1.021, 3.021, 10.333, 22.00 : Introduction to Modeling and Simulation : Spring 2011

Part II – Quantum Mechanical Methods : Lecture 2

Quantum Mechanics: Practice Makes Perfect

Jeffrey C. Grossman

Department of Materials Science and Engineering
Massachusetts Institute of Technology

Part II Outline

theory & practice

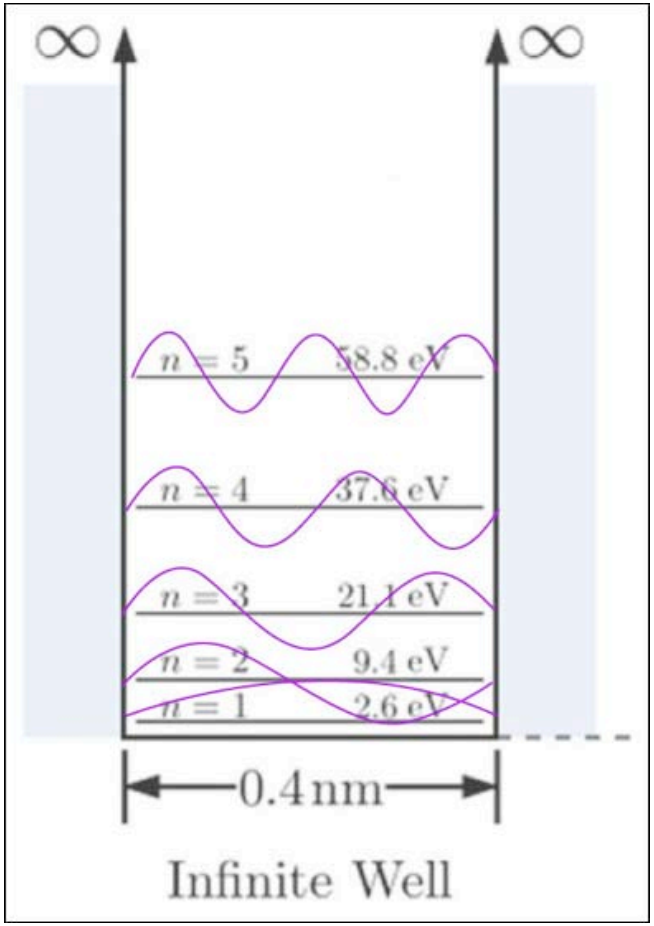
1. It's A Quantum World: The Theory of Quantum Mechanics
2. Quantum Mechanics: Practice Makes Perfect
3. From Many-Body to Single-Particle; Quantum Modeling of Molecules
4. From Atoms to Solids
5. Quantum Modeling of Solids: Basic Properties
6. Advanced Prop. of Materials: What else can we do?

example applications

7. Nanotechnology
8. Solar Photovoltaics: Converting Photons into Electrons
9. Thermoelectrics: Converting Heat into Electricity
10. Solar Fuels: Pushing Electrons up a Hill
11. Hydrogen Storage: the Strength of Weak Interactions
12. Review

Motivation

electron in box



Courtesy ESA and NASA. Image from Wikimedia Commons, http://commons.wikimedia.org.

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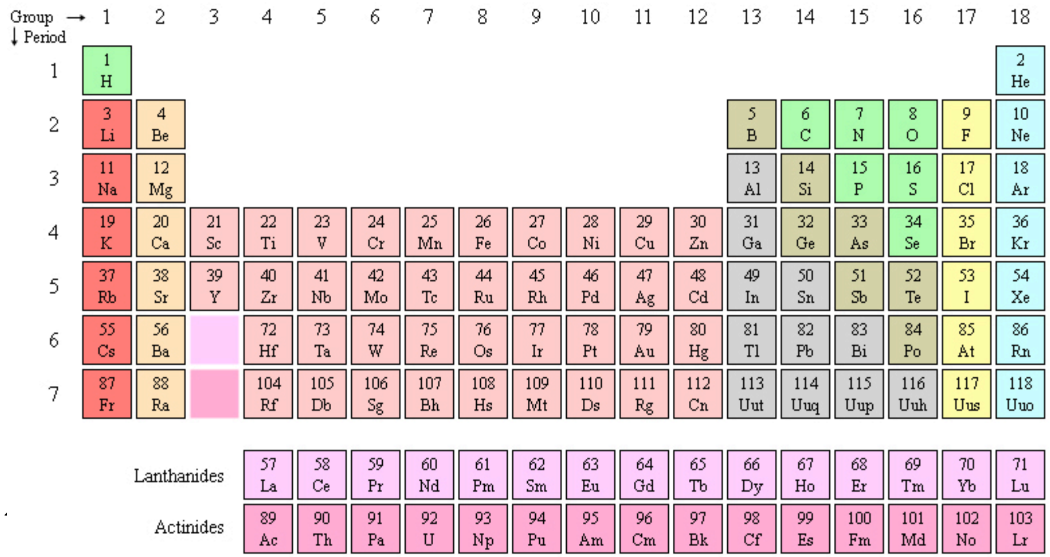
Lesson outline

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



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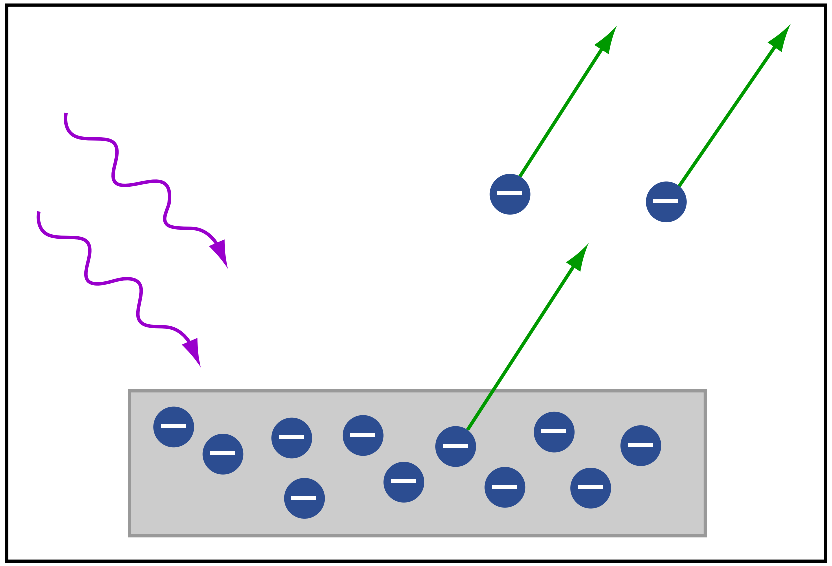
Review: Why QM?

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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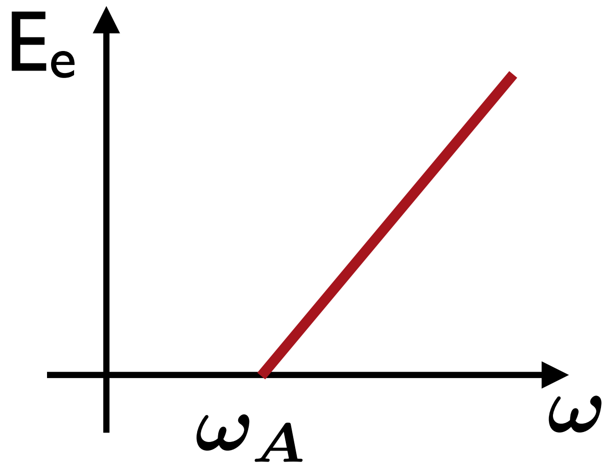
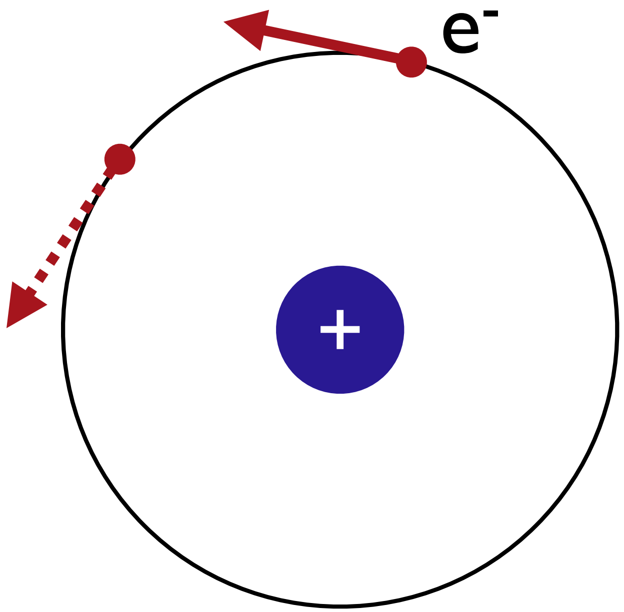


$$E = \hbar(\omega - \omega_A) = h(\nu - \nu_A)$$

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

Einstein: photon $E = \hbar\omega$

“Classical atoms”



hydrogen atom

problem:
accelerated charge causes radiation, atom not stable!

Liénard-Wiechert potential

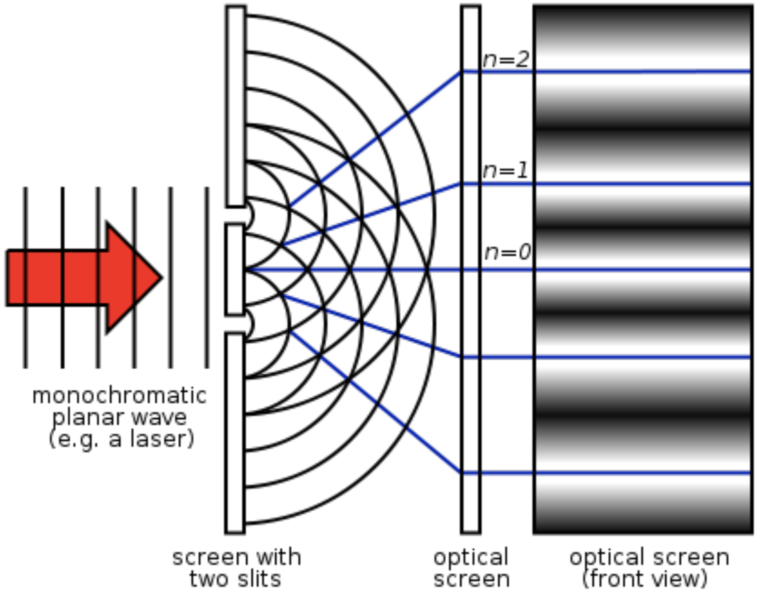
http://en.wikipedia.org/wiki/Li%C3%A9nard%E2%80%93Wiechert_potential#Implications.

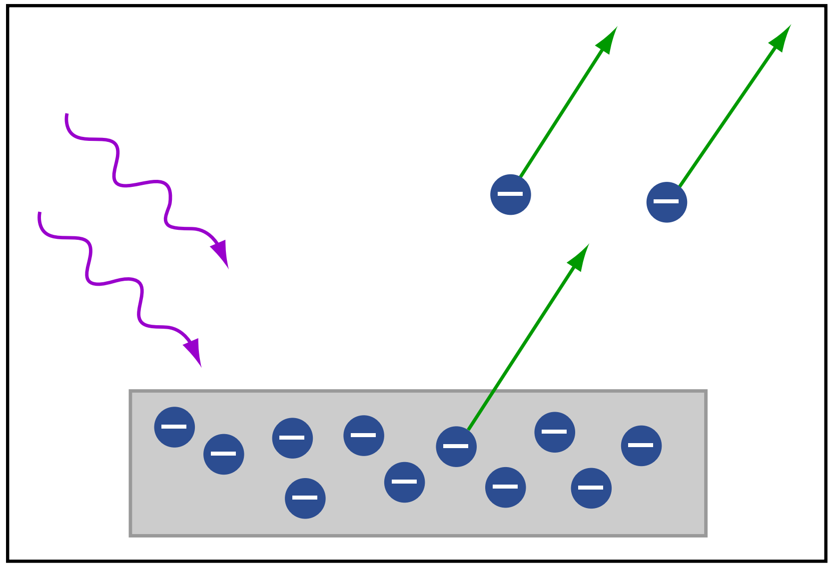
Review: Wave aspect

light matter

wave character

particle character





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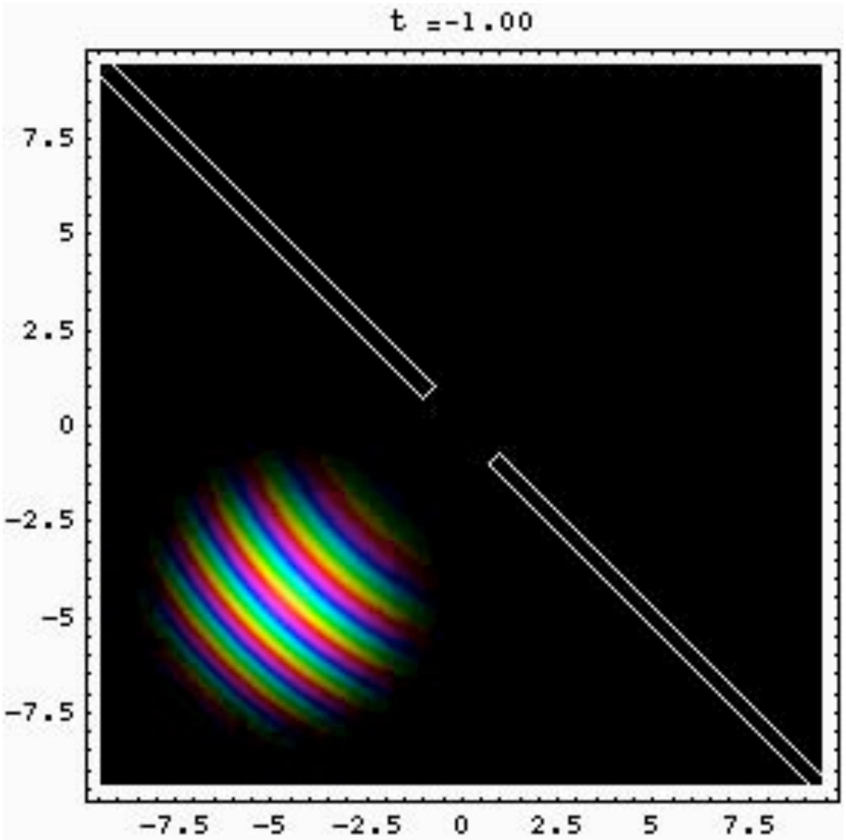
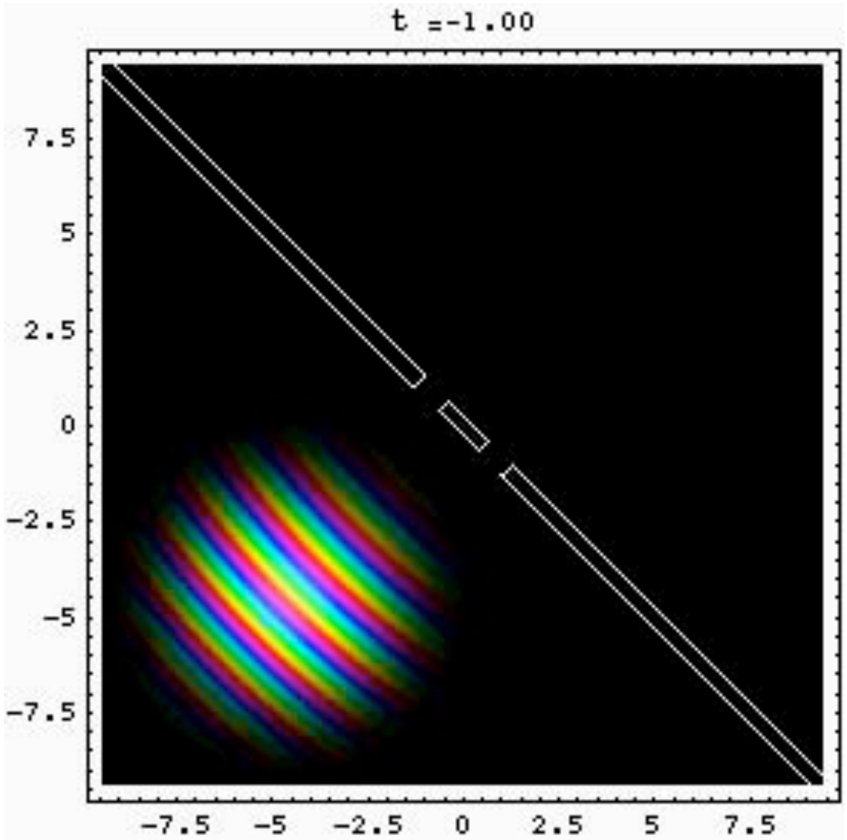
Double-Slit



t =-1.00
7.5
5
2.5
0
-2.5
-5
-7.5
-7.5
-5
-2.5
0
2.5
5
7.5



t =-1.00
7.5
5
2.5
0
-2.5
-5
-7.5
-7.5
-5
-2.5
0
2.5
5
7.5

Review: Wave aspect

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

wave:

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

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!

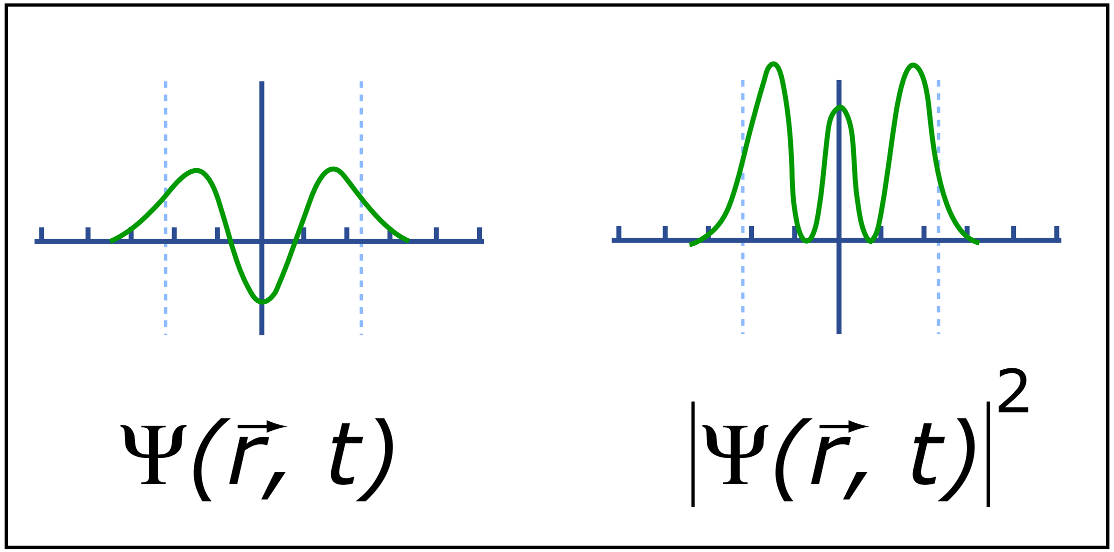


Image by MIT OpenCourseWare.

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

Review: Schrödinger equation

a wave equation:

second derivative in space
first derivative in time

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

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

Hamiltonian

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

Schrödinger...

http://en.wikipedia.org/wiki/Schrodinger_equation#Historical_background_and_development.

Review: Schrödinger equation

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

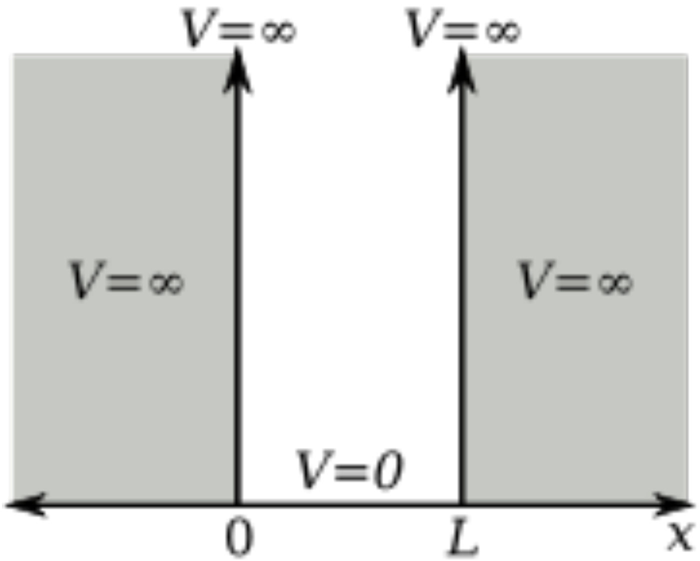
$$i\hbar \frac{\dot{f}(t)}{f(t)} = \frac{H\psi(\vec{r})}{\psi(\vec{r})} = \text{const.} = E$$

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

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

time independent Schrödinger equation
stationary Schrödinger equation

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

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

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

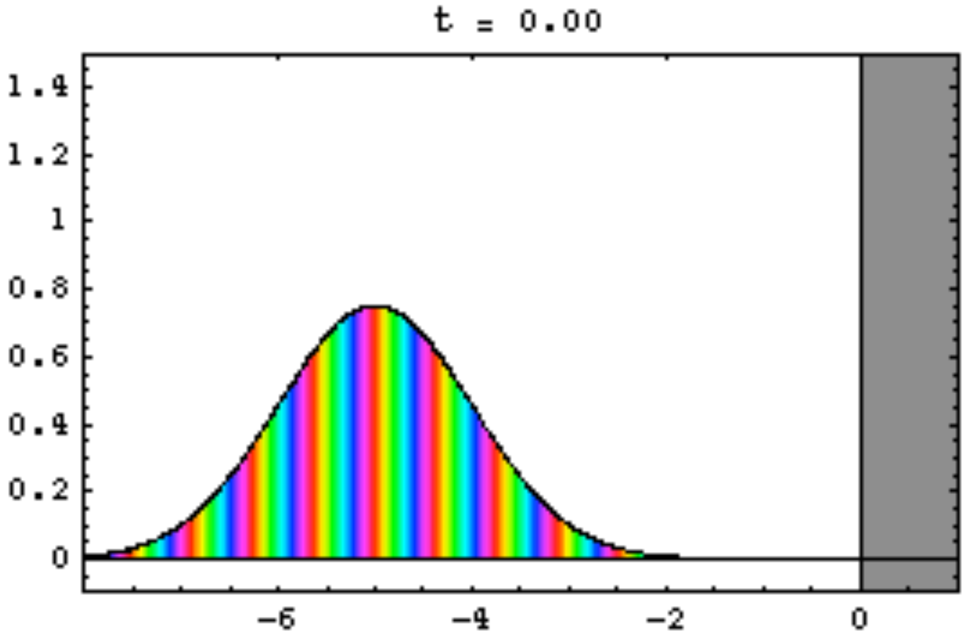
$$\psi(L) = A\sin(kL) = 0 \quad (6)$$

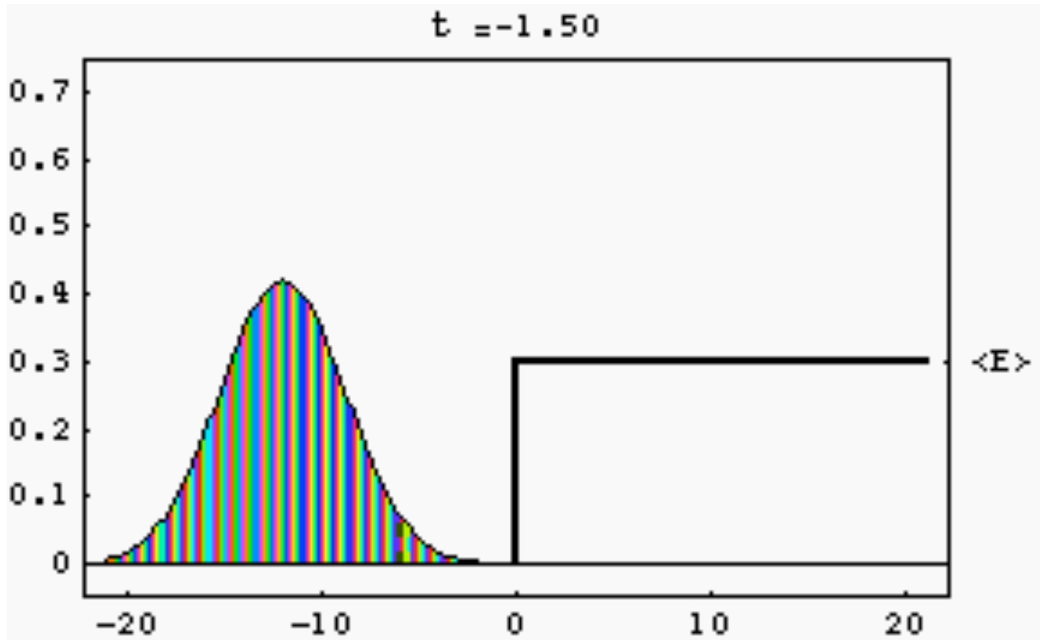
general solution

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

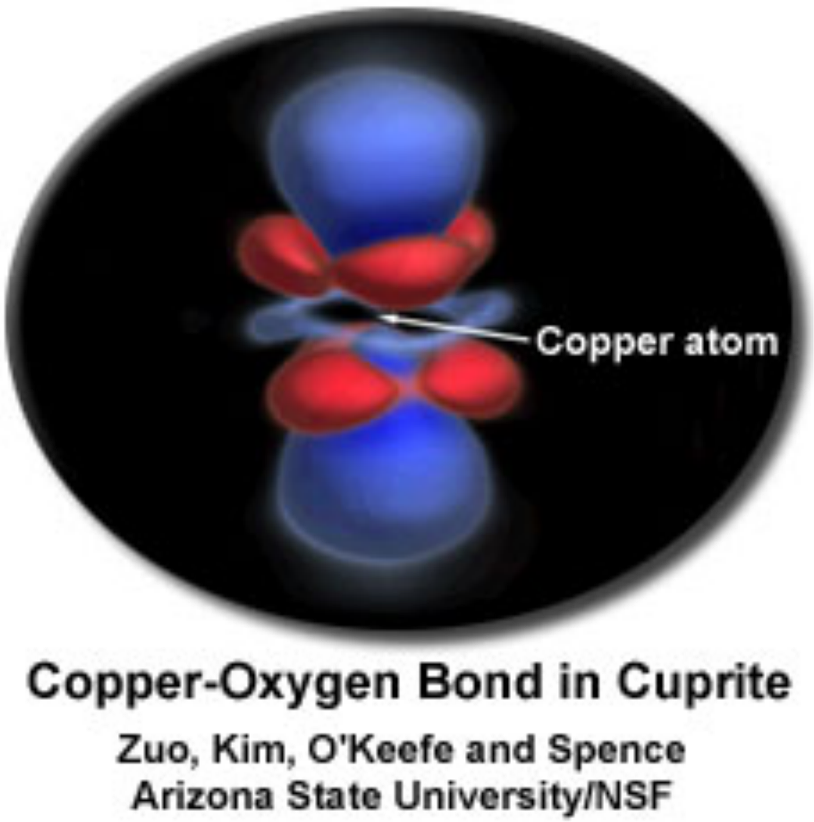
$$E = \frac{k^2\hbar^2}{2m} \quad (3)$$

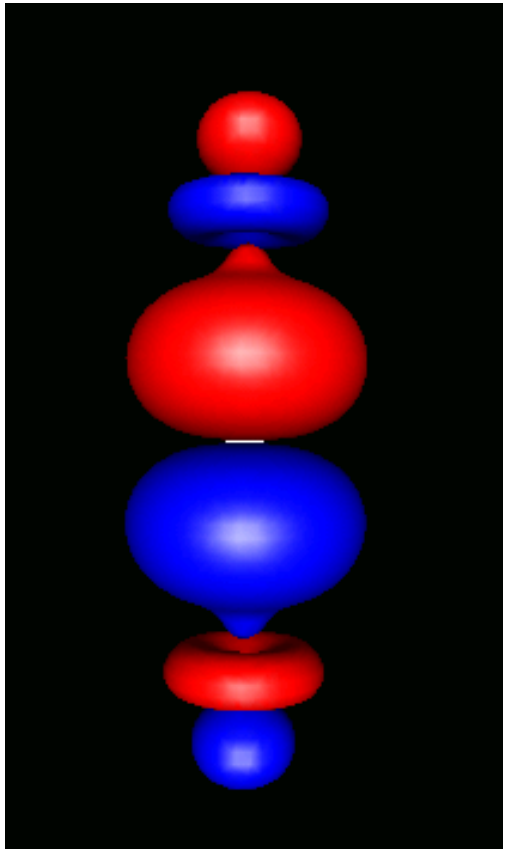
Wave Particles Hitting a Wall





It's real!





Cu-O Bond
(experiment)

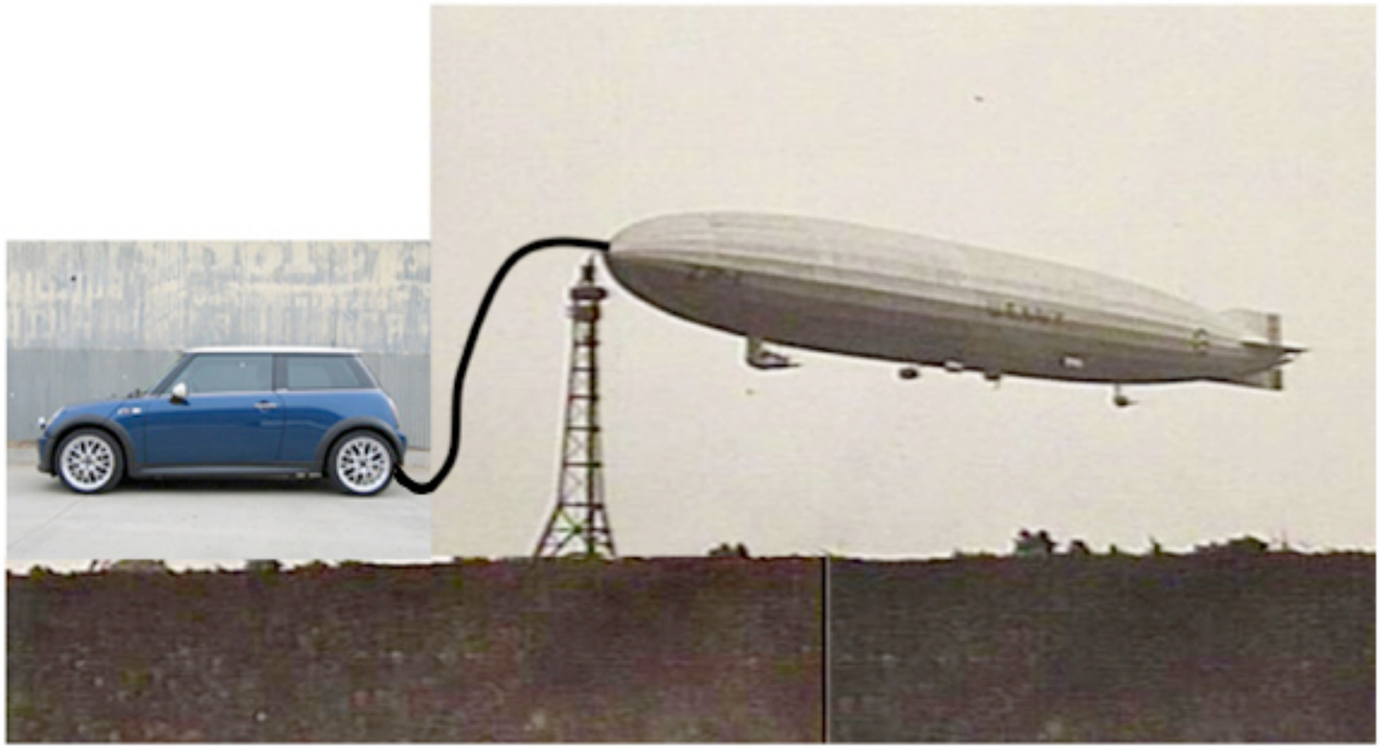
Ti-O Bond
(theory)

Screenshot of Scientific American article removed due to copyright restrictions;
read the article online: http://www.scientificamerican.com/article.cfm?id=observing--orbitals.

What's this good for?

Hydrogen:
a real world
example.

The Hydrogen Future?



History of Hydrogen

Screenshot of timeline of hydrogen technology removed due to copyright restrictions.

How large of a gas tank do we want?

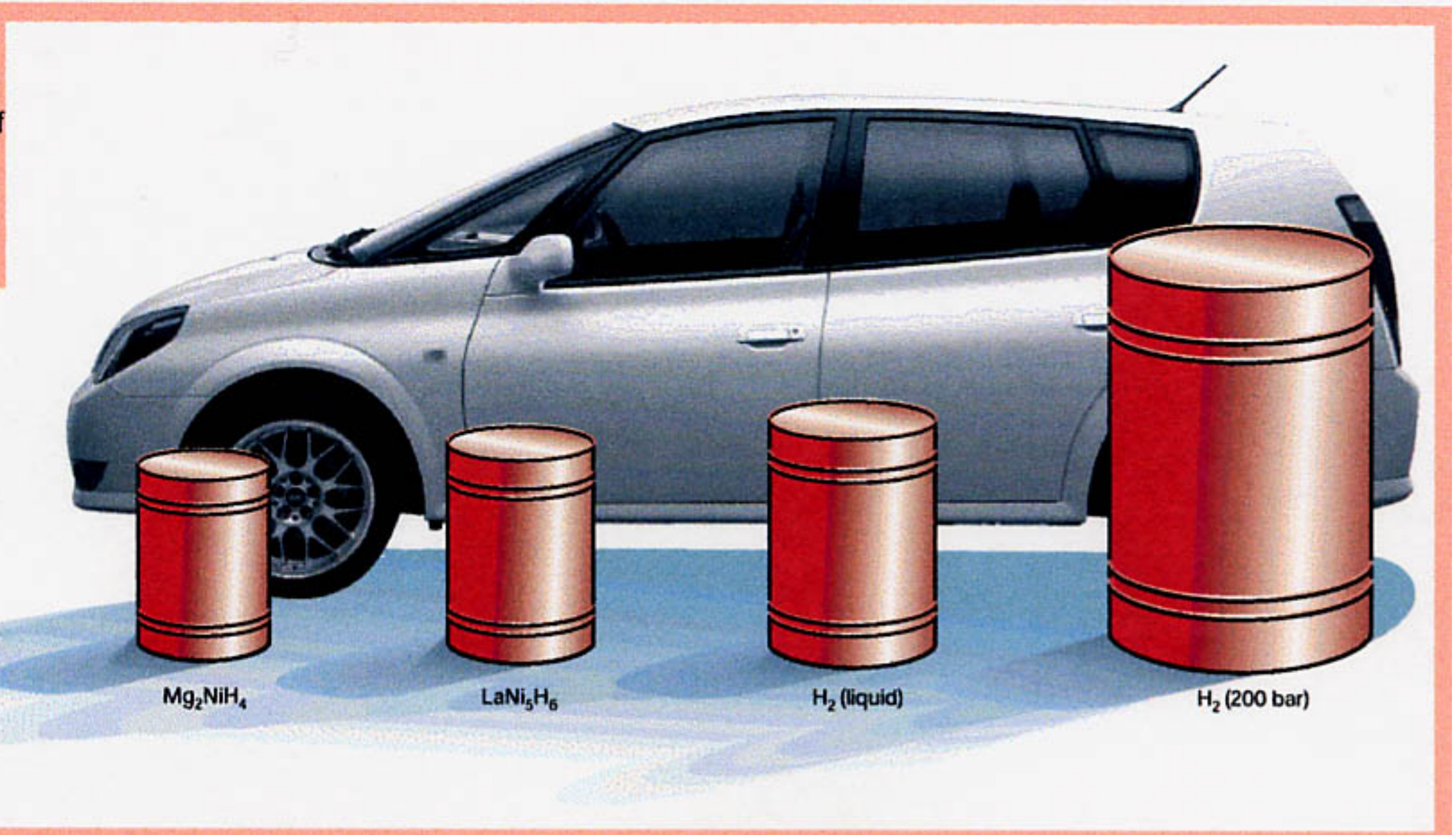
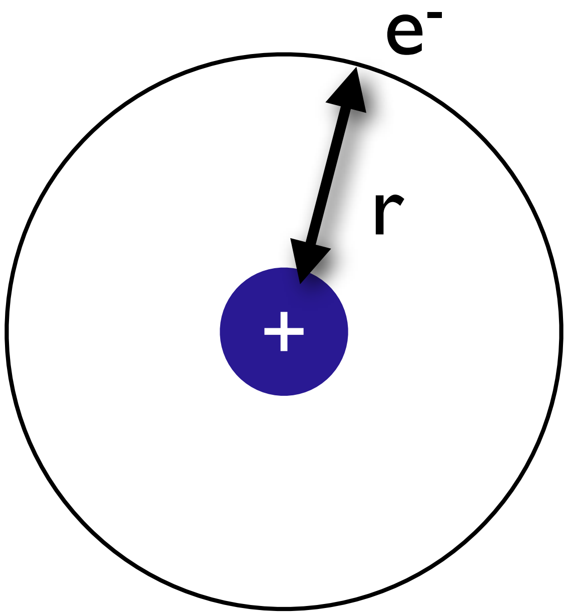


Figure 1 Volume of 4 kg of hydrogen compacted in different ways, with size relative to the size of a car. (Image of car courtesy of Toyota press information, 33rd Tokyo Motor Show, 1999.)

The hydrogen atom



electrostatics:
Coulomb potential

sta ry
Schrödin equation

wave functions
possible energies

The hydrogen atom

stationary
Schrödinger equation

$$H\psi = E\psi$$

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

just solve ☺

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

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

The hydrogen atom

choose a more suitable coordinate system:

spherical coordinates

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

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

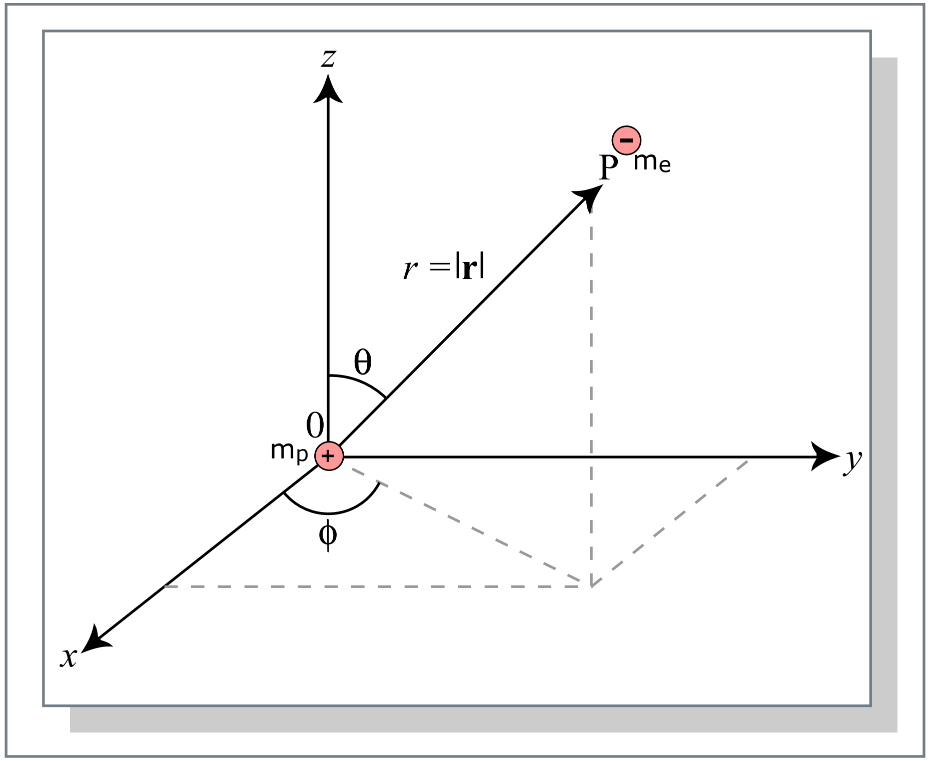


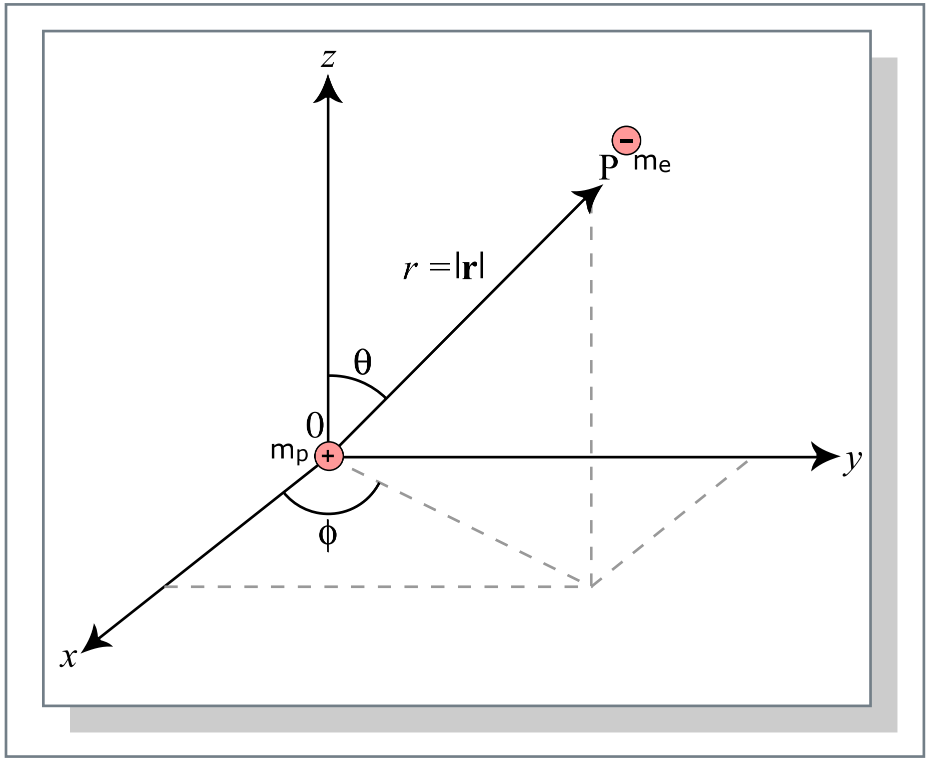
Image by MIT OpenCourseWare.

The hydrogen atom

Schrödinger equation in spherical coordinates:

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

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



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The hydrogen atom

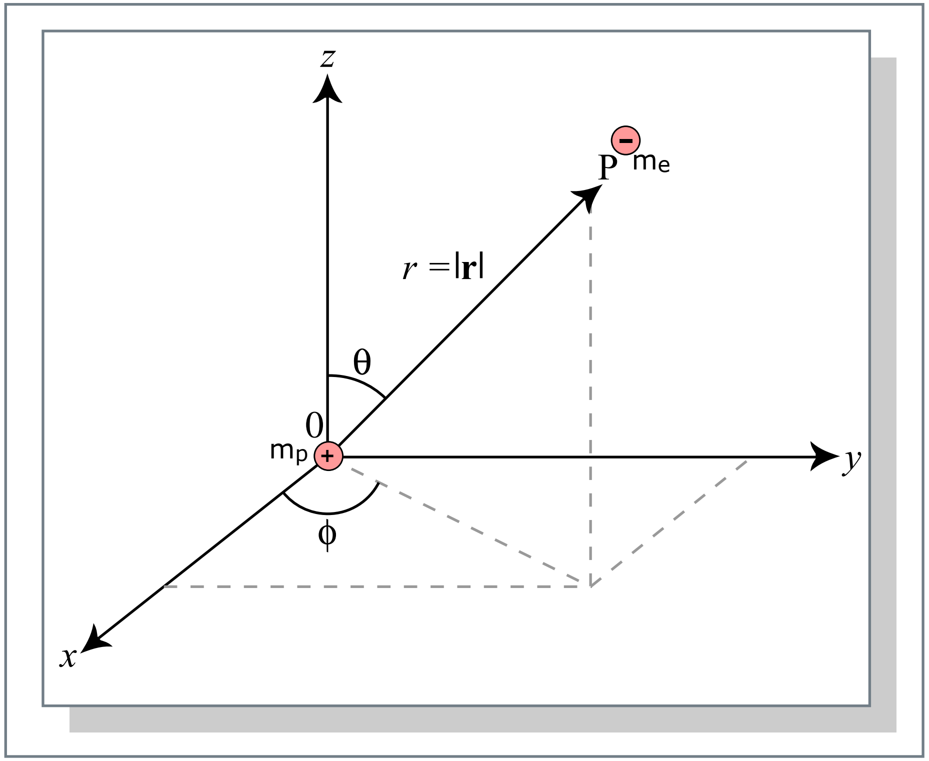


Image by MIT OpenCourseWare.

solve by separation of variables:

$$\Psi(r,\theta,\phi) = R(r)P(\theta)F(\phi)$$

n	ℓ	m_ℓ
principal quantum number	orbital quantum number	magnetic quantum number

The hydrogen atom

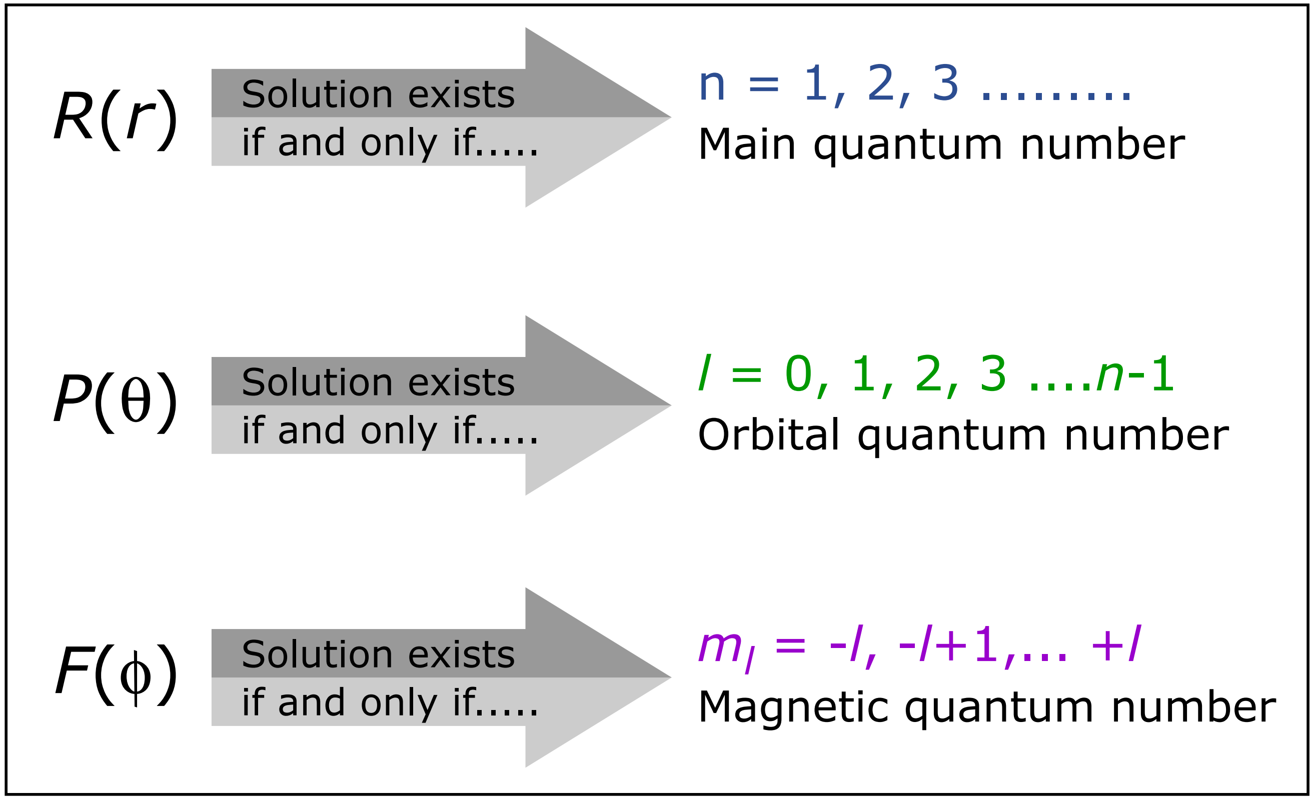
separation of variables

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

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

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

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

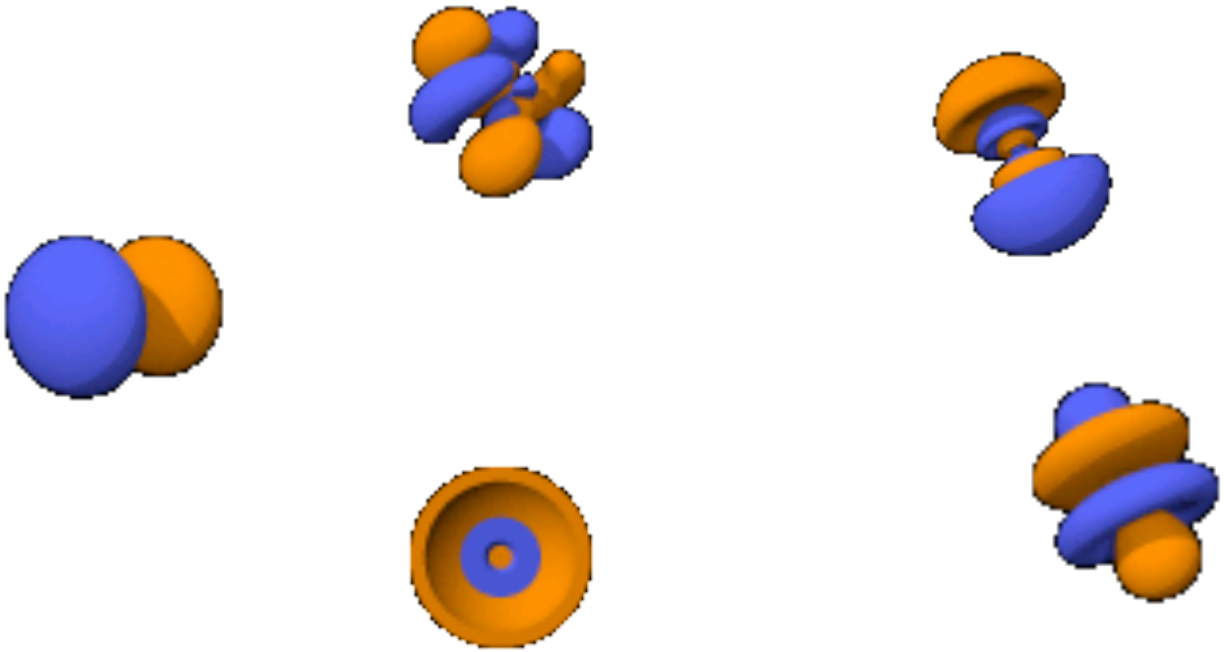
quantum numbers

n	l	m_l	Atomic Orbital	$\psi_{n\,l\,m_l}(r, \theta, \phi)$
1	0	0	1s	$\frac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0}$
2	0	0	2s	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \left[2 - \frac{r}{a_0}\right] e^{-r/2a_0}$
2	1	0	2p	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos\theta$
2	1	±1	2p	$\frac{1}{8\sqrt{\pi}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin\theta\, e^{\pm i\phi}$

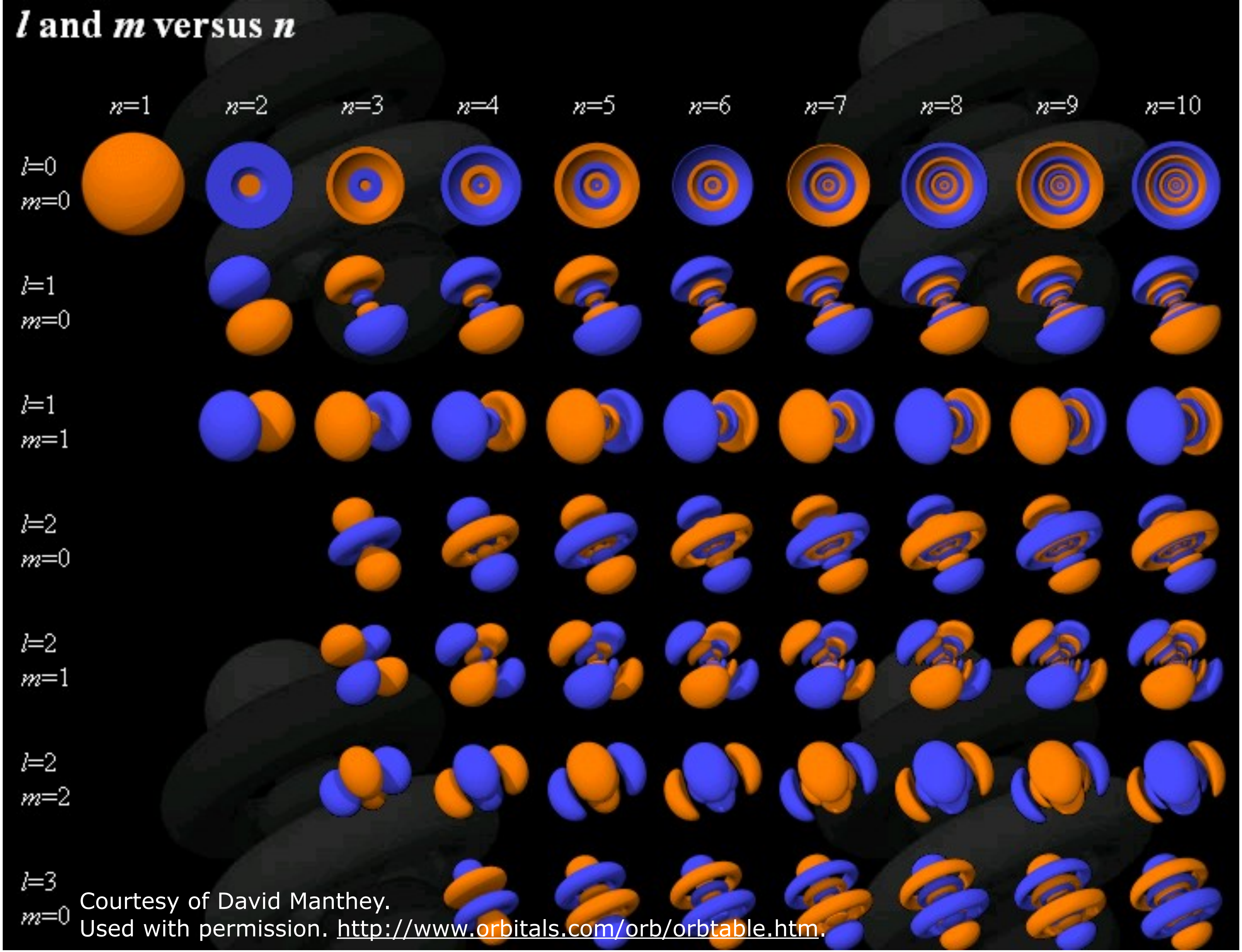
$$a_0 = \frac{\hbar^2}{me^2} = .0529 \text{ nm} = \text{first Bohr radius}$$

The hydrogen atom

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



Courtesy of David Manthey. Used with permission. http://www.orbitals.com/orb/orbtable.htm.

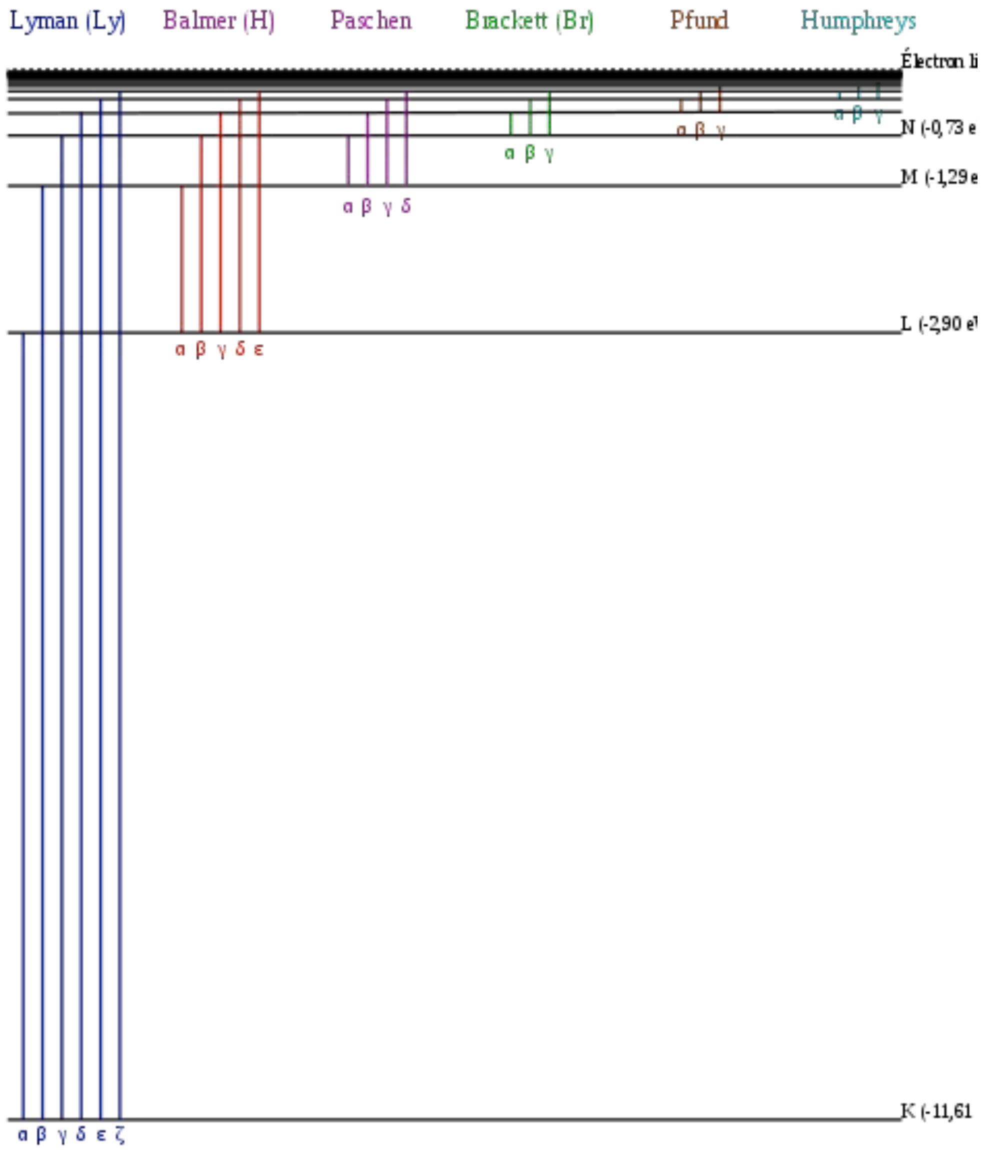

l and m versus n
n=1
n=2
n=3
n=4
n=5
n=6
n=7
n=8
n=9
n=10
l=0 m=0
l=1 m=0
l=1 m=1
l=2 m=0
l=2 m=1
l=2 m=2
l=3 m=0

The hydrogen atom

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

Please see http://hyperphysics.phy-astr.gsu.edu/hbase/imgmod/hyde4.gif.

The hydrogen atom



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The hydrogen atom

Please see http://hyperphysics.phy-astr.gsu.edu/hbase/imgmod/hydspe.gif.

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

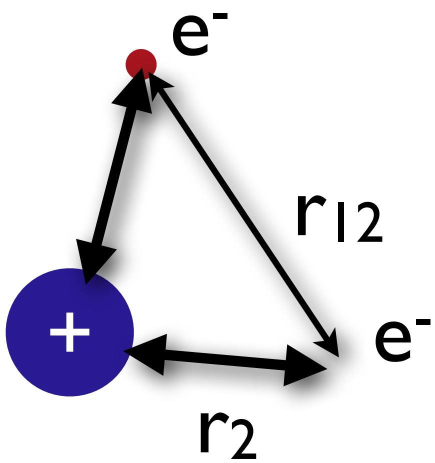
Atomic units (a.u.):

Energies in Ry

Distances in Bohr

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

Next? Helium!



$$H\psi = E\psi$$

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

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

$$\Big[-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}\Big]\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

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)

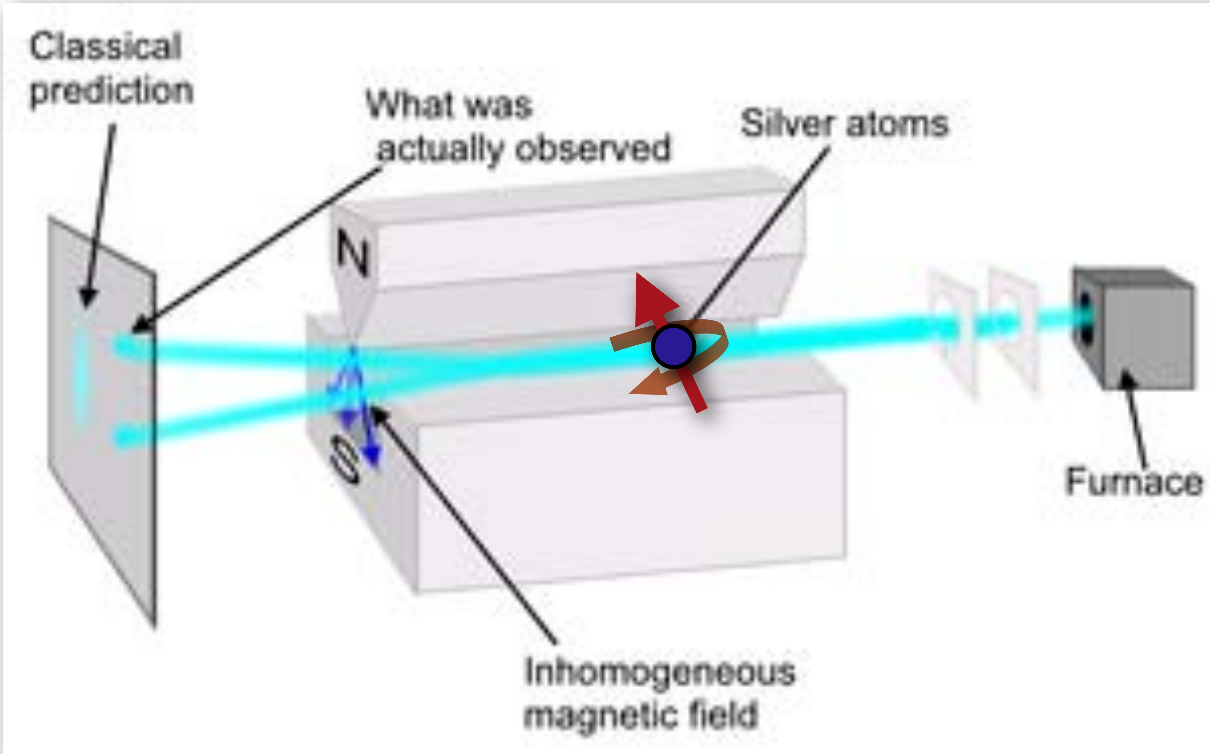
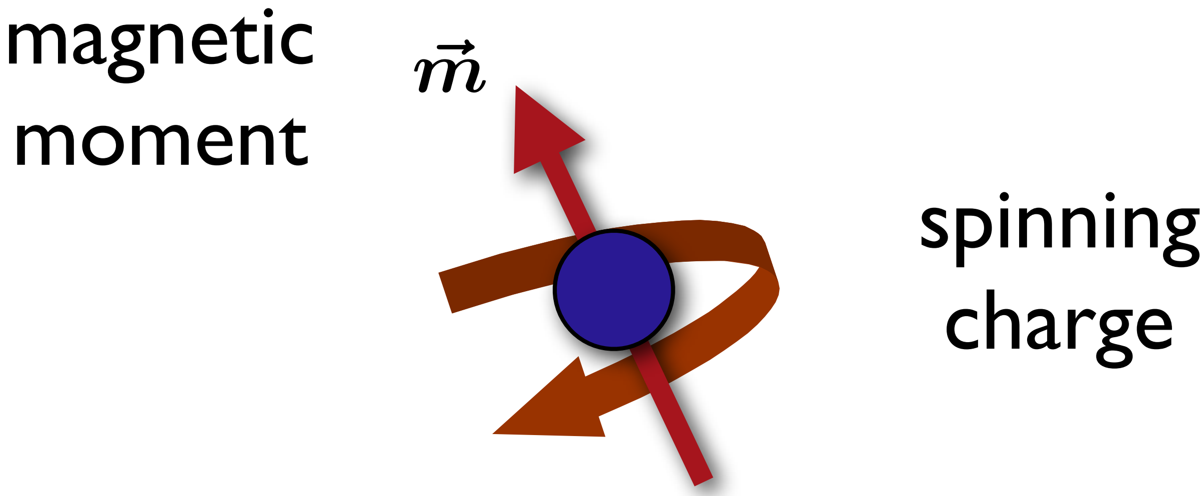


Image courtesy Teresa Knott.

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

Discovered in 1926 by
Goudsmit and Uhlenbeck

Part of a letter by L. H. Thomas to Goudsmit on March 25, 1926:
http://www.lorentz.leidenuniv.nl/history/spin/thomas.gif.

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

Group → / ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

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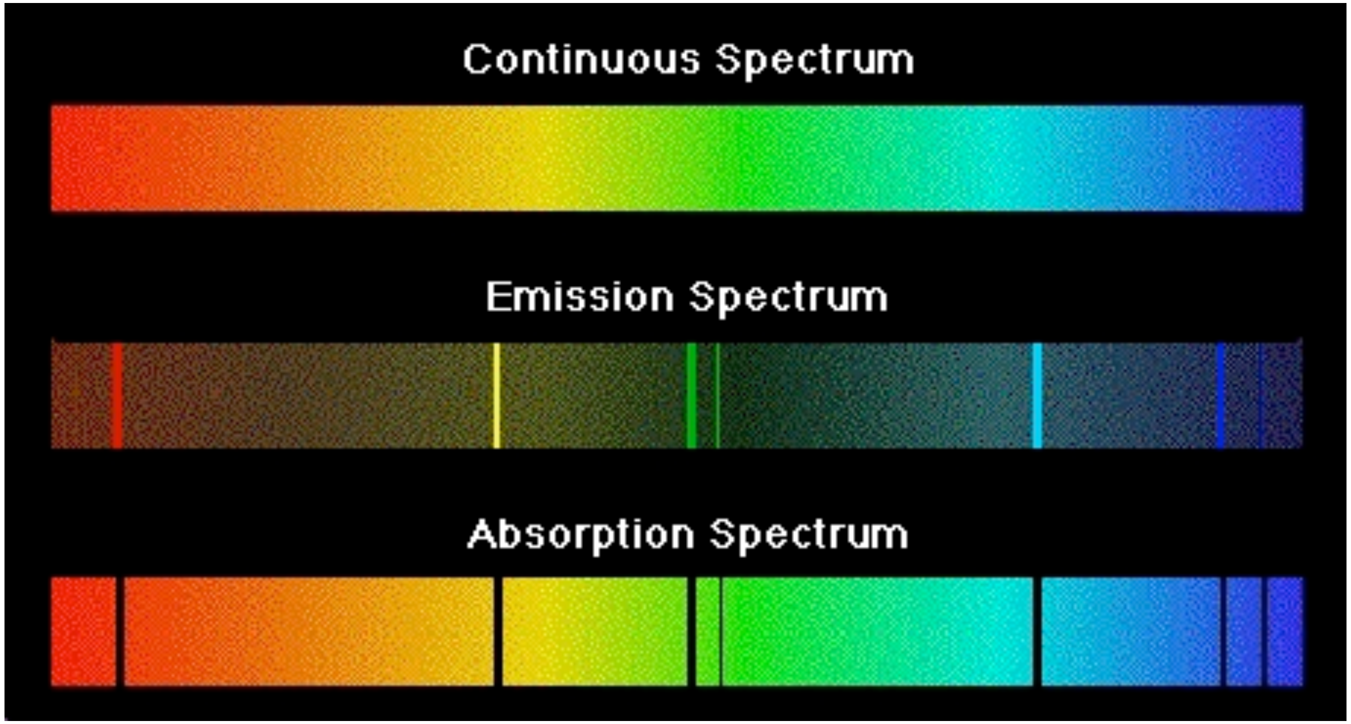
Connection to materials?

optical properties of gases



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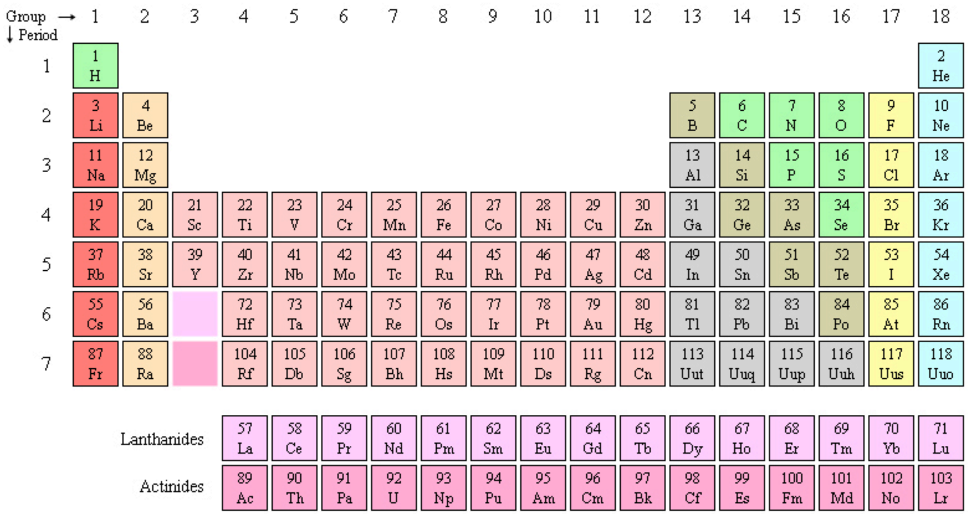
Review

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



Group → / ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

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Literature

- Greiner, Quantum Mechanics: An Introduction
- Feynman, The Feynman Lectures on Physics
- wikipedia, “hydrogen atom”, “Pauli exclusion principle”, “periodic table”, ...

Part II Outline

theory & practice

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. From Atoms to Solids
5. Quantum Modeling of Solids: Basic Properties
6. Advanced Prop. of Materials: What else can we do?

example applications

7. Nanotechnology
8. Solar Photovoltaics: Converting Photons into Electrons
9. Thermoelectrics: Converting Heat into Electricity
10. Solar Fuels: Pushing Electrons up a Hill
11. Hydrogen Storage: the Strength of Weak Interactions
12. Review