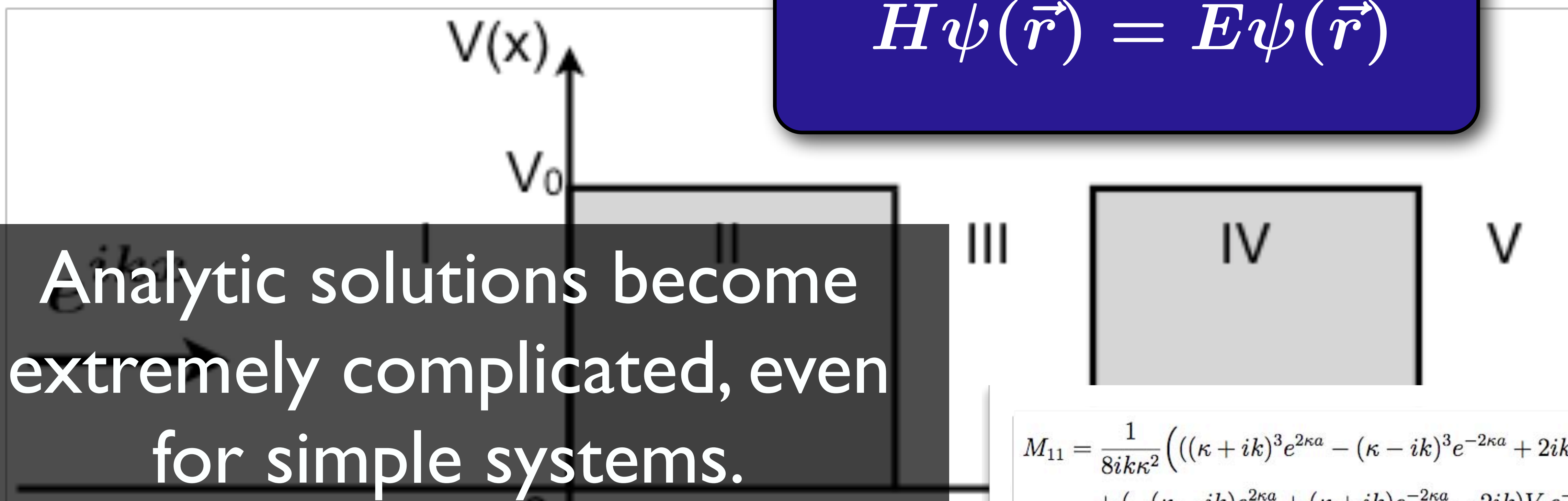
Atomic units (a.u.):

Energies in Ry
Distances in Bohr

Also in use: 1Å=10^{-10}m, nm= 10^{-9}m

Slightly Increased Complexity

$$H\psi(\vec{r}) = E\psi(\vec{r})$$



Analytic solutions become extremely complicated, even for simple systems.

$$\begin{aligned}
x = 0: \quad & 1 + R &=& A + B \\
& ik - ikR &=& \kappa A - \kappa B \\
x = a: \quad & Ae^{\kappa a} + Be^{-\kappa a} &=& Ce^{ika} + De^{-ika} \\
& \kappa Ae^{\kappa a} - \kappa Be^{-\kappa a} &=& ikCe^{ika} - ikDe^{-ika} \\
x = a + b: \quad & Ce^{ik(a+b)} + De^{-ik(a+b)} &=& Fe^{\kappa(a+b)} + Ge^{-\kappa(a+b)} \\
& ikCe^{ik(a+b)} - ikDe^{-ik(a+b)} &=& \kappa Fe^{\kappa(a+b)} - \kappa e^{-\kappa(a+b)} \\
x = 2a + b: \quad & Fe^{\kappa(2a+b)} + Ge^{-\kappa(2a+b)} &=& Te^{ik(2a+b)} \\
& \kappa Fe^{\kappa(2a+b)} - \kappa Ge^{-\kappa(2a+b)} &=& ikTe^{ik(2a+b)}.
\end{aligned}$$

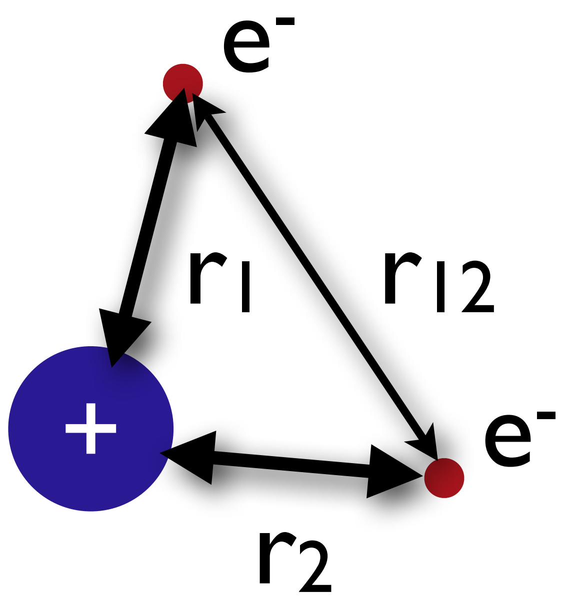
$$M_{11} = \frac{1}{8ik\kappa^2}\Big(\big((\kappa+ik)^3 e^{2\kappa a} - (\kappa-ik)^3 e^{-2\kappa a} + 2ikV_1\big)e^{ikb} + \big(-(\kappa-ik)e^{2\kappa a} + (\kappa+ik)e^{-2\kappa a} - 2ik\big)V_1 e^{-ikb}\Big)$$

$$M_{12} = \frac{1}{8ik\kappa^2}\Big(\big((\kappa+ik)e^{2\kappa a} - (\kappa-ik)e^{-2\kappa a} - 2ik\big)V_1 e^{ikb} + \big(-(\kappa-ik)^3 e^{2\kappa a} + (\kappa+ik)^3 e^{-2\kappa a} + 2ikV_1\big)e^{-ikb}\Big)$$

$$M_{21} = \frac{1}{8ik\kappa}\Big(\big((\kappa+ik)^3 e^{2\kappa a} + (\kappa-ik)^3 e^{-2\kappa a} - 2\kappa V_1\big)e^{ikb} - \big((\kappa-ik)e^{2\kappa a} + (\kappa+ik)e^{-2\kappa a} - 2\kappa\big)V_1 e^{-ikb}\Big)$$

$$M_{22} = \frac{1}{8ik\kappa}\Big(\big((\kappa+ik)e^{2\kappa a} + (\kappa-ik)e^{-2\kappa a} - 2\kappa\big)V_1 e^{ikb} + \big(-(\kappa-ik)^3 e^{2\kappa a} - (\kappa+ik)^3 e^{-2\kappa a} + 2\kappa V_1\big)e^{-ikb}\Big)$$

Next? Helium!



$$H\psi = E\psi$$

$$\Big[H_1 + H_2 + W\Big]\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

$$\Big[T_1 + V_1 + T_2 + V_2 + W\Big]\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

$$\Big[-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}\Big]\psi(r_1, r_2) = E\psi(r_1, r_2)$$

cannot be solved analytically

problem!

Solution in general?

Only a few problems are solvable analytically.

We need approximate approaches:

perturbation theory

matrix eigenvalue equation

Solution in general?

Perturbation theory:

$$H = H_0 + \lambda H_1$$

small

wave functions and energies are known

wave functions and energies will be similar to those of H_o

Solution in general?

Matrix eigenvalue equation:

$$\psi = \sum_i c_i \phi_i$$

expansion in orthonormalized basis functions

$$H\psi = E\psi$$

$$H \sum_i c_i \phi_i = E \sum_i c_i \phi_i$$

$$\int d\vec{r}\, \phi_j^* H \sum_i c_i \phi_i = E \int d\vec{r}\, \phi_j^* \sum_i c_i \phi_i$$

$$\sum_i H_{ji} c_i = E c_j$$

$$\mathcal{H}\vec{c} = E\vec{c}$$

Everything is spinning ...

$$\vec{F} = -\nabla E$$
$$= \nabla\, \vec{m} \cdot \vec{B}$$

Stern–Gerlach experiment (1922)

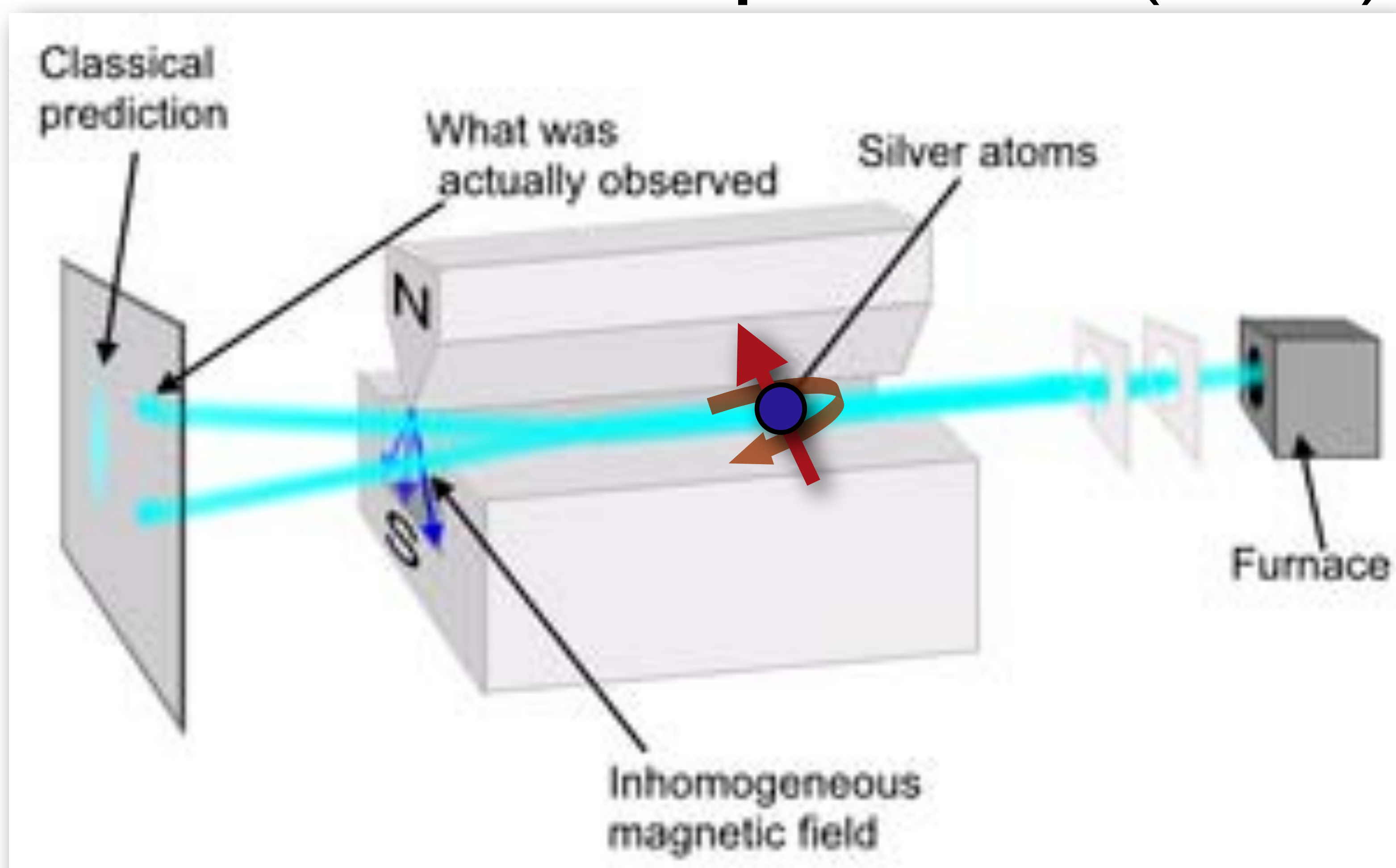
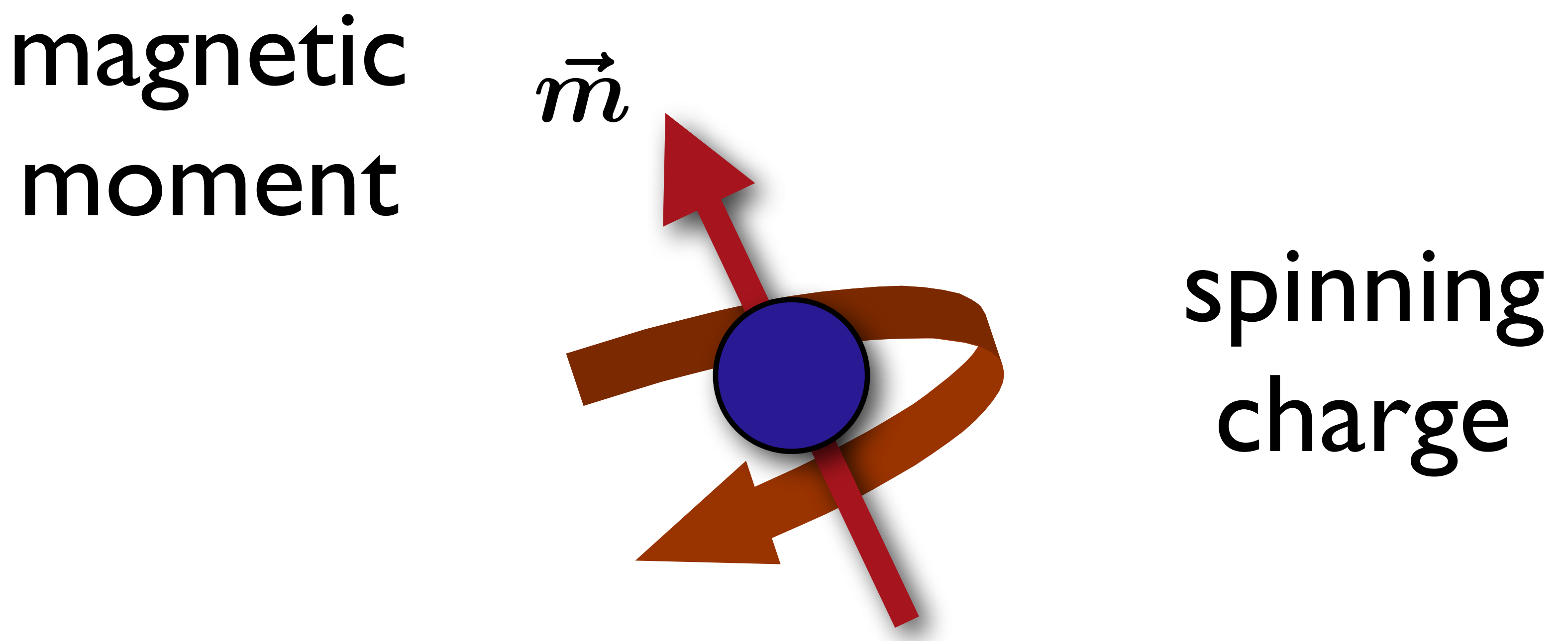


Image courtesy of Teresa Knott.

Everything is spinning ...

In quantum mechanics particles can have a magnetic moment and a ”spin”



Everything is spinning ...

conclusion from the
Stern-Gerlach experiment

for electrons: spin can ONLY be

up down

Everything is spinning ...

new quantum number: spin quantum number

for electrons: spin quantum number can ONLY be

up

down

Spin History

I think you and Uhlenbeck have been very lucky to get your spinning electron published and talked about before Pauli heard of it. It appears that more than a year ago Kronig believed in the spinning electron and worked out something; the first person he showed it to was Pauli. Pauli ridiculed the whole thing so much that the first person became also the last and no one else heard anything of it. Which all goes to show that the infallibility of the Deity does not extend to his self-styled vicar on earth.

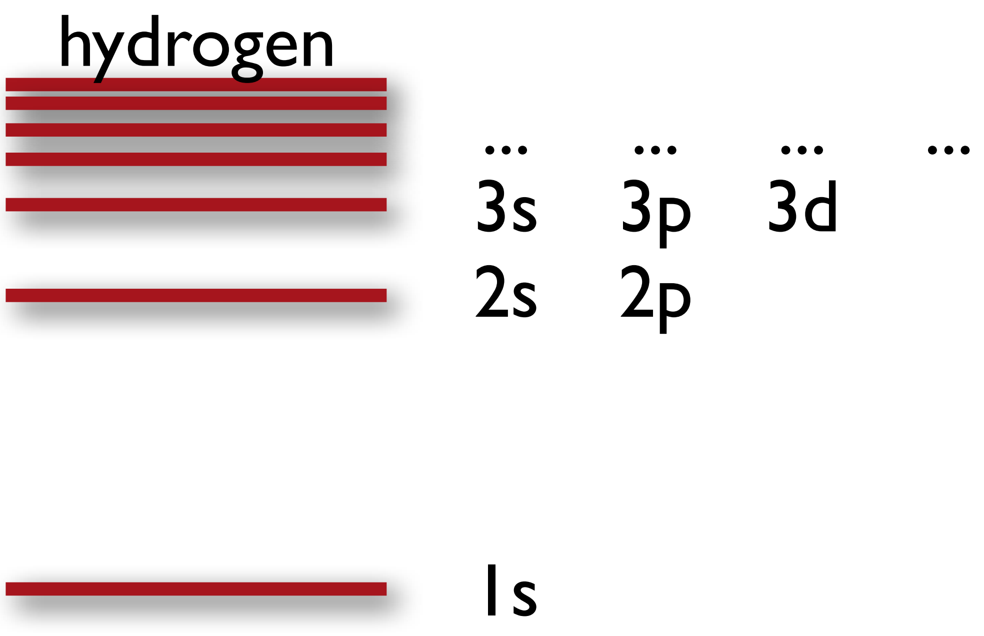
Part of a letter by L.H. Thomas to Goudsmit on March 25 1926 (source: Wikipedia).

Discovered in 1926 by Goudsmit and Uhlenbeck

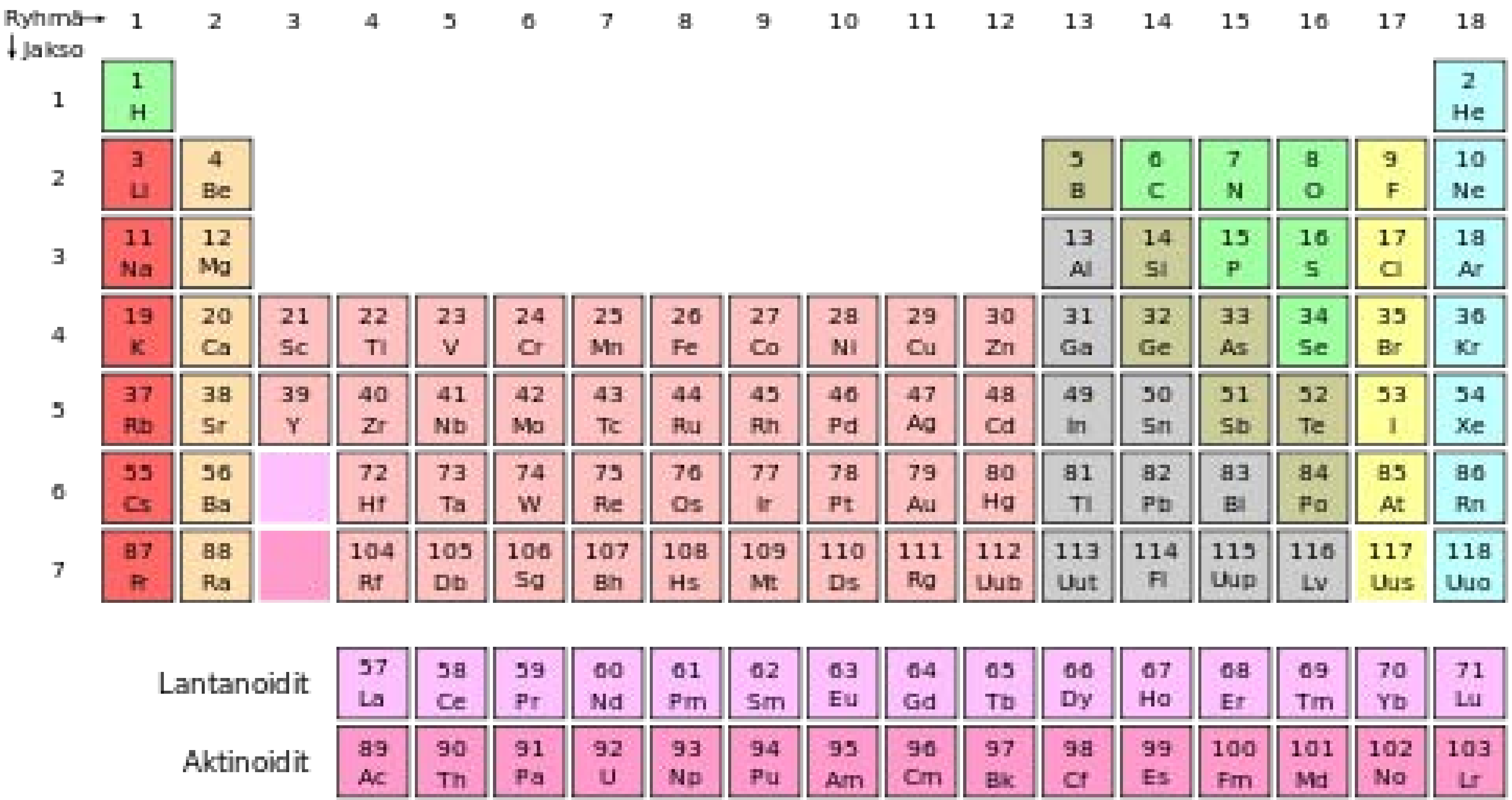
Pauli's exclusions principle

Two electrons in a system cannot have the same quantum numbers!

quantum numbers:
main n: 1,2,3 ...
orbital l: 0,1,...,n-1
magnetic m: -l,...,l
spin: up, down

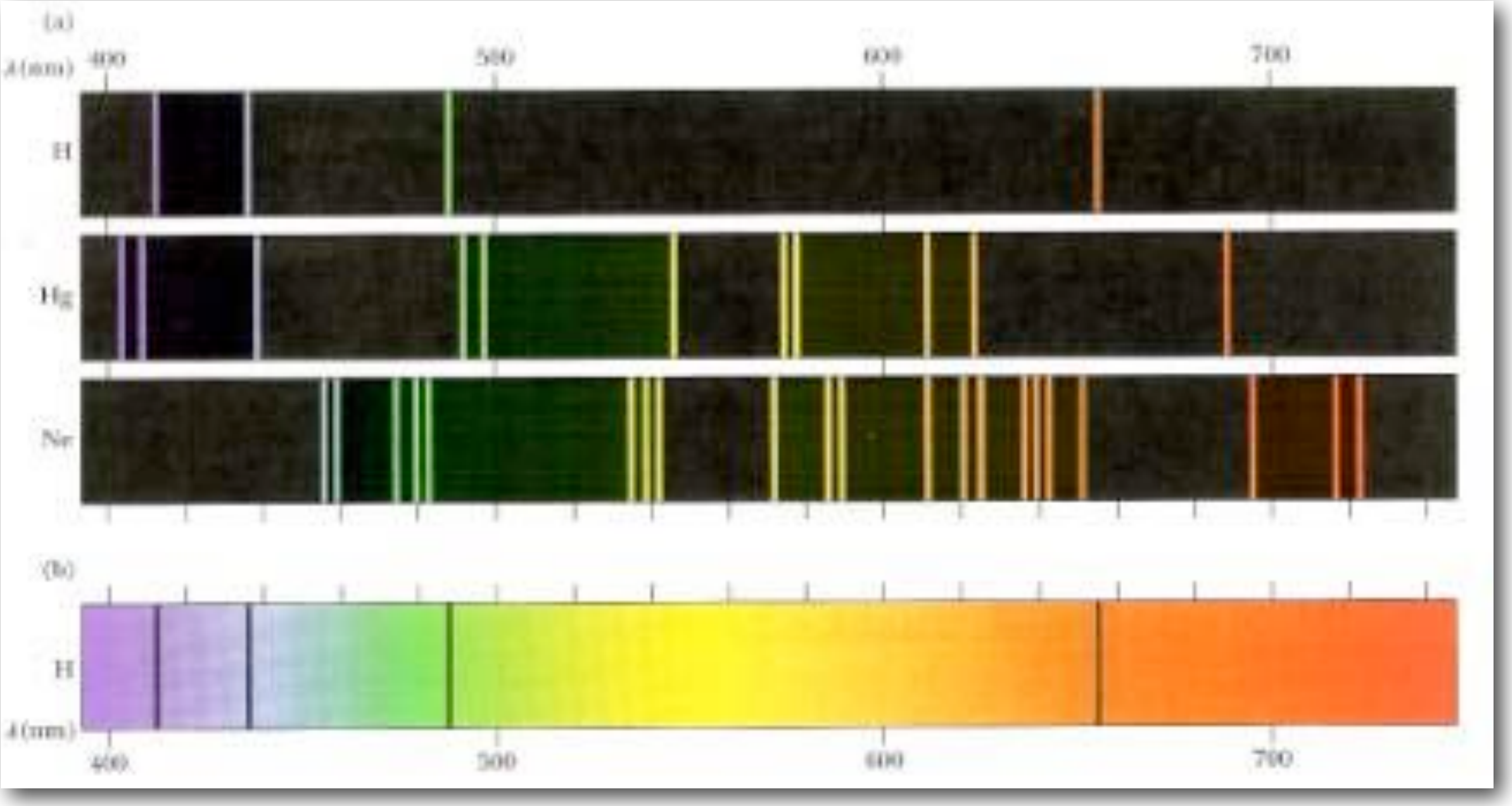


Periodic table of elements



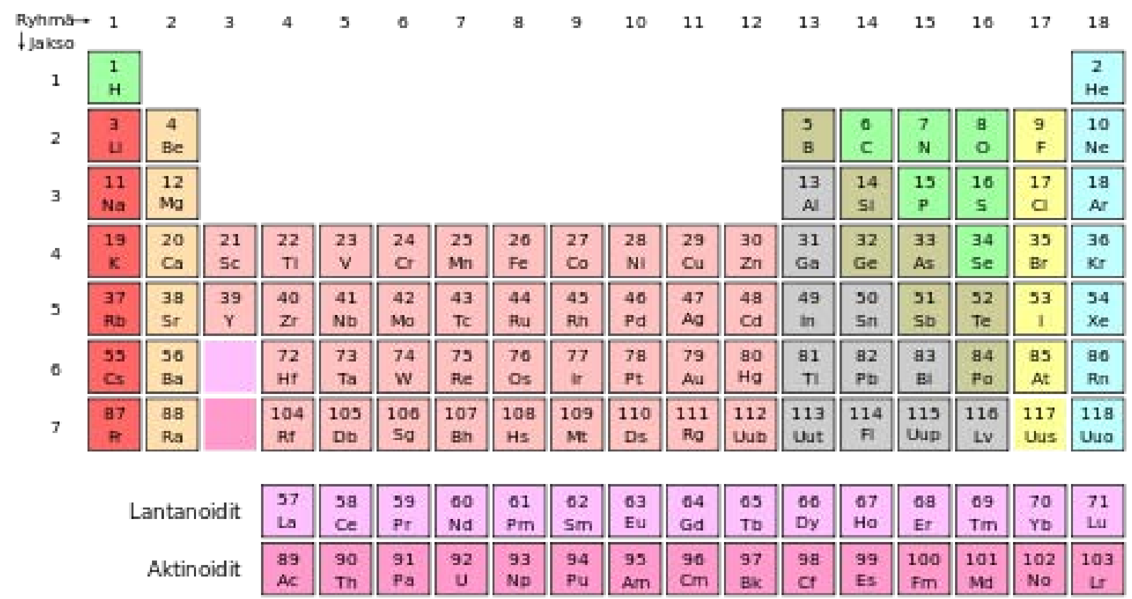
Connection to materials?

optical properties of gases



Review

- Review
- A real world example!
- Everything is spinning
- Pauli's exclusion
- Periodic table of elements



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Literature

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- wikipedia, "hydrogen atom", "Pauli exclusion principle", "periodic table", ...