近代原子與分子物理

Modern Atomic and Molecular Physics

Course:

(1) 222 U2130 (2011 Fall semester)

(2) Three credits for senior undergraduate and graduate students

(3) Pre-requirement: quantum physics (量子物理) or equivalent

(4) Lecture: Tuesday 09:10 ~ 10:00;
Friday 09:10 ~ 10:00 & 10:20 ~ 11:10
[First lecture: Sept. 13, 2011 & Last lecture: Jan. 6, 2012; total 48 hrs.]

(5) Midterm exam.: Nov. 11, 2011 ; Final exam.: Jan. 13, 2012
[Both are open book]

Reference books:

(1) C. Foot, “Atomic Physics”, Oxford U. Press, 2007
(2) W. Demtroder, “Molecular Physics”, Wiley-VCH, 2005

	Topics	References	Lecturer	(hrs)
1.	Atomic structure and atom-atom interactions	(1), Chapt, 2-6	張銘顯	9 hrs
2.	Atom-field interaction	(1), Chapt. 7	陳應誠	9 hrs
3	Recent developments in atomic physics		林育如	6 hrs
4.	Molecular structure	(2), Chapt. 2, 3	高橋開人	12 hrs
5.	Molecular spectroscopy	(2), Chapt. 4, 6	林倫年	6 hrs
6.	Non Born-Oppenheimer phenomena		林倫年	3 hrs
7.	Experiment aspects in molecular physics		林志民	3 hrs
				Total: 48 hrs

Note:

(1). “hr” means 50 minutes for each lecture.
(2). Please set your own “office hour” and homework.
(3). Grade: Homework (40%), Midterm exam. (30%), Final exam. (30%)

近代原子與分子物理
Modern Atomic and Molecular Physics

Course # 222 U2130 (2011 Fall semester)
Three credits for senior undergraduate and graduate students
Pre-requirement: quantum physics or equivalent

Lecture: New Physics/CCMS Bldg, Room 406
新物/凝態館, 406室
Tuesday 09:10 ~ 10:00;
Friday 09:10 ~ 10:00 & 10:20 ~ 11:10

Midterm exam.: Nov. 11, 2011 ; Final exam.: Jan. 13, 2012.

Recent Nobel Prizes in (Atomic) Physics

1989 N. F. Ramsey *(for the separated oscillatory fields method in hydrogen maser and other atomic clocks)*

H. G. Dehmelt & W. Paul *(for ion trap techniques)*

1997 S. Chu, C. Cohen-Tannoudji, & W. D. Phillips

(for laser cooling and trapping of atoms)

2001 E. A. Cornell, W. Ketterle, & C. E. Wieman

(for Bose-Einstein condensates)

2005 R. J. Glauber *(for optical coherence);*

J. L. Hall & T. W. Hansch *(for precision spectroscopy, including optical frequency comb technique)*

Recent Nobel Prizes in Chemistry (Molecular Physics)

1991	R. R. Ernst *(for high resolution NMR spectroscopy)*
1992	R. A. Marcus, *(for electron transfer in chemical systems)*
1995	P. J. Crutzen, M. J. Molina & F. S. Rowland *(for atmosphere chemistry and ozone destruction)*
1996	R. E. Curl, Jr., H. W. Kroto & R. E. Smalley *(for* C_{60}*)*
1998	W. Kohn *(for density functional theory)* J. A. Pople *(for computational quantum chemistry)*
1999	A. Zewail *(for femtochemistry)*

Recent Nobel Prizes in Chemistry (Molecular Physics)

2002 J. Fenn *(for electrosprayed mass spectrometry)*

K. Tanaka *(for laser-desorption mass spectrometry)*

K. Wuthrich *(for NMR determination of 3D structure in solution)*

2007 G. Ertl *(for chemical processes on solid surfaces)*

Textbooks:

(1) C. Foot, "Atomic Physics", Oxford U. Press, 2007
(2) W. Demtroder, "Molecular Physics", Wiley-VCH, 2005

	Topics	References	Lecturer	(hrs)
I.	Atomic Structure	(1), Chapt, 2-6	張銘顯	9 hrs
II.	Atom-field Interaction	(1), Chapt. 7	陳應誠	9 hrs
III.	Recent developments in Atomic Physics		林育如	6 hrs
IV.	Molecular Structure	(2), Chapt. 2, 3	高橋開人	12 hrs
V.	Spectroscopy	(2), Chapt. 4, 6	林倫年	6 hrs
VI.	Non Born-Oppenheimer phenomena and other theoretical aspects		林倫年	3 hrs
VII.	Experiment techniques in molecular physics		林志民	6 hrs

Total: 48 hrs

Atomic Physics

Hydrogen atom; Helium; Alkalis; LS-coupling; hyperfine structure; atom-atom interactions; Interaction of atoms with radiation; Laser cooling & trapping; Bose-Einstein condensation; other hot topics.

Molecular Physics

Molecular electronic states; Rotation & vibration of diatomic molecules; Spectroscopy of diatomic molecules; Rotation & vibration of polyatomic molecules.

Non-adiabatic phenomena; Molecules in external fields; Modern experimental techniques in molecular physics.

Final Notes:

(1) Each lecturer will set his/her own **office hours**.

(2) Discussion and/or group study are encouraged. But, copying the homework is prohibited.

(3) Grade: Homework (40%), Midterm exam. (30%), Final exam. (30%).

(4) Both midterm and final examinations will be **2 hours** and **open book**.

Atomic Structure

Sep 13th – Sep. 30th

Instructor I: Ming-Shien Chang (張銘顯)
Email: msc@gate.sinica.edu.tw
Phone: 2366-8206 / 2366-8220
Office Hour: Tue 2:00 pm – 4:00 pm
Office Location: IAMS bldg, R206/R107 (原分所, 206室/107室)

Textbook:
C. Foot, “Atomic Physics,” Oxford U. Press (2007)

Other References:
W. Demtroder, “Atoms, Molecules and Phtons,” Springer
B.H. Bransden & C.J. Joachain, “Physics of Atoms and Molecules,” Prentice Hall
H. Haken and H. C. Wolf, “The Physics of Atoms and Quanta”, Springer-Verlag
C. Cohen-Tannoudji, J. Dupont-Roc & G Grynberg, “Atom-Photon Interactions,” Wiley
P.F. Bernath, “Spectra of Atoms and Molecules”, Oxford University Press
H.S. Friedrich, “Theoretical Atomic Physics”, Springer-Verlag
...

Syllabus (Sep 13th – Sep. 30th)

Introduction

Atomic structure: Ch2 ~ Ch6 of C. Foot's book

- Ch 2. The hydrogen atom
- Ch 3. The helium atom
- Ch 4. The alkali atoms
- Ch 5. The L-S and JJ coupling
- Ch 6. Hyperfine structure

Atomic interaction

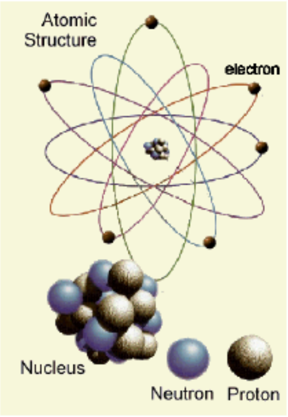
- Atomic collisions

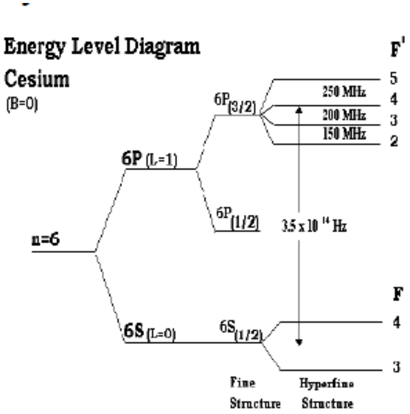
Introduction

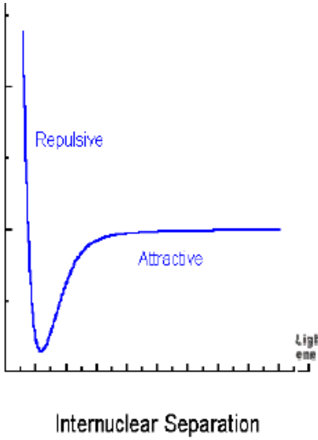
- Contents and importance of atomic physics
- Relation to other fields
- Recent trends in modern atomic physics
- The concept of the atom
  - Proofs for the existence of atoms
  - Can one see atoms?

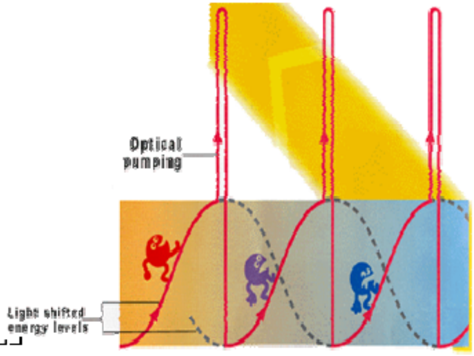
Contents and importance of atomic physics

- Goals
  - Full understanding of the macroscopic properties of matter on the basis of its microscopic composition of the atoms and a quantitative description of the relations between microscopic and macroscopic features
- Content
  - understanding the properties of microscopic building block of matter: atoms, including their structures, interaction with electromagnetic fields, mutual interaction, and dynamics (time-dependent properties).

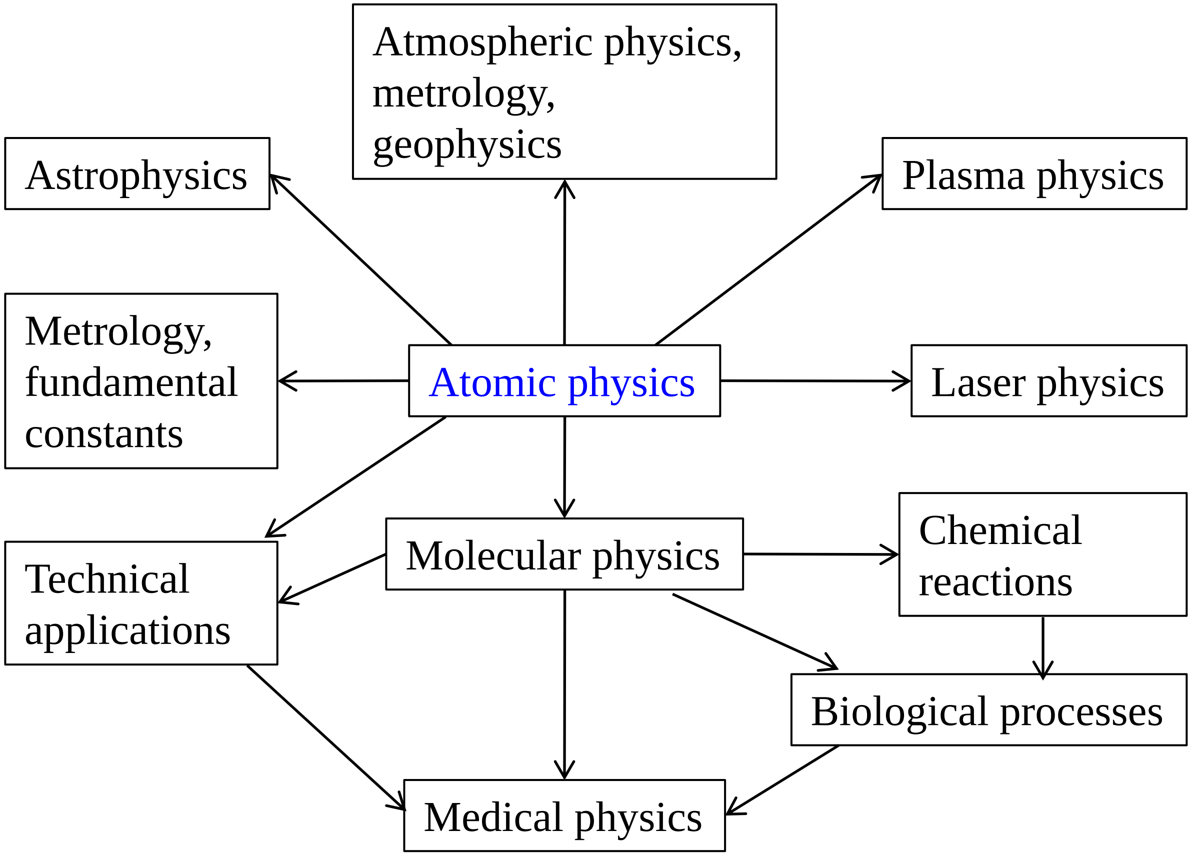








Relation to other fields



Atmospheric physics, metrology, geophysics

Astrophysics

Plasma physics

Metrology, fundamental constants

Atomic physics

Laser physics

Molecular physics

Chemical reactions

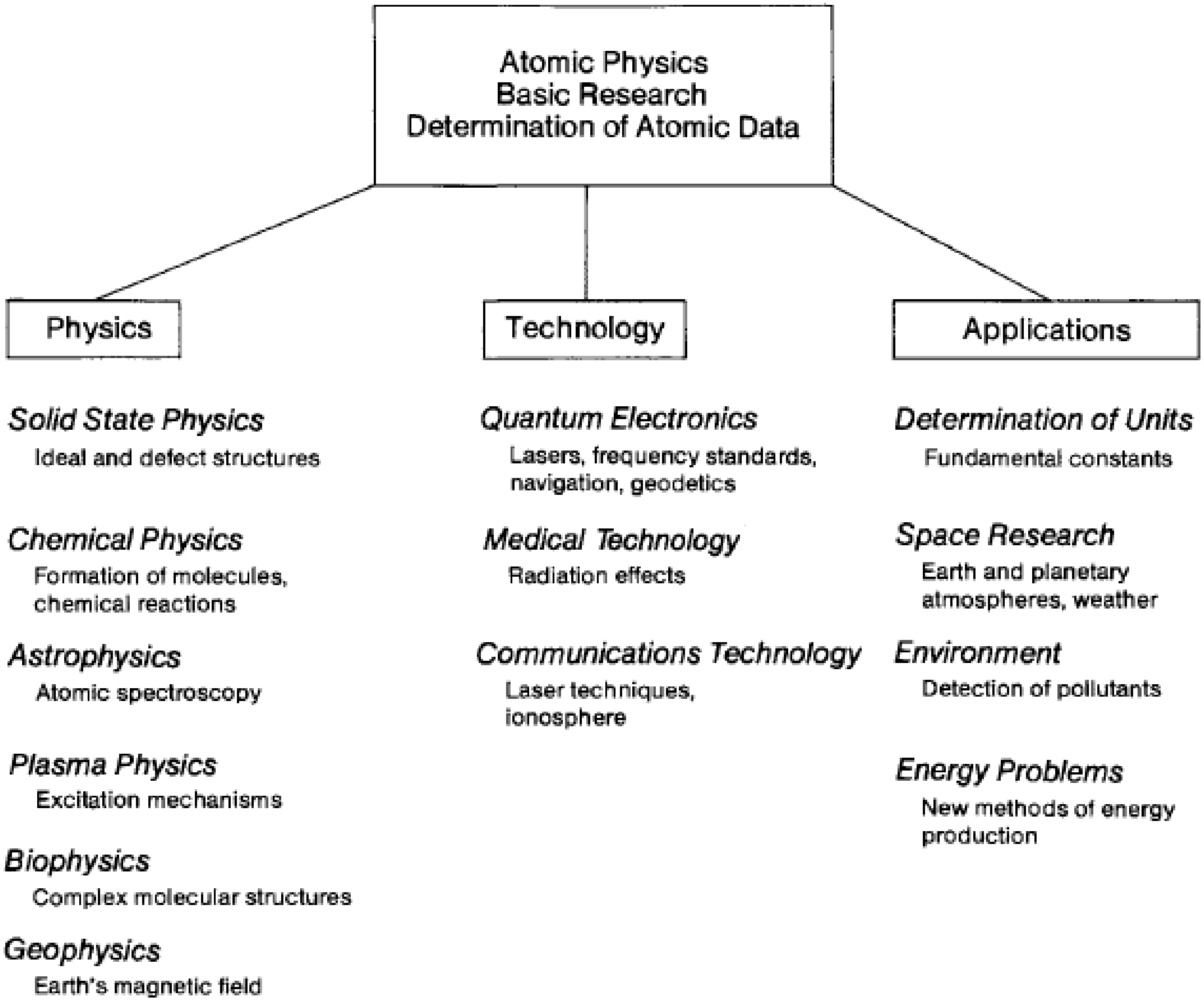
Technical applications

Biological processes

Medical physics

W. Demtröder

Relation to other fields (alternative)



Atomic Physics
Basic Research
Determination of Atomic Data

Physics

Solid State Physics
Ideal and defect structures

Chemical Physics
Formation of molecules, chemical reactions

Astrophysics
Atomic spectroscopy

Plasma Physics
Excitation mechanisms

Biophysics
Complex molecular structures

Geophysics
Earth's magnetic field

Technology

Quantum Electronics
Lasers, frequency standards, navigation, geodetics

Medical Technology
Radiation effects

Communications Technology
Laser techniques, ionosphere

Applications

Determination of Units
Fundamental constants

Space Research
Earth and planetary atmospheres, weather

Environment
Detection of pollutants

Energy Problems
New methods of energy production

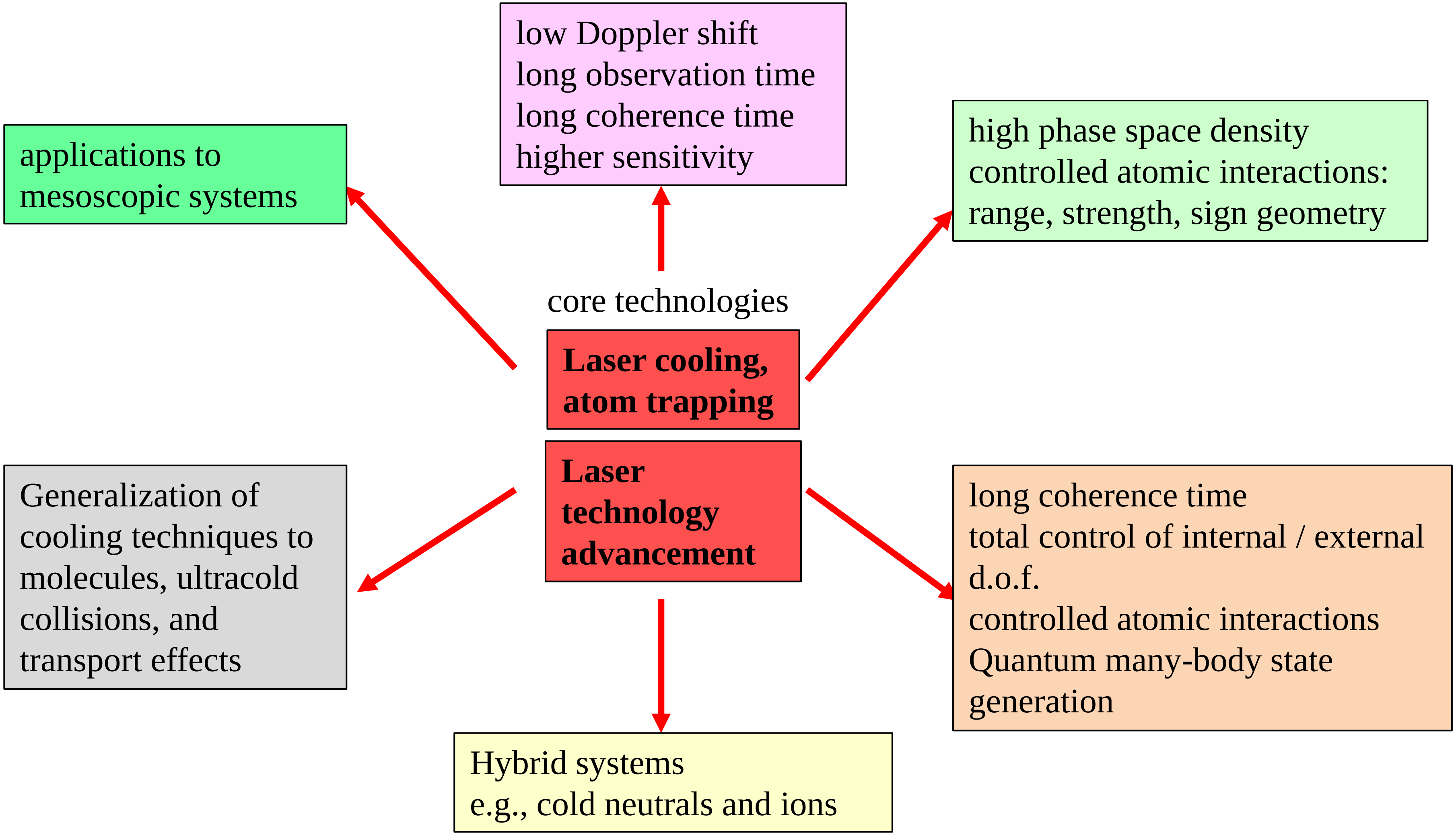
H. Haken & H. Wolf

Six compelling research opportunities for AMO science

- Revolutionary new methods to measure the nature of space and time with extremely high precision have emerged within the last decade from a convergence of technologies in the control of the coherence of ultrafast lasers and ultracold atoms. this new capability creates unprecedented new research opportunities.
- Ultracold AMO physics was the most spectacularly successful new AMO research area of the past decade and led to the development of coherent quantum gases. this new field is poised to make major contributions to resolving important fundamental problems in condensed matter science and in plasma physics, bringing with it new interdisciplinary opportunities.
- High-intensity and short-wavelength sources such as new x-ray free-electron lasers promise significant advances in AMO science, condensed matter physics and materials research, chemistry, medicine, and defense-related science.
- Ultrafast quantum control will unveil the internal motion of atoms within molecules, and of electrons within atoms, to a degree thought impossible only a decade ago. this is sparking a revolution in the imaging and coherent control of quantum processes and will be among the most fruitful new areas of AMO science in the next 10 years.
- Quantum engineering on the nanoscale of tens to hundreds of atomic diameters has led to new opportunities for atom-by-atom control of quantum structures using the techniques of AMO science. there are compelling opportunities in both molecular science and photon science that are expected to have far-reaching societal applications.
- Quantum information is a rapidly growing research area in AMO science and one that faces special challenges owing to its potential application in data security and encryption. Multiple approaches to quantum computing and communication are likely to be fruitful in the coming decade, and open international exchange of people and information is critical in order to realize the maximum benefit.

NRC report, Controlling the quantum world (2006)

Recent trends in modern atomic physics



low Doppler shift
long observation time
long coherence time
higher sensitivity

applications to
mesoscopic systems

high phase space density
controlled atomic interactions:
range, strength, sign geometry

core technologies

Laser cooling, atom trapping

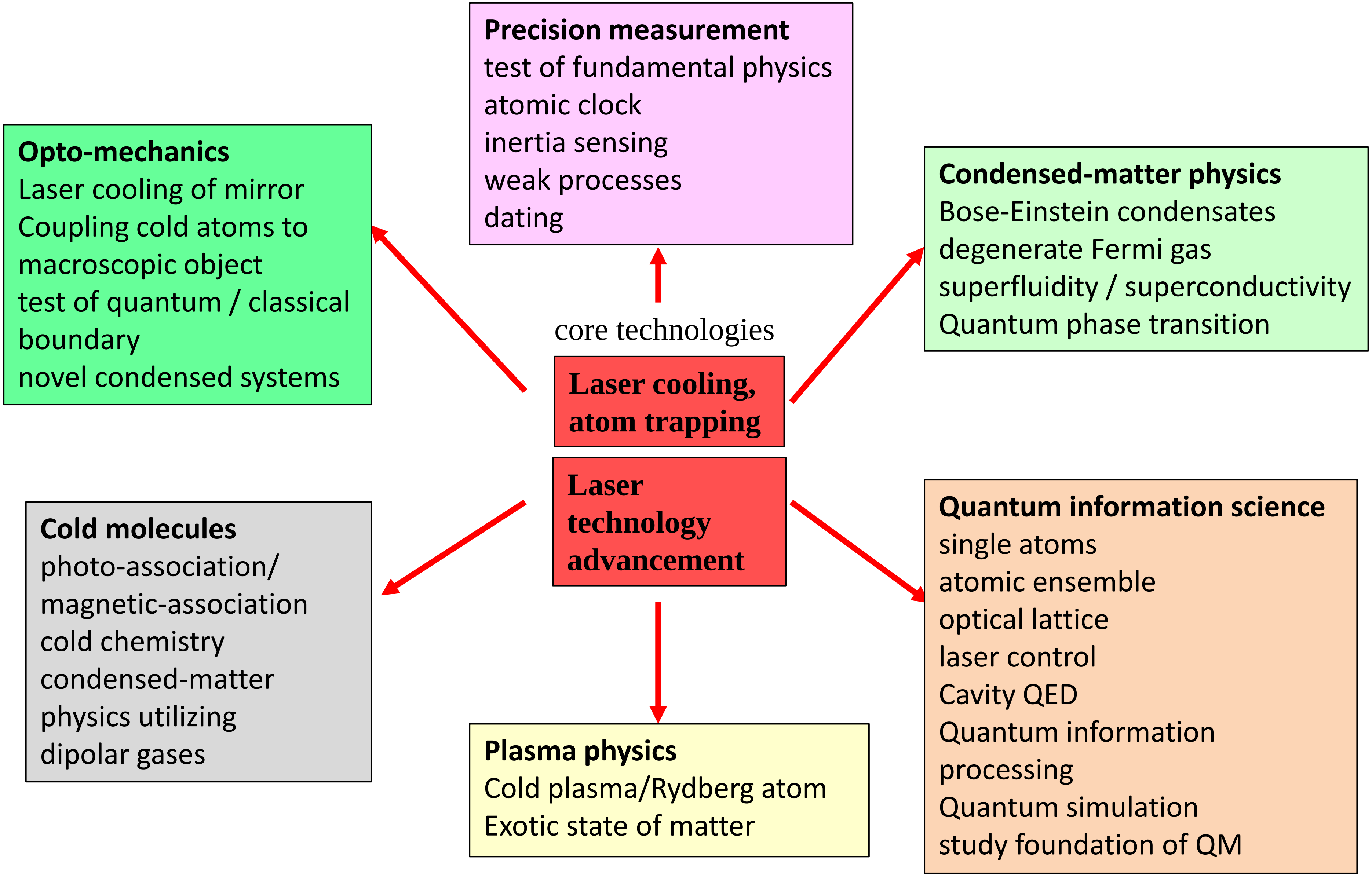
Laser technology advancement

Generalization of cooling techniques to molecules, ultracold collisions, and transport effects

long coherence time
total control of internal / external d.o.f.
controlled atomic interactions
Quantum many-body state generation

Hybrid systems
e.g., cold neutrals and ions

Recent trends in modern atomic physics



core technologies

Laser cooling, atom trapping

Laser technology advancement

Precision measurement
test of fundamental physics
atomic clock
inertia sensing
weak processes
dating

Opto-mechanics
Laser cooling of mirror
Coupling cold atoms to macroscopic object
test of quantum / classical boundary
novel condensed systems

Condensed-matter physics
Bose-Einstein condensates
degenerate Fermi gas
superfluidity / superconductivity
Quantum phase transition

Cold molecules
photo-association/ magnetic-association
cold chemistry
condensed-matter physics utilizing dipolar gases

Quantum information science
single atoms
atomic ensemble
optical lattice
laser control
Cavity QED
Quantum information processing
Quantum simulation
study foundation of QM

Plasma physics
Cold plasma/Rydberg atom
Exotic state of matter

Cold atoms: much more than just cool atomic physics

Long interaction times, slow velocities

- Frequency metrology
  - Atomic clocks
  - EDM/parity violations
  - Time variation of fundamental constants
  - Tests of general relativity

$$\delta\omega \sim \frac{1}{T\sqrt{N}}$$

- Inertial sensitivities
  - Accelerometers, gravity gradiometers, gyroscopes
- Study of rare isotopes and weak processes
  - Radioactive isotopic dating
  - Parity non-conserving (forbidden) transitions

ensemble of non-interacting atoms

Single atom physics

High phase space densities

- Quantum degenerate gases

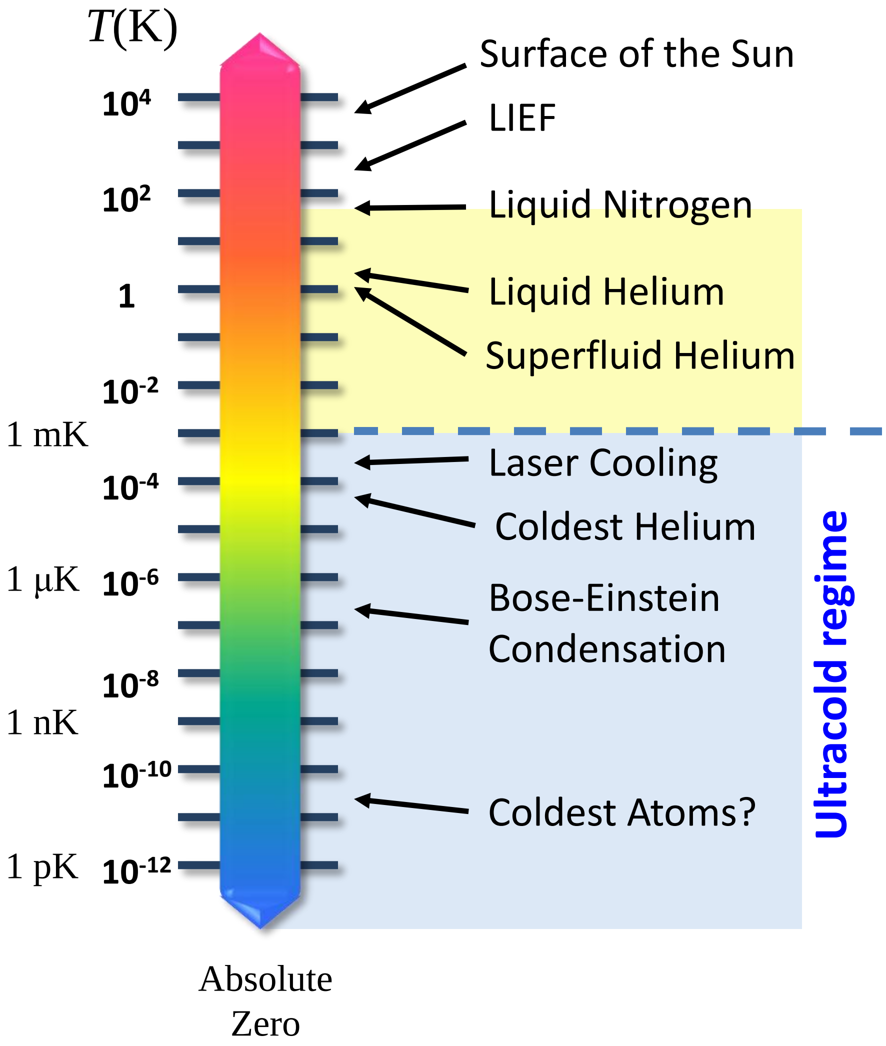
Total control over internal and external quantum states of system

- Many-atom quantum state engineering
- Test foundation of QM
- Quantum metrology
- Quantum communication
- Quantum simulation
- Quantum computation

Requires / main feature

controlled atom-atom interactions

Define the “Ultracold”



- Laboratory energy scales
  - 1 peV < energy < 1 TeV

BEC

Tevatron, Fermilab

Atomic velocities

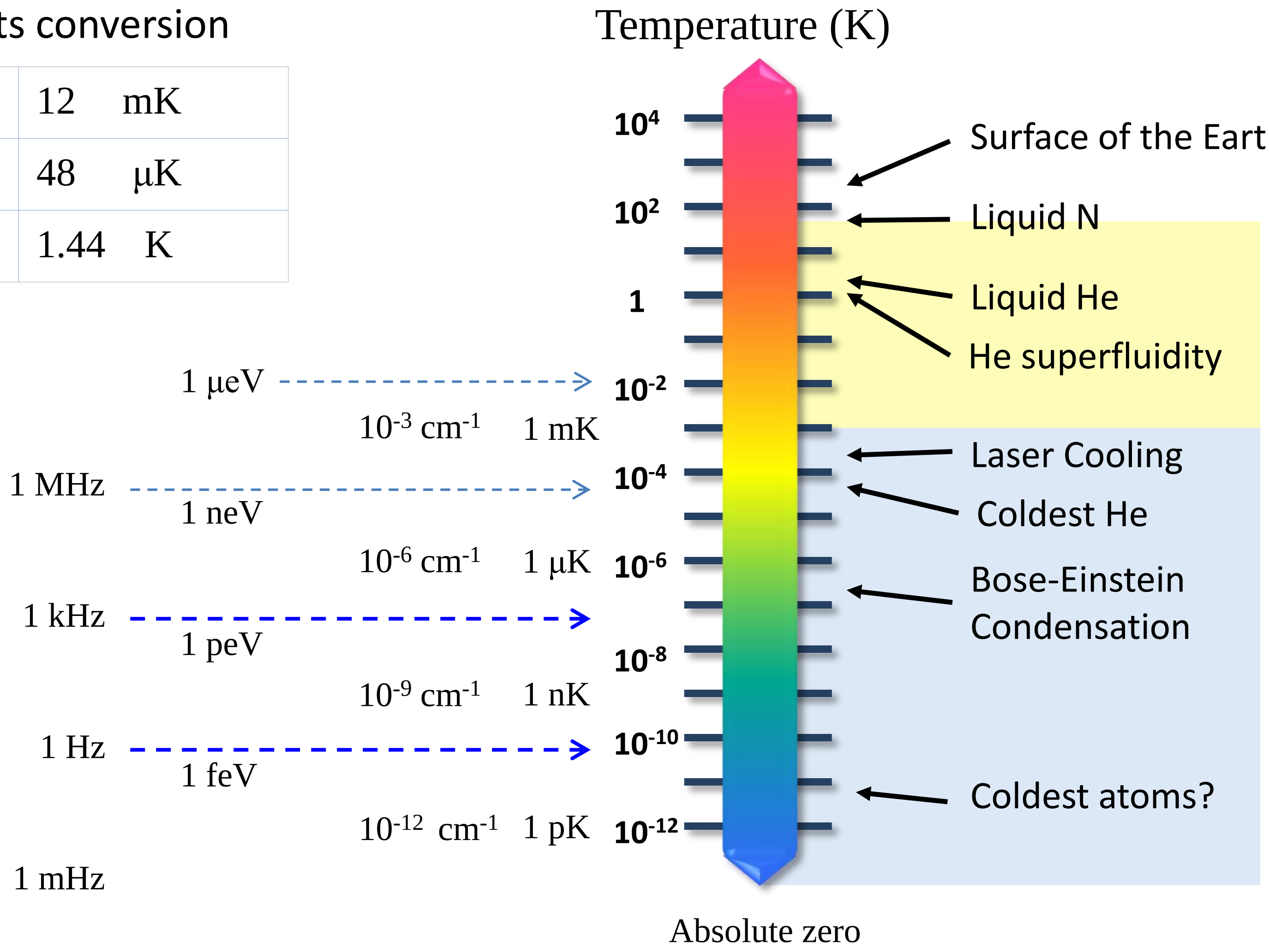
room temperature gas:	**300 meters/sec**
ultracold gas:	**6 meters/hour**

$$\tfrac{1}{2}mv^2 = k_B T$$

Relevant energy scale for ultracold atomic physics

Energy units conversion

1	μeV	12	mK
1	MHz	48	μK
1	cm^{-1}	1.44	K



Temperature (K)

10^4

10^2

1

10^{-2}

10^{-4}

10^{-6}

10^{-8}

10^{-10}

10^{-12}

Absolute zero

Surface of the Earth

Liquid N

Liquid He

He superfluidity

Laser Cooling

Coldest He

Bose-Einstein Condensation

Coldest atoms?

1 μeV

10^{-3} cm^{-1} 1 mK

1 MHz

1 neV

10^{-6} cm^{-1} 1 μK

1 kHz

1 peV

10^{-9} cm^{-1} 1 nK

1 Hz

1 feV

10^{-12} cm^{-1} 1 pK

1 mHz

Proofs for the existence of atoms

- Atoms are much smaller then the wavelength of visible light, detection often needs indirect methods (experiment) + careful interpretation (theory), Through iterative processes of modeling

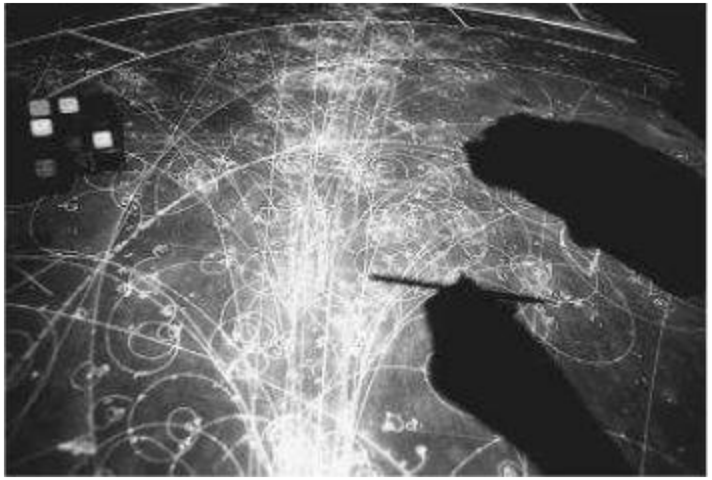
- Gay-Lussac’s law of constant proportions of gas volume (1805) and Avogadro’s interpretation: definition of molecules (1811)
- Dalton’s law of constant proportions of mass (1808)
- Kinetic gas theory: Bernoulli (1738), Joule (1848) , Clausius (1857), Maxwell (1870),
- Statistical physics foundation: Boltzmann (1884)
- Brownian motion (1827) and Einstein’s explanation (1905)
- Faraday’s electrolysis law (1834)

Can one see atoms?

- Cloud chamber
- Microscopes with atomic resolution
  - Field emission microscope
  - Transmission electron microscope
  - Scanning electron microscope
  - Scanning tunneling microscope
  - Atomic force microscope

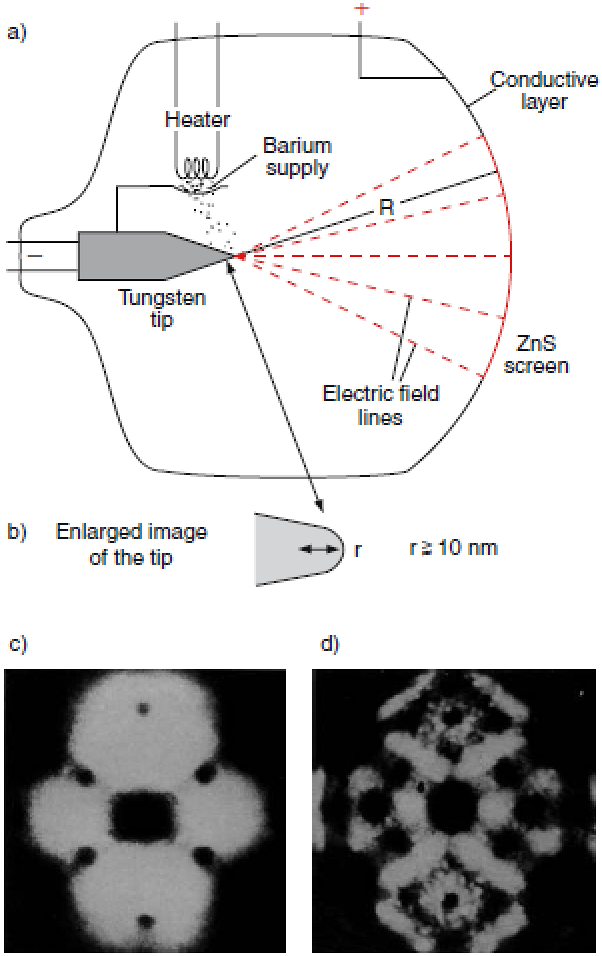
Cloud chamber

- Developed by C.T. Wilson (1911)
- Allows one to view spur of fast atoms, ions, or electrons
- Mechanism: incident particles with sufficient kinetic energy can ionize the supersaturated water vapor in the chamber. When the chamber is illuminated by light, the scattering by droplet makes the particle track visible.
- Doesn’t allow direct view of the incident particles.



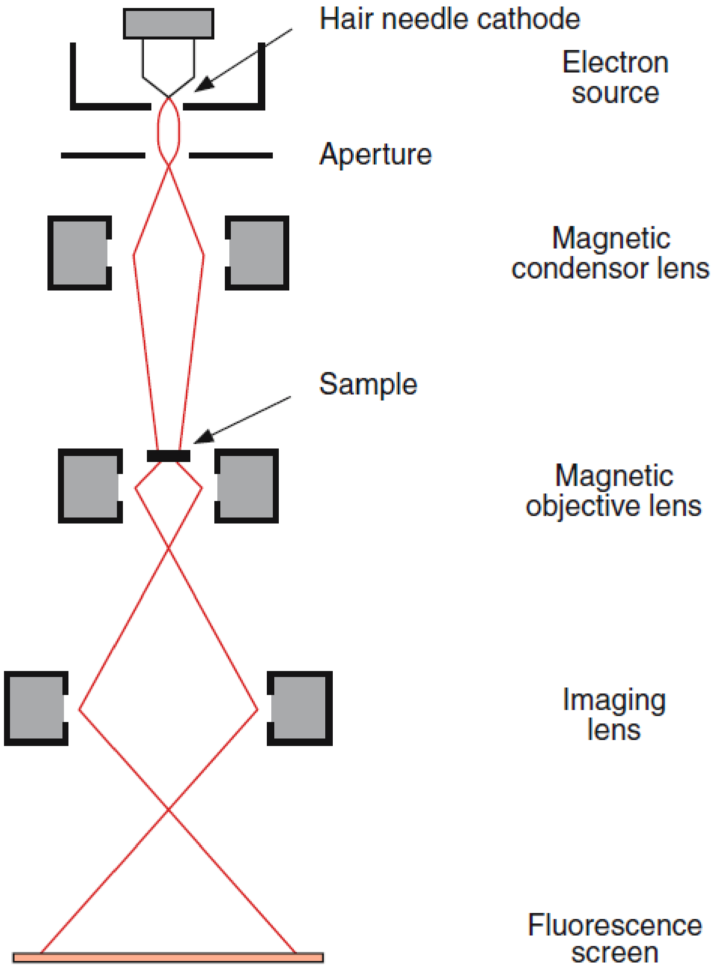
Field emission microscope

- Developed by E. Muller (1937)
- On a sharp metal tip, very high electric field induces ejection of electrons to the screen. Pattern on the screen reveals the atomic structure on the tip.
- The magnification ratio is R/r ~ 10 cm / 10 nm = 10^7.
- Only the emitted electrons are detected, no direct info about atomic information
- Prof. 鄭天佐 of 中研院物理所 is an expert in this field.



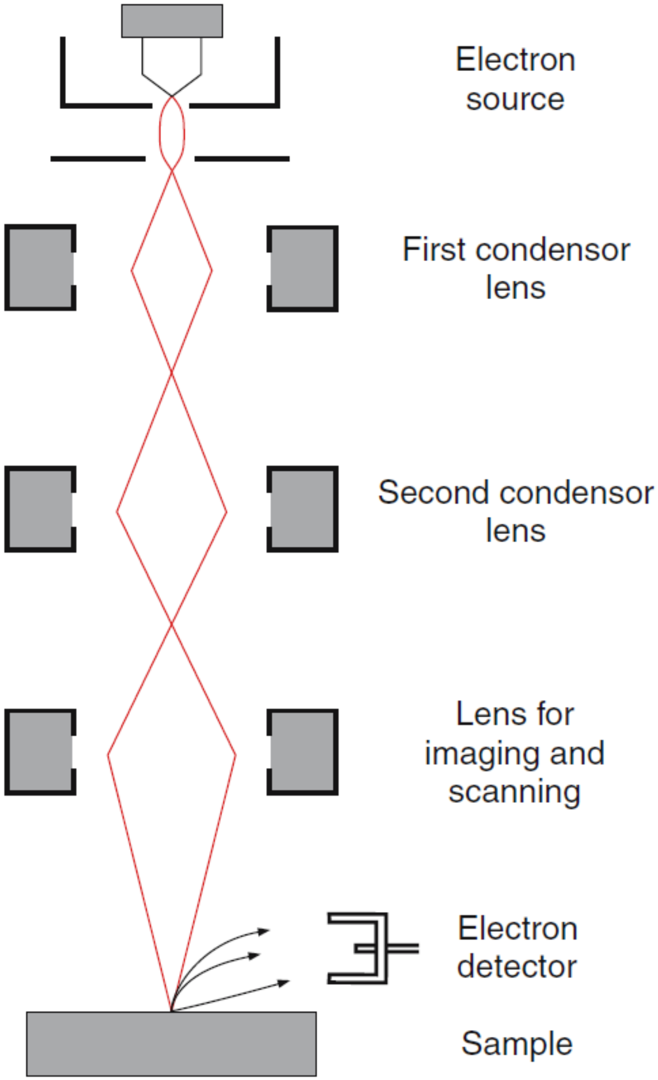
Transmission electron microscope

- Invented by E. Ruska (1932, 1986 Nobel Prize)
- Resolution to 1 Å
- Electron energy up to 500 kV (deBrogie wavelength ~ 10^{-12} m).
- Electron deflected by collisions with sample
- Near point electron source emission from sharp tungsten tip
- Drawbacks
  - Need to prepare sample in thin sheet
  - Need intense electron beam to obtain high contrast image
  - Might damage the sample especially for biological ones



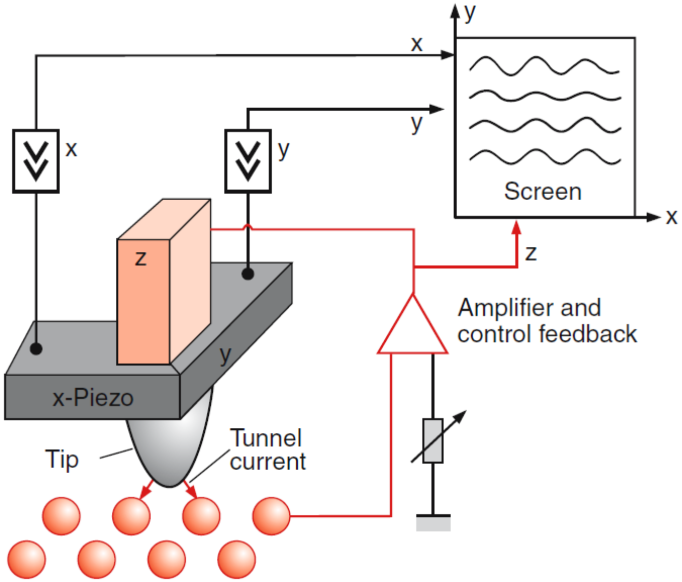
Scanning electron microscope

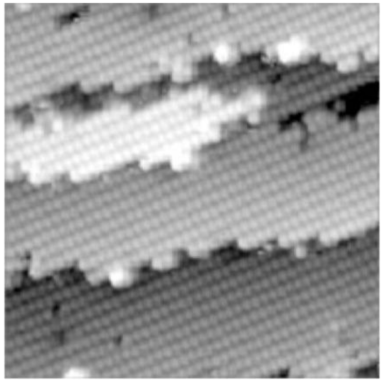
- Electron beam on the surface of sample to produce light emission or secondary electron
- Electron beam is scanned over the surface
- Light signal can be detected by optical microscope and secondary electron



Scanning tunneling microscope

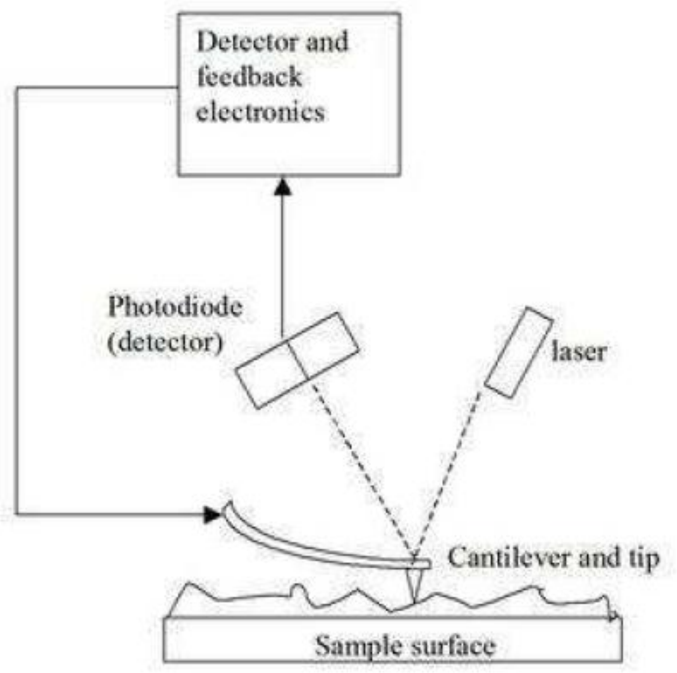
- Invented by G. Binning and H. Rochrer (1984, 1986 Nobel Prize)
- Achieved the highest spatial resolution: real atomic resolution!
- Sharp tungsten tip scanned by piezo, electron tunneling current being measured when applying voltage between sample and tip.
- Lock-in detection and tunneling current being feedback locked

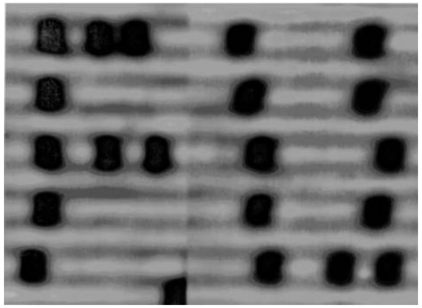




Atomic force microscope

- STM can only be used for a conducting surface, AFM can be used for a non-conductor
- The force between sample and the tip is measured by monitoring, through the reflection of a laser beam, the small upwards or downwards shift through of the balanced lever carrying a sharp tip





Atomic mass and mass spectrometer

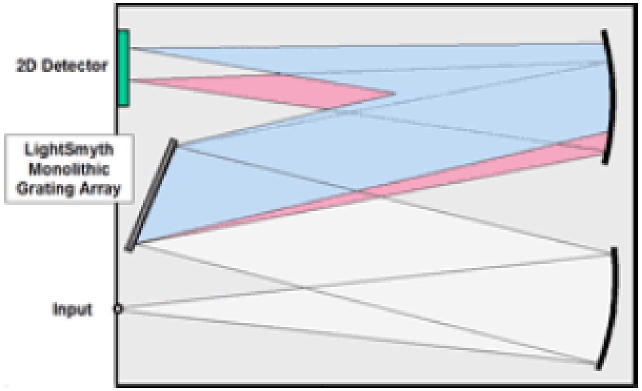
- J.J. Thomson’s parabola spectrograph
- Time-of-flight mass spectrometer
- Quadrupole mass spectrometer
- ion-cyclotron-resonance spectrometer
- Isotopes
- In mass spectrometry, one usually measure the effect on ions by E or B fields
- Mass spectrometer is widely used as a diagnostic tool in vacuum technology or chemical dynamics

The hydrogen atom

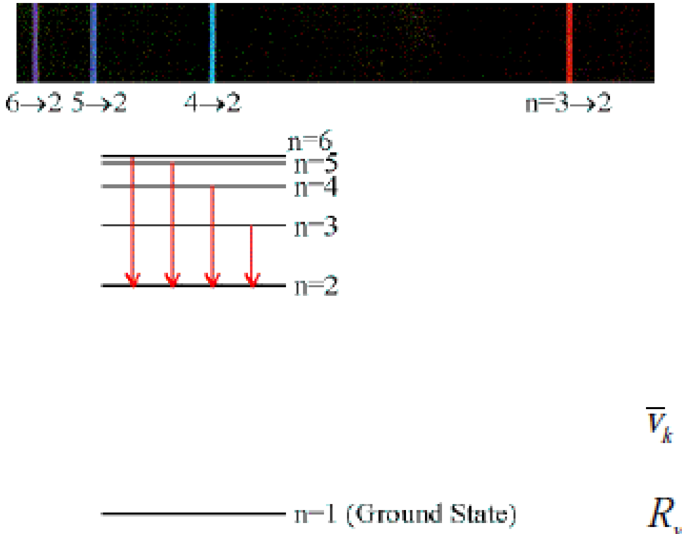
- The only exactly solvable atom, provides theoretical understanding of the atomic structure
- Simplest model system to test new theories
- Higher precision spectroscopy probes finer structure of the atom!

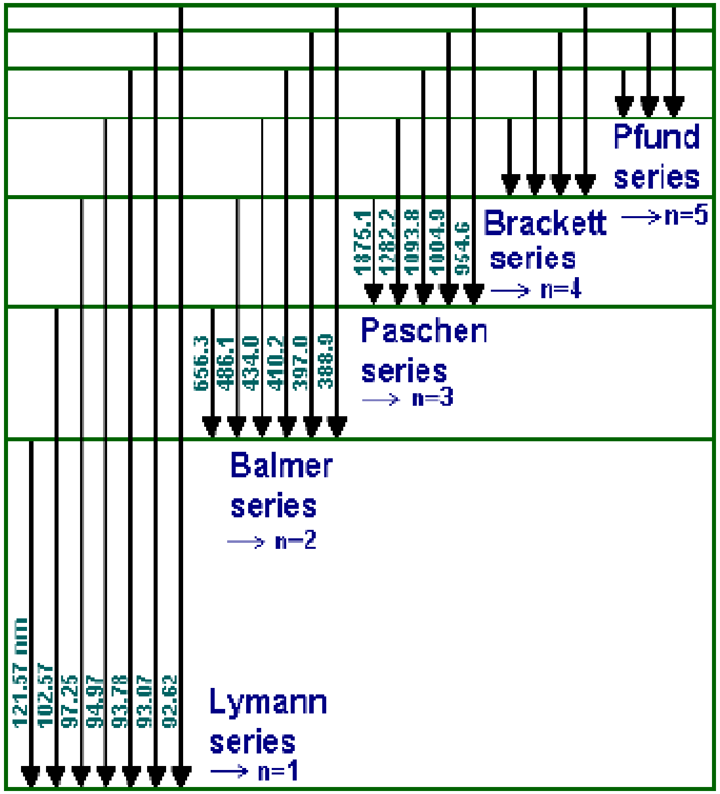
- Spectroscopic observations & Bohr’s model
- Schrodinger equation for the Hydrogen atom
- Spin-orbit coupling and fine-structure
- Relativistic effect
- Quantum Electrodynamic effect: Lamb shift
- Transition selection rules
- Hyperfine structure (will be introduced latter)

Hydrogen Spectrum (1/2)



Grating Spectrometer



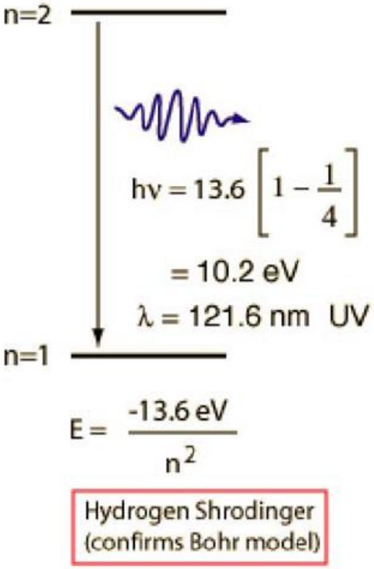


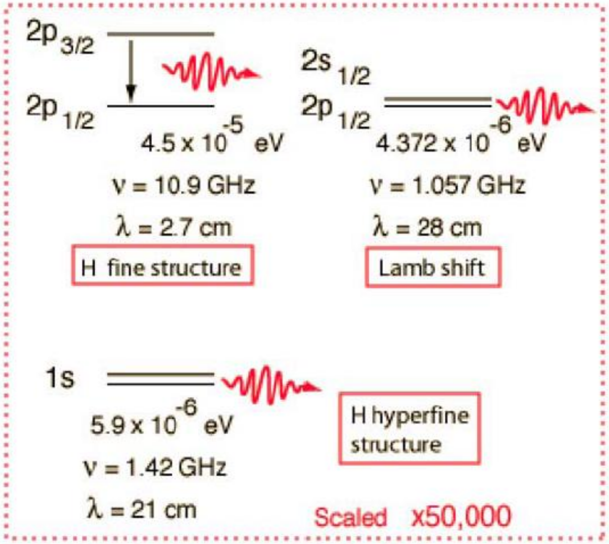
$$\bar{v}_k = R_y\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

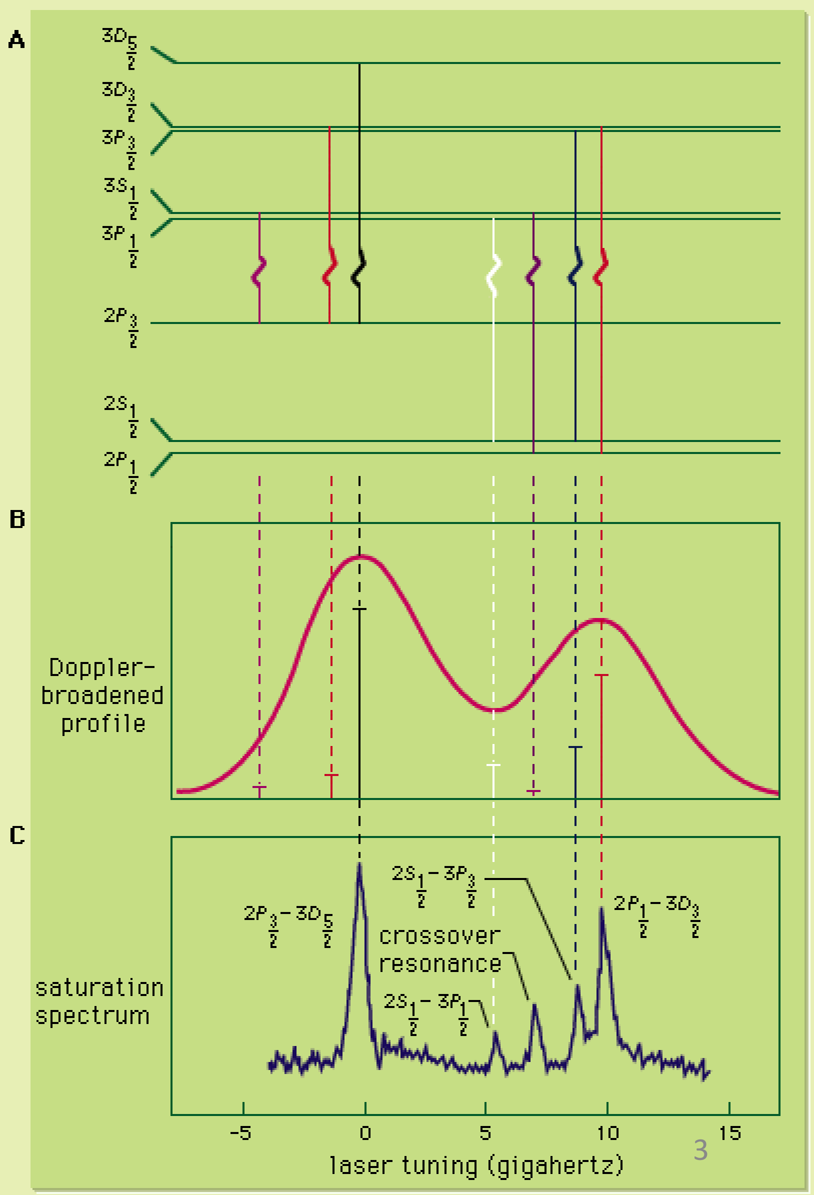
$$R_y = 109678 cm^{-1}$$

Hydrogen Spectrum (2/2)

- Higher precision spectrum probes finer structure of the hydrogen atom:
  - Fine structure, hyperfine structure, Zeeman effect, QED shift, finite nuclear size effect…



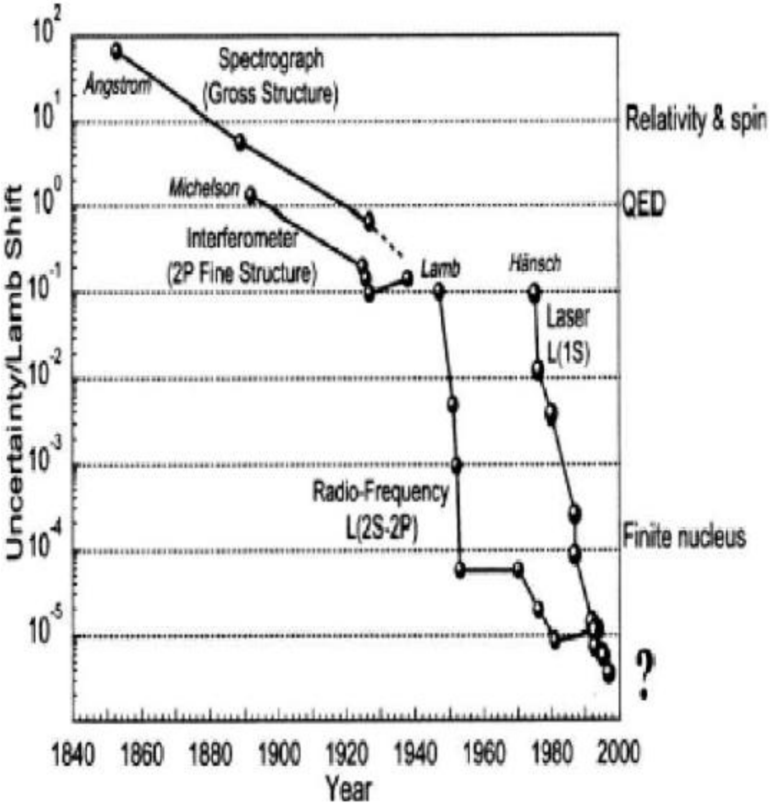




Experimental Improvements in High-Resolution Spectroscopy

- From grating spectrometer to laser spectroscopy.
- Elimination of broadening mechanisms
  - Doppler broadening: atomic beam, Doppler-free spectroscopy, atom cooling
  - Transit-time broadening: Ramsey’s method, atom trapping
- Lasers with narrower linewidth
- Careful considerations of all systematic effect
- Endless improvements…
- Powerful techniques developed, e.g. atomic clock, laser cooling, comb laser…

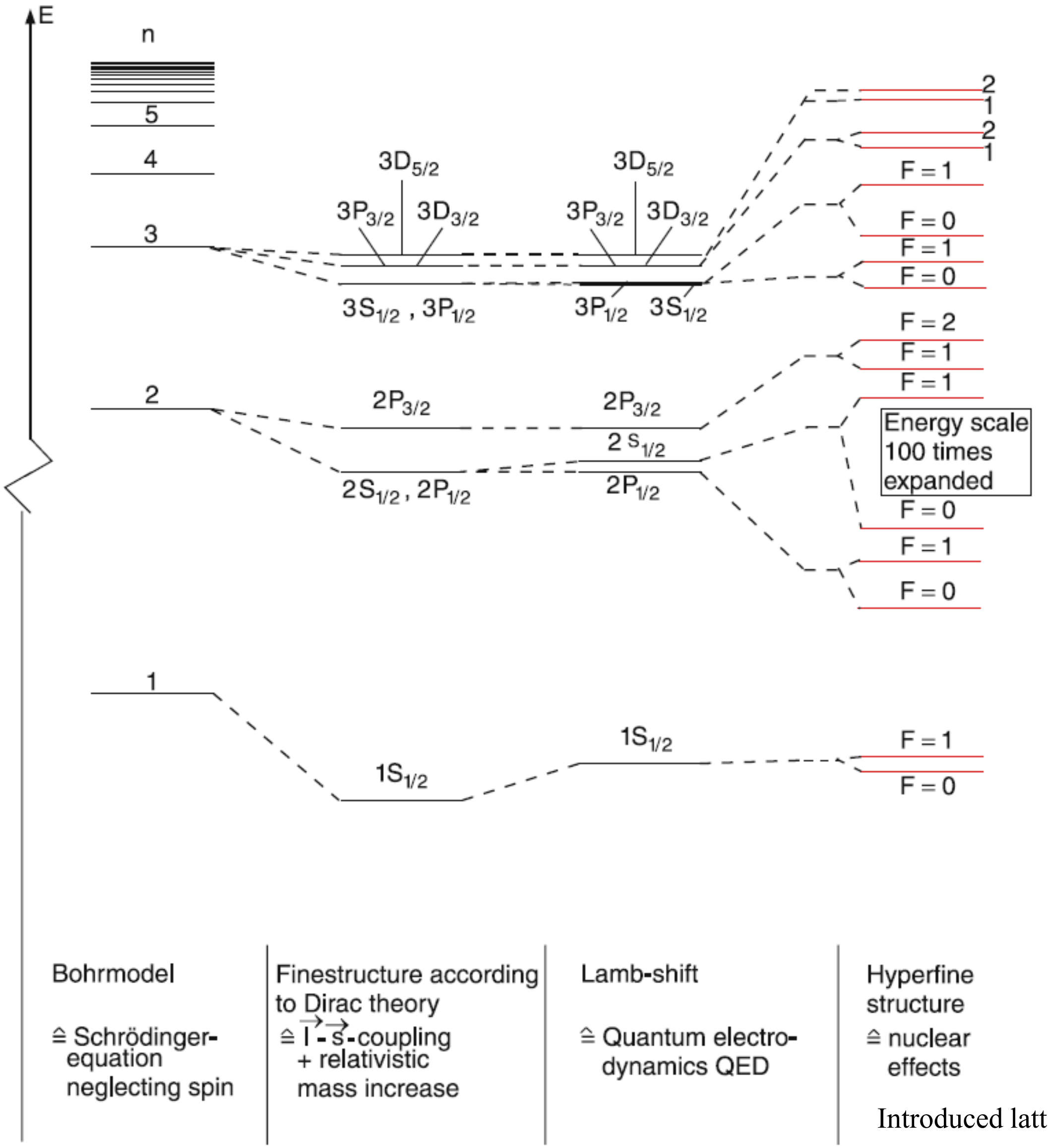
- “Passion for precision” see, T. Hansch, Nobel Lecture, Rev. Mod. Phys. 78,1297(2006).



Overview of Hydrogen Energy Level Splitting

- Atomic structures arise from electromagnetic interactions, finer splittings reveal finer structures of the electron, nucleus, and EM field.
- Bohr model or Schrodinger equation: Coulomb force
- Fine structure: coupling of electron spin magnetic moment with magnetic field produced by relativistic motion of the electron around the nucleus.
- Hyperfine structure: Higher order electromagnetic coupling between the nucleus and the electron, including magnetic dipole moment, quadrupole moment, etc.
- Quantum electrodynamic effect: coupling of electron with the vacuum fluctuation of quantized EM field.
- Finite nuclear size effect: the nucleus is not a point charge but with a certain radius.

Atomic structure of the Hydrogen atom



Introduced latter…

Spectroscopic notation

$n^{2s+1}X_J$

$X : s(l=0), p(l=1), d(l=2), f(l=3)\ldots$

$J = |L-S| \sim L+S$

$F = |J-I| \sim J+I$

Bohr’s model

- Coulomb force $\frac{\mu v^2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2} \Rightarrow r = \frac{Ze^2}{4\pi\varepsilon_0 \mu v^2}$
- Standing-wave condition $2\pi r = n\lambda_{dB} ; \lambda_{dB} = \frac{h}{\mu v}$
- Angular momentum $\Rightarrow \mu v r = n\hbar$
- Radius of electron $r_n = \frac{n^2 h^2 \varepsilon_0}{\pi\mu Ze^2} = \frac{n^2}{Z} a_0 ; a_0 \sim 0.53 A$
- Kinetic energy $E_{kin} = \frac{\mu}{2} v^2 = \frac{1}{2}\frac{Ze^2}{4\pi\varepsilon_0 r} = -\frac{1}{2}U$
- Total energy $E_{tot} = E_{kin} + U = \frac{1}{2}U = -\frac{1}{2}\frac{Ze^2}{4\pi\varepsilon_0 r}$
- Energy levels $E_n = -\frac{\mu e^4 Z^2}{8\varepsilon_0^2 h^2 n^2} = -R_y^* \frac{Z^2}{n^2}$
- Rydbergy constant $R_y^* = hcR_y = \frac{\mu e^4}{8\varepsilon_0^2 h^2}$
- Excitation frequency $h\nu_{ik} = E_k - E_i$
- Atomic spectra $\nu_{ik} = \frac{R_y^*}{h} Z^2 (\frac{1}{n_i^2} - \frac{1}{n_k^2})$

2006 CODATA, physics.nist.gov/hdel

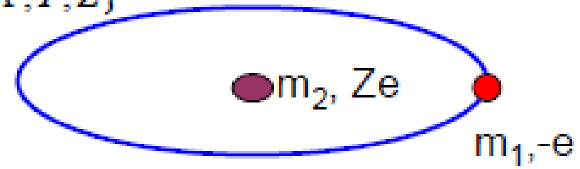
$$R_\infty = R_y \frac{M_p}{M_p + m_e}$$

$$= \frac{1}{hc}\frac{m_e e^4}{8\varepsilon_0^2 h^2} = 10973731.568527(37) m^{-1}$$

Schrodinger equation for the Hydrogen atom

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi(\vec{r}_1,\vec{r}_2)-\frac{\hbar^2}{2m_2}\nabla_2^2\psi(\vec{r}_1,\vec{r}_2)-\frac{Ze^2}{4\pi\varepsilon_0 r}\psi(\vec{r}_1,\vec{r}_2)=E\psi(\vec{r}_1,\vec{r}_2)$$

Center of mass coordinate $\vec{R}=\frac{m_1\vec{r}_1+m_2\vec{r}_2}{M}, M=m_1+m_2, \vec{R}=\{X,Y,Z\}$



Relative coordinate $r=\{x,y,z\}=|\vec{r}_1-\vec{r}_2|$

$$\vec{r}_1=\vec{R}+\frac{m_2}{M}\vec{r}, \vec{r}_2=\vec{R}-\frac{m_1}{M}\vec{r}$$

After some treatments,

$$[-\frac{\hbar^2}{2M}\nabla_R^2+\frac{\hbar^2}{2\mu}\nabla_r^2]\psi+U(r)\psi=E\psi$$

Try separation of variables,

$$\psi(\vec{R},\vec{r})=f(\vec{r})g(\vec{R})$$

$$-\frac{\hbar^2}{2M}\frac{\nabla_R^2 g}{g}=\frac{\hbar^2}{2\mu}\frac{\nabla_r^2 f}{f}+E-U(r)$$

Unless,

$$\frac{\hbar^2}{2M}\frac{\nabla_R^2 g}{g}=const=-E_g$$

$$\frac{\hbar^2}{2\mu}\frac{\nabla_r^2 f}{f}-U(r)=const=-E_f$$

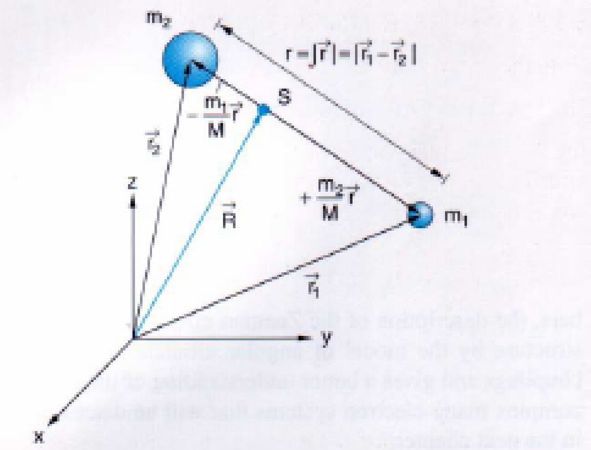


Fig. 5.1. Transformation of laboratory frame into the center-of-mass coordinate system

Ignore the center of mass (external) motion, and focus on the Schrodinger eqn for the electron (internal)

$$\left\{ \frac{-\hbar^2}{2m_e} \nabla^2 + V(r) \right\} \psi = E\psi \,. \tag{2.1}$$

with $V(r) = \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r}$, and $Z = 1.$

$$\text{Laplacian:} \quad \begin{cases} \nabla^2 = \dfrac{1}{r^2} \dfrac{\partial}{\partial r} \left(r^2 \dfrac{\partial}{\partial r} \right) - \dfrac{1}{r^2} \mathrm{l}^2 \,, & (2.2) \\[2ex] \mathrm{l}^2 = - \left\{ \dfrac{1}{\sin\theta} \dfrac{\partial}{\partial \theta} \left(\sin\theta \, \dfrac{\partial}{\partial \theta} \right) + \dfrac{1}{\sin^2\theta} \dfrac{\partial^2}{\partial \phi^2} \right\} , & (2.3) \end{cases}$$

Let the solution $\psi = R(r) Y(\theta, \phi)$,

and by separation of variables, we arrive at

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2m_e r^2}{\hbar^2} \{ V(r) - E \} = \frac{1}{Y} \mathrm{l}^2 Y \,. \tag{2.4}$$

$$\mathrm{l}^2 Y = bY \,. \tag{2.5}$$

Solution of the angular equation

Angular eqn: $$l^2 Y = bY\,. \tag{2.5}$$

Substitute $Y = \Theta(\theta)\Phi(\phi)$ into Eq. (2.5),

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\Theta}{\partial\theta}\right) + b\sin^2\theta = -\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = \text{const}\,. \tag{2.6}$$

Φ follows a simple harmonic motion and can be written as

$$\Phi = A\mathrm{e}^{im\phi} + B\mathrm{e}^{-im\phi}\,. \tag{2.7}$$

Wavefunction must be single-valued at each point:

$\Phi(\phi + 2\pi) = \Phi(\phi)$, so m must be an integer.

Introduce ladder operators: $l_+ = l_x + \mathrm{i}l_y$ and $l_- = l_x - \mathrm{i}l_y$

$$\hbar l_z = -\mathrm{i}\hbar \frac{\partial}{\partial \phi} \,. \tag{2.8}$$

$$l_\pm = e^{\pm i\phi}(\pm \frac{\partial}{\partial \theta} + i \cot\theta \frac{\partial}{\partial \phi}) \tag{2.9}$$

$$l_\pm Y_{l,m} \propto Y_{l,m\pm 1} \text{ , and } m_{\max} = l,$$

$$Y_{l,l} \propto \sin^l \theta \, e^{il\phi} \;. \tag{2.10}$$

Which is the eigenfunction of eqn 2.5, with eigenvalue $b = l(l+1)$.

So the solution of the angular eqn is

$$Y_{l,m} \propto (l_-)^{l-m} \sin^l \theta \, \mathrm{e}^{\mathrm{i}l\phi} \,. \tag{2.11}$$

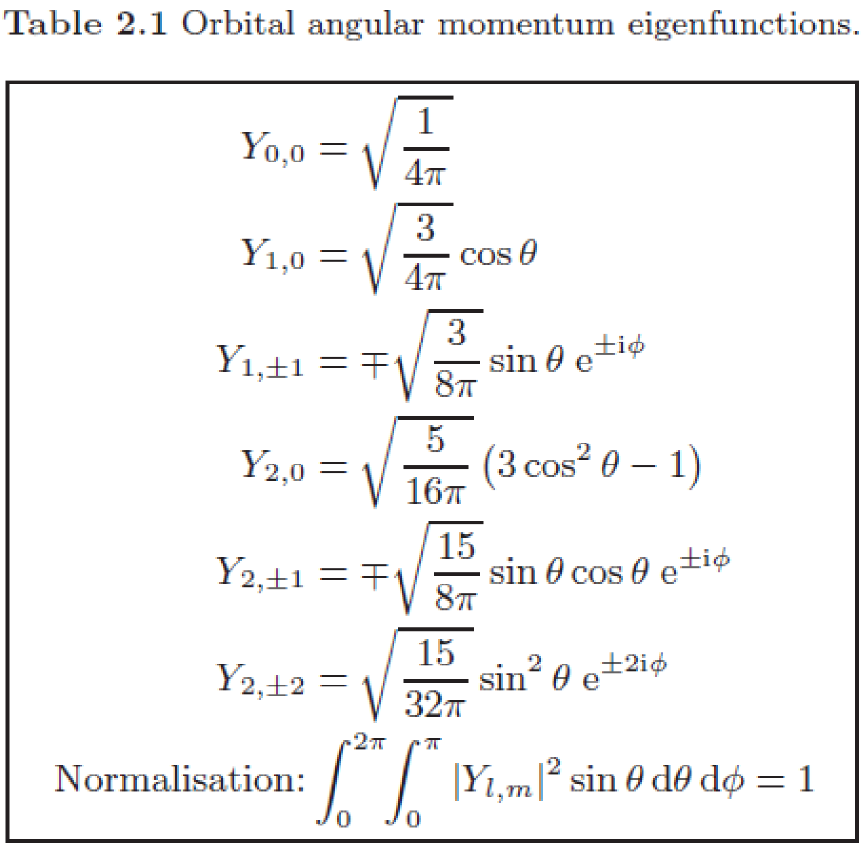


Table 2.1 Orbital angular momentum eigenfunctions.

$$Y_{0,0} = \sqrt{\frac{1}{4\pi}}$$

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$Y_{1,\pm 1} = \mp\sqrt{\frac{3}{8\pi}} \sin\theta \, \mathrm{e}^{\pm \mathrm{i}\phi}$$

$$Y_{2,0} = \sqrt{\frac{5}{16\pi}} \left(3\cos^2\theta - 1\right)$$

$$Y_{2,\pm 1} = \mp\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta \, \mathrm{e}^{\pm \mathrm{i}\phi}$$

$$Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta \, \mathrm{e}^{\pm 2\mathrm{i}\phi}$$

$$\text{Normalisation:} \int_0^{2\pi}\int_0^{\pi} |Y_{l,m}|^2 \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi = 1$$

The spherical harmonic functions

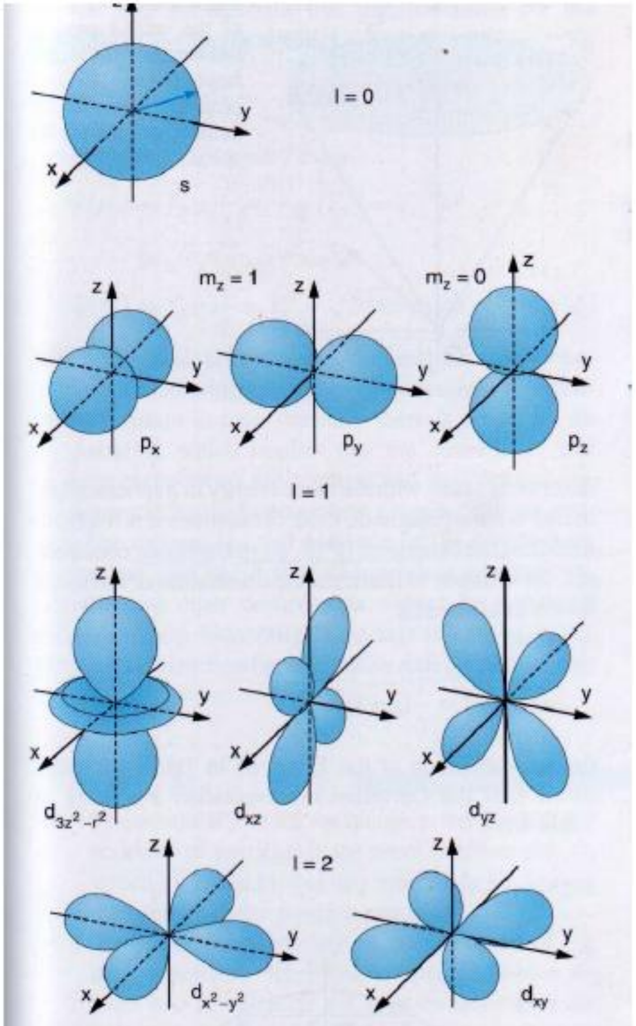


Fig. 4.28. Absolute squares $|Y_l^m(\vartheta, \varphi)|^2$, which are proportional to the spatial probability density of a particle in a spherical symmetric potential, are plotted here in Cartesian coordinates

$$
\begin{aligned}
Y_{1,0} &\propto \frac{z}{r}\,, \\
Y_{1,1} &\propto \frac{x+\mathrm{i}y}{r}\,, \\
Y_{1,-1} &\propto \frac{x-\mathrm{i}y}{r}\,.
\end{aligned}
\tag{2.13}
$$

$$Y_{1,0} \;\propto\; z/r$$

$$Y_{1,-1} - Y_{1,1} \propto \frac{x}{r} = \sin\theta\,\cos\phi\,, \tag{2.14}$$

$$Y_{1,-1} + Y_{1,1} \propto \frac{y}{r} = \sin\theta\,\sin\phi\,. \tag{2.15}$$

Referred to as p-orbitals in chemistry.

Total wavefunction

$$|\psi\,(r,\theta,\phi)|^2 = R_{n,l}^2\,(r)\,|Y_{l,m}\,(\theta,\phi)|^2\;. \tag{2.12}$$

$|\psi|^2$ is the probability distribution of the electron, and

$-e\,|\psi|^2$ is the electronic charge distribution.

Solution of the radial equation

Recall Coulomb potential $V(r) = -e^2/4\pi\epsilon_0 r.$

Substitute $P(r) = rR(r)$:

$$-\frac{\hbar^2}{2m_e}\frac{d^2P}{dr^2} + \left\{\frac{\hbar^2}{2m_e}\frac{l(l+1)}{r^2} - \frac{e^2/4\pi\epsilon_0}{r} - E\right\}P = 0\,. \qquad (2.16)$$

centrifugal barrier potential > 0, when $l \neq 0$

$$\rho^2 = \frac{2m_e|E|r^2}{\hbar^2} \qquad (2.17)$$

$$\frac{d^2P}{d\rho^2} + \left\{-\frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho} - 1\right\}P = 0\,. \qquad (2.18)$$

$$\lambda = \frac{e^2}{4\pi\epsilon_0}\sqrt{\frac{2m_e}{\hbar^2|E|}}\,. \qquad (2.19)$$

$$\left\langle\frac{1}{r}\right\rangle = \frac{1}{n^2}\left(\frac{Z}{a_0}\right). \qquad (2.24)$$

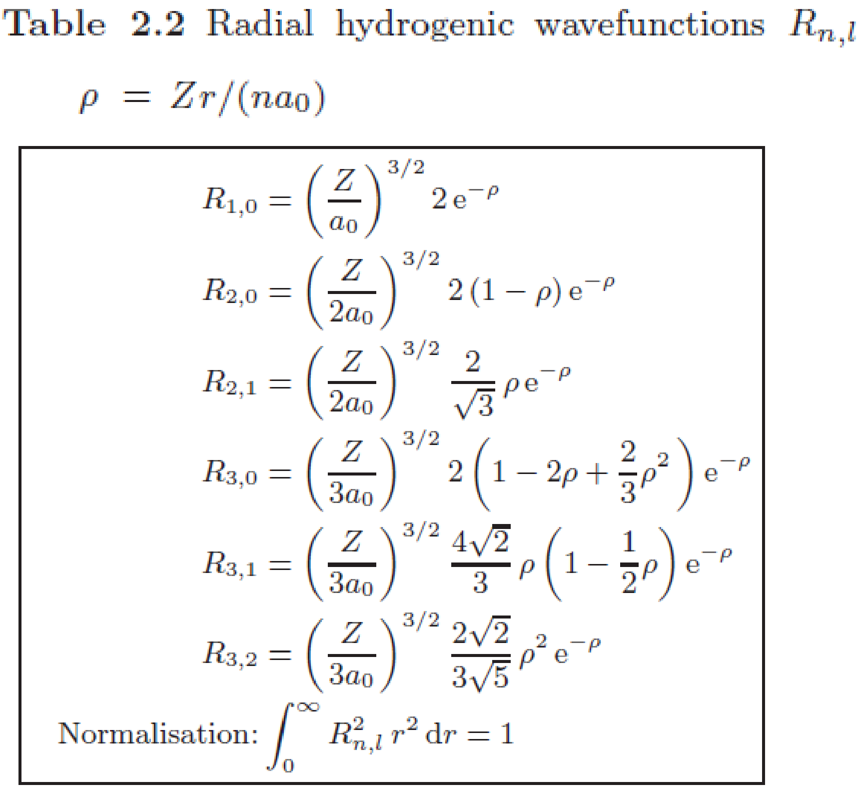


Table 2.2 Radial hydrogenic wavefunctions $R_{n,l}$

$$\rho = Zr/(na_0)$$

$$R_{1,0} = \left(\frac{Z}{a_0}\right)^{3/2} 2\,\mathrm{e}^{-\rho}$$

$$R_{2,0} = \left(\frac{Z}{2a_0}\right)^{3/2} 2\,(1-\rho)\,\mathrm{e}^{-\rho}$$

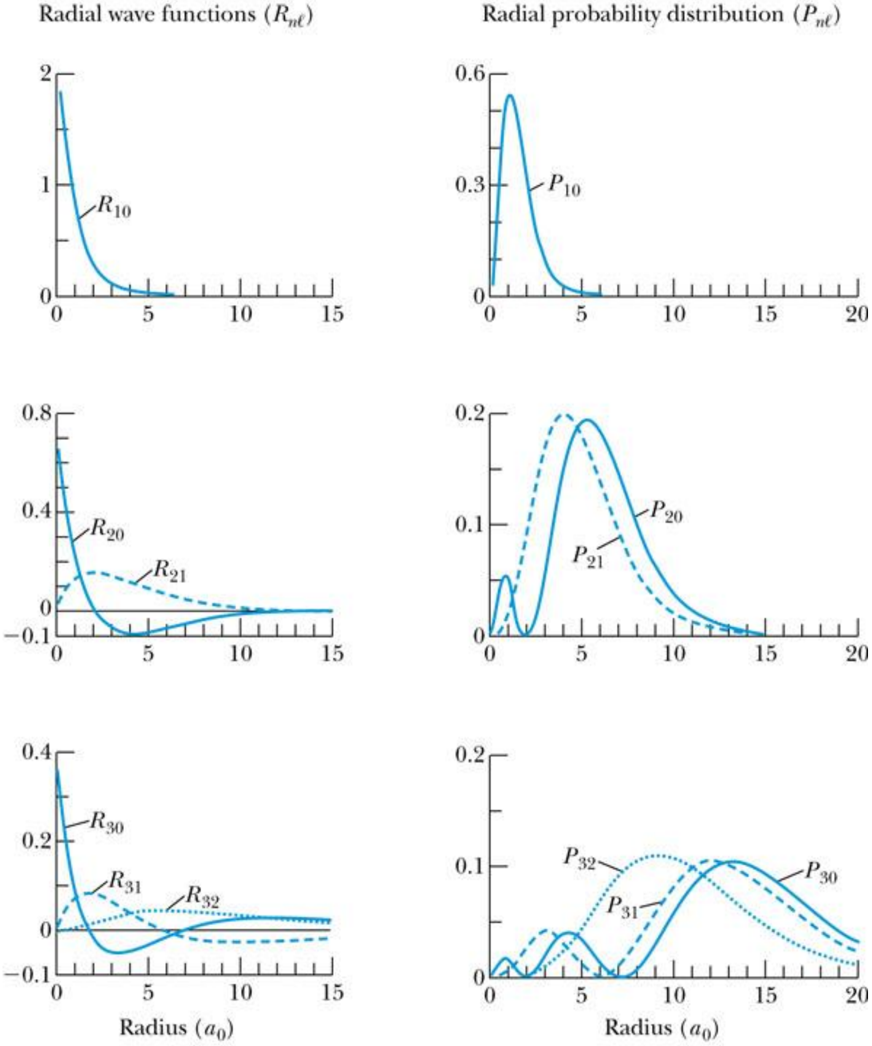
$$R_{2,1} = \left(\frac{Z}{2a_0}\right)^{3/2} \frac{2}{\sqrt{3}}\,\rho\,\mathrm{e}^{-\rho}$$

$$R_{3,0} = \left(\frac{Z}{3a_0}\right)^{3/2} 2\left(1-2\rho+\frac{2}{3}\rho^2\right)\mathrm{e}^{-\rho}$$

$$R_{3,1} = \left(\frac{Z}{3a_0}\right)^{3/2} \frac{4\sqrt{2}}{3}\,\rho\left(1-\frac{1}{2}\rho\right)\mathrm{e}^{-\rho}$$

$$R_{3,2} = \left(\frac{Z}{3a_0}\right)^{3/2} \frac{2\sqrt{2}}{3\sqrt{5}}\,\rho^2\,\mathrm{e}^{-\rho}$$

Normalisation: $\int_0^\infty R_{n,l}^2\, r^2\, \mathrm{d}r = 1$



$$R_{n,0}(0) \neq 0!$$

s-electrons can be used to probe nucleus.

Probability to find an electron between r and r+dr

$$P(r)dr = r^2 \left|R_{nl}(r)\right|^2 dr$$

Transitions

Let’s consider the transition between the stationary states when the atom interacts with an electromagnetic radiation,

$$\mathbf{E}(t) = |\mathbf{E}_0| \operatorname{Re}\left(\mathrm{e}^{-\mathrm{i}\omega t}\, \widehat{\mathbf{e}}_{\mathrm{rad}}\right) \qquad (2.25)$$

with constant amplitude $|\mathbf{E}_0|$ and polarization vector $\widehat{\mathbf{e}}_{\mathrm{rad}}$.

The interaction Hamiltonian: $H' = e\mathbf{r} \cdot \mathbf{E}(t)$

$$\text{Rate} \propto |e\mathbf{E}_0|^2 \left| \int \psi_2^* \left(\mathbf{r} \cdot \widehat{\mathbf{e}}_{\mathrm{rad}}\right) \psi_1 \, \mathrm{d}^3\mathbf{r} \right|^2 \equiv |e\mathbf{E}_0|^2 \times |\langle 2| \mathbf{r} \cdot \widehat{\mathbf{e}}_{\mathrm{rad}} |1\rangle|^2 . \qquad (2.26)$$

$$\langle 2| \mathbf{r} \cdot \widehat{\mathbf{e}}_{\mathrm{rad}} |1\rangle = D_{12}\, \mathcal{I}_{\mathrm{ang}} . \qquad (2.27)$$

$$D_{12} = \int_0^\infty R_{n_2,l_2}(r)\, r\, R_{n_1,l_1}(r)\, r^2 \, \mathrm{d}r . \qquad (2.28)$$

The angular integral is

$$\mathcal{I}_{\mathrm{ang}} = \int_0^{2\pi} \int_0^{\pi} Y_{l_2,m_2}^*(\theta,\phi)\, \widehat{\mathbf{r}} \cdot \widehat{\mathbf{e}}_{\mathrm{rad}}\, Y_{l_1,m_1}(\theta,\phi) \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi , \qquad (2.29)$$

Selection rules

dipole operator
(position op.)

$$\widehat{\mathbf{r}} = \frac{1}{r}\left(x\widehat{\mathbf{e}}_x + y\widehat{\mathbf{e}}_y + z\widehat{\mathbf{e}}_z\right)$$
$$= \sin\theta\cos\phi\,\widehat{\mathbf{e}}_x + \sin\theta\sin\phi\,\widehat{\mathbf{e}}_y + \cos\theta\,\widehat{\mathbf{e}}_z\,. \qquad (2.30)$$

$$\sin\theta\cos\phi = \sqrt{\frac{2\pi}{3}}\left(Y_{1,-1} - Y_{1,1}\right),$$
$$\sin\theta\sin\phi = \mathrm{i}\sqrt{\frac{2\pi}{3}}\left(Y_{1,-1} + Y_{1,1}\right), \qquad (2.31)$$
$$\cos\theta = \sqrt{\frac{4\pi}{3}}Y_{1,0}\,,$$

leads to

$$\widehat{\mathbf{r}} \propto Y_{1,-1}\frac{\widehat{\mathbf{e}}_x + \mathrm{i}\widehat{\mathbf{e}}_y}{\sqrt{2}} + Y_{1,0}\widehat{\mathbf{e}}_z + Y_{1,1}\frac{-\widehat{\mathbf{e}}_x + \mathrm{i}\widehat{\mathbf{e}}_y}{\sqrt{2}}\,. \qquad (2.32)$$

We write the general polarization vector as

$$\widehat{\mathbf{e}}_{\mathrm{rad}} = A_{\sigma-}\frac{\widehat{\mathbf{e}}_x - \mathrm{i}\widehat{\mathbf{e}}_y}{\sqrt{2}} + A_\pi\widehat{\mathbf{e}}_z + A_{\sigma+}\left(-\frac{\widehat{\mathbf{e}}_x + \mathrm{i}\widehat{\mathbf{e}}_y}{\sqrt{2}}\right), \qquad (2.33)$$

$$\widehat{\mathbf{r}}\cdot\widehat{\mathbf{e}}_{\mathrm{rad}} \propto A_{\sigma-}Y_{1,-1} + A_z Y_{1,0} + A_{\sigma+}Y_{1,+1}\,. \qquad (2.34)$$

π-transitions

$$\widehat{\mathrm{e}}_{\mathrm{rad}} \cdot \widehat{\mathrm{e}}_z = \cos\theta$$

$$\mathcal{I}_{\mathrm{ang}}^{\pi} = \int_0^{2\pi}\int_0^{\pi} Y_{l_2,m_2}^{*}(\theta,\phi)\,\cos\theta\, Y_{l_1,m_1}(\theta,\phi)\,\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\,. \qquad (2.35)$$

$$\mathcal{I}_{\mathrm{ang}}^{\pi} = \mathrm{e}^{\mathrm{i}(m_1-m_2)\phi_0}\mathcal{I}_{\mathrm{ang}}^{\pi}\,. \qquad (2.36)$$

System has cylindrical symmetry.

This equation is satisfied if either $\mathcal{I}_{\mathrm{ang}}^{\pi} = 0$ or $m_{l_1} = m_{l_2}$.

σ-transitions

$$\mathcal{I}_{\mathrm{ang}}^{\sigma^+} = \int_0^{2\pi}\int_0^{\pi} Y_{l_2,m_2}^{*}(\theta,\phi)\,\sin\theta\,\mathrm{e}^{\mathrm{i}\phi}\, Y_{l_1,m_1}(\theta,\phi)\,\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\,. \qquad (2.37)$$

Using the same cylindrical symmetry argument,

$$\mathcal{I}_{\mathrm{ang}}^{\sigma^+} = 0 \text{ unless } m_{l_1} - m_{l_2} + 1 = 0.$$

Also taking $\mathrm{e}^{\mathrm{i}\phi} \rightarrow \mathrm{e}^{-\mathrm{i}\phi}$

$$\mathcal{I}_{\mathrm{ang}}^{\sigma^-} = 0 \text{ unless } m_{l_1} - m_{l_2} - 1 = 0.$$

Parity consideration

The parity transformation is an inversion through the origin given by $\mathbf{r} \rightarrow -\mathbf{r}$

In polar coordinate, this is equivalent to $\begin{cases} \theta \longrightarrow \pi - \theta : & \text{a reflection}, \\ \phi \longrightarrow \phi + \pi : & \text{a rotation}. \end{cases}$

Given Parity operator $\widehat{P}$ and its eigenvalue P

$$\widehat{P}\,\psi = P\,\psi\,, \tag{2.40}$$

Operate twice: $\mathbf{r} \rightarrow -\mathbf{r} \rightarrow \mathbf{r}.$

Therefore, $\widehat{P}^2\,\psi = P^2\,\psi = \psi$, and $P^2 = 1$, or $P = \pm 1.$

$$\widehat{P}\,\psi = \psi \qquad \text{or} \qquad \widehat{P}\,\psi = -\,\psi\,.$$

(even) (odd)

$$\widehat{P}\,Y_{l,m} = (-1)^{\,l}\,Y_{l,m}\,. \tag{2.41}$$

$$\mathcal{I}_{\text{ang}} = (-1)^{\,l_2+l_1+1}\,\mathcal{I}_{\text{ang}}\,. \tag{2.42}$$

The integral is zero unless the initial and final states have different parity.

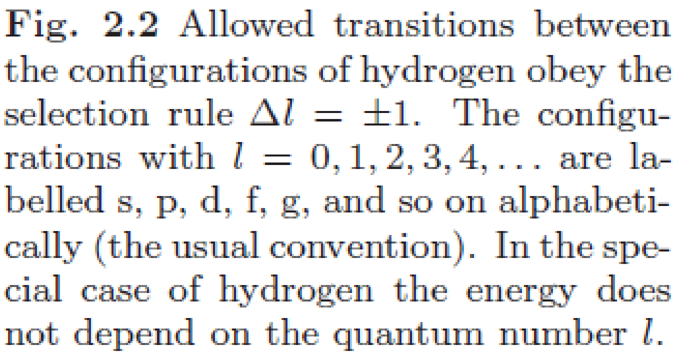


Fig. 2.2 Allowed transitions between the configurations of hydrogen obey the selection rule $\Delta l = \pm 1$. The configurations with $l = 0, 1, 2, 3, 4, \ldots$ are labelled s, p, d, f, g, and so on alphabetically (the usual convention). In the special case of hydrogen the energy does not depend on the quantum number l.

E.g., the long lived 2s state enabled determination of the Lamb shift.

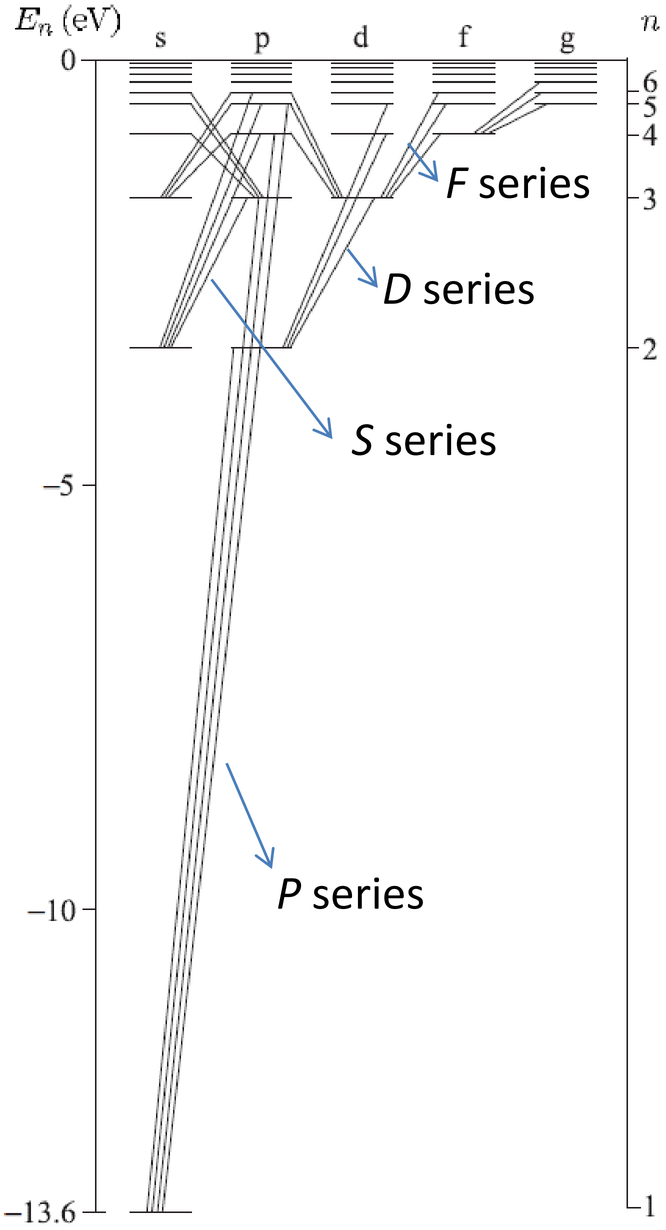
2s lifetime is ~ 0.125 s ~ 10^8 of 2p lifetime

Muonic hydrogen

2s -> 2p transition

Proton might be smaller than we thought

Nature **466 ,** 213–216 (08 July 2010)



The “normal” Zeeman effect

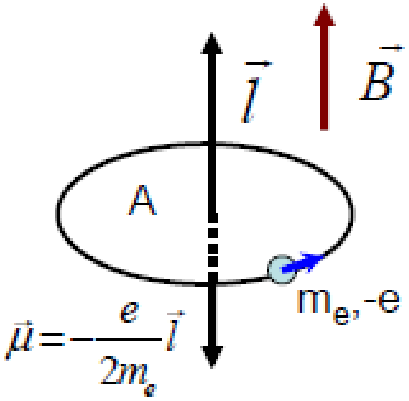
- Relation between magnetic moment & angular momentum by classical physics.

$$I = \frac{dQ}{dt} = \frac{-e}{T} = \frac{-ev}{2\pi r}$$

$$\vec{\mu} = I\vec{A} = I\pi r^2 \hat{n} = -\frac{evr}{2}\hat{n}$$

$$\vec{l} = \vec{r} \times \vec{p} = m_e rv\,\hat{n}$$

$$\Rightarrow \vec{\mu} = -\frac{e}{2m_e}\vec{l} = -\frac{\mu_B}{\hbar}\vec{l}$$



- Magnetic potential energy,

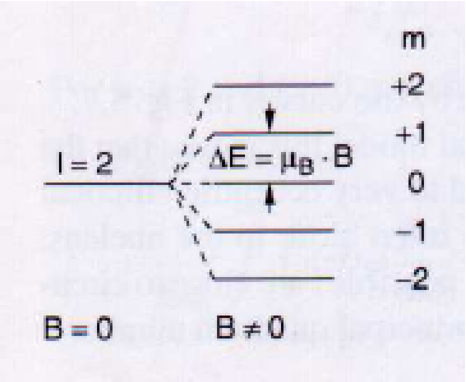
$$H_{Zeeman} = -\vec{\mu} \bullet \vec{B} = \frac{e}{2m_e}\vec{l} \bullet \vec{B} = \frac{e}{2m_e} l_z B = \frac{e\hbar}{2m_e} mB = \mu_B mB$$

- Bohr magneton

$$\mu_B = \frac{e\hbar}{2m_e} = 9.274015 \times 10^{-24} J/T$$

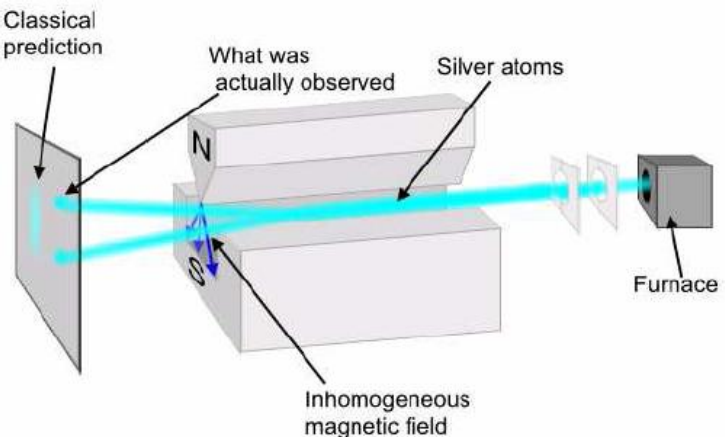
$$\Delta f = \frac{\mu_B B}{h} \approx 1.4\,MHz \;/\; Gauss$$

- Zeeman shift spacing



Electron spin and the “anomalous ” Zeeman effect

- Demonstrated with silver atom in *s* state by *Stern & Gerlach* (1921).
- Goundsmit & Uhlenbeck proposed the spin concept (1925).
- Interpretation as mechanical spin will runs into serious difficulties.
- Pauli suggested it as an intrinsic angular momentum of electron.
- Being included in the Dirac equation.



Magnetic moment due to its orbital motion:

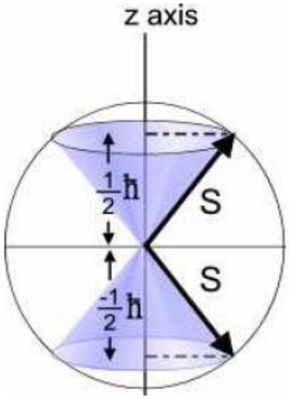
$$\vec{\mu}_L = -\frac{e}{2m}\vec{L} = -\frac{\mu_B}{\hbar}\vec{L}$$

Magnetic moment due to its intrinsic spin:

$$\vec{\mu}_s = -\frac{e}{m}\vec{S} = -g_s\frac{\mu_B}{\hbar}\vec{S},$$

g_s = 2.00231930436146(56).

PRL v.100,120801(2008)



intrinsic spin of the electron

$$s = \frac{1}{2}$$

$$|\vec{s}| = \sqrt{s(s+1)}\hbar = \frac{1}{2}\sqrt{3}\hbar$$

$$s_z = \pm\frac{1}{2}\hbar$$

Zeeman energy in a *B* field

$$V_B = -\vec{\mu}_s \cdot \vec{B} = +\frac{e}{m}\vec{S}\cdot\vec{B}$$

Spin matrics

- Commutation relation for spin operator : $[\vec{S}_i, \vec{S}_j] = i\hbar\varepsilon_{ijk}\vec{S}_k\,(works\ \ , \vec{S} \rightarrow \vec{L})$
- Matrix representation of spin operator : Pauli matrices

$$\vec{S} = \hbar\vec{\sigma}/2; \sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix},$$

- Identity for spin matrix : (can be easily checked by commutation relation)
- If ***A*** and ***B*** are two operators that commute with σ

$$(\vec{\sigma}\bullet\vec{A})(\vec{\sigma}\bullet\vec{B}) = (\vec{A}\bullet\vec{B}) + i\vec{\sigma}\bullet(\vec{A}\times\vec{B})$$

$$(\vec{A} - (\vec{\sigma}\bullet\vec{A})\vec{\sigma})\bullet\vec{B} = -i\vec{\sigma}\bullet(\vec{A}\times\vec{B}) = -i(\vec{\sigma}\times\vec{A})\bullet\vec{B}, \forall\vec{B}$$

$$\Rightarrow \vec{A} - (\vec{\sigma}\bullet\vec{A})\vec{\sigma} = i\vec{A}\times\vec{\sigma}; similarly, \Rightarrow \vec{\sigma}(\vec{\sigma}\bullet\vec{A}) - \vec{A} = i\vec{A}\times\vec{\sigma}$$

$$\Rightarrow [\vec{\sigma}, \vec{\sigma}\bullet\vec{A}] = 2i\vec{A}\times\vec{\sigma}$$

- $[\vec{\sigma}, \vec{L}] = 0$, since σ and ***L*** belongs to different space.

$[\vec{\sigma}, \vec{\sigma}\bullet\vec{L}] = 2i\vec{L}\times\vec{\sigma} \neq 0$

$[\vec{L}, \vec{\sigma}\bullet\vec{L}] = i\hbar\vec{\sigma}\times\vec{L} \neq 0$ (can be proved using commutation relation for ***S*** &***L***)

$[\vec{J}, \vec{\sigma}\bullet\vec{L}] = [\vec{L}, \vec{\sigma}\bullet\vec{L}] + \hbar/2[\vec{\sigma}, \vec{\sigma}\bullet\vec{L}] = 0$

$[\vec{J}, \vec{L}^2] = [\vec{L}, \vec{L}^2] + [\vec{S}, \vec{L}^2] = 0; [\vec{J}, \vec{S}^2] = [\vec{L}, \vec{S}^2] + [\vec{S}, \vec{S}^2] = 0$

- {***J*,*L*.*S*,*L*^{2},*S*^{2}**} are commute, one can choose {***J*,*L*^{2},*S*^{2}**} as complete set !

Spin-orbit interaction

$$\mathbf{B} = -\frac{1}{c^2}\mathbf{v}\times\mathbf{E}\,. \tag{2.45}$$

(e.g., Griffths eqn 10.120)

$$\mathbf{E} = \frac{1}{e}\frac{\partial V}{\partial r}\frac{\mathbf{r}}{r}\,. \tag{2.46}$$

$$\mathbf{B} = \frac{1}{m_e c^2}\left(\frac{1}{er}\frac{\partial V}{\partial r}\right)\mathbf{r}\times m_e\mathbf{v} = \frac{\hbar}{m_e c^2}\left(\frac{1}{er}\frac{\partial V}{\partial r}\right)\mathbf{l}\,, \tag{2.47}$$

where $\hbar\mathbf{l} = \mathbf{r}\times m_e\mathbf{v}$

$$\begin{aligned} H &= -\boldsymbol{\mu}\cdot\mathbf{B} \\ &= g_s\mu_B\mathbf{s}\cdot\frac{\hbar}{m_e c^2}\left(\frac{1}{er}\frac{\partial V}{\partial r}\right)\mathbf{l}\,. \end{aligned} \tag{2.48}$$

Bohr magneton ($\mu_B = e\hbar/2m_e$)

Thomas precession— replacing g_s with $g_s - 1 \simeq 1$ (e.g. Appendix C of Eisberg & Resnick)

$$H_{s-o} = (g_s - 1)\frac{\hbar^2}{2m_e^2c^2}\left(\frac{1}{r}\frac{\partial V}{\partial r}\right)\mathbf{s}\cdot\mathbf{l}\,. \tag{2.49}$$

$$\frac{1}{r}\frac{\partial V}{\partial r} = \frac{e^2/4\pi\epsilon_0}{r^3}\,. \qquad (2.50)$$

$$E_{\mathrm{s-o}} = \frac{\hbar^2}{2m_{\mathrm{e}}^2c^2}\,\frac{e^2}{4\pi\epsilon_0}\left\langle\frac{1}{r^3}\right\rangle\langle\mathbf{s}\cdot\mathbf{l}\rangle\,. \qquad (2.51)$$

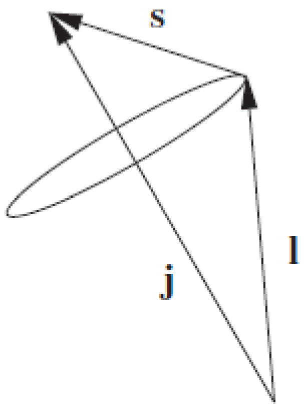
$$\left\langle\frac{1}{r^3}\right\rangle = \int_0^\infty \frac{1}{r^3}R_{n,l}^2\,(r)\,r^2\,\mathrm{d}r = \frac{1}{l\left(l+\frac{1}{2}\right)(l+1)}\left(\frac{Z}{na_0}\right)^3\,. \qquad (2.23)$$

$$\langle\mathbf{s}\cdot\mathbf{l}\rangle = \frac{1}{2}\left\{j\,(j+1) - l\,(l+1) - s\,(s+1)\right\}. \qquad (2.53)$$

$$E_{\mathrm{s-o}} = \frac{\beta}{2}\left\{j\,(j+1) - l\,(l+1) - s\,(s+1)\right\}, \qquad (2.54)$$

$$\beta = \frac{\hbar^2}{2m_{\mathrm{e}}^2c^2}\,\frac{e^2}{4\pi\epsilon_0}\,\frac{1}{(na_0)^3\,l\left(l+\frac{1}{2}\right)(l+1)}\,. \qquad (2.55)$$

$$\begin{aligned}\Delta E_{\mathrm{s-o}} &= E_{j=l+\frac{1}{2}} - E_{j=l-\frac{1}{2}}\\ &= \beta\left(l+\tfrac{1}{2}\right) = \frac{\alpha^2 hcR_\infty}{n^3l\,(l+1)}\,. \qquad (2.56)\\ &= \frac{\alpha^2}{n\,l\,(l+1)}E\,(n)\,.\end{aligned}$$



$$\mathbf{j} = \mathbf{l} + \mathbf{s}\,.$$

s=1/2

$$j = l + \frac{1}{2} \quad \text{or} \quad l - \frac{1}{2}\,.$$

Electronic configuration after L-S coupling

for $n = 2$ and $l = 1$

Before L-S coupling: $2\mathrm{p}$

$j = 1/2$ and $j = 3/2$

After L-S coupling: $2\mathrm{p}\,{}^2\mathrm{P}_{1/2}$ and $2\mathrm{p}\,{}^2\mathrm{P}_{3/2}$

Here we introduce Russell Saunders notation

$$^{2S+1}L_J$$

Transitions between fine-structure levels

Examples of allowed transitions:

$$2\,\mathrm{P}_{3/2} - 3\,\mathrm{S}_{1/2}\,,$$
$$2\,\mathrm{P}_{3/2} - 3\,\mathrm{D}_{3/2}\,,$$
$$2\,\mathrm{P}_{3/2} - 3\,\mathrm{D}_{5/2}\,,$$
$$2\,\mathrm{S}_{1/2} - 3\,\mathrm{P}_{1/2}\,,$$
$$2\,\mathrm{P}_{1/2} - 3\,\mathrm{S}_{1/2}\,,$$
$$2\,\mathrm{S}_{1/2} - 3\,\mathrm{P}_{3/2}\,,$$
$$2\,\mathrm{P}_{1/2} - 3\,\mathrm{D}_{3/2}\,.$$

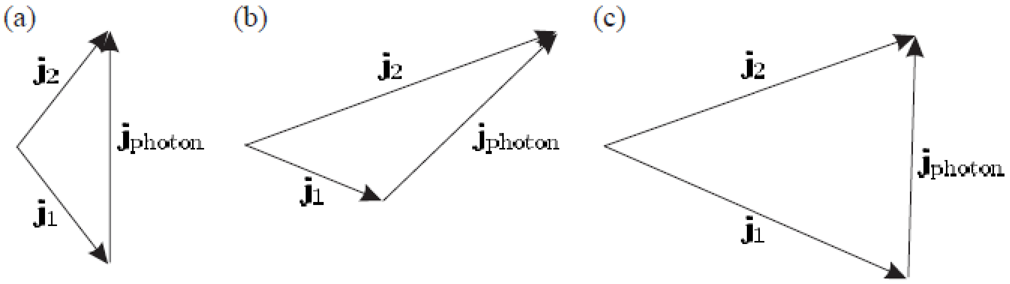
$$\Delta l = \pm 1$$

$$\Delta j = 0, \pm 1.$$

$$\Delta m_j = 0, \pm 1.$$

Selection rules summary

Electric dipole transitions	Magnetic dipole transitions
$\Delta J = 0, \pm 1$ (but not $J = 0$ to $J' = 0$)	$\Delta J = 0, \pm 1$ (but not $J = 0$ to $J' = 0$)
$\Delta M_J = 0, \pm 1$	$\Delta M_J = 0, \pm 1$
Parity change	No parity change
$\Delta l = \pm 1$	$\Delta l = 0$ } No change of
Any Δn	$\Delta n = 0$ } configuration
$\Delta L = 0, \pm 1$	$\Delta L = 0$
$\Delta S = 0$	$\Delta S = 0$



Relativistic correction

$$E_{kin} = \frac{\vec{p}^2}{2m} \to E_{kin,re} = \sqrt{m^2c^4 + c^2p^2} - mc^2$$

$$E_{kin,re} = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \cdots = E_{kin,nr} - \Delta E_{re}$$

$$\Delta E_{re} = \frac{\hbar^4}{8m^3c^2}\int \psi^*_{nlm}\nabla^4\psi_{nlm}d^3r = E_{nr}\ \frac{Z\alpha^2}{n}[\frac{3}{4n} - \frac{1}{l+1/2}]$$

(left as a homework)

So up to now we have Hamiltonian

$$H = \frac{\vec{p}^2}{2m} + V(r) \underbrace{- \frac{\vec{p}^4}{8m^3c^2}}_{\text{relativistic kinetic}} + \underbrace{\frac{\hbar^2}{2m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{l}\cdot\vec{s}}_{\text{L-S coupling}}$$

Darwin term

- Due to zitterbewegung tumbling motion
- Exist only for *l*=0 states with non-zero wavefunction at *r* = 0.
- This term follows from Dirac equation
- No classical analogue
- cf Sakurai “Advanced Quantum Mechanics” 3-3 & 3-7.

$$H_D = -\frac{\hbar^2}{8m^2c^2}\nabla^2 V(r), \quad \text{where} \quad V(r) = -\frac{Ze^2}{r}$$

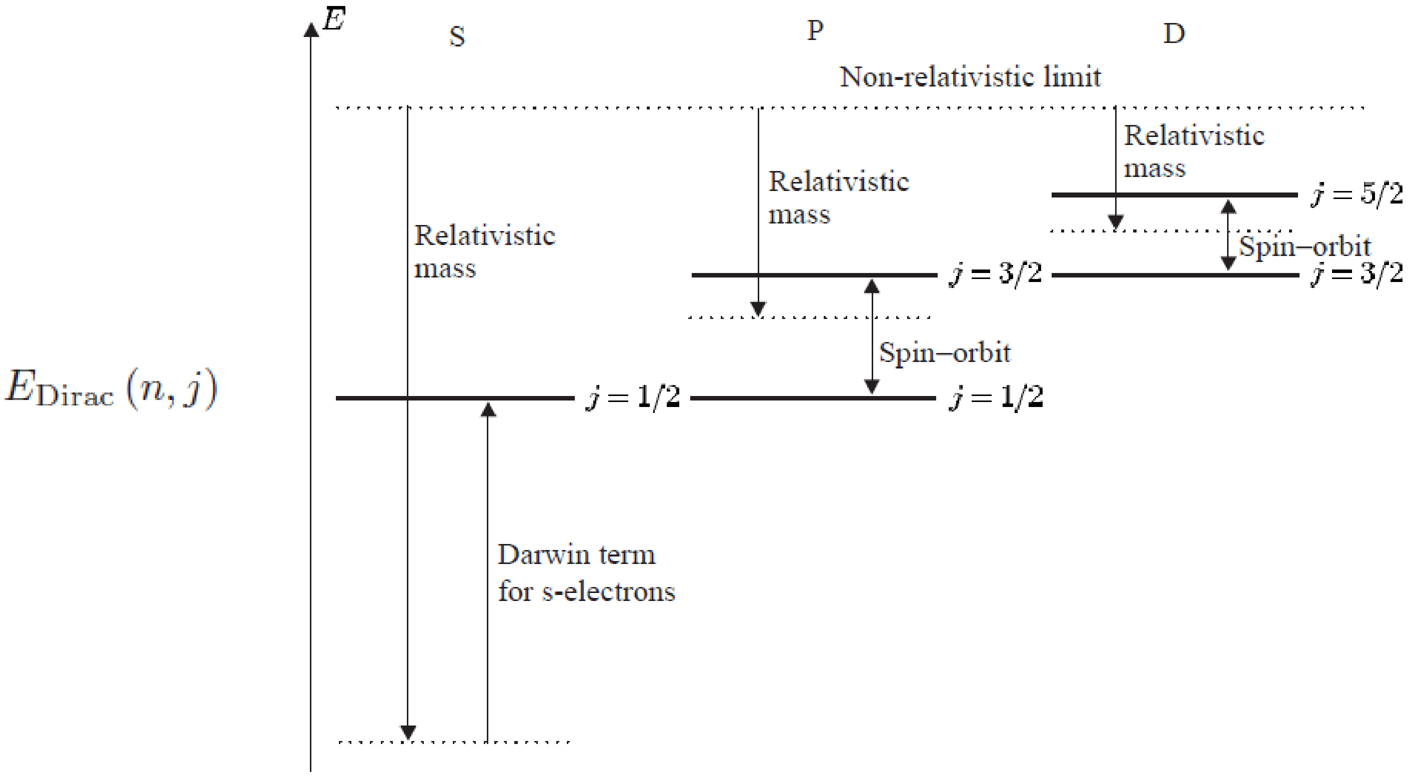
$$H_D = \frac{Ze^2\hbar^2}{8m^2c^2}\delta^{(3)}(\vec{r})$$

$$\langle\psi(r)|H_D|\psi(r)\rangle = \frac{Ze^2\hbar^2}{8m^2c^2}|\psi(0)|^2$$

$$\langle H_D\rangle_{n00} = (Z\alpha)^4 mc^2 \frac{1}{2n^3} = E_n\frac{Z^2\alpha^2}{n}$$

Where fine structure constant $\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$

Hydrogen structure given by the Dirac equation



$$H = \frac{\vec{p}^2}{2m} + V(r) - \frac{\vec{p}^4}{8m^3c^2} + \frac{\hbar^2}{2m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{l}\cdot\vec{s} + \frac{Ze^2\hbar^2}{8m^2c^2}4\pi\delta^{(3)}(\vec{r})$$

$$E_{n,j} = E_n[1 + \frac{Z^2\alpha^2}{n}(\frac{1}{j+1/2} - \frac{3}{4n})]$$

Lamb shift

Fluctuations in the EM fields associated with the vacuum is a perturbation of the electron in an H atom from the standard orbits of the Coulomb potential $-e^2/4\pi\varepsilon_0 r$ due to the proton.

$$\Delta V = V(\mathbf{r}+\delta\mathbf{r}) - V(\mathbf{r})$$

$$= \delta\mathbf{r}\cdot\nabla V + \frac{1}{2}(\delta\mathbf{r}\cdot\nabla)^2 V + \ldots$$

The fluctuations are isotropic, $\langle \delta\mathbf{r} \rangle_{vac} = 0,$ the first term can be neglected. Moreover,

due to the isotropy again, $\left\langle (\delta\mathbf{r}\cdot\nabla)^2 \right\rangle_{vac} = \frac{1}{3}\left\langle \delta\mathbf{r}^2 \right\rangle_{vac} \nabla^2.$ Therefore

$$\langle \Delta V \rangle = \frac{1}{6}\left\langle \delta\mathbf{r}^2 \right\rangle_{vac} \left\langle \nabla^2 \frac{-e^2}{4\pi\varepsilon_0 r} \right\rangle_{at}$$

$$\left\langle \nabla^2 \frac{-e^2}{4\pi\varepsilon_0 r} \right\rangle_{at} = \frac{-e^2}{4\pi\varepsilon_0} \int d\mathbf{r}\, \psi^*_{2s}(\mathbf{r}) \nabla^2 \frac{1}{r} \psi_{2s}(\mathbf{r})$$

$$= \frac{e^2}{\varepsilon_0} \left| \psi_{2s}(0) \right|^2 = \frac{e^2}{8\pi\varepsilon_0 a^3}$$

Here we use

$$a_0 = 4\pi\varepsilon_0 \hbar^2 / me^2$$

$$\nabla^2 \frac{1}{r} = -4\pi\delta(\mathbf{r})$$

$$\psi_{2s}(0) = \frac{1}{(8\pi a_0^3)^{1/2}}$$

Lamb shift

Next we consider the contribution $\left\langle \delta \mathbf{r}^2 \right\rangle_{vac}$ due to the vacuum fluctuations. The classical equation of motion for the electron displacement $\left\langle \delta \mathbf{r} \right\rangle_{\mathbf{k}}$ induced by a single mode of the field of wave vector **k** and the frequency ν is

$$m \frac{d^2}{dt^2} \left\langle \delta \mathbf{r} \right\rangle_{\mathbf{k}} = -eE_{\mathbf{k}}$$

Use ansatz: $\delta r(t) \cong \delta r(0) e^{i\nu t} + \text{c.c.}$

Given the quantized field $E_{\mathbf{k}} = \sum_{\mathbf{k}} \sqrt{\frac{\hbar c k}{2\varepsilon_0 V}} (\hat{a}_{\mathbf{k}} e^{-i(\mathbf{k}\cdot\mathbf{r}-\nu t)} + \text{c.c.})$

$$\left\langle (\delta \mathbf{r})^2 \right\rangle_{vac} = \sum_{\mathbf{k}} (\frac{e^2}{mc^2k^2})^2 \left\langle 0 \right| E_{\mathbf{k}}^2 \left| 0 \right\rangle$$

$$= \sum_{\mathbf{k}} (\frac{e^2}{mc^2k^2})^2 \frac{\hbar c k}{2\varepsilon_0 V}$$

Replace the sum with an integral

$$\left\langle (\delta \mathbf{r})^2 \right\rangle_{vac} = 2 \frac{V}{(2\pi)^3} 4\pi \int (\frac{e^2}{mc^2k^2})^2 \frac{\hbar c k}{2\varepsilon_0 V} k^2 dk$$

Lamb shift

Take the integration limits as follows:

(wavelength shorter than the Bohr orbit)

$\nu > c/a_0$ or $k > 1/a_0$

(wavelength longer than the Compton wavelength)

$\hbar k < mc$ or $k < mc/\hbar$

$$\left\langle (\delta \mathbf{r})^2 \right\rangle_{vac} \cong \frac{1}{2\varepsilon_0 \pi^2} \frac{e^2}{\hbar c} \left(\frac{\hbar}{mc}\right)^2 \ln \frac{1}{\alpha}$$

$$\left\langle \Delta V \right\rangle = \frac{4}{3} \frac{e^2}{4\pi\varepsilon_0} \frac{e^2}{4\pi\varepsilon_0 \hbar c} \left(\frac{\hbar}{mc}\right)^2 \frac{1}{8\pi a_0^3} \ln \frac{1}{\alpha}$$

$$= \frac{mc^2 \alpha^5}{6\pi} \ln \frac{1}{\alpha}$$

$$\cong 1 \text{ GHz}$$

We have used

$$\alpha = \frac{e^2 / 4\pi\varepsilon_0}{\hbar c}$$

$$a_0 = \frac{\hbar}{mc\alpha}$$

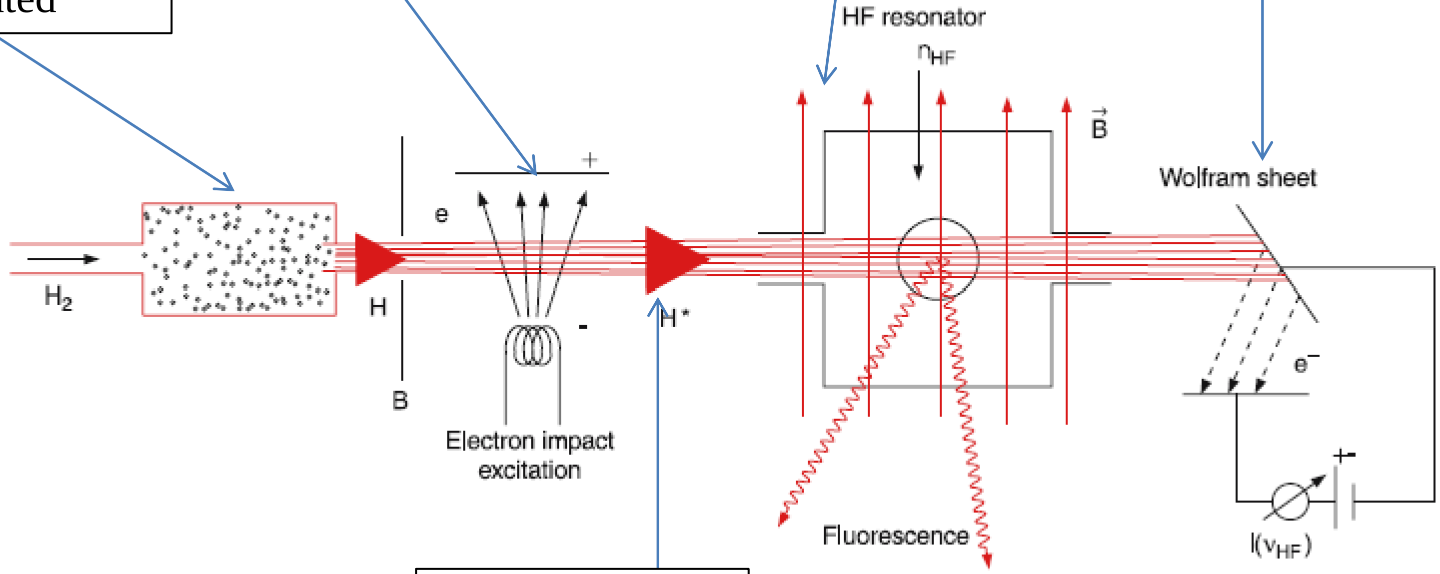
Lamb-Retherford Experiment

Oven T~2500K
64% H_2 molecules disassociated

Electron beam w/ ~ 10.2 eV; excite H to n=2

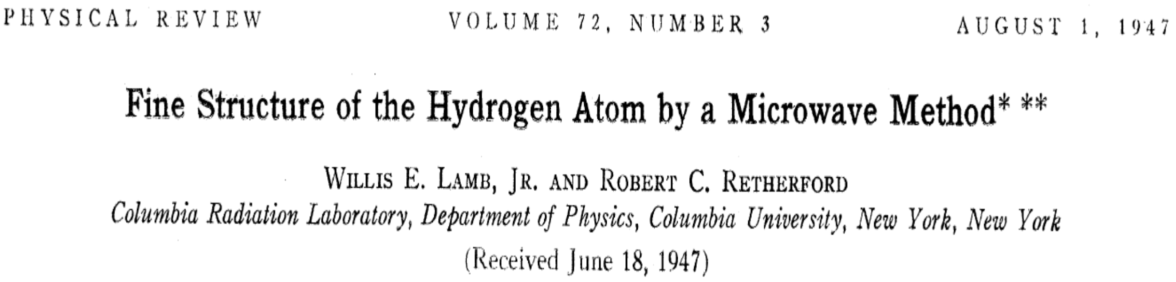
B field tuning & radio wave to drive $2S_{1/2} \rightarrow 2P_{3/2}$ transitions, followed by fast decay to deplete $2S_{1/2}$ population

W metal plate
W ionization energy E(I)~ 10.2 eV,
can detect $2S_{1/2}$ H



H in meta-stable $2S_{1/2}$ state

Resolution is limited by the 2*p* state linewidth ~ 100 MHz (1/lifetime of 2*p* state)

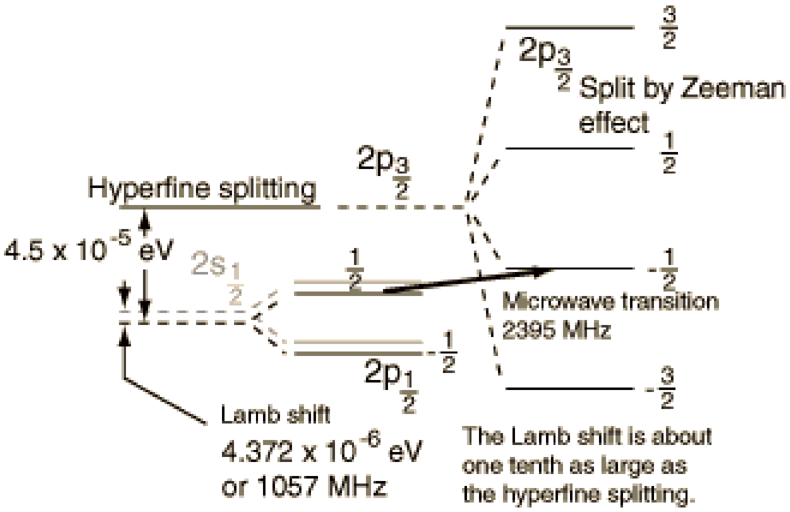


PHYSICAL REVIEW VOLUME 72, NUMBER 3 AUGUST 1, 1947

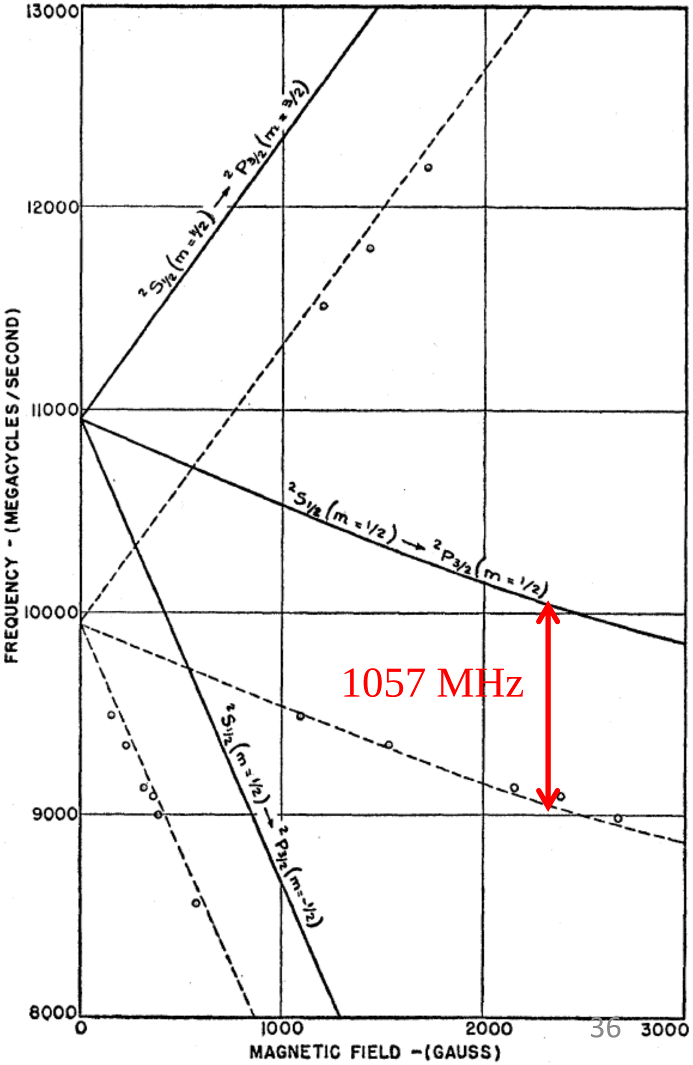
Fine Structure of the Hydrogen Atom by a Microwave Method* **

WILLIS E. LAMB, JR. AND ROBERT C. RETHERFORD
Columbia Radiation Laboratory, Department of Physics, Columbia University, New York, New York

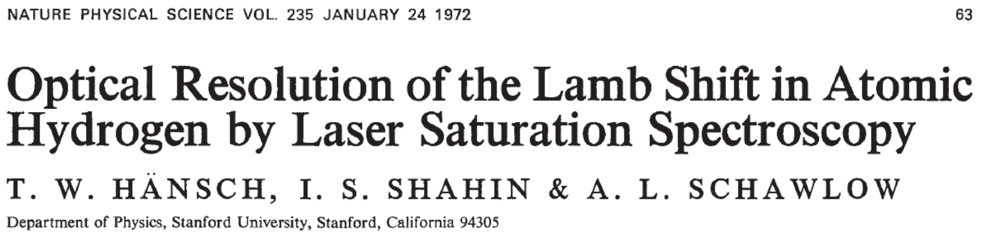
(Received June 18, 1947)



The Lamb shift is about one tenth as large as the hyperfine splitting.



Measuring Lamb shift using a laser



NATURE PHYSICAL SCIENCE VOL. 235 JANUARY 24 1972 63

Optical Resolution of the Lamb Shift in Atomic Hydrogen by Laser Saturation Spectroscopy

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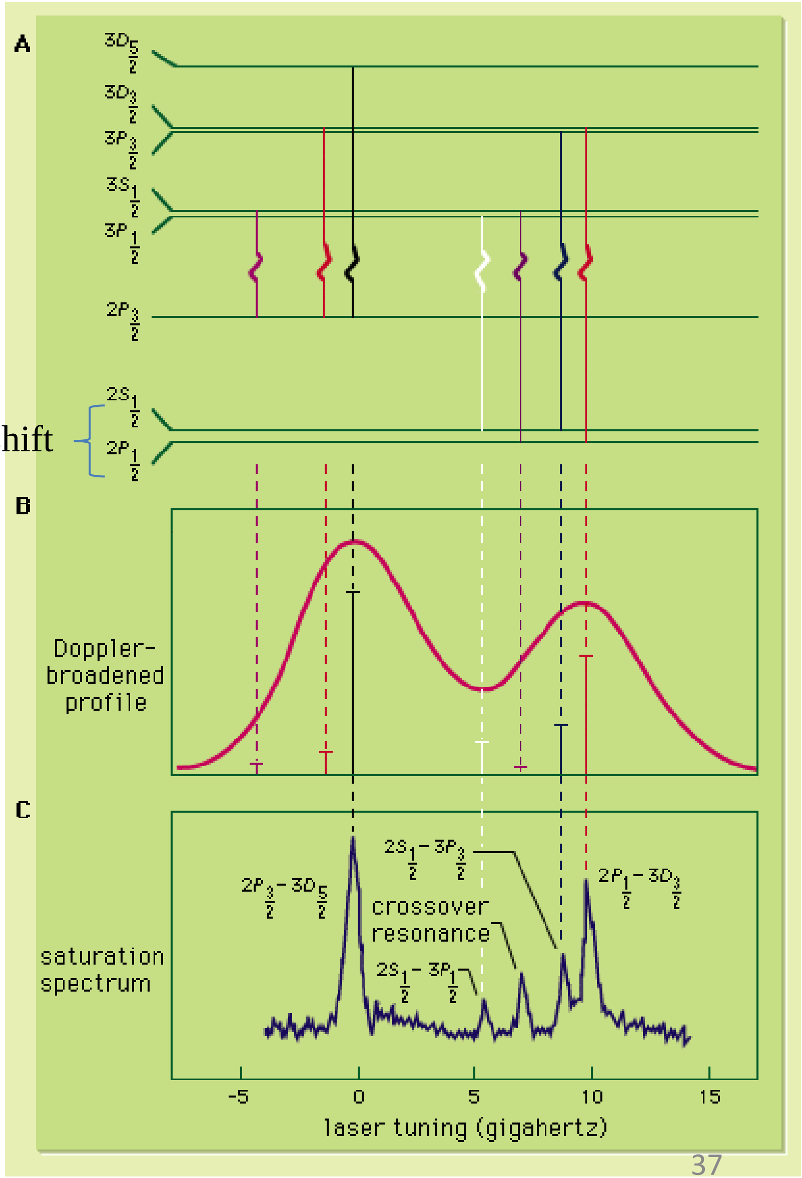
Department of Physics, Stanford University, Stanford, California 94305

- Hydrogen excited in a discharge lamp
- Saturation spectroscopy : eliminate Doppler broadening, and H_α (Balmer line) fine structure was resolved

Lamb shift ~

$$E(^3P_{3/2} \rightarrow {}^2S_{1/2}) - E(^3D_{3/2} \rightarrow {}^2P_{1/2})$$

Many more Lamb shift were measured later, utilizing laser spectroscopy techniques, such as two-photon transition for E(1s → 2s).



Lamb shift

Helium

Multi-electron Atoms

We wish to address the following issues:

- The role of identical particles: bosons, fermions, and symmetry requirements for the total wavefunction of electrons.
- Theoretical models for multi-electron atoms
- Electron configuration and coupling of angular momenta
- Periodic Table
- Excited states of multi-electron atoms

Helium Atom

- Study in detail the implication of Pauli exclusion principle.
- Various approximations used in atomic structure calculations can be explained most easily and tested accurately.

Identical Particles (1/2)

- Identical particles are indistinguishable for their internal states are quantized, and their quantum numbers (rest mass, charge, spin, lifetime…) are the same.
- For a many-body system containing many identical particles, permutation symmetry arises, such that the Hamiltonian is unchanged under exchange of two particles, e.g.,

$$H = \frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{|\vec{r}_1|} - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{|\vec{r}_2|} + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

$$P_{12}\,|q_1, q_2> \equiv |q_2, q_1>; [P_{12}, H] = 0$$

- The permutation operator commutes with the Hamiltonian and it is a constant of motion. Then a eigenstate of ***H*** *is also a eigenstate of* ***P***$\boldsymbol{P_{12}}$ *with eigenvalues +1 or* – 1 for operator $\boldsymbol{P_{12}}$.

$$P_{ij}\psi(q_1, q_2, \ldots q_i, \ldots q_j \ldots q_N) \equiv \psi(q_1, q_2, \ldots q_j, \ldots q_i \ldots q_N) = \lambda\psi$$

$$P_{ij}^2\psi = \psi = \lambda^2\psi \Rightarrow \lambda = \pm 1$$

- The symmetric or antisymmetric wavefunction with eigenvalus of 1 and -1 for P_{12} are

$$|k'k''>_+ = 1/\sqrt{2}(|k'>|k''> + |k''>|k'>)$$

$$|k'k''>_- = 1/\sqrt{2}(|k'>|k''> - |k''>|k'>)$$

k are a collection of quantum number

Identical Particles (2/2)

- Natural particles can be categorized into two types:
- *Pij |N identical bosons>=|N identical bosons>,* ***Bose-Einstein statistics***
- *Pij| N identical fermions> = -| N identical fermions>,* ***Fermi-Dirac statistics***
- Pauli **spin-statistics theorem:** Half-integer spin particles cannot be bosons. Integer spin particles cannot be fermions.
- Particles can be **composite,** not just elementary particles!
- For a system of two fermions occupying two states, *k' and k",* there is only one allowed state $\frac{1}{\sqrt{2}}\left(|k'\rangle|k''\rangle - |k''\rangle|k'\rangle\right)$
- For a system of two bosons occupying two, k' and k'', there are three allowed states:

$$|k'\rangle|k'\rangle, \; |k''\rangle|k''\rangle, \; \frac{1}{\sqrt{2}}\left(|k'\rangle|k''\rangle + |k''\rangle|k'\rangle\right)$$

- Pauli exclusion principle: no two fermions can occupy the same states.
- Symmerty requirement determines the possible number of atoms occupying the same state with occupation number n. For fermion n= 0 or 1; for boson n= 0,1,2…
- This property sets the quantum statistics!

Helium atom

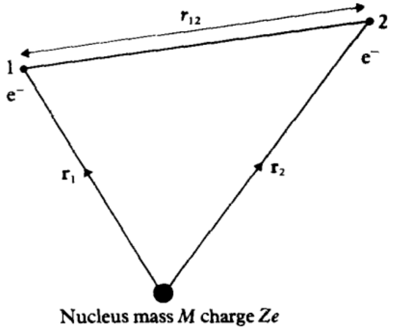
The Schrodinger equation for two electrons in the Coulomb potential of a charge *Ze is*,

$$\left[\frac{-\hbar^2}{2\mu}\nabla_{\mathbf{r}_1}^2+\frac{-\hbar^2}{2\mu}\nabla_{\mathbf{r}_2}^2+\frac{-\hbar^2}{M}\nabla_{\mathbf{r}_1}\cdot\nabla_{\mathbf{r}_2}-\frac{Ze^2}{4\pi\varepsilon_0 r_1}-\frac{Ze^2}{4\pi\varepsilon_0 r_2}+\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right]\psi(r_1,r_2)=E\psi(r_1,r_2)$$

Mass polarization term, $\frac{-\hbar^2}{M}\nabla_{\mathbf{r}_1}\cdot\nabla_{\mathbf{r}_2}$, is small and can be omitted.

Assume M is infinite, then $\mu = m.$

$$\left\{\frac{-\hbar^2}{2m}\nabla_1^2+\frac{-\hbar^2}{2m}\nabla_2^2+\frac{e^2}{4\pi\epsilon_0}\left(-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_{12}}\right)\right\}\psi = E\psi\,. \qquad (3.1)$$



The Hamiltonian is unchanged under permutation operation.

According to slide #2, the symmetrized wave functions are such that

$$\psi(\mathbf{r}_2,\,\mathbf{r}_1) = \pm\psi(\mathbf{r}_1,\,\mathbf{r}_2)$$

"+": space symmetric, para state
"-": space anti-symmetric, orth state

Approx. I: independent particle model

Separate the Hamiltonian into

$$H = H_0 + H',$$

$$H_0 = \left(\frac{-\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{Z}{r_1}\right) + \left(\frac{-\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{Z}{r_2}\right) = H_1 + H_2$$

$$H' = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{12}}\right) \quad \text{(perturbation)}$$

Later we will see that H' is not very small compared to H_0.

Unperturbed solution

Unperturbed Schrodinger eqn.

$$(H_1 + H_2)\,\psi = E^{(0)}\psi\,, \tag{3.2}$$

where

$$H_1 \equiv \frac{-\hbar^2}{2m}\nabla_1^2 - \frac{Z\,e^2}{4\pi\epsilon_0 r_1} \tag{3.3}$$

Write the atomic wavefunction as $\psi = \psi(1)\,\psi(2),$ then eqn. (3.2) can be separated into

$$H_1\psi(1) = E_1\psi(1) \tag{3.4}$$

and a similar eqn. for $\psi(2)$ with eigenvalue E_2.

For Helium Z=2, and the ground state energy $E_1 = E_2 = -4hcR_\infty = -54.4$ eV.

The total energy is $$E^{(0)} = E_1 + E_2 = -109\,\mathrm{eV}\,. \tag{3.5}$$

Perturbed solution

$$\psi_{1s^2} = R_{1s}^{Z=2}(r_1)\, R_{1s}^{Z=2}(r_2) \times \frac{1}{4\pi}\,, \qquad (3.6)$$

with $R_{1,0} = \left(\frac{Z}{a_0}\right)^{3/2} 2\,\mathrm{e}^{-\rho}$, (Table 2.2)

$$<H'> = \frac{e^2}{4\pi\epsilon_0}\int_0^\infty\int_0^\infty \psi^*_{1s^2}\,\frac{1}{r_{12}}\psi_{1s^2}\, r_1^2\,\mathrm{d}r_1\, r_2^2\,\mathrm{d}r_2 = 34\,\mathrm{eV}\,. \qquad (3.7)$$

(see slide 9-13 for detailed calculations)

$E(1s^2)$ = -109 + 34 = -75 eV. (energy takes for: He → He^{++}).

$E(He^+ \rightarrow He^{++}) = -4hcR_\infty = -54.4$ eV. (2^{nd} ionization energy)

$E(He \rightarrow He^+) \approx 75 - 54.4 = 21$ eV. (1^{st} ionization energy)

The measured 1st ionization energy, 24.6 eV.

Better solution is needed…

A general solution

Let’s consider one electron is excited to state (*n*, *l*, *m*), then the unperturbed single-particle spatial wavefunctions are

$$u_{1\mathrm{s}}(1) = R_{1\mathrm{s}}(r_1) \times \frac{1}{\sqrt{4\pi}},$$
$$u_{nl}(2) = R_{nl}(r_2) Y_{l,m}(\theta_2, \phi_2)$$

An easy total spatial wavefunction is

$$\psi_{\mathrm{space}} = u_{1\mathrm{s}}(1) u_{nl}(2) \,. \qquad (3.8)$$

$$\psi_{\mathrm{space}} = u_{1\mathrm{s}}(2) u_{nl}(1) \,. \qquad (3.9)$$

A general expression for the total spatial wavefunction is

$$\psi = a\, u_{1\mathrm{s}}(1) u_{nl}(2) + b\, u_{1\mathrm{s}}(2) u_{nl}(1) \,. \qquad (3.13)$$

General formalism for perturbation

$$(H_0 + H')\,\psi = E\psi\,, \tag{3.10}$$

$$E^{(0)} = E_1 + E_2 \qquad H_0\psi = E^{(0)}\psi\,, \tag{3.11}$$

$$\Delta E = E - E^{(0)} \qquad H'\psi = \Delta E\,\psi\,. \tag{3.12}$$

$$\psi = a\,u_{1\mathrm{s}}(1)u_{nl}(2) + b\,u_{1\mathrm{s}}(2)u_{nl}(1)\,. \tag{3.13}$$

$$\begin{pmatrix} J & K \\ K & J \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \Delta E \begin{pmatrix} a \\ b \end{pmatrix}. \tag{3.14}$$

$$\begin{aligned} J &= \frac{1}{4\pi\epsilon_0}\iint |u_{1\mathrm{s}}(1)|^2\,\frac{e^2}{r_{12}}\,|u_{nl}(2)|^2\,\mathrm{dr}_1^3\,\mathrm{dr}_2^3 \\ &= \frac{1}{4\pi\epsilon_0}\iint \frac{\rho_{1\mathrm{s}}(r_1)\rho_{nl}(r_2)}{r_{12}}\,\mathrm{dr}_1^3\,\mathrm{dr}_2^3\,, \end{aligned} \tag{3.15}$$

$$\rho_{1\mathrm{s}}(1) = -e\,|u_{1\mathrm{s}}(1)|^2$$

$$K = \frac{1}{4\pi\epsilon_0}\iint u_{1\mathrm{s}}^*(1)u_{nl}^*(2)\,\frac{e^2}{r_{12}}\,u_{1\mathrm{s}}(2)u_{nl}(1)\,\mathrm{dr}_1^3\,\mathrm{dr}_2^3\,. \tag{3.16}$$

(exchange integral)

Solve for the eigen equations:

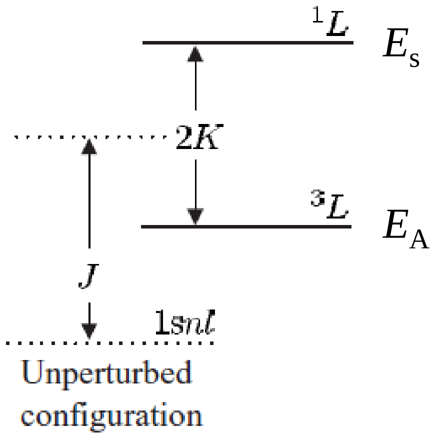
$$\begin{vmatrix} J - \Delta E & K \\ K & J - \Delta E \end{vmatrix} = 0 . \qquad (3.17)$$

$$\Delta E = J \pm K .$$

$$\psi^{\mathrm{S}}_{\mathrm{space}} = \frac{1}{\sqrt{2}} \{ u_{1\mathrm{s}}(1) u_{nl}(2) + u_{1\mathrm{s}}(2) u_{nl}(1) \} , \quad E^{(0)} + J + K$$

$$\psi^{\mathrm{A}}_{\mathrm{space}} = \frac{1}{\sqrt{2}} \{ u_{1\mathrm{s}}(1) u_{nl}(2) - u_{1\mathrm{s}}(2) u_{nl}(1) \} . \quad E^{(0)} + J - K$$

$E_s - E_A = 2K$



Electrons obey Pauli exclusion principle, and the total wavefunction must be antisymmetric,

$$\psi = \psi^{\mathrm{S}}_{\mathrm{space}} \psi^{\mathrm{A}}_{\mathrm{spin}} \quad \text{or} \quad \psi^{\mathrm{A}}_{\mathrm{space}} \psi^{\mathrm{S}}_{\mathrm{spin}} . \qquad (3.18)$$

Spin wave functions: χ

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2, \text{ and } S_z = S_{1,z} + S_{2,z}; \quad S_z \chi = M_S \chi$$

$$\mathbf{S}^2 = \mathbf{S}_1^2 + \mathbf{S}_2^2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2 = \frac{3}{2} + 2\mathbf{S}_1 \cdot \mathbf{S}_2 .$$

$$\mathbf{S}_1 \cdot \mathbf{S}_2 = S_{1,z} S_{2,z} + \tfrac{1}{2}(S_1^+ S_2^- + S_1^- S_2^+),$$

$$S_1^{\pm} = S_x \pm i S_y .$$

Spin function χ	$\boldsymbol{S}_z\chi$	$\boldsymbol{S}^2\chi$
$\chi_1(1,2) = \lvert\uparrow\uparrow\rangle$	χ_1	$2\chi_1$
$\chi_2(1,2) = \lvert\uparrow\downarrow\rangle$	0	$\chi_2+\chi_3$
$\chi_3(1,2) = \lvert\downarrow\uparrow\rangle$	0	$\chi_2+\chi_3$
$\chi_4(1,2) = \lvert\downarrow\downarrow\rangle$	$-\chi_4$	$2\chi_4$

χ_2 and χ_3 are not the eigen states of $\boldsymbol{S}^2$

	Spin function	$\boldsymbol{S}$	$\boldsymbol{M_S}$
singlet: Ψ^A_{spin}	$\chi_{0,0} = 1/\sqrt{2}\ [\ \lvert\uparrow\downarrow\rangle - \lvert\downarrow\uparrow\rangle\ ]$	*0*	*0*
triplet: Ψ^S_{spin}	$\chi_{1,1} = \lvert\uparrow\uparrow\rangle$	1	*0*
	$\chi_{1,0} = 1/\sqrt{2}\ [\ \lvert\uparrow\downarrow\rangle = \lvert\downarrow\uparrow\rangle\ ]$	1	*0*
	$\chi_{1,-1} = \lvert\downarrow\downarrow\rangle$	*1*	*-1*

after symmetrization
eigenstates of $\boldsymbol{S}^2$ operator!

Ground state

$$V_{12}\left(r_2\right)=\int_0^{r_2}\frac{1}{4\pi\epsilon_0 r_{12}}\rho(r_1)\,\mathrm{d}^3\mathbf{r}_1\,. \tag{3.21}$$

$$V_{12}\left(r_2\right)=\frac{Q\left(r_2\right)}{4\pi\epsilon_0 r_2}\,,$$

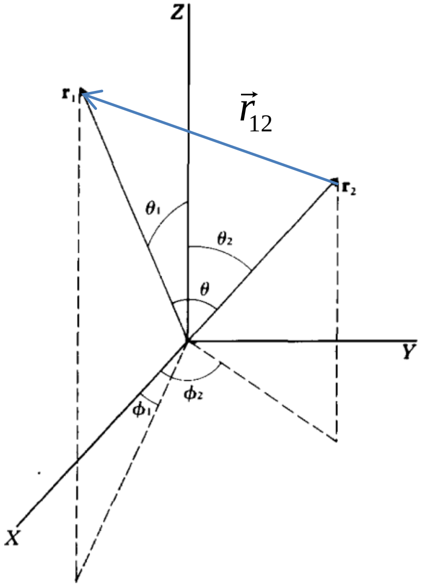
$$Q\left(r_2\right)=\int_0^{r_2}\rho\left(r_1\right)4\pi r_1^2\,\mathrm{d}r_1\,. \tag{3.22}$$

$$E_{12}=\int_0^{\infty}V_{12}\left(r_2\right)\rho\left(r_2\right)4\pi r_2^2\,\mathrm{d}r_2\,. \tag{3.23}$$

$$\begin{aligned}J_{1\mathrm{s}^2}&=2\times\frac{e^2}{4\pi\epsilon_0}\int_0^{\infty}\left\{\int_0^{r_2}\frac{1}{r_1}4Z^3\mathrm{e}^{-(Z/a_0)2r_1}r_1^2\,\mathrm{d}r_1\right\}4Z^3\mathrm{e}^{-(Z/a_0)2r_2}r_2^2\,\mathrm{d}r_2\\&=\frac{e^2/4\pi\epsilon_0}{2a_0}\frac{5}{4}Z=(13.6\,\mathrm{eV})\times\frac{5}{4}Z\,.\end{aligned} \tag{3.24}$$

For helium this gives $J_{1\mathrm{s}^2}^{Z=2}=34\,\mathrm{eV}$.

Useful formula



$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{(r_<)^l}{(r_>)^{l+1}} P_l(\cos\theta)$$

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} \frac{(r_<)^l}{(r_>)^{l+1}} Y^*_{lm}(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2)$$

Let's compute electron interaction energy.

$$E_0^{(1)} = \int \left|\psi_{1s}(r_1)^2\right| \frac{e^2}{4\pi\varepsilon_0} \frac{1}{r_{12}} \left|\psi_{1s}(r_2)^2\right| d\vec{r}_1 d\vec{r}_2$$

$$\begin{aligned} E_0^{(1)} &= \frac{Z^6}{\pi^2} \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{(4\pi)^2}{2l+1} \int_0^{\infty} \mathrm{d}r_1 r_1^2 \int_0^{\infty} \mathrm{d}r_2 r_2^2 \exp[-2Z(r_1+r_2)] \frac{(r_<)^l}{(r_>)^{l+1}} \\ &\quad \times \int \mathrm{d}\Omega_1 Y^*_{lm}(\theta_1, \phi_1) Y_{00} \int \mathrm{d}\Omega_2 Y_{00} Y_{lm}(\theta_2, \phi_2) \\ &= \frac{Z^6}{\pi^2} \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{(4\pi)^2}{2l+1} \int_0^{\infty} \mathrm{d}r_1 r_1^2 \int_0^{\infty} \mathrm{d}r_2 r_2^2 \exp[-2Z(r_1+r_2)] \\ &\quad \times \frac{(r_<)^l}{(r_>)^{l+1}} \delta_{l,0}\, \delta_{m,0} \end{aligned}$$

$$E_0^{(1)} = 16Z^2 \int_0^{\infty} dr_1 r_1^2 \int_0^{\infty} dr_2 r_2^2 e^{-2Z(r_1+r_2)} \frac{1}{r_>}$$

$$= 16Z^2 \int_0^{\infty} dr_1 r_1^2 e^{-2Zr_1} \left[\frac{1}{r_1} \int_0^{r_1} dr_2 r_2^2 e^{-2Zr_2} + \int_0^{r_1} dr_2 r_2 e^{-2Zr_2} \right]$$

After some calculations,

$$\mathrm{E}_0^{(1)} = \frac{5}{8} \text{ a.u.}$$

$$1 \text{ a.u.} = \frac{e^2/4\pi\varepsilon_0}{a_0} = 27.2 \text{ eV}$$

Recall Hydrogenic atom energy

$$E_n = -\frac{1}{2}\frac{Z^2}{n^2} \quad \text{a.u.}$$

Excited states: the direct integral

Hamiltonian $H = H_{0a} + H'_a$

$$H_{0a} = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{r_1} + \frac{1}{r_2}\right) \tag{3.25}$$

→ due to screening

$$H'_a = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{12}} - \frac{1}{r_2}\right). \tag{3.26}$$

$$J_{1snl} = \frac{e^2}{4\pi\epsilon_0}\iint\left(\frac{1}{r_{12}} - \frac{1}{r_2}\right)\left|u_{1s}(1)\right|^2\left|u_{nlm}(2)\right|^2\,\mathrm{d}^3\mathbf{r}_1\,\mathrm{d}^3\mathbf{r}_2\,. \tag{3.27}$$

$$J_{1snl} = \frac{e^2}{4\pi\epsilon_0}\int_0^\infty\int_0^\infty J(r_1, r_2)\;R_{10}^2(r_1)R_{nl}^2(r_2)r_1^2\,\mathrm{d}r_1\,r_2^2\,\mathrm{d}r_2\,, \tag{3.28}$$

angular parts

$$J(r_1, r_2) = \int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi}\int_0^{\pi}\left(\frac{1}{r_{12}} - \frac{1}{r_2}\right)\frac{1}{4\pi}\left|Y_{lm}(\theta_2, \phi_2)\right|^2 \times \sin\theta_1\,\mathrm{d}\theta_1\,\mathrm{d}\phi_1\,\sin\theta_2\,\mathrm{d}\theta_2\,\mathrm{d}\phi_2\,. \tag{3.29}$$

$$J(r_1, r_2) = \begin{cases} 0 & \text{for } r_1 < r_2\,, \\ 1/r_1 - 1/r_2 & \text{for } r_1 > r_2\,. \end{cases}$$

$$J_{1snl} = \frac{e^2}{4\pi\epsilon_0}\int_0^\infty\left\{\int_{r_2}^\infty\left(\frac{1}{r_1} - \frac{1}{r_2}\right)R_{10}^2(r_1)r_1^2\,\mathrm{d}r_1\right\}R_{nl}^2(r_2)r_2^2\,\mathrm{d}r_2\,. \tag{3.31}$$

Excited states: the exchange integral

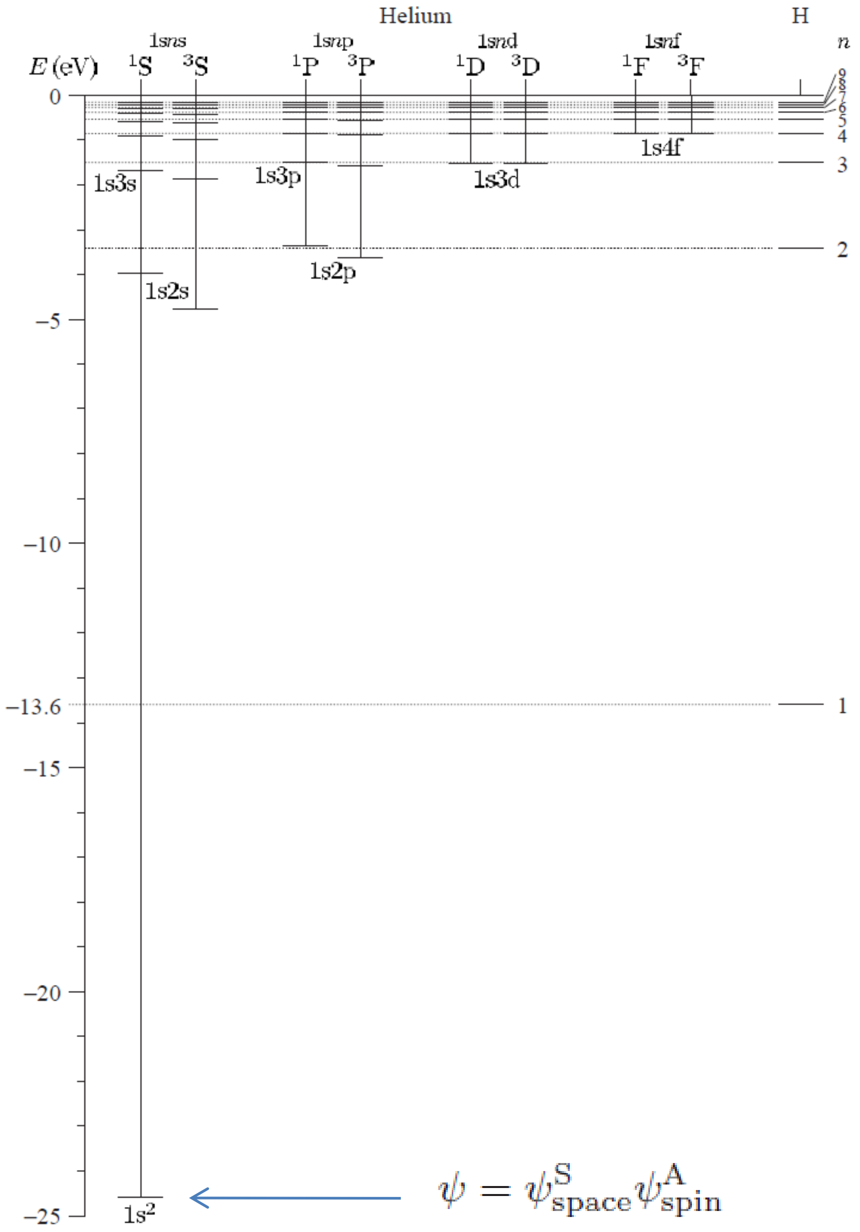
$$K_{1snl} = \frac{e^2}{4\pi\epsilon_0} \iint K(r_1, r_2) R_{1s}(r_1) R_{nl}(r_1) R_{1s}(r_2) R_{nl}(r_2) r_1^2 \, \mathrm{d}r_1 \, r_2^2 \, \mathrm{d}r_2 \, . \tag{3.32}$$

angular parts:

$$K(r_1, r_2) = \iiiint \frac{1}{r_{12}} Y_{lm}^*(\theta_1, \phi_1) \frac{1}{4\pi} Y_{lm}(\theta_2, \phi_2) \times \sin\theta_1 \, \mathrm{d}\theta_1 \, \mathrm{d}\phi_1 \, \sin\theta_2 \, \mathrm{d}\theta_2 \, \mathrm{d}\phi_2 \, . \tag{3.33}$$

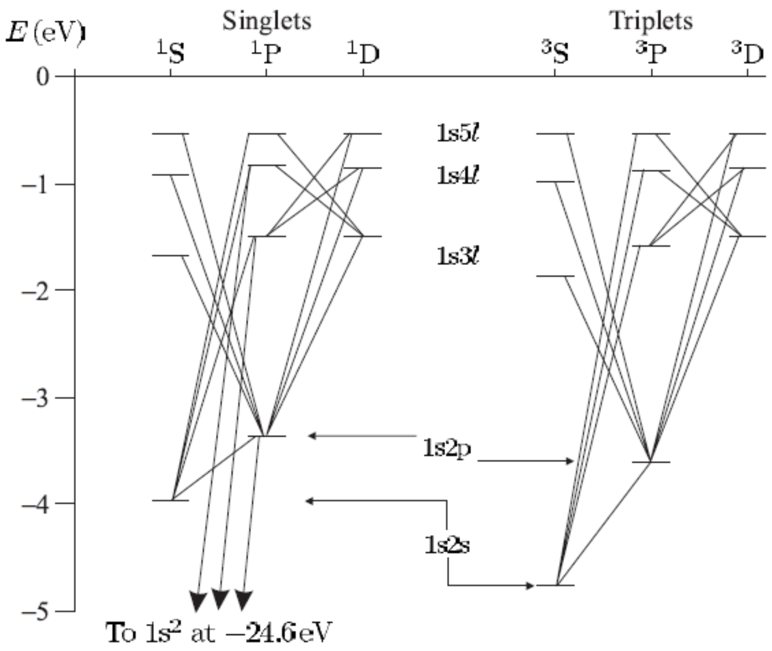
$$K(r_1, r_2) = \begin{cases} r_1/3r_2^2 & \text{for } r_1 < r_2 \, , \\ r_2/3r_1^2 & \text{for } r_2 < r_1 \, . \end{cases} \tag{3.34}$$

Energy levels of Helium



$$\psi = \psi^{S}_{\text{space}}\psi^{A}_{\text{spin}}$$

Allowed transitions



Dipole allowed transition:

$$\langle \psi_{\text{final}} | r | \psi_{\text{initial}} \rangle \neq 0$$

Electric dipole interaction should not affect the spin, so singlet to triplet transition is not allowed!

$$\begin{aligned} \text{selection rule } \Delta S &= 0 \\ \Delta l &= \pm 1 \end{aligned}$$

Rayleigh-Ritz variational method

Goal is to find the correct wavefunction, which minimizes the system energy

Let the trial function ϕ

Energy functional: $E[\phi] = \dfrac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle}$

We should have ground state energy

$$E_0 \le E[\phi] < 0$$

In the ground state, both are *s* electrons (*l*=0), the the wavefunction should be of the form:

$$\phi(r_1, r_2) = \psi_{1s}^{Z_e}(r_1)\psi_{1s}^{Z_e}(r_2) \propto Z_e^3 e^{-Z_e(r_1+r_2)}$$

Z_e: effective nucleus charge number

$$E[\phi] = \left\langle \phi \middle| T_1 + T_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \middle| \phi \right\rangle$$

Kinetic:

$$\langle \phi | T_1 | \phi \rangle = \left\langle \psi_{1s}^{Z_e} \middle| T_1 \middle| \psi_{1s}^{Z_e} \right\rangle = \frac{1}{2} Z_e^2$$

$$\langle \phi | T_1 | \phi \rangle = \langle \phi | T_2 | \phi \rangle$$

Potential:

$$\langle \phi | \frac{1}{r_1} | \phi \rangle = \left\langle \psi_{1s}^{Z_e} \middle| \frac{1}{r_1} \middle| \psi_{1s}^{Z_e} \right\rangle = Z_e$$

$$\langle \phi | \frac{1}{r_1} | \phi \rangle = \langle \phi | \frac{1}{r_2} | \phi \rangle$$

Interaction: $\langle \phi | \dfrac{1}{r_{12}} | \phi \rangle = \dfrac{5}{8} Z_e$

Energy is only dependent on Z_e

$$E[\phi] \equiv E(Z_e) = Z_e^2 - 2ZZ_e + \frac{5}{8} Z_e.$$

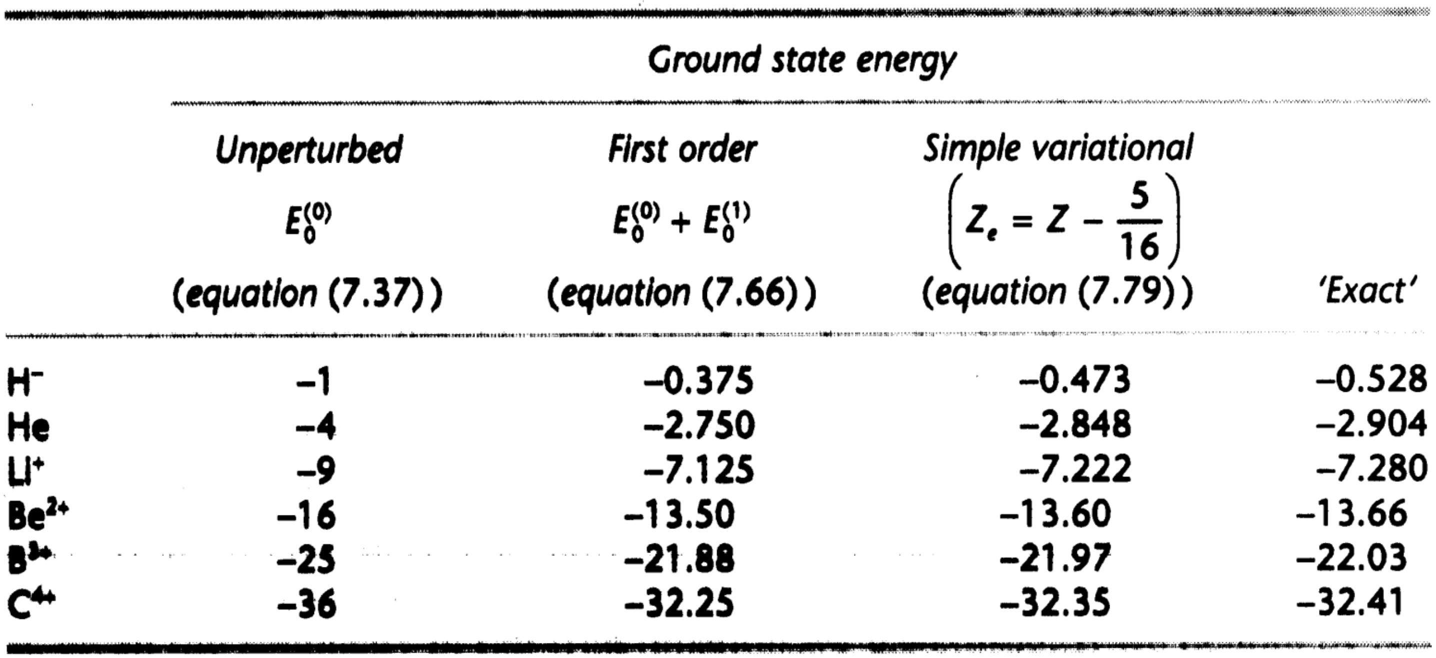
We should now minimize the energy w.r.t. the variational parameter Z_e

$$\frac{\partial E}{\partial Z_e} = 2Z_e - 2Z + \frac{5}{8} = 0 \quad \Rightarrow \quad Z_e = Z - \frac{5}{16}$$

We find the ground state energy

$$E(Z_e = Z - \frac{5}{16}) = -(Z - \frac{5}{16})^2 \text{ a.u.}$$

Theory comparison



	Ground state energy			
	Unperturbed $E_0^{(0)}$ (*equation (7.37)*)	*First order* $E_0^{(0)} + E_0^{(1)}$ (*equation (7.66)*)	*Simple variational* $\left(Z_e = Z - \frac{5}{16}\right)$ (*equation (7.79)*)	*'Exact'*
H^-	−1	−0.375	−0.473	−0.528
He	−4	−2.750	−2.848	−2.904
Li^+	−9	−7.125	−7.222	−7.280
Be^{2+}	−16	−13.50	−13.60	−13.66
B^{3+}	−25	−21.88	−21.97	−22.03
C^{4+}	−36	−32.25	−32.35	−32.41

unit: a.u.

$$1 \text{ a.u.} = \frac{e^2/4\pi\varepsilon_0}{a_0} = 27.2 \text{ eV}$$