# Atomes et molécules - L3

***Supporting slides***

# Atomic & molecular physics - *timeline*

**1885**: J. Balmer discovers the mathematical formula for hydrogen emission lines (Balmer series);
**1881-1887**: A. Michelson & E. Morley observe the fine and hyperfine structures of atomic lines;
**1896**: P. Zeeman discovers the splitting of hydrogen lines with a magnetic field (Zeeman effect);
**1900**: Rydberg formula for the hydrogen emission lines (introduction of the Rydberg constant);
**1906**: Lyman discovers the Lyman series of hydrogen emission lines;
**1908**: Paschen discovers the Paschen series of hydrogen emission lines;
**1908-1913**: Rutherford discovers that the atom is made of a dense nucleus surrounded by electrons (=> planetary model of the atom);
**1913**: N. Bohr formulates his quantum model of the hydrogen atom;
**1913**: J. Stark shows the splitting of hydrogen emissions lines with an electric field (Stark effect);
**1916**: A. Sommerfeld explains the fine structure as a relativistic effect;
**1925: Birth of modern quantum mechanics**
**1925**: W. Pauli formulates its exclusion principle for fermions;
**1926**: E. Schrödinger solves the non-relativistic quantum theory of the hydrogen atom;
**1927**: F. Hund formulates Hund's rules
**1927**: W. Heitler & F. London formulate the quantum theory of the chemical bond;
**1927**: D. Hartree formulates the Hartree equations (wrong!) for N-electron atoms;
**End of 1920's**: L. Pauling formulates his theory of the chemical bond (orbital hybridization);
**1928**: C. Darwin & W. Gordon solve the Dirac equation for hydrogen (quantitative explanation of the fine structure);
**1929-1930**: J. Slater develops the determinant form of the N-electron wavefunction;
**1930**: V. Fock develops the Hartree-Fock method;
**1939:** L. Pauling publishes "*The Nature of the Chemical Bond*";
**1947:** Lamb & Retherford discover the Lamb shift of hydrogen eigenstates

**>1950:** laser spectroscopy, nuclear magnetic / electron spin resonance, atomic clocks, computational quantum chemistry, laser cooling and trapping of ultra-cold gases, ultra-cold chemistry, atom interferometers, etc. etc.

# Atomes & molécules - *Nobel prizes (est. 1901)*

## The Nobel Prize in Physics 1902

Photo from the Nobel Foundation archive.

Hendrik Antoon Lorentz

Prize share: 1/2

Photo from the Nobel Foundation archive.

Pieter Zeeman

Prize share: 1/2

The Nobel Prize in Physics 1902 was awarded jointly to Hendrik Antoon Lorentz and Pieter Zeeman "in recognition of the extraordinary service they rendered by their researches into the influence of magnetism upon radiation phenomena."

## The Nobel Prize in Physics 1907

Photo from the Nobel Foundation archive.

Albert Abraham Michelson

Prize share: 1/1

The Nobel Prize in Physics 1907 was awarded to Albert Abraham Michelson "for his optical precision instruments and the spectroscopic and metrological investigations carried out with their aid."

## The Nobel Prize in Physics 1919

Photo from the Nobel Foundation archive.

Johannes Stark

Prize share: 1/1

The Nobel Prize in Physics 1919 was awarded to Johannes Stark "for his discovery of the Doppler effect in canal rays and the splitting of spectral lines in electric fields."

## The Nobel Prize in Physics 1922

Photo from the Nobel Foundation archive.

Niels Henrik David Bohr

Prize share: 1/1

The Nobel Prize in Physics 1922 was awarded to Niels Henrik David Bohr "for his services in the investigation of the structure of atoms and of the radiation emanating from them."

# Atomes & molécules - *Nobel prizes (est. 1901)*

## The Nobel Prize in Physics 1932

Photo from the Nobel Foundation archive.
Werner Karl Heisenberg
Prize share: 1/1

The Nobel Prize in Physics 1932 was awarded to Werner Karl Heisenberg "for the creation of quantum mechanics, the application of which has, inter alia, led to the discovery of the allotropic forms of hydrogen."

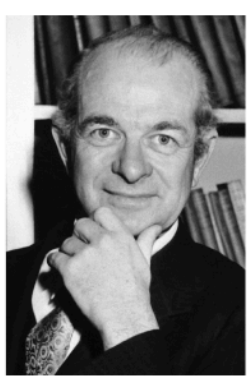
## The Nobel Prize in Physics 1933

Photo from the Nobel Foundation archive.
Erwin Schrödinger
Prize share: 1/2

Photo from the Nobel Foundation archive.
Paul Adrien Maurice Dirac
Prize share: 1/2

The Nobel Prize in Physics 1933 was awarded jointly to Erwin Schrödinger and Paul Adrien Maurice Dirac "for the discovery of new productive forms of atomic theory."

## The Nobel Prize in Chemistry 1954



Linus Carl Pauling
Prize share: 1/1

The Nobel Prize in Chemistry 1954 was awarded to Linus Carl Pauling "for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances."

## The Nobel Prize in Physics 1955

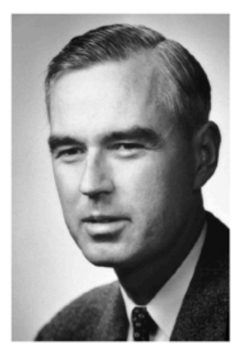


Photo from the Nobel Foundation archive.
Willis Eugene Lamb
Prize share: 1/2

Photo from the Nobel Foundation archive.
Polykarp Kusch
Prize share: 1/2

The Nobel Prize in Physics 1955 was divided equally between Willis Eugene Lamb "for his discoveries concerning the fine structure of the hydrogen spectrum" and Polykarp Kusch "for his precision determination of the magnetic moment of the electron."

## The Nobel Prize in Chemistry 1966

Photo from the Nobel Foundation archive.
Robert S. Mulliken
Prize share: 1/1

The Nobel Prize in Chemistry 1966 was awarded to Robert S. Mulliken "for his fundamental work concerning chemical bonds and the electronic structure of molecules by the molecular orbital method."

# Atomes & molécules - *Nobel prizes (est. 1901)*

## The Nobel Prize in Physics 1966

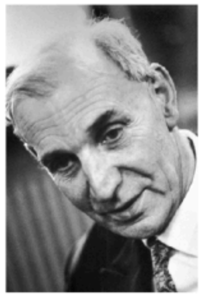


Photo from the Nobel Foundation archive.
Alfred Kastler
Prize share: 1/1

The Nobel Prize in Physics 1966 was awarded to Alfred Kastler "for the discovery and development of optical methods for studying Hertzian resonances in atoms."

## The Nobel Prize in Physics 1981

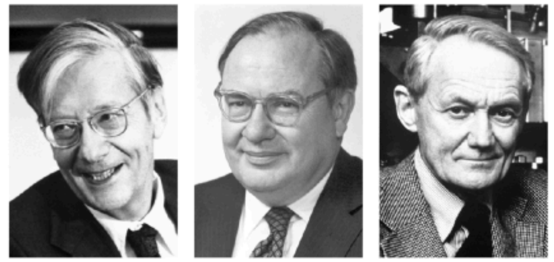


Photo from the Nobel Foundation archive.
Nicolaas Bloembergen
Prize share: 1/4

Photo from the Nobel Foundation archive.
Arthur Leonard Schawlow
Prize share: 1/4

Photo from the Nobel Foundation archive.
Kai M. Siegbahn
Prize share: 1/2

The Nobel Prize in Physics 1981 was divided, one half jointly to Nicolaas Bloembergen and Arthur Leonard Schawlow "for their contribution to the development of laser spectroscopy" and the other half to Kai M. Siegbahn "for his contribution to the development of high-resolution electron spectroscopy."

## The Nobel Prize in Physics 1989

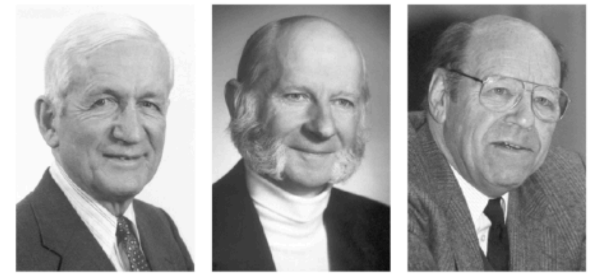


Photo from the Nobel Foundation archive.
Norman F. Ramsey
Prize share: 1/2

Photo from the Nobel Foundation archive.
Hans G. Dehmelt
Prize share: 1/4

Photo from the Nobel Foundation archive.
Wolfgang Paul
Prize share: 1/4

The Nobel Prize in Physics 1989 was divided, one half awarded to Norman F. Ramsey "for the invention of the separated oscillatory fields method and its use in the hydrogen maser and other atomic clocks", the other half jointly to Hans G. Dehmelt and Wolfgang Paul "for the development of the ion trap technique."

## The Nobel Prize in Physics 1997

Photo from the Nobel Foundation archive.
Steven Chu
Prize share: 1/3

Photo from the Nobel Foundation archive.
Claude Cohen-Tannoudji
Prize share: 1/3

Photo from the Nobel Foundation archive.
William D. Phillips
Prize share: 1/3

The Nobel Prize in Physics 1997 was awarded jointly to Steven Chu, Claude Cohen-Tannoudji and William D. Phillips "for development of methods to cool and trap atoms with laser light."

## The Nobel Prize in Chemistry 1998

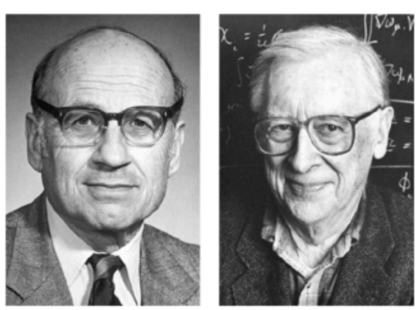


Photo from the Nobel Foundation archive.
Walter Kohn
Prize share: 1/2

Photo from the Nobel Foundation archive.
John A. Pople
Prize share: 1/2

The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn "for his development of the density-functional theory" and John A. Pople "for his development of computational methods in quantum chemistry."

## The Nobel Prize in Physics 2001

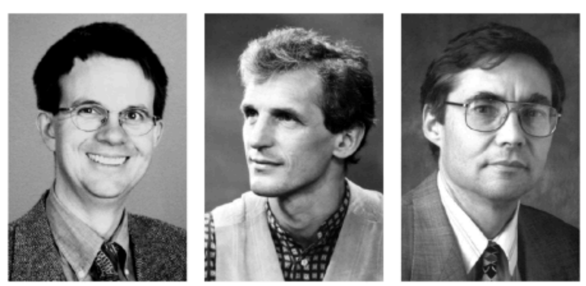


Photo from the Nobel Foundation archive.
Eric A. Cornell
Prize share: 1/3

Photo from the Nobel Foundation archive.
Wolfgang Ketterle
Prize share: 1/3

Photo from the Nobel Foundation archive.
Carl E. Wieman
Prize share: 1/3

The Nobel Prize in Physics 2001 was awarded jointly to Eric A. Cornell, Wolfgang Ketterle and Carl E. Wieman "for the achievement of Bose-Einstein condensation in dilute gases of alkali atoms, and for early fundamental studies of the properties of the condensates."

## The Nobel Prize in Physics 2005

Photo: J.Reed
Roy J. Glauber
Prize share: 1/2

Photo: Sears.P.Studio
John L. Hall
Prize share: 1/4

Photo: F.M. Schmidt
Theodor W. Hänsch
Prize share: 1/4

The Nobel Prize in Physics 2005 was divided, one half awarded to Roy J. Glauber "for his contribution to the quantum theory of optical coherence", the other half jointly to John L. Hall and Theodor W. Hänsch "for their contributions to the development of laser-based precision spectroscopy, including the optical frequency comb technique."

## The Nobel Prize in Physics 2012

© The Nobel Foundation. Photo: U. Montan
Serge Haroche
Prize share: 1/2

© The Nobel Foundation. Photo: U. Montan
David J. Wineland
Prize share: 1/2

The Nobel Prize in Physics 2012 was awarded jointly to Serge Haroche and David J. Wineland "for ground-breaking experimental methods that enable measuring and manipulation of individual quantum systems."

**(...)**

# Atomes & molécules - *Nobel prizes (est. 1901)*

## The Nobel Prize in Physics 2022

Ill. Niklas Elmehed © Nobel Prize Outreach

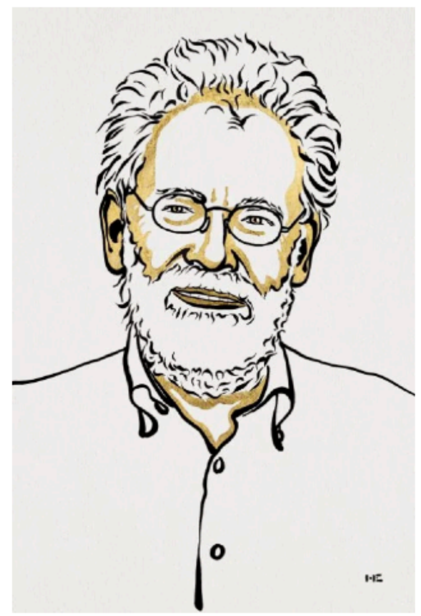
Alain Aspect

Prize share: 1/3

Ill. Niklas Elmehed © Nobel Prize Outreach

John F. Clauser

Prize share: 1/3

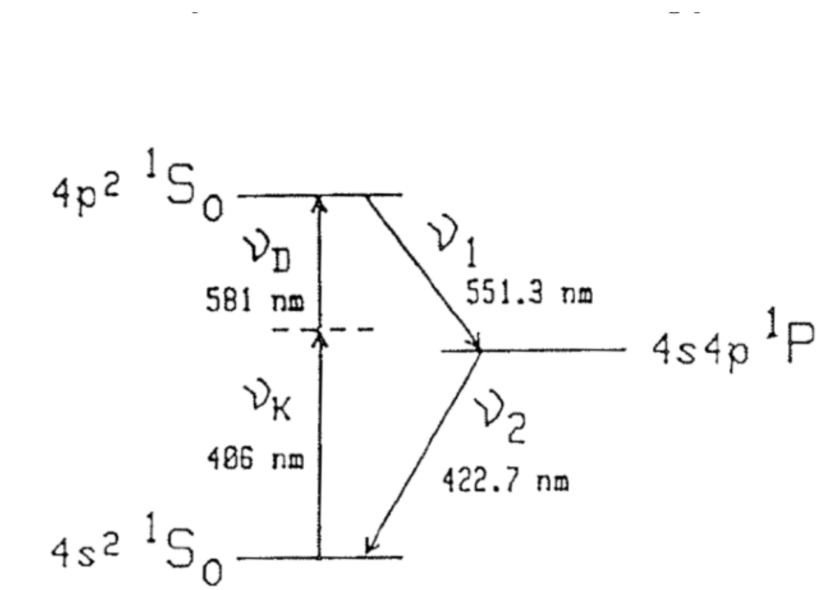


Ill. Niklas Elmehed © Nobel Prize Outreach

Anton Zeilinger

Prize share: 1/3

The Nobel Prize in Physics 2022 was awarded jointly to Alain Aspect, John F. Clauser and Anton Zeilinger "for experiments with entangled photons, establishing the violation of Bell inequalities and pioneering quantum information science"



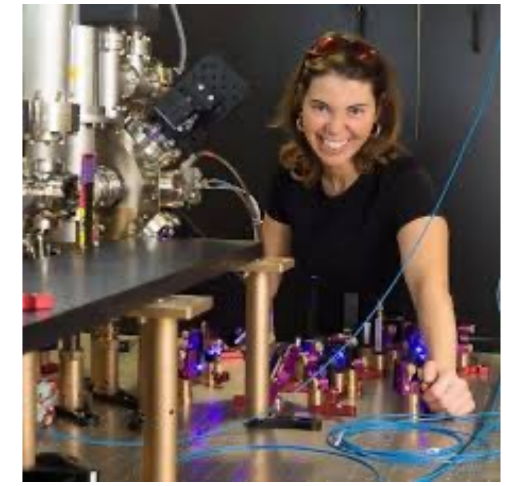

entangled photons from the radiative cascade of $^{40}Ca$ atoms

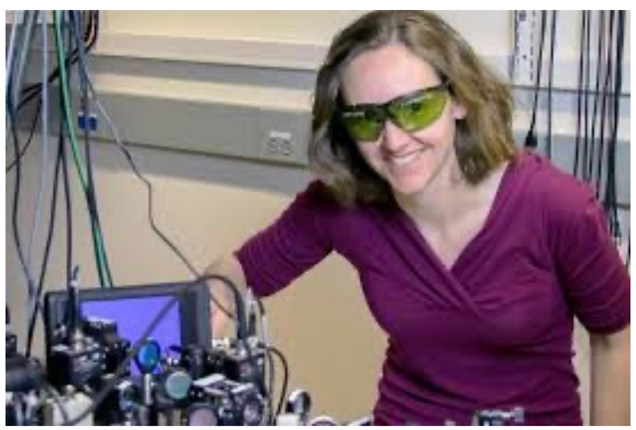
# “The times, they are a-changing”

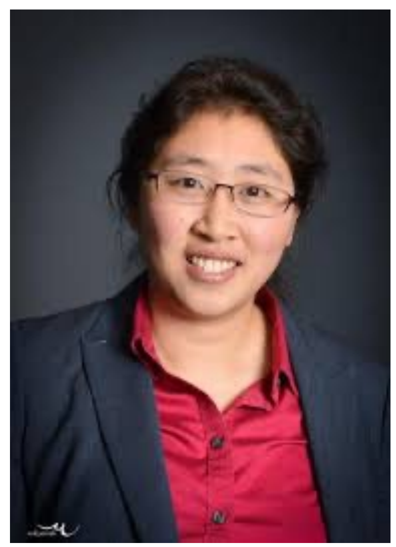

Debbie Jin (JILA, Boulder)

Michèle Leduc (Paris)

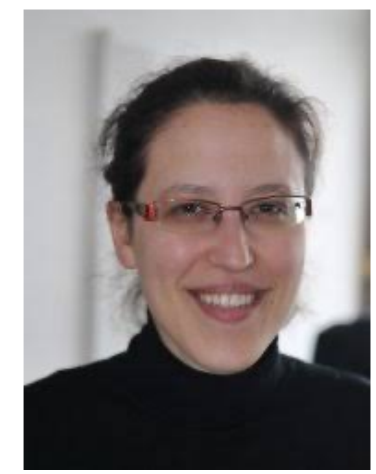

Monika Schleier-Smith (Stanford)


Francesca Ferlaino (Innsbruck)


Cindy Regal (JILA, Boulder)


Kang-Kuen Ni (Harvard)

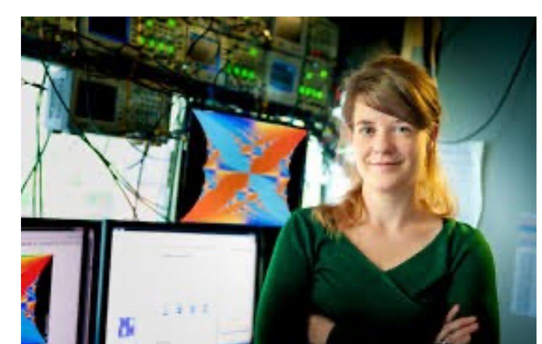

Lauriane Chomaz (Heidelberg)


Juliette Billy (Toulouse)


Isabelle Bouchoule (Palaiseau)


Hélène Perrin (Villetaneuse)

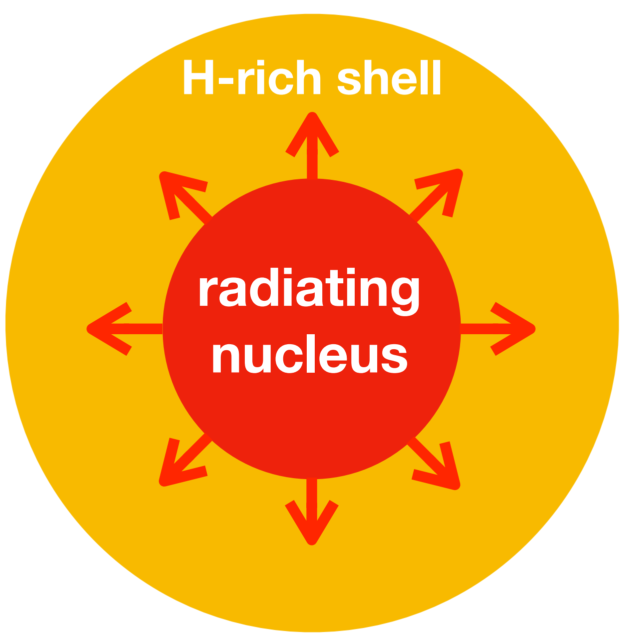

Caroline Champenois (Marseille)


Monika Aidelsburger (Munich)

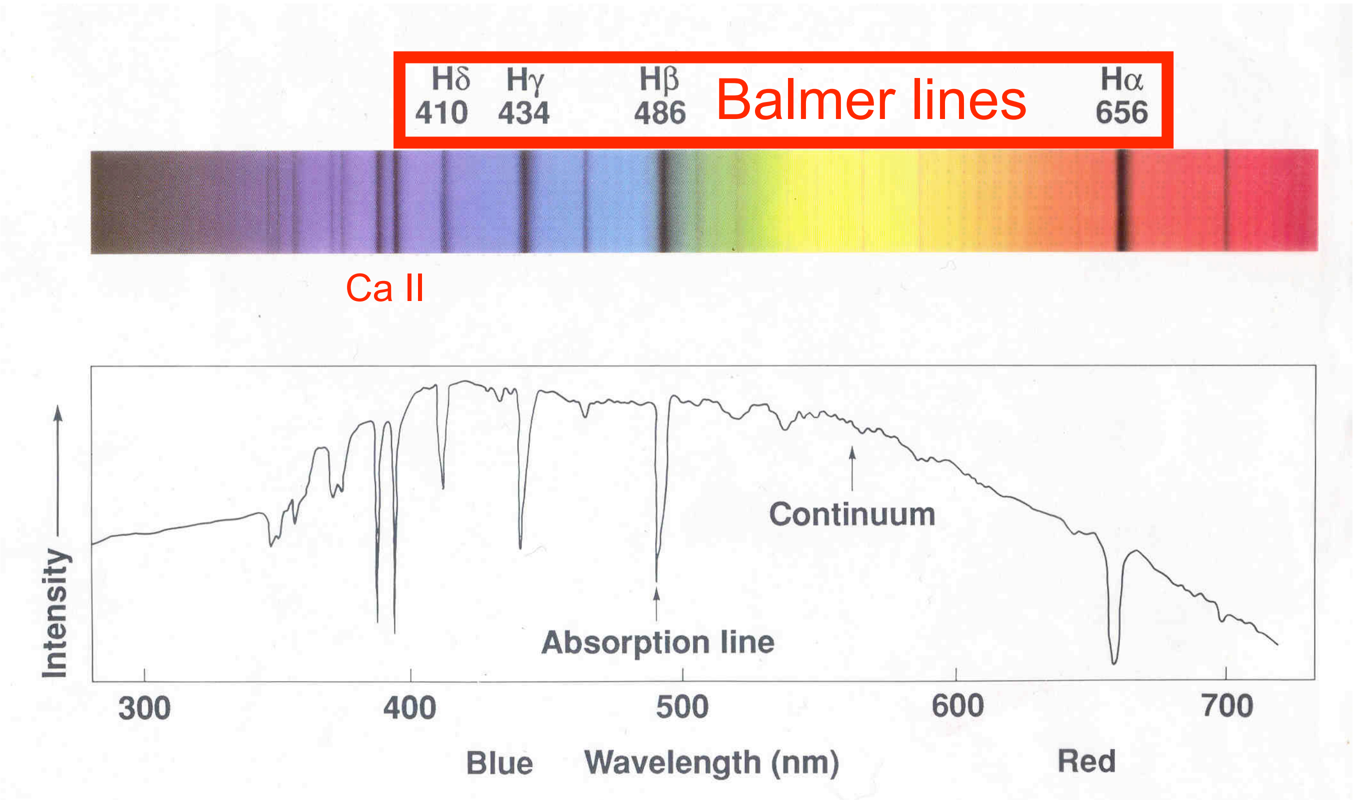
(…)

# Emission/absorption spectrum of atomic hydrogen (1885 - )

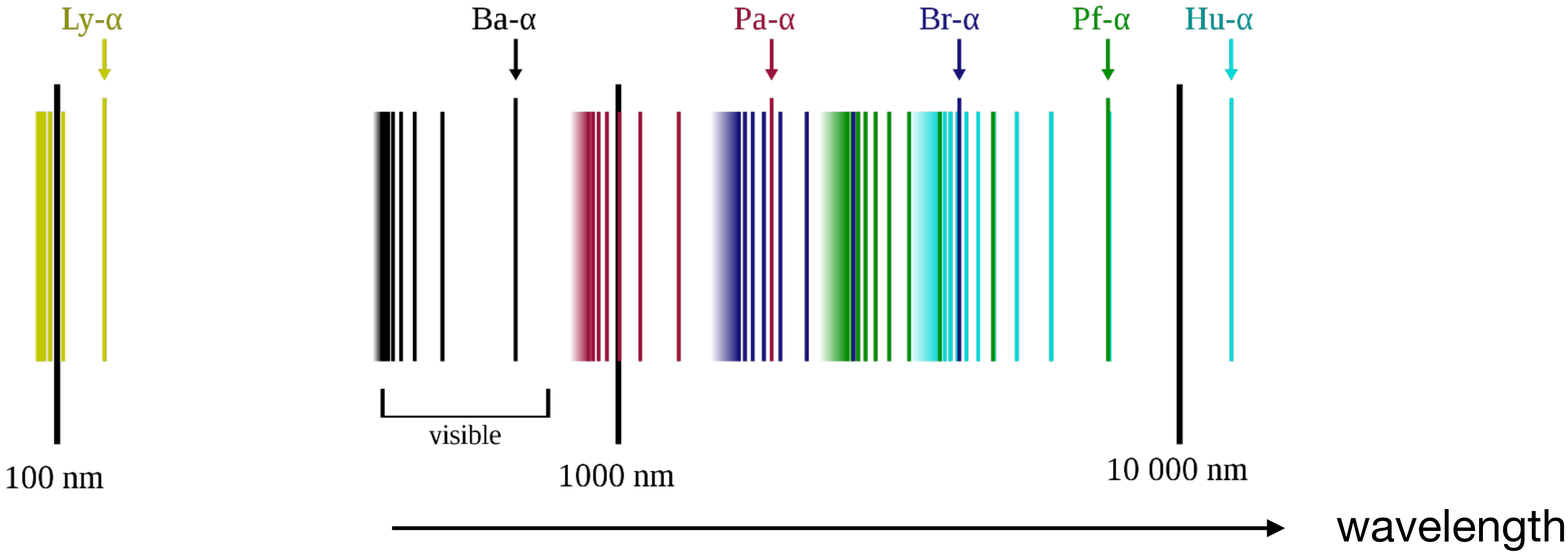

visible Balmer-series lines

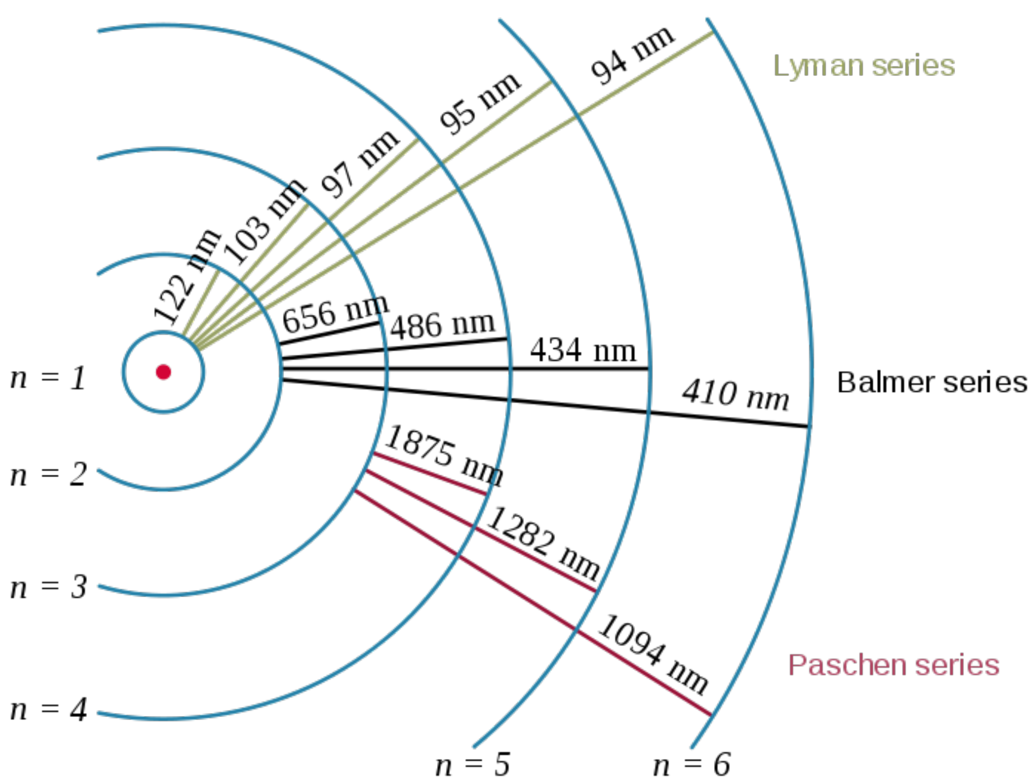



Star emission spectrum



# Emission spectrum of atomic hydrogen

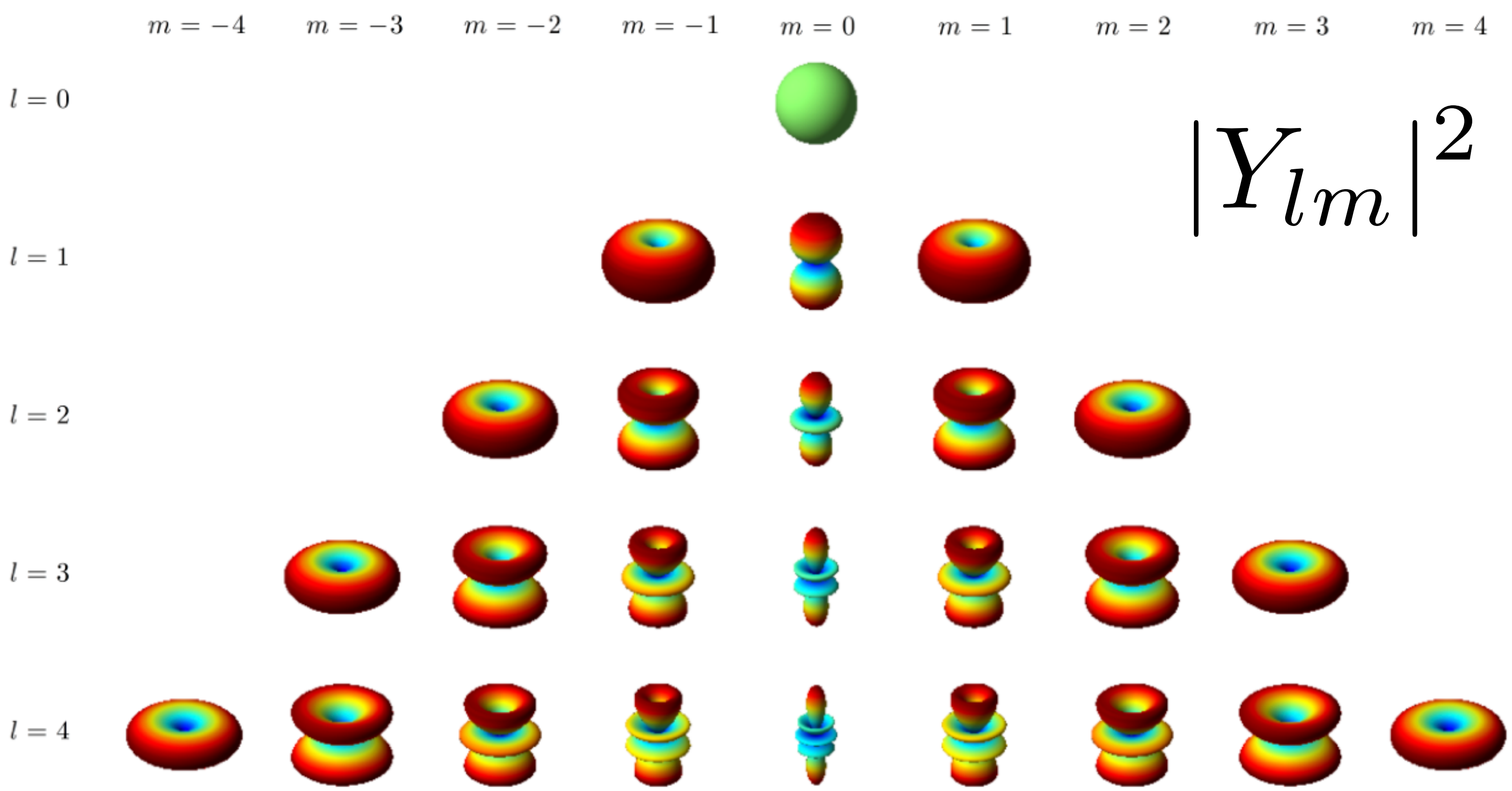


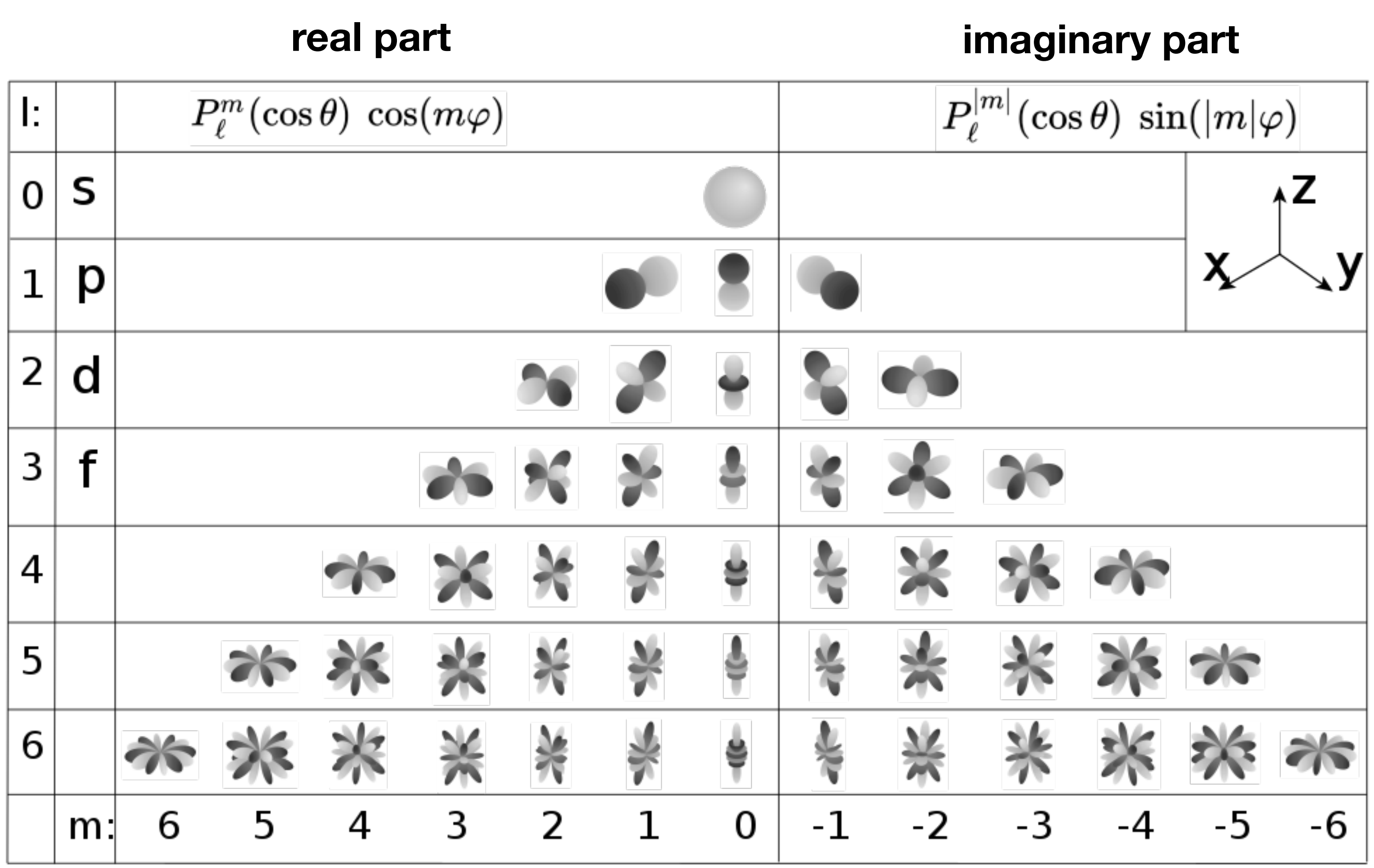




further series:
Brackett’s series (n’=4)
Pfund’s series (n’=5)
Humphrey’s series (n’=6)
etc.

(from Wikipedia)

# Spherical harmonics




$l=0$

$$Y_0^0 = \frac{1}{(4\pi)^{1/2}}$$

$l=1$

$$Y_1^1 = -\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{-i\phi}$$

$l=2$

$$Y_2^1 = -\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{i\phi}$$

$$Y_2^2 = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{2i\phi}$$

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$$

$$Y_2^{-1} = \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{-i\phi}$$

$$Y_2^{-2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{-2i\phi}$$

**(...)**

# Hydrogen radial wavefunctions and probability densities

$$R_{10} = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0}$$

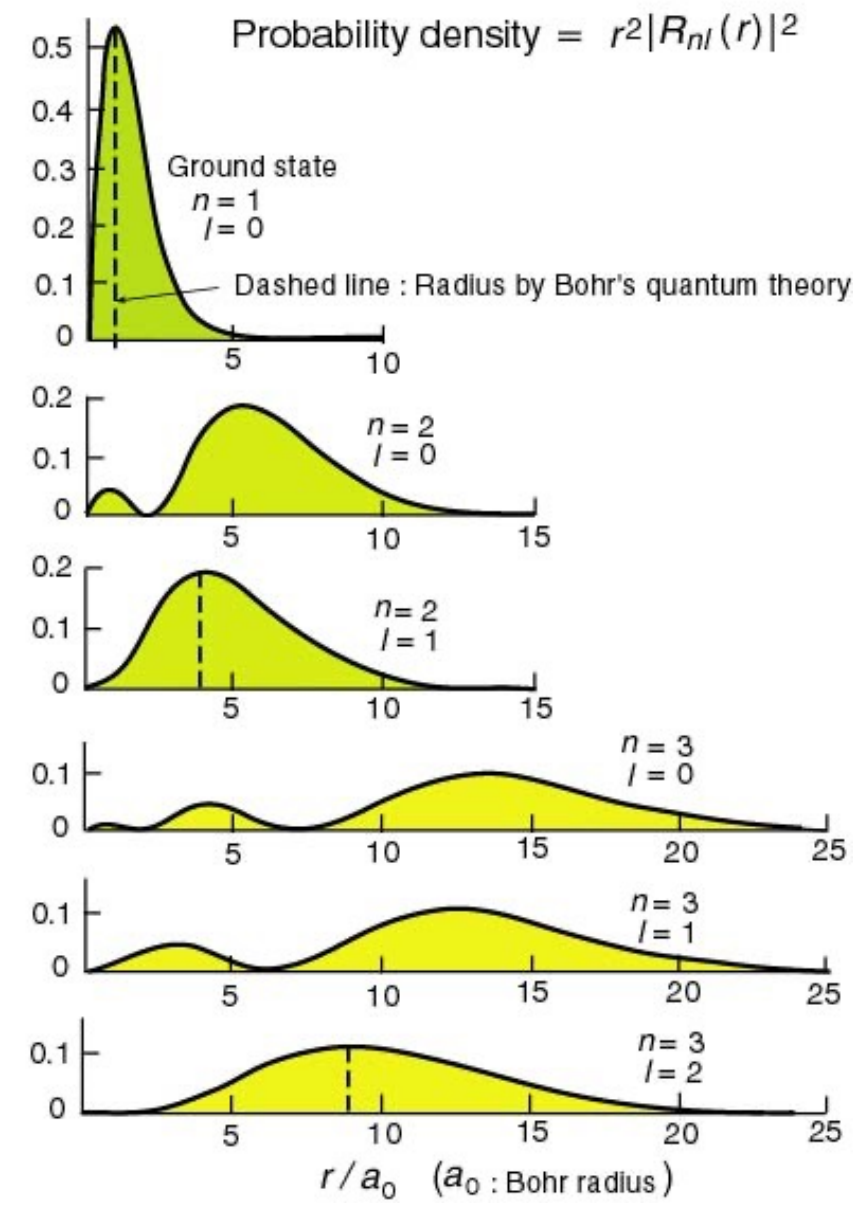
$$R_{21} = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$$R_{20} = 2\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(1-\frac{Zr}{2a_0}\right) e^{-Zr/2a_0}$$

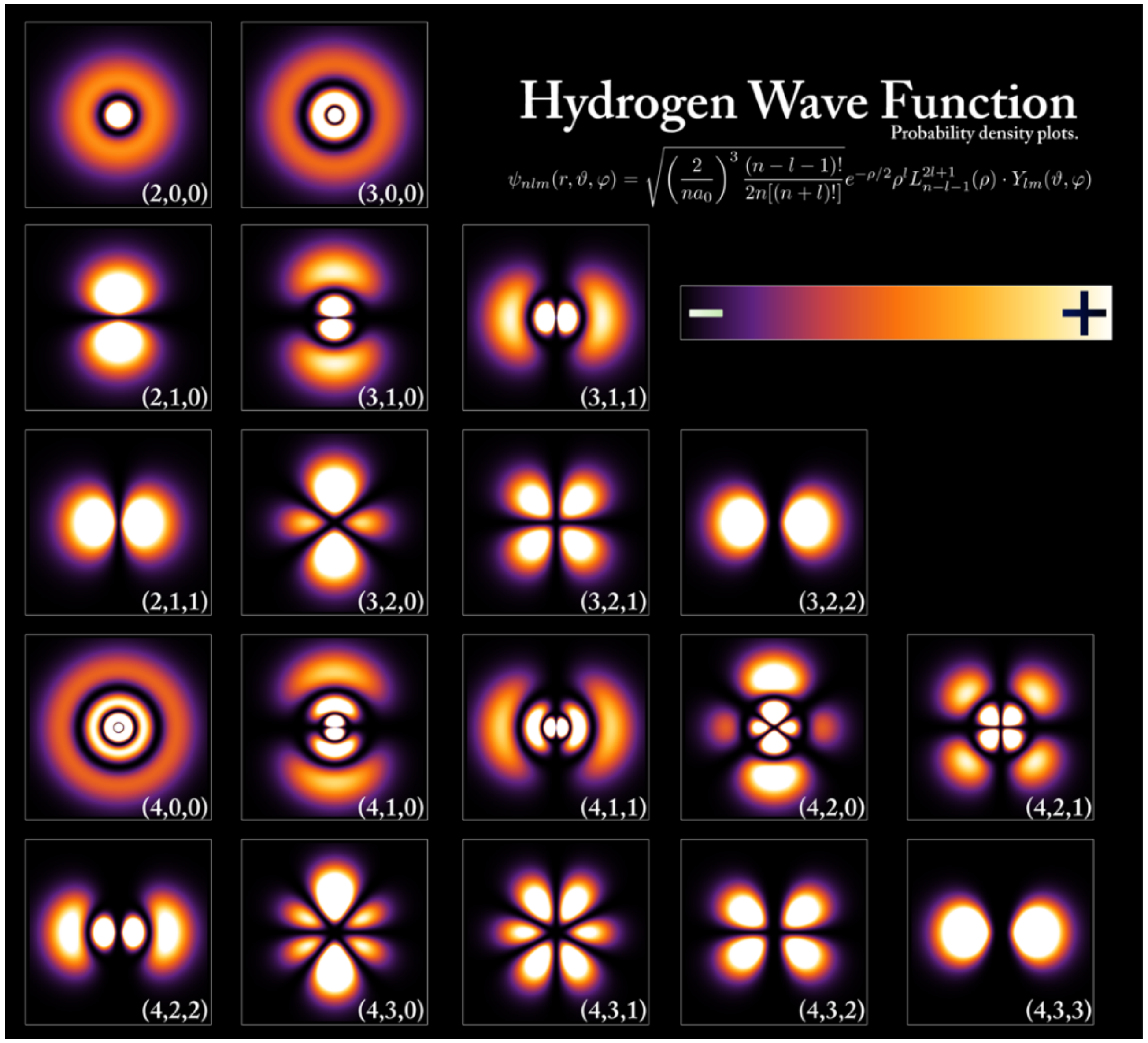
$$R_{32} = \frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$$

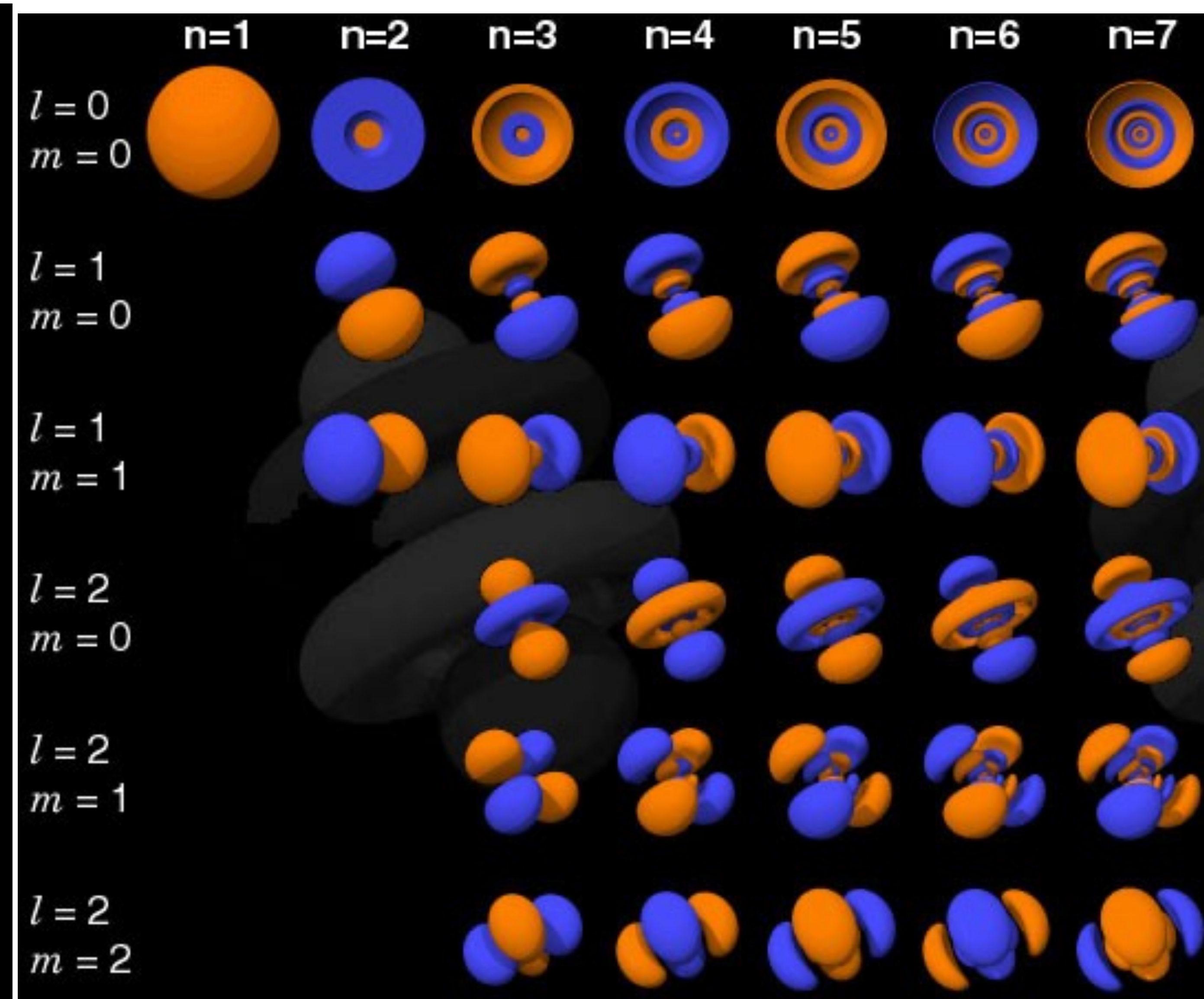
$$R_{31} = \frac{4\sqrt{2}}{3}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)\left(1-\frac{Zr}{6a_0}\right) e^{-Zr/3a_0}$$

$$R_{30} = 2\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(1-\frac{2Zr}{3a_0}+\frac{2\left(Zr\right)^2}{27a_0^2}\right) e^{-Zr/3a_0}$$



# Hydrogen wavefunctions



# Hydrogen atom: main structure and fine structure

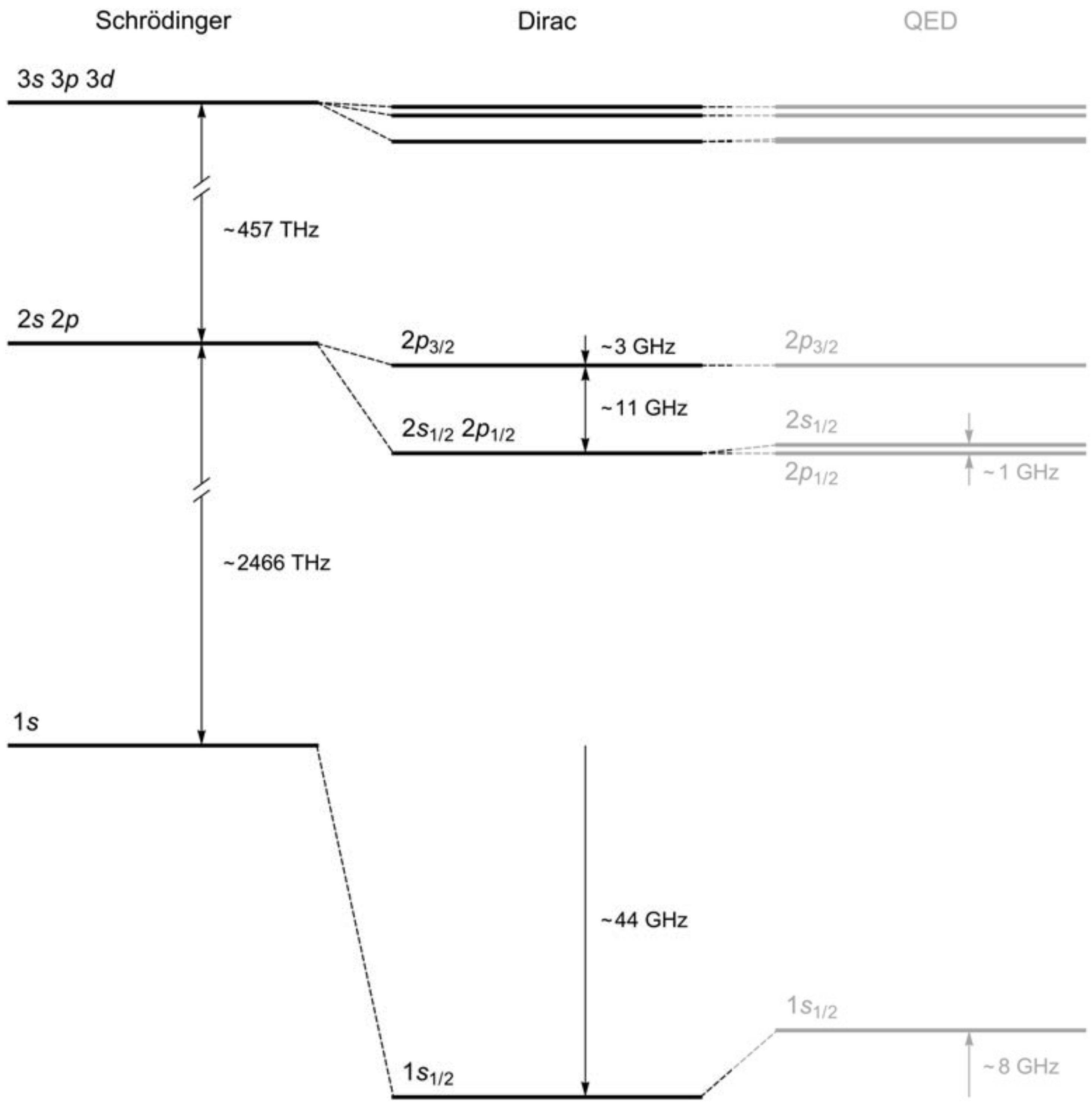



**Fig. 1.4** Scheme of relativistic (fine-structure) corrections and QED corrections to the energy of hydrogen $n = 1$ and $n = 2$ levels.

# Hydrogen atom: main structure, fine structure and Lamb shift

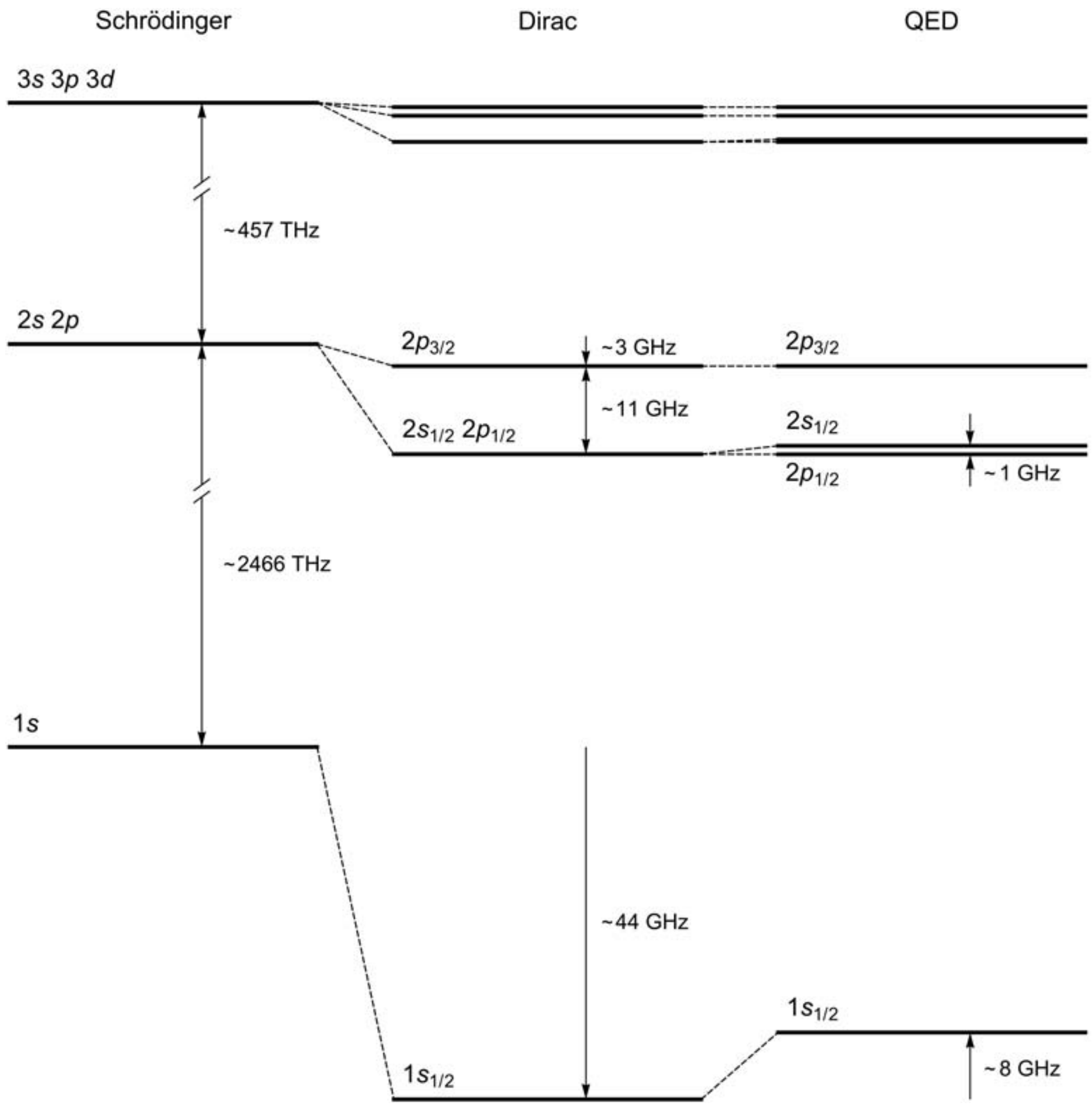
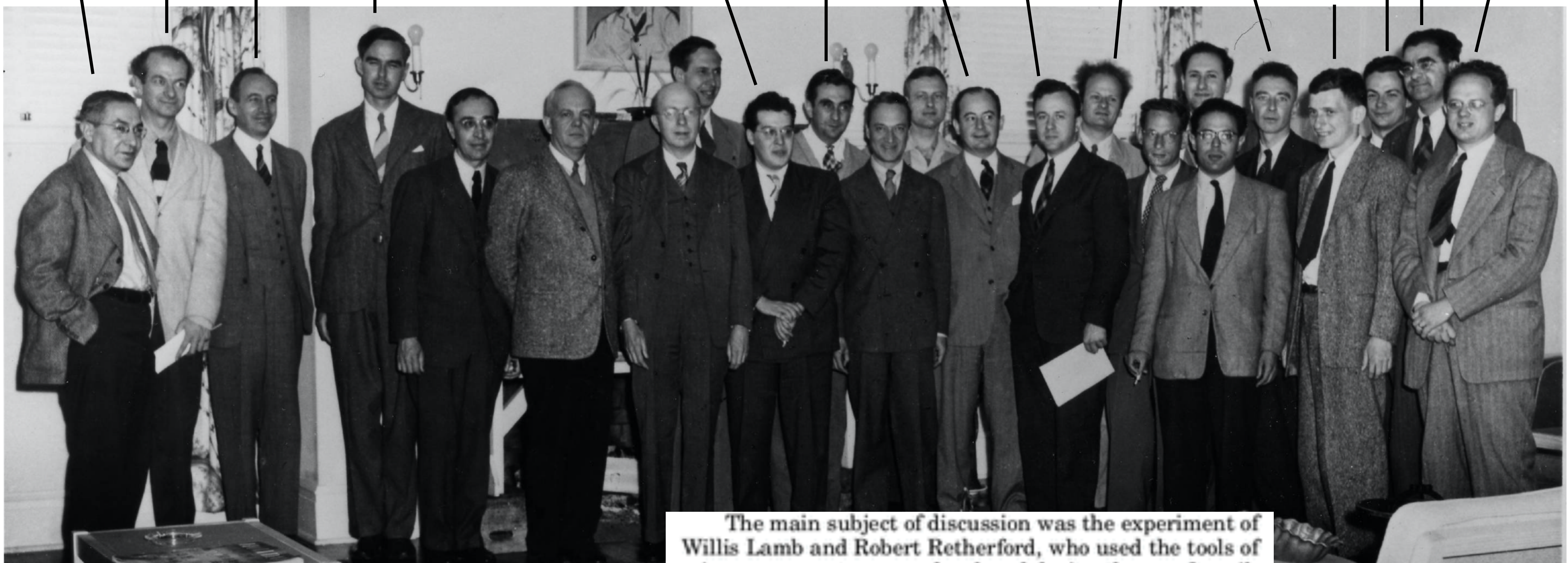



**Fig. 1.4** Scheme of relativistic (fine-structure) corrections and QED corrections to the energy of hydrogen $n = 1$ and $n = 2$ levels.

# The Shelter Island Conference, 1947

## *Fundamental problems of quantum mechanics*




## From Physics Today, 2005

Freeman Dyson

From 2 to 4 June 1947, a carefully selected group of distinguished physicists assembled at Shelter Island, a small and secluded spot near the eastern tip of Long Island, to discuss the outstanding problems of physics. This was the first serious meeting of physicists who had played leading roles in World War II and then returned to the pursuit of peaceful science. The Shelter Island Conference succeeded in its purpose: It set the direction for physics for the next 30 years.

The main subject of discussion was the experiment of Willis Lamb and Robert Retherford, who used the tools of microwave spectroscopy, developed during the war for military purposes, to measure the fine structure of the energy levels of the hydrogen atom. The results showed a clear de-

After the meeting, Bethe traveled by train from New York to Schenectady, a distance of 75 miles. On the train he finished a calculation of the Lamb shift for a real electron. The value that he found was 1040 megahertz, a result agreeing pretty well with Lamb's experiment. On 9 June he wrote a paper summarizing his calculation,[1] and sent it to the other participants of the Shelter Island meeting. The paper, two pages long with only 12 equations, was received by the *Physical Review* on 27 June and published on 15 August. It was a turning point in the history of physics. Before it appeared, the prevailing view of such ex-

# Definition of the second: hyperfine levels

WIKIPEDIA
The Free Encyclopedia

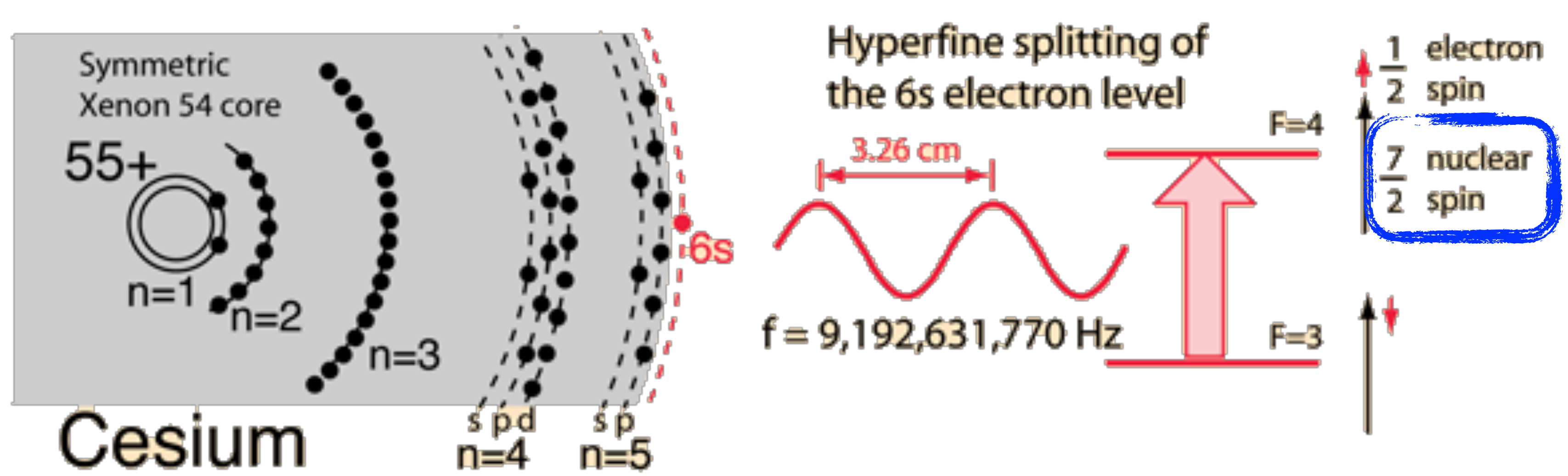
Article | Talk

## Second

From Wikipedia, the free encyclopedia

Although the historical definition of the unit was based on this division of the Earth's rotation cycle, the formal definition in the International System of Units (SI) is a much steadier timekeeper:

> *The second is defined as being equal to the time duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the fundamental unperturbed ground-state of the caesium-133 atom.*[1][2]



# He spectrum: perturbation theory

**Table 3.1** Energies of low lying excited states in neutral He, as calculated by first-order perturbation theory, compared with experimental values from [5]. The tabled values refer to the double ionisation energies, as in figure 3.1.

| Energy level | First-order correction | Calculated energy | Experimental value |
|---|---|---|---|
| $E_{1s2s_-}$ | $J_{1s:2s} - K_{1s:2s}$ | -57.8 eV | -59.19 eV |
| $E_{1s2s_+}$ | $J_{1s:2s} + K_{1s:2s}$ | -55.4 eV | -58.39 eV |
| $E_{1s2p_-}$ | $J_{1s:2p} - K_{1s:2p}$ | -55.7 eV | -58.04 eV |
| $E_{1s2p_+}$ | $J_{1s:2p} + K_{1s:2p}$ | -53.9 eV | -57.79 eV |

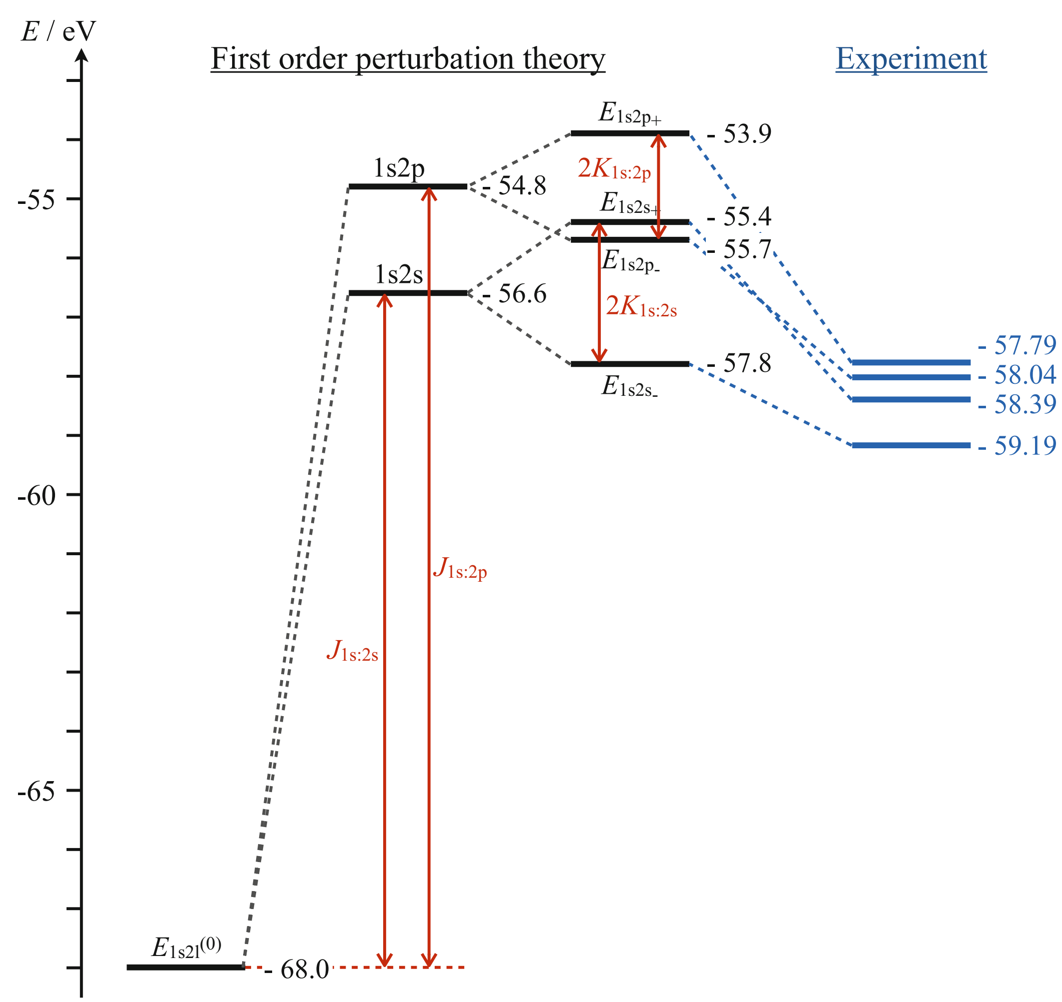



**Fig. 3.1** Energies of the levels in the 1s2s and 1s2p configurations of neutral He, calculated with first-order perturbation theory, and compared with experimentally measured values [5]. Zero energy is taken as that for both electrons being removed to infinity, as in table 3.1.

# He spectrum

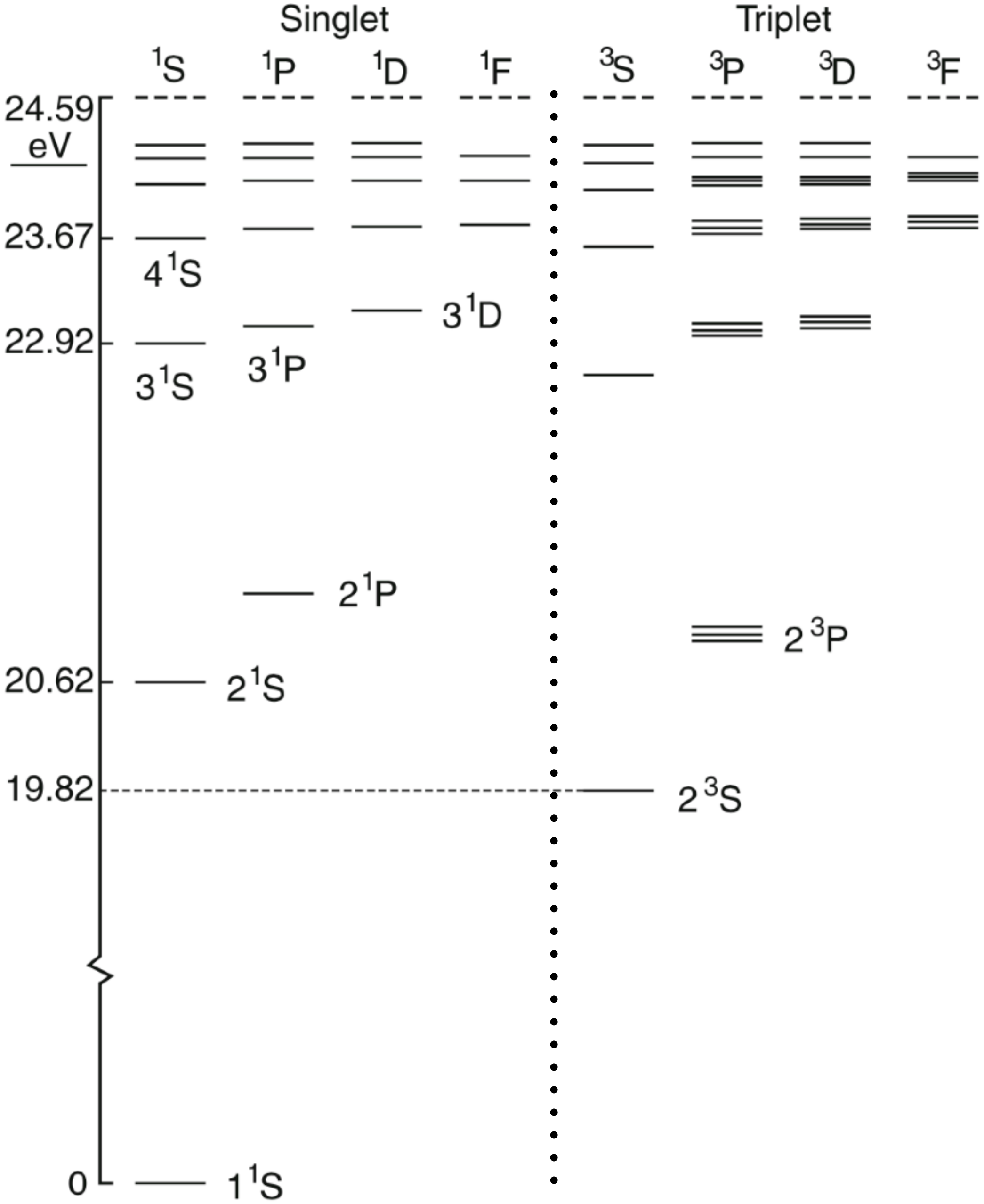
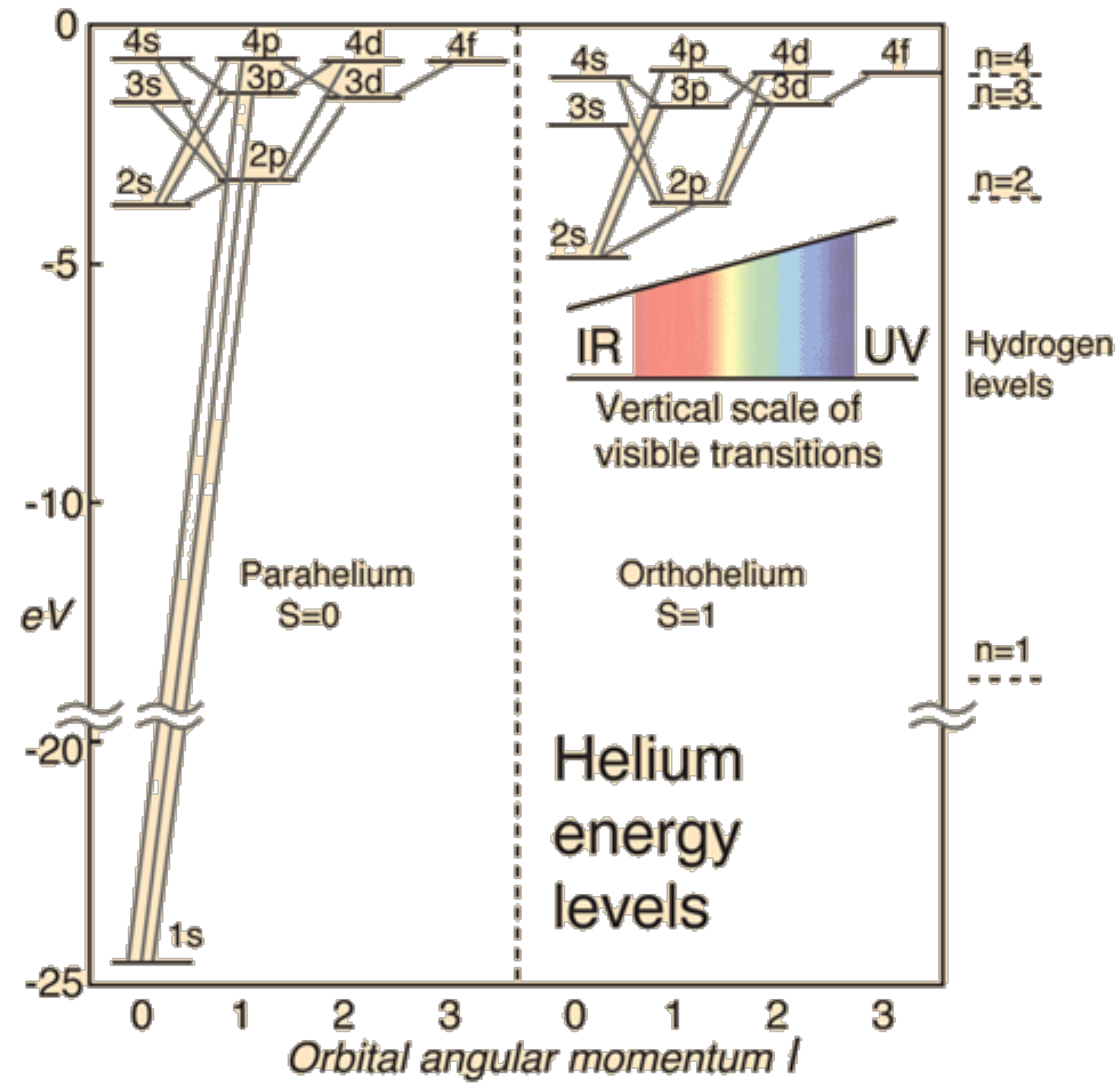
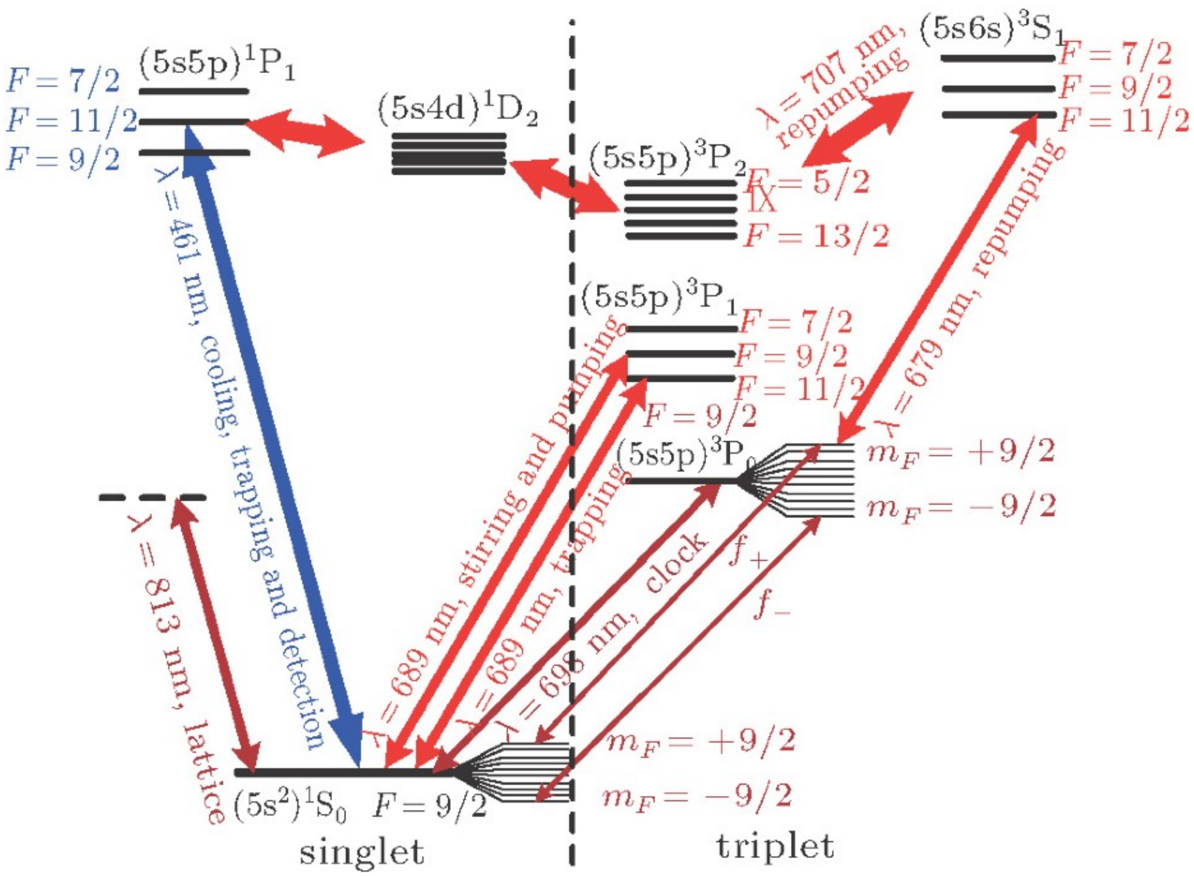
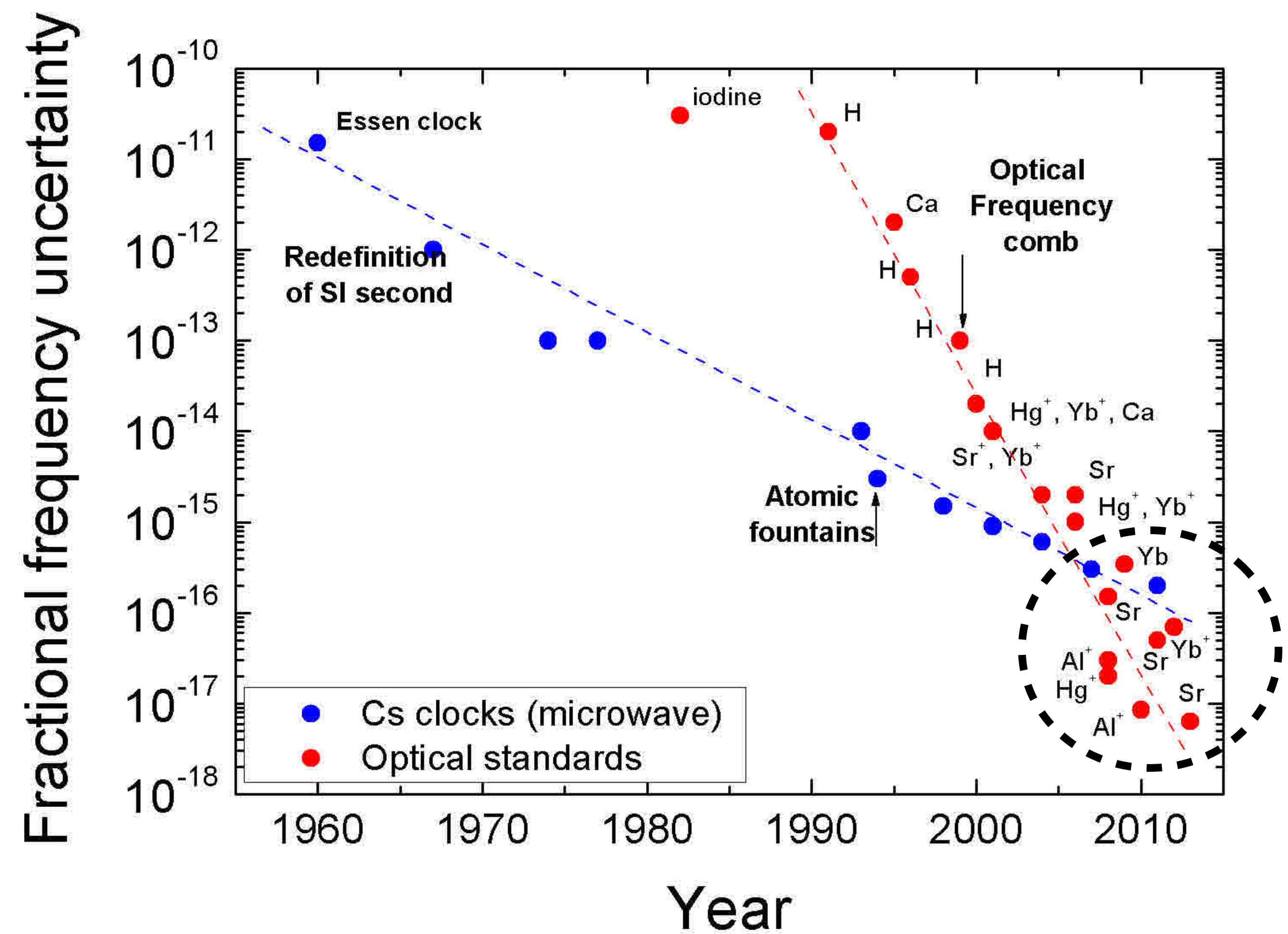



**Fig. 6.9** Level scheme of singlet and triplet states of the helium atom from $L = 0$ up to $L = 3$. The ground state $1^1S_0$ is chosen to have the energy $E = 0$



# Strontium and other “2-electron atoms”: atomic clocks




N. Poli et al., Riv. Nuovo Cimento 36, 555 (2013)

Article | Published: 24 March 2021

## Frequency ratio measurements at 18-digit accuracy using an optical clock network

Boulder Atomic Clock Optical Network (BACON) Collaboration*

Nature **591**, 564–569 (2021) | Cite this article

Here we operate a network of optical clocks based on $^{27}$Al$^+$ (ref. 6), $^{87}$Sr (ref. 7) and $^{171}$Yb (ref. 8), and measure their frequency ratios with fractional uncertainties at or below $8 \times 10^{-18}$.

# Atomic "Aufbau"

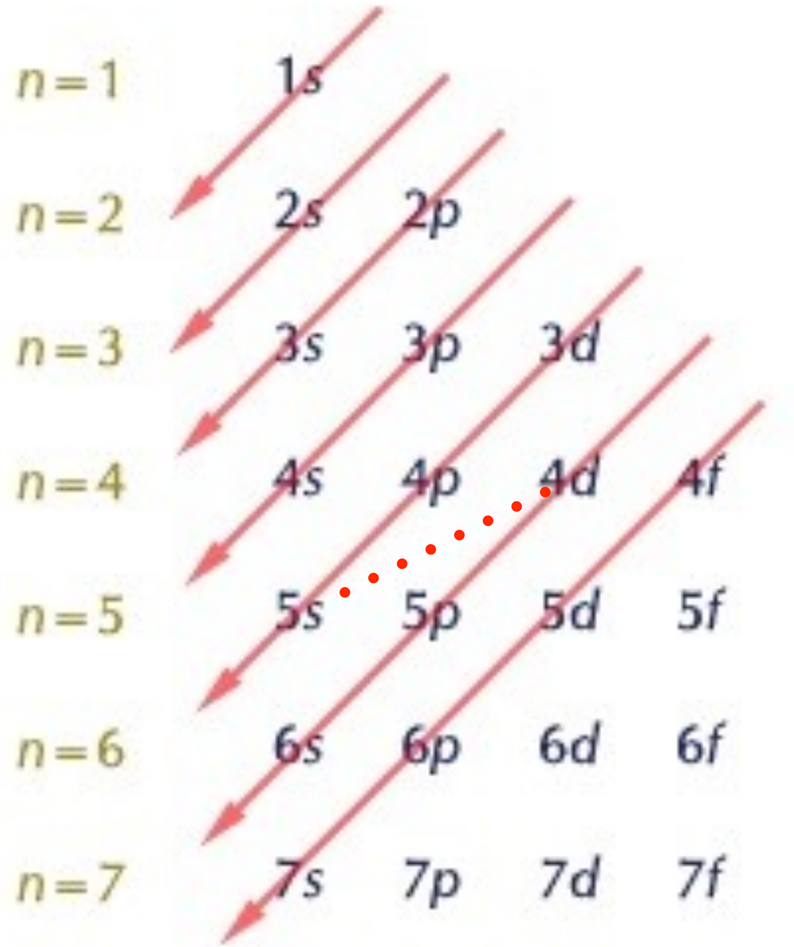



**Table 6.2** Electron configuration in the ground states of the chemical elements

| Shell | | | K | L | | M | | | O |
|---|---|---|---|---|---|---|---|---|---|
| Z | | Element | 1s | 2s | 2p | 3s | 3p | 3d | 4s |
| 1 | H | Hydrogen | 1 | | | | | | |
| 2 | He | Helium | 2 | | | | | | |
| 3 | Li | Lithium | 2 | 1 | | | | | |
| 4 | Be | Beryllium | 2 | 2 | | | | | |
| 5 | B | Boron | 2 | 2 | 1 | | | | |
| 6 | C | Carbon | 2 | 2 | 2 | | | | |
| 7 | N | Nitrogen | 2 | 2 | 3 | | | | |
| 8 | O | Oxygen | 2 | 2 | 4 | | | | |
| 9 | F | Fluorine | 2 | 2 | 5 | | | | |
| 10 | Ne | Neon | 2 | 2 | 6 | | | | |
| 11 | Na | Sodium | 2 | 2 | 6 | 1 | | | |
| 12 | Mg | Magnesium | 2 | 2 | 6 | 2 | | | |
| 13 | Al | Aluminum | 2 | 2 | 6 | 2 | 1 | | |
| 14 | Si | Silicon | 2 | 2 | 6 | 2 | 2 | | |
| 15 | P | Phosphorus | 2 | 2 | 6 | 2 | 3 | | |
| 16 | S | Sulfur | 2 | 2 | 6 | 2 | 4 | | |
| 17 | Cl | Chlorine | 2 | 2 | 6 | 2 | 5 | | |
| 18 | Ar | Argon | 2 | 2 | 6 | 2 | 6 | | |
| 19 | K | Potassium | 2 | 2 | 6 | 2 | 6 | | 1 |
| 20 | Ca | Calcium | 2 | 2 | 6 | 2 | 6 | | 2 |
| 21 | Sc | Scandium | 2 | 2 | 6 | 2 | 6 | 1 | 2 |
| 22 | Ti | Titanium | 2 | 2 | 6 | 2 | 6 | 2 | 2 |
| 23 | V | Vanadium | 2 | 2 | 6 | 2 | 6 | 3 | 2 |
| 24 | Cr | Chromium | 2 | 2 | 6 | 2 | 6 | 5 | 1 |
| 25 | Mn | Manganese | 2 | 2 | 6 | 2 | 6 | 5 | 2 |
| 26 | Fe | Iron | 2 | 2 | 6 | 2 | 6 | 6 | 2 |
| 27 | Co | Cobalt | 2 | 2 | 6 | 2 | 6 | 7 | 2 |

| Shell | | | K | L | | M | | | N | | | O | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Z | | Element | 1s | 2s | 2p | 3s | 3p | 3d | 4s | 4p | 4d | 5s | 5p |
| 28 | Ni | Nickel | 2 | 2 | 6 | 2 | 6 | 8 | 2 | | | | |
| 29 | Cu | Copper | 2 | 2 | 6 | 2 | 6 | 10 | 1 | | | | |
| 30 | Zn | Zink | 2 | 2 | 6 | 2 | 6 | 10 | 2 | | | | |
| 31 | Ga | Gallium | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 1 | | | |
| 32 | Ge | Germanium | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 2 | | | |
| 33 | As | Arsenic | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 3 | | | |
| 34 | Se | Selenium | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 4 | | | |
| 35 | Br | Bromium | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 5 | | | |
| 36 | Kr | Krypton | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | | | |
| 37 | Rb | Rubidium | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | | 1 | |
| 38 | Sr | Strontium | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | | 2 | |
| 39 | Y | Yttrium | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 1 | 2 | |
| 40 | Zr | Zirconium | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 2 | 2 | |
| 41 | Nb | Niobium | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 4 | 1 | |
| 42 | Mo | Molybdenum | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 5 | 1 | |
| 43 | Tc | Technetium | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 6 | 1 | |
| 44 | Ru | Ruthenium | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 7 | 1 | |
| 45 | Rh | Rhodium | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 8 | 1 | |
| 46 | Pd | Palladium | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | | |
| 47 | Ag | Silver | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | 1 | |
| 48 | Cd | Cadmium | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | 2 | |
| 49 | In | Indium | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | 2 | 1 |
| 50 | Sn | Tin | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | 2 | 2 |
| 51 | Sb | Antimony | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | 2 | 3 |
| 52 | Te | Tellurium | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | 2 | 4 |
| 53 | I | Iodine | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | 2 | 5 |
| 54 | Xe | Xenon | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | 2 | 6 |

| Shell | | | N | O | | | | P |
|---|---|---|---|---|---|---|---|---|
| Z | | Element | 4f | 5s | 5p | 5d | 5f | 6s |
| 55 | Cs | Cesium | | 2 | 6 | | | 1 |
| 56 | Ba | Barium | | 2 | 6 | | | 2 |
| 57 | La | Lanthanium | | 2 | 6 | 1 | | 2 |
| 58 | Ce | Cerium | 2 | 2 | 6 | | | 2 |
| 59 | Pr | Praseodymium | 3 | 2 | 6 | | | 2 |
| 60 | Nd | Neodymium | 4 | 2 | 6 | | | 2 |
| 61 | Pm | Promethium | 5 | 2 | 6 | | | 2 |
| 62 | Sm | Samarium | 6 | 2 | 6 | | | 2 |
| 63 | Eu | Europium | 7 | 2 | 6 | | | 2 |
| 64 | Gd | Gadolinium | 7 | 2 | 6 | 1 | | 2 |
| 65 | Tb | Terbium | 9 | 2 | 6 | | | 2 |
| 66 | Dy | Dysprosium | 10 | 2 | 6 | | | 2 |
| 67 | Ho | Holmium | 11 | 2 | 6 | | | 2 |
| 68 | Er | Erbium | 12 | 2 | 6 | | | 2 |
| 69 | Tm | Thulium | 13 | 2 | 6 | | | 2 |
| 70 | Yb | Ytterbium | 14 | 2 | 6 | | | 2 |
| 71 | Lu | Lutetium | 14 | 2 | 6 | 1 | | 2 |
| 72 | Hf | Hafnium | 14 | 2 | 6 | 2 | | 2 |
| 73 | Ta | Tantalium | 14 | 2 | 6 | 3 | | 2 |
| 74 | W | Tungsten | 14 | 2 | 6 | 4 | | 2 |
| 75 | Re | Rhenium | 14 | 2 | 6 | 5 | | 2 |
| 76 | Os | Osmium | 14 | 2 | 6 | 6 | | 2 |
| 77 | Ir | Iridium | 14 | 2 | 6 | 7 | | 2 |
| 78 | Pt | Platinum | 14 | 2 | 6 | 9 | | 1 |
| 79 | Au | Gold | 14 | 2 | 6 | 10 | | 1 |

| Shell | | | N | O | | | | P | | | Q |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Z | | Element | 4f | 5s | 5p | 5d | 5f | 6s | 6p | 6d | 7s |
| 80 | Hg | Mercury | 14 | 2 | 6 | 10 | | 2 | | | |
| 81 | Tl | Thallium | 14 | 2 | 6 | 10 | | 2 | 1 | | |
| 82 | Pb | Lead | 14 | 2 | 6 | 10 | 2 | 2 | | | |
| 83 | Bi | Bismuth | 14 | 2 | 6 | 10 | | 2 | 3 | | |
| 84 | Po | Polonium | 14 | 2 | 6 | 10 | | 2 | 4 | | |
| 85 | At | Astatine | 14 | 2 | 6 | 10 | | 2 | 5 | | |
| 86 | Rn | Radon | 14 | 2 | 6 | 10 | | 2 | 6 | | |
| 87 | Fr | Francium | 14 | 2 | 6 | 10 | | 2 | 6 | | 1 |
| 88 | Ra | Radium | 14 | 2 | 6 | 10 | | 2 | 6 | | 2 |
| 89 | Ac | Actinium | 14 | 2 | 6 | 10 | | 2 | 6 | 1 | 2 |
| 90 | Th | Thorium | 14 | 2 | 6 | 10 | | 2 | 6 | 2 | 2 |
| 91 | Pa | Protactinium | 14 | 2 | 6 | 10 | 2 | 2 | 6 | 1 | 2 |
| 92 | U | Uranium | 14 | 2 | 6 | 10 | 3 | 2 | 6 | 1 | 2 |
| 93 | Np | Neptunium | 14 | 2 | 6 | 10 | 5 | 2 | 6 | | 2 |
| 94 | Pu | Plutonium | 14 | 2 | 6 | 10 | 6 | 2 | 6 | | 2 |
| 95 | Am | Americium | 14 | 2 | 6 | 10 | 7 | 2 | 6 | | 2 |
| 96 | Cm | Curium | 14 | 2 | 6 | 10 | 7 | 2 | 6 | 1 | 2 |
| 97 | Bk | Berkelium | 14 | 2 | 6 | 10 | 8 | 2 | 6 | 1 | 2 |
| 98 | Cf | Californium | 14 | 2 | 6 | 10 | 10 | 2 | 6 | | 2 |
| 99 | Es | Einsteinium | 14 | 2 | 6 | 10 | 11 | 2 | 6 | | 2 |
| 100 | Fm | Fermium | 14 | 2 | 6 | 10 | 12 | 2 | 6 | | 2 |
| 101 | Md | Mendelevium | 14 | 2 | 6 | 10 | 13 | 2 | 6 | | 2 |
| 102 | No | Nobelium | 14 | 2 | 6 | 10 | 14 | 2 | 6 | | 2 |
| 103 | Lr | Lawrencium | 14 | 2 | 6 | 10 | 14 | 2 | 6 | 1 | 2 |
| 104 | Rf | Rutherfordium | 14 | 2 | 6 | 10 | 14 | 2 | 6 | 2 | 2 |

# Alkali atoms: quantum defects



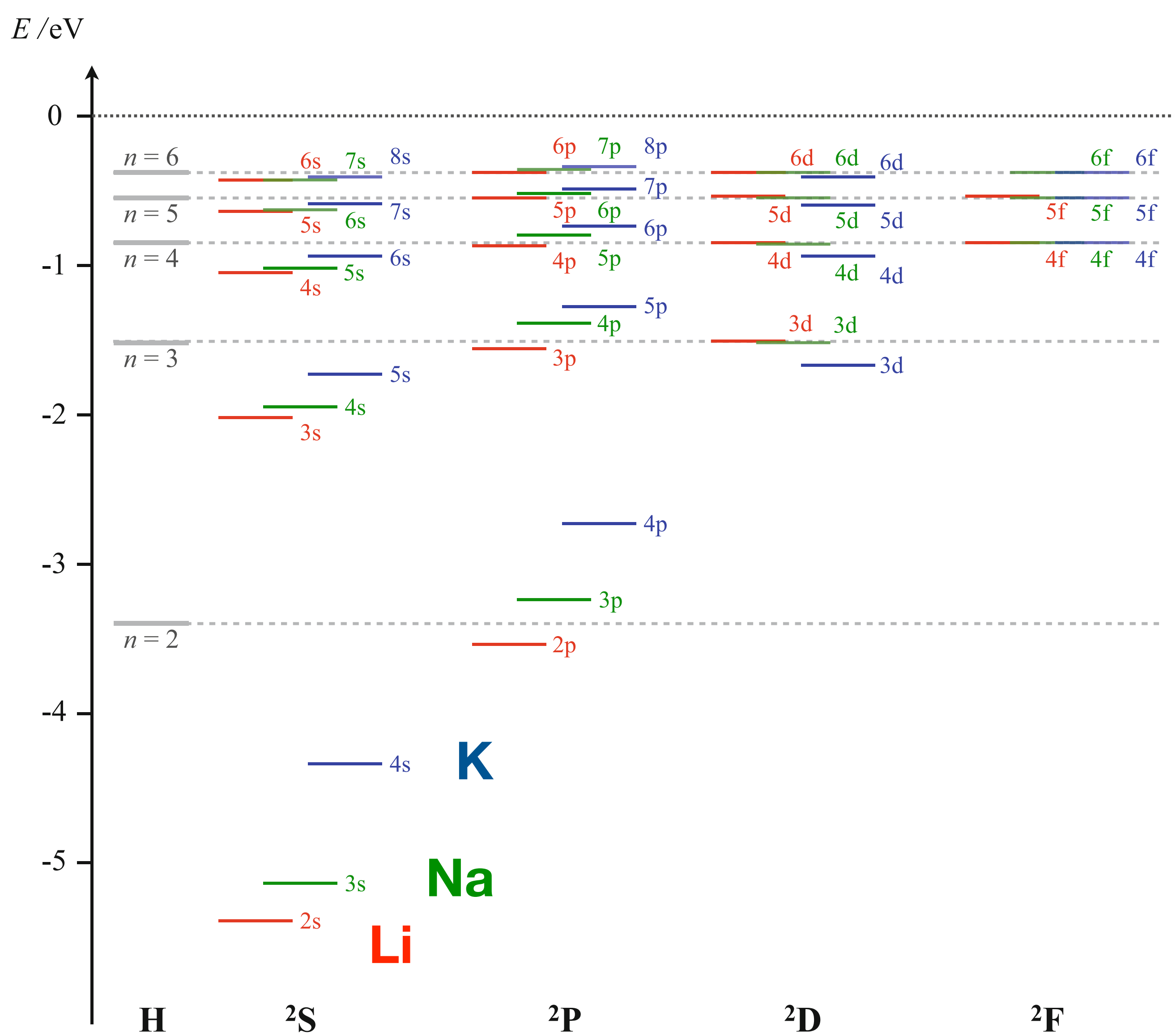



**Fig. 5.3** Experimentally reported energies (in eV) of the lowest energy states, with $l \leq 3$, for Li (red), Na (green) and K (blue) [4]. To the left, in grey, are the energy levels for H. In this graph, the respective ionisation limits have been chosen as a common zero point for the energy scale. The states 2s, 3s and 4s are the electronic ground states for Li, Na and K, and the energies of these correspond to the first ionisation energy for the respective atoms. For low energy states, the valence electron is more strongly bound for the shown alkalis than the hydrogenic version of the same level. This is due to significant penetration of the wave function into the screening charge cloud of the filled orbital electrons. The horizontal scale is organised after the value of $l$ of the valence electron (and the corresponding atomic term — see chapter 6).

$$\delta_{nl}$$

| | | | | | |
|---|---|---|---|---|---|
| | | | Li | | |
| | $n = 2$ | 3 | 4 | 5 | 6 |
| $l = 0$ | 0.411 | 0.404 | 0.402 | 0.402 | 0.401 |
| 1 | 0.040 | 0.045 | 0.046 | 0.047 | 0.048 |
| 2 | | 0.002 | 0.002 | 0.003 | 0.003 |
| 3 | | | 0.000 | 0.00 | |
| | | | Na | | |
| | $n = 3$ | 4 | 5 | 6 | 7 |
| $l = 0$ | 1.373 | 1.358 | 1.353 | 1.352 | 1.352 |
| 1 | 0.884 | 0.868 | 0.863 | 0.860 | 0.859 |
| 2 | 0.011 | 0.013 | 0.014 | 0.015 | 0.015 |
| 3 | | 0.002 | 0.002 | 0.002 | 0.003 |
| | | | K | | |
| | $n = 3$ | 4 | 5 | 6 | 7 |
| $l = 0$ | | 2.230 | 2.199 | 2.191 | 2.187 |
| 1 | | 1.768 | 1.738 | 1.728 | 1.723 |
| 2 | 0.147 | 0.204 | 0.232 | 0.247 | 0.255 |
| 3 | | 0.008 | 0.009 | 0.009 | 0.010 |
| | | | Rb | | |
| | $n = 4$ | 5 | 6 | 7 | 8 |
| $l = 0$ | | 3.196 | 3.156 | 3.144 | 3.140 |
| 1 | | 2.721 | 2.684 | 2.672 | 2.667 |
| 2 | 1.234 | 1.295 | 1.318 | 1.328 | 1.334 |
| 3 | 0.012 | 0.014 | 0.015 | 0.017 | 0.017 |
| | | | Cs | | |
| | $n = 4$ | 5 | 6 | 7 | 8 |
| $l = 0$ | | | 4.131 | 4.081 | 4.067 |
| 1 | | | 3.671 | 3.627 | 3.612 |
| 2 | | 2.453 | 2.473 | 2.476 | 2.476 |
| 3 | 0.023 | 0.027 | 0.029 | 0.031 | 0.032 |

$$E_{nl} = -\frac{\text{Ry}}{(n - \delta_{nl})^2}$$

# Ground-state energies from the Hartree-Fock approximation

Table I. Total and Correlation Energies (in au) for Some Atoms

| Element | Total Energy: Corrected Hartree-Fock | Corrected Dirac-Hartree-Fock[9] | Exact[10] | Correlation Energy[a] |
|---|---|---|---|---|
| He | −2.8617480 | −2.8617350 | −2.9037843 | 0.0420363 |
| Li | −7.4332736 | | −7.4785707 | 0.0452971 |
| Be | −14.575209 | −14.575199 | −14.669349 | 0.094140 |
| B | −24.535061 | | −24.659145 | 0.124084 |
| C | −37.702196 | | −37.857424 | 0.155228 |
| N | −54.427812 | | −54.614112 | 0.186300 |
| O | −74.858218 | | −75.112455 | 0.254237 |
| F | −99.491039 | | −99.808790 | 0.317751 |
| Ne | −128.67513 | −128.67526 | −129.06016 | 0.385030 |
| A | −528.53560 | −528.55144 | | |
| Zn | −1793.4731 | −1793.8535 | | |
| Kr | −2786.2073 | −2787.4402 | | |

[a] Defined as the difference between the corrected Hartree-Fock and the exact energies

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