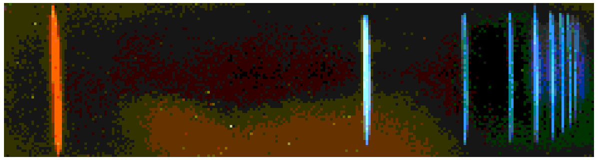
3.4 Hydrogenic atom

In 1885, Swiss mathematician Balmer 巴耳末 discovered the visible spectrum lines of hydrogen atoms

Balmer series 巴耳末系 $\lambda = 365.46 \dfrac{n^2}{n^2 - 2^2}\ \mathrm{nm}, \qquad n = 3,4,5,\cdots$

Rydberg 里德伯 rewrite the equation into this form



$$\sigma = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \qquad n = 3,4,5,\cdots$$

$\sigma=1/\lambda$: wavenumber 波数, R: Rydberg constant,

$R = 1.097\,373\,153\,4\times10^{7}\mathrm{m}^{-1}$

Ultraviolet spectrum

Lyman series 莱曼系 (1916) $\sigma = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right), \quad n = 2,3,4, \cdots$

Infrared spectrum

Paschen series 莱曼系 (1908) $\sigma = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right), \quad n = 4,5,6, \cdots$

Brackett series 布拉开系 (1922) $\sigma = R\left(\frac{1}{4^2} - \frac{1}{n^2}\right), \quad n = 5,6,7, \cdots$

Pfund series 普丰德系 (1924) $\sigma = R\left(\frac{1}{5^2} - \frac{1}{n^2}\right), \quad n = 6,7,8, \cdots$

A general formula

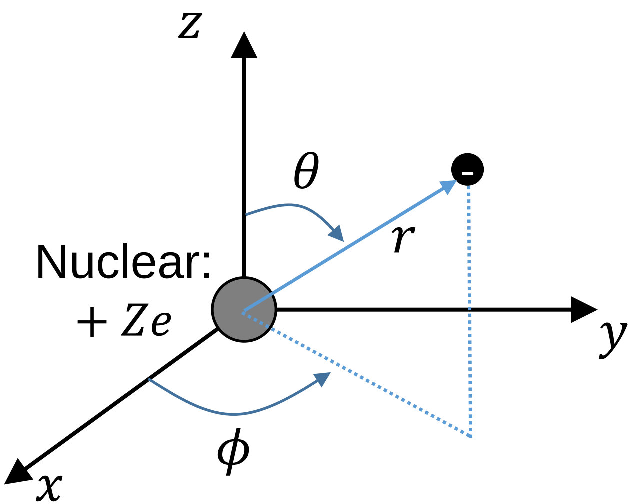
$$\sigma = R\left(\frac{1}{n_j^2} - \frac{1}{n_i^2}\right)$$

n_j (=1,2,3, …)

n_i: n_j+1,n_j+2, …

The spectrum of hydrogen atoms should reveal its internal atomic structure.

What's the behavior of electrons in a hydrogenic (hydrogen-like) atom: nuclear charge $+Ze$, 1 electron.



Potential energy:

$$V = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

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

Radial part

Spherical harmonic

$$\boldsymbol{\psi(r, \theta , \phi) = R(r)Y(\theta , \phi)}$$

Radial part $R(r)$ depends on n and ℓ.

Spherical harmonic $Y(\theta , \phi)$ depends on ℓ and m_ℓ.

Principle quantum number: $n = 1, 2, 3, \ldots$

Orbital angular momentum quantum number: $\ell = 0, 1, 2, 3, \ldots , n - 1$

Magnetic quantum number: $m_\ell = -\ell,\ -(\ell - 1), \ldots , 0, \ldots , \ell - 1, \ell$

Principle quantum number: $n = 1, 2, 3, \ldots$

Orbital angular momentum quantum number: $\ell = 0, 1, 2, 3, \ldots, n-1$

Magnetic quantum number: $m_\ell = -\ell,\ -(\ell-1), \ldots, 0, \ldots, \ell-1, \ell$

	ℓ				
$\boldsymbol{n}$	0	1	2	3	4
1	1*s*				
2	2*s*	2*p*			
3	3*s*	3*p*	3*d*		
4	4*s*	4*p*	4*d*	4*f*	
5	5*s*	5*p*	5*d*	5*f*	5*g*

The solution of Schrodinger equation

n	ℓ	$R(r)$	m_ℓ	$Y(\theta, \phi)$
1	0	$\left(\frac{1}{a_0}\right)^{3/2} 2\exp\left(-\frac{r}{a_0}\right)$	0	$\frac{1}{2\sqrt{\pi}}$
2	0	$\left(\frac{1}{2a_0}\right)^{\frac{3}{2}} (2-\frac{r}{a_0})\exp\left(-\frac{r}{2a_0}\right)$	0	$\frac{1}{2\sqrt{\pi}}$
2	1	$\left(\frac{1}{2a_0}\right)^{\frac{3}{2}} (\frac{r}{\sqrt{3}a_0})\exp\left(-\frac{r}{2a_0}\right)$	0	$\propto \cos\theta$
			1	$\propto \sin\theta\cos\phi$
			-1	$\propto \sin\theta\sin\phi$

$$a_0 = 0.0529 \text{ nm}$$

The probability of finding the electron in the shell from r to $r + \delta r$

$$|R_{n,\ell}(r)\overline{Y_{\ell,m_\ell}(\theta\,,\phi)}|^2 \times 4\pi r^2 \delta r$$

$$\because\ \ |\overline{Y_{\ell,m_\ell}(\theta\,,\phi)}|^2 = \frac{1}{4\pi}$$

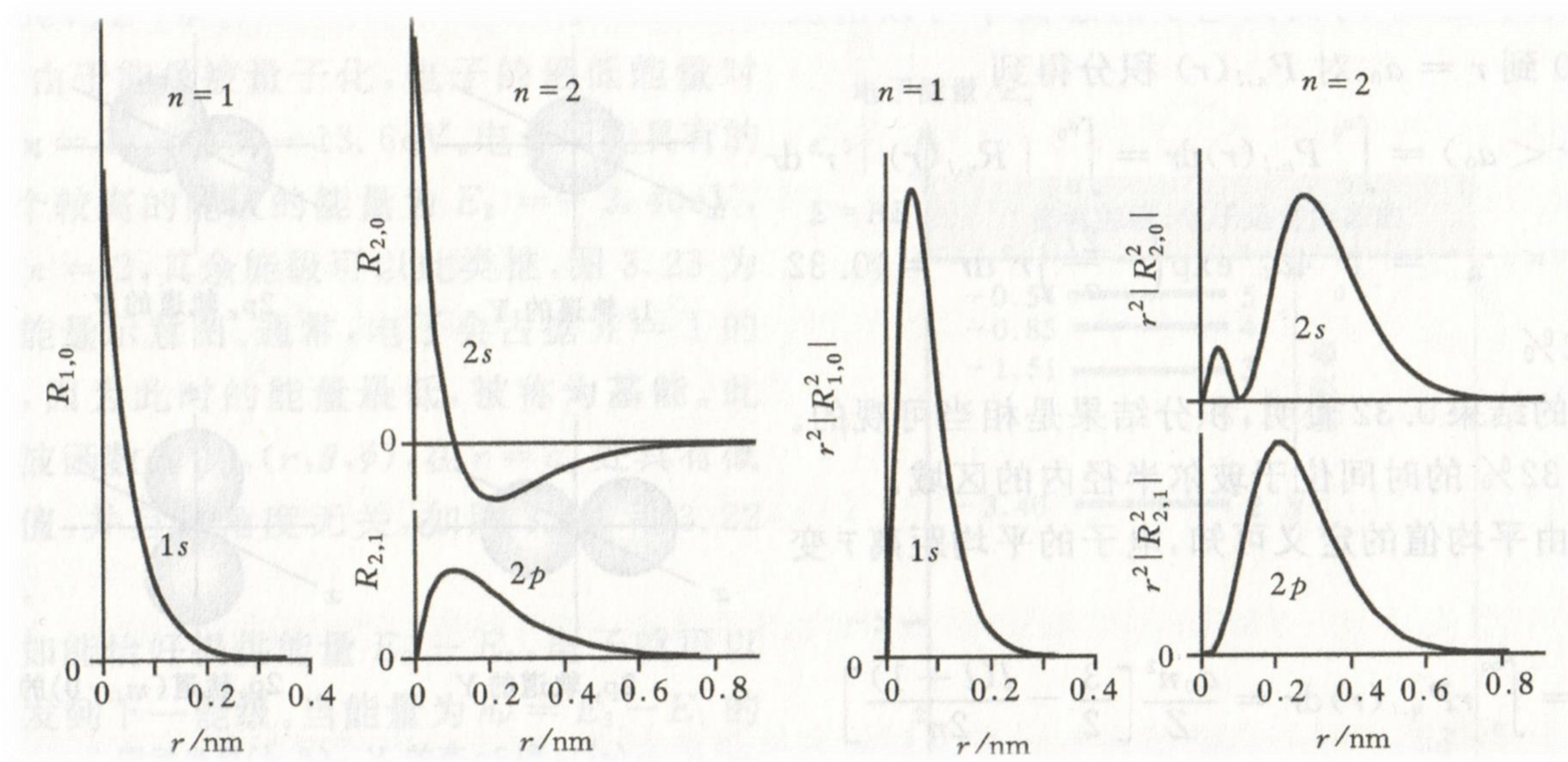
$$\therefore |R_{n,\ell}(r)Y_{\ell,m_\ell}(\theta\,,\phi)|^2 \times 4\pi r^2 \delta r = |R_{n,\ell}(r)|^2 r^2 \delta r$$

The radial probability density: $P_{n,\ell}(r)$

Defined as the probability per unit radial distance.

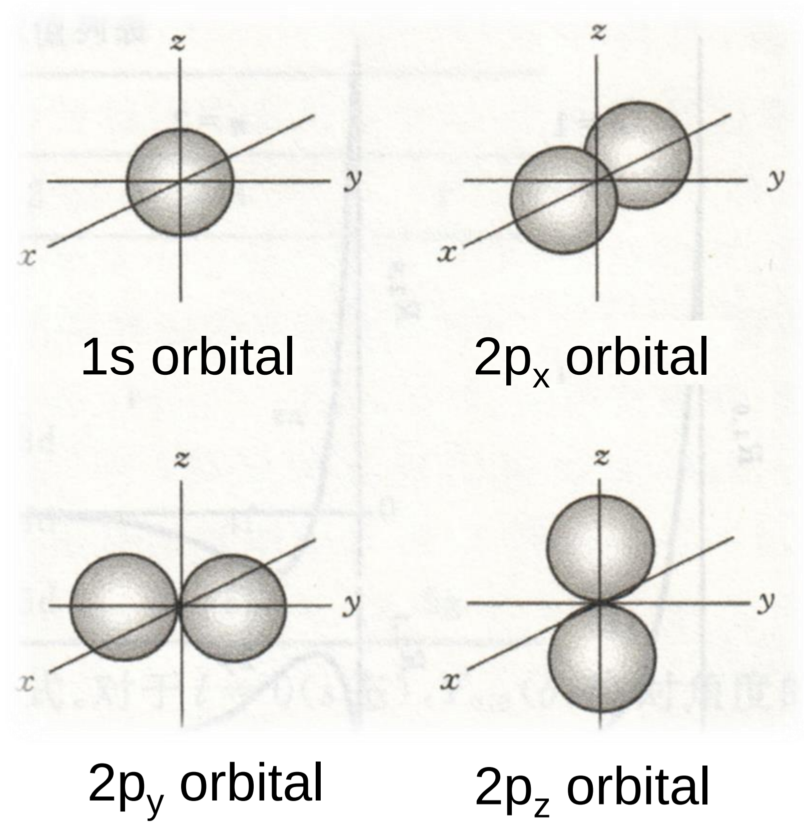
$$P_{n,\ell}(r) = |R_{n,\ell}(r)|^2 r^2$$

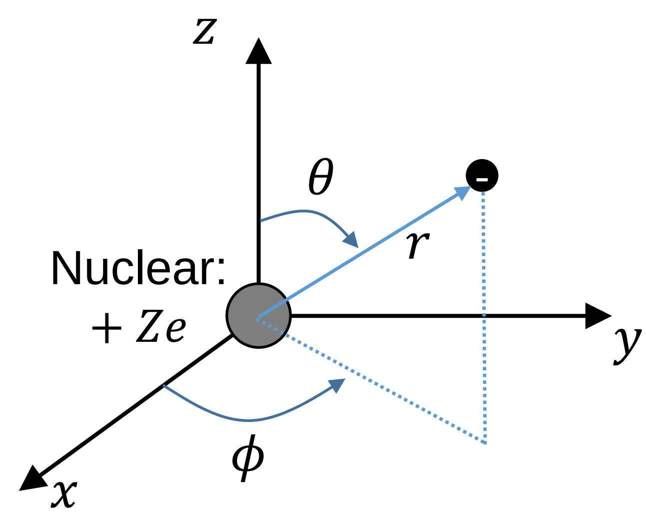
The radial part $R_{n,\ell}(r)$ and radial probability $P_{n,\ell}(r)$ in a hydrogenic atom



The radius *r* with maximum probability $P_{n,\ell}(r)$ is called the **Bohr radius**.

The spherical harmonic $Y(\theta, \phi)$ in a hydrogenic atom

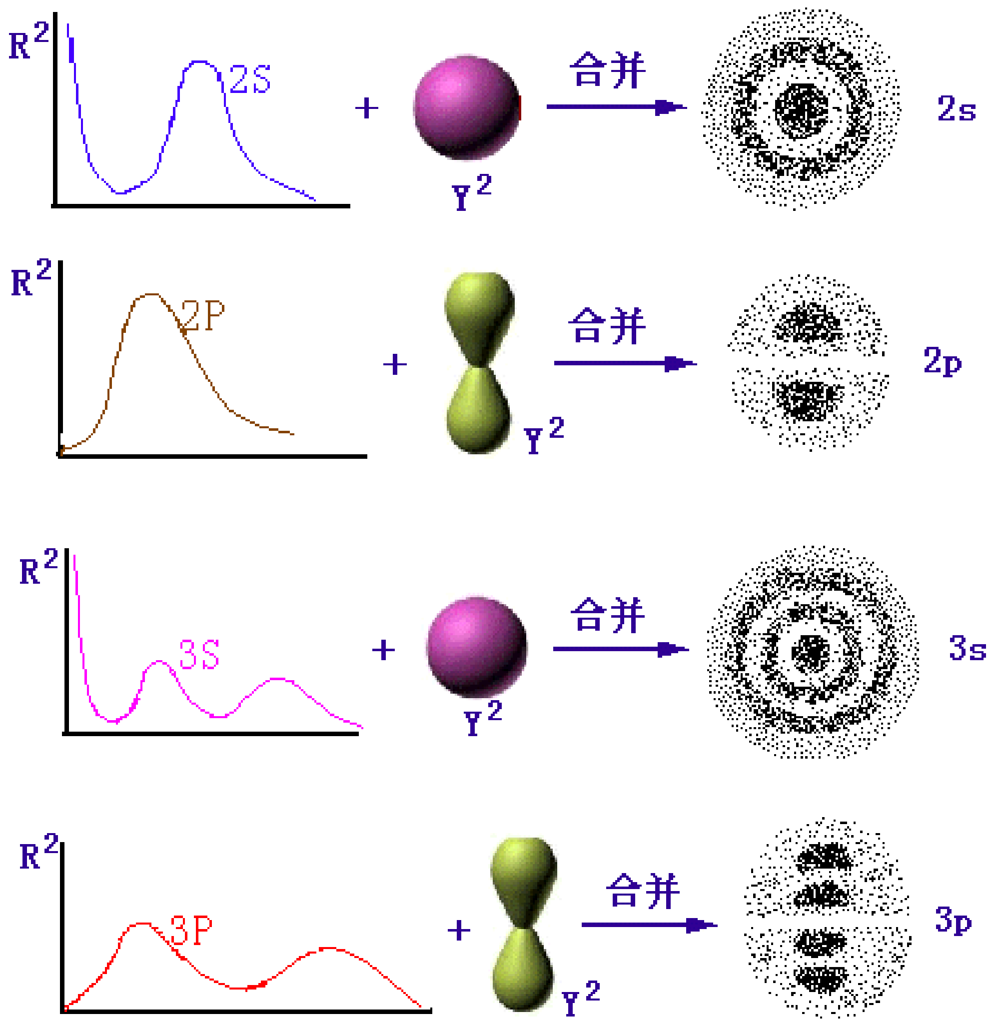




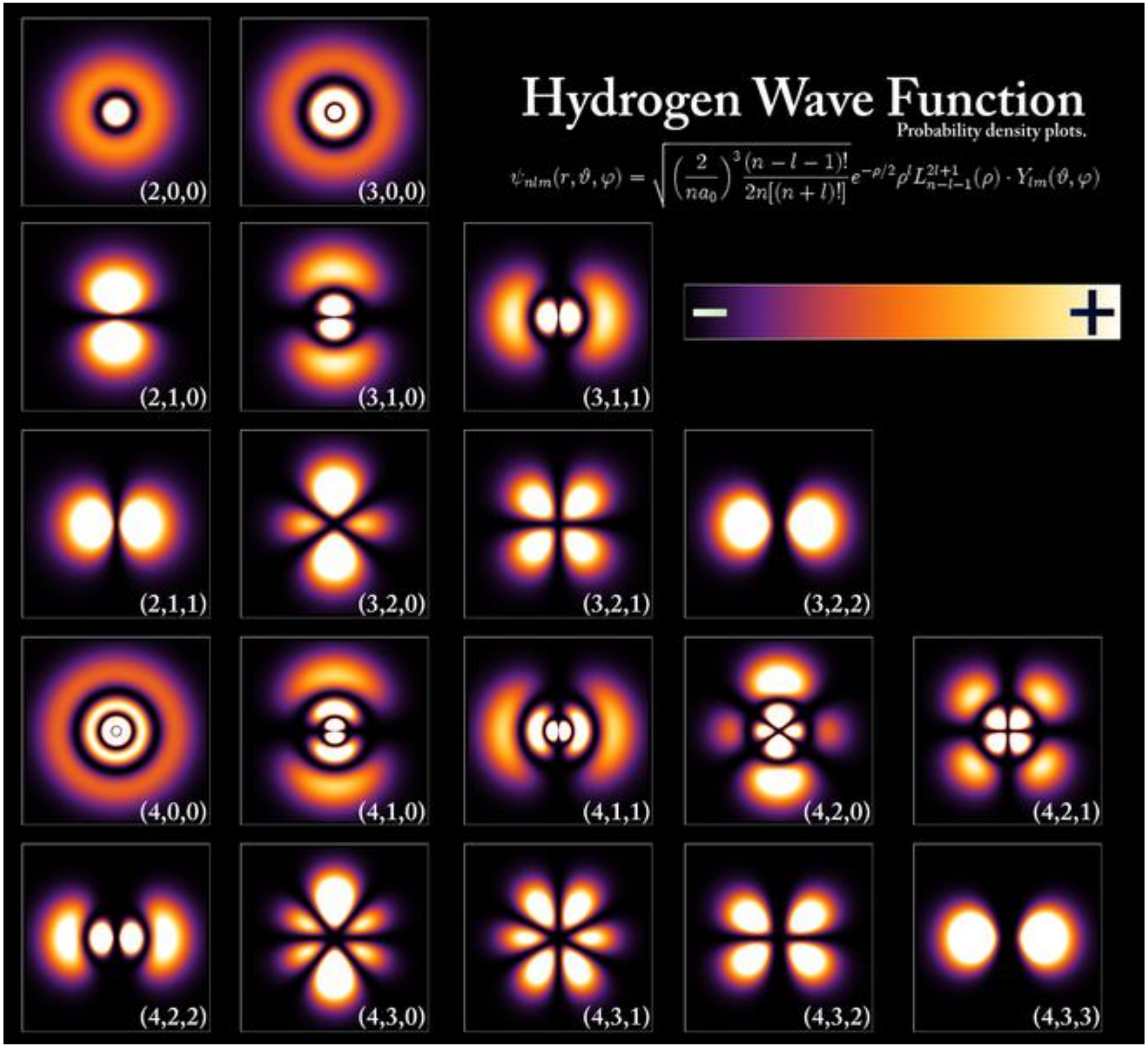
p$_z$: $m_\ell = 0$

p$_x$, p$_y$: $m_\ell = \pm 1$

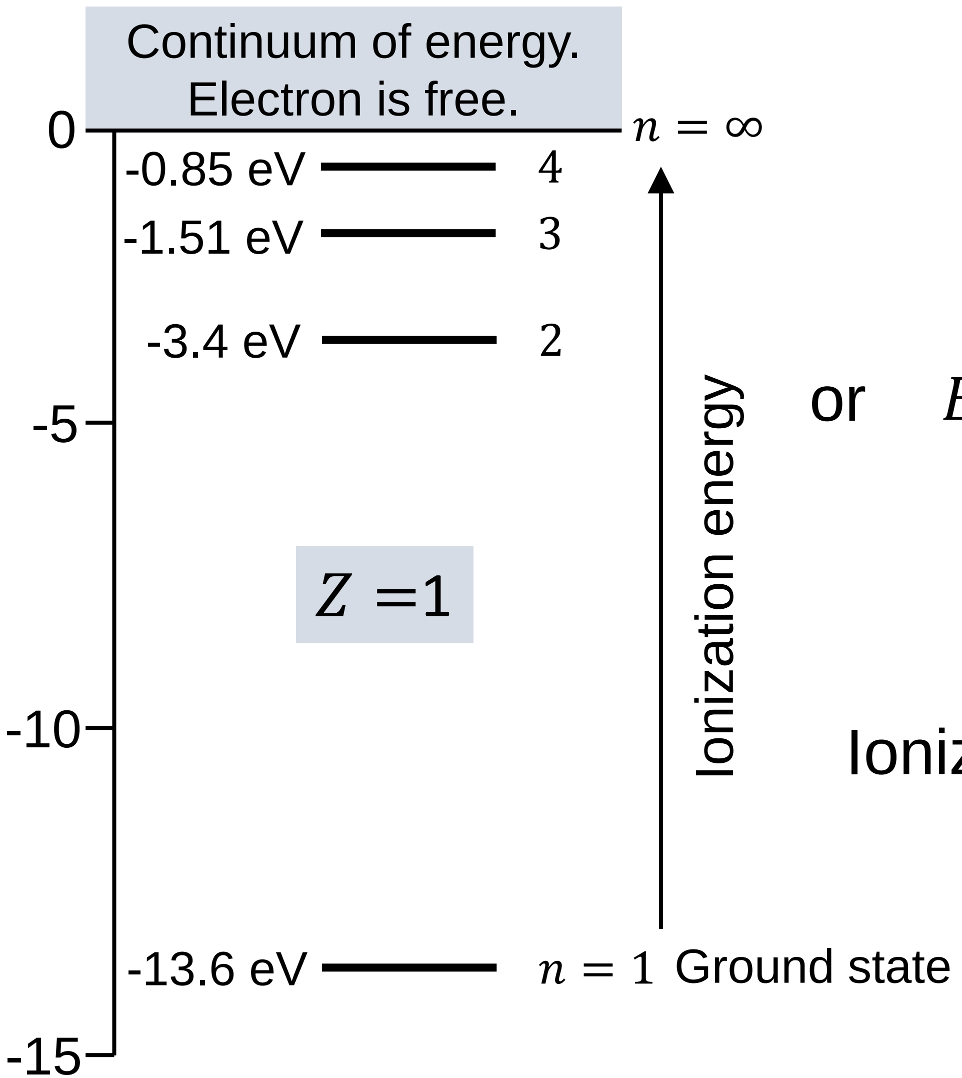
$$\psi(r,\theta,\phi) = R_{n,l}(r)Y_{l,m_l}(\theta,\phi)$$



e orbital: e cloud (simulated)



The eigenenergy in hydrogenic atom



$$E_{\mathrm{n}} = -\frac{m_{\mathrm{e}} e^4 Z^2}{8 \varepsilon_0{}^2 h^2 n^2}$$

or

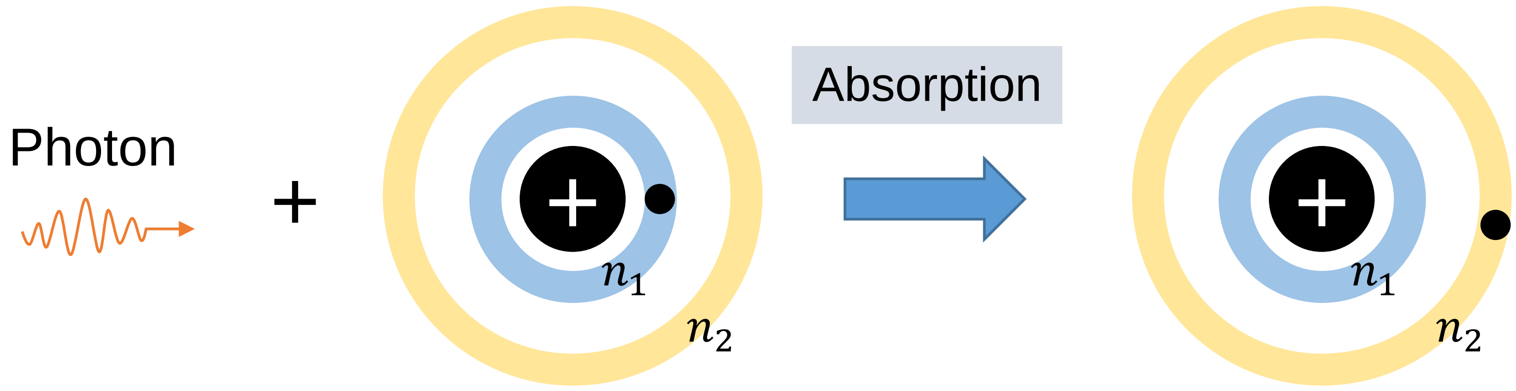
$$E_{\mathrm{n}} = -\frac{Z^2 E_{\mathrm{I}}}{n^2} = -\frac{Z^2 (13.6\ \mathrm{eV})}{n^2}$$

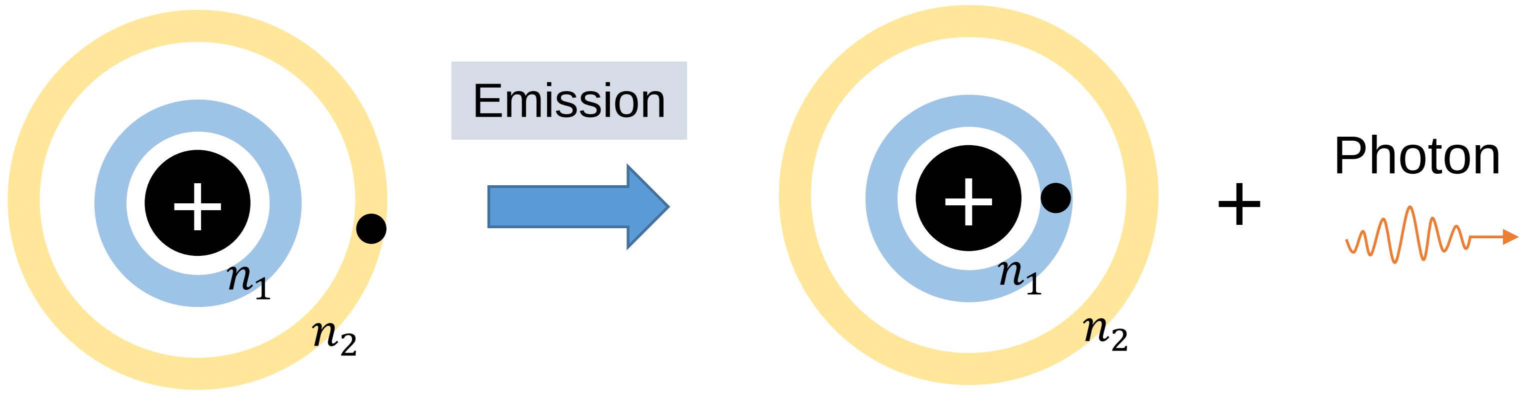
$n = 1$: Ground energy

Ionization energy for the n^{th} shell:

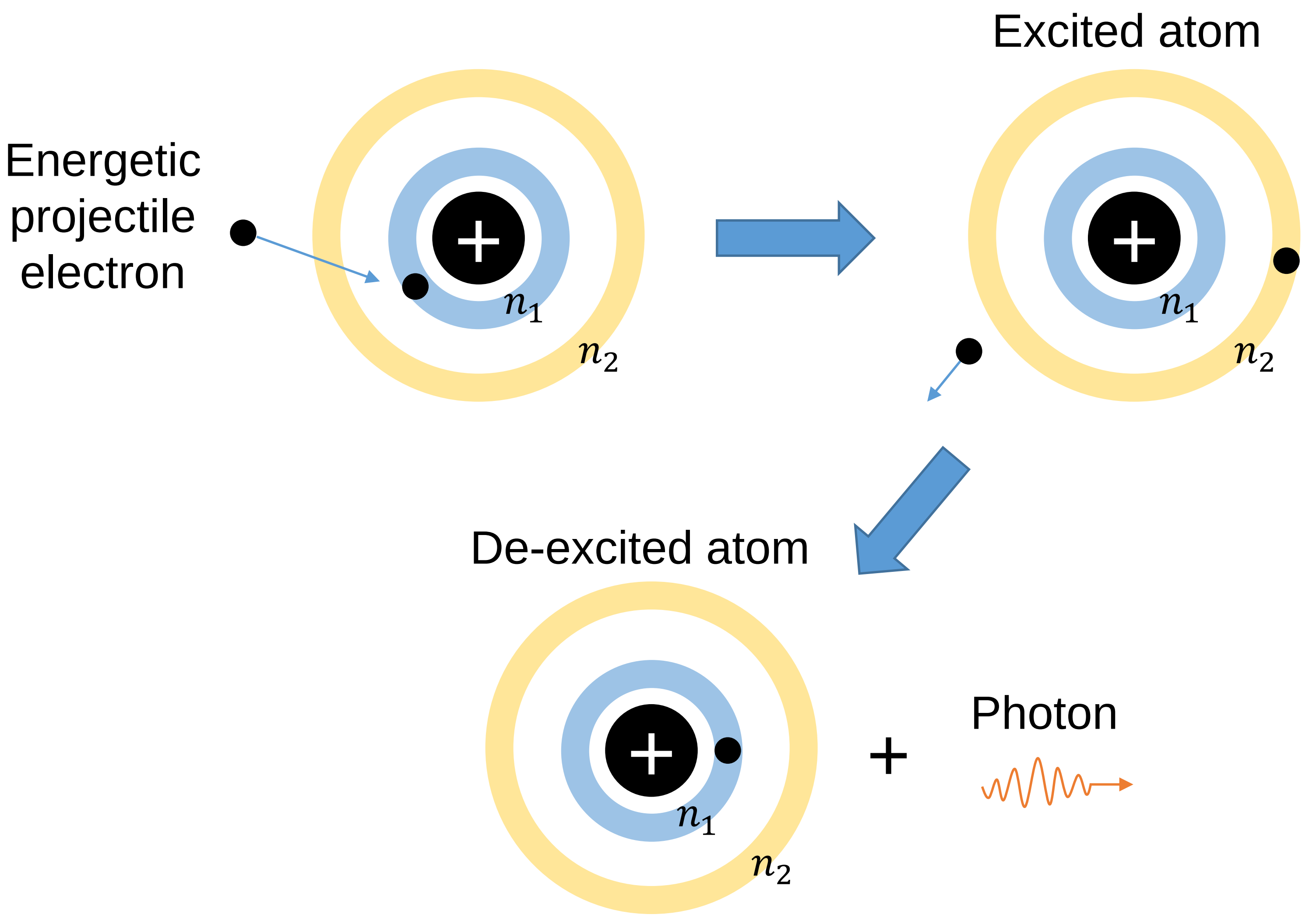
$$\frac{13.6 Z^2}{n^2}\ \mathrm{eV}$$

The physical origin of absorption and emission spectra

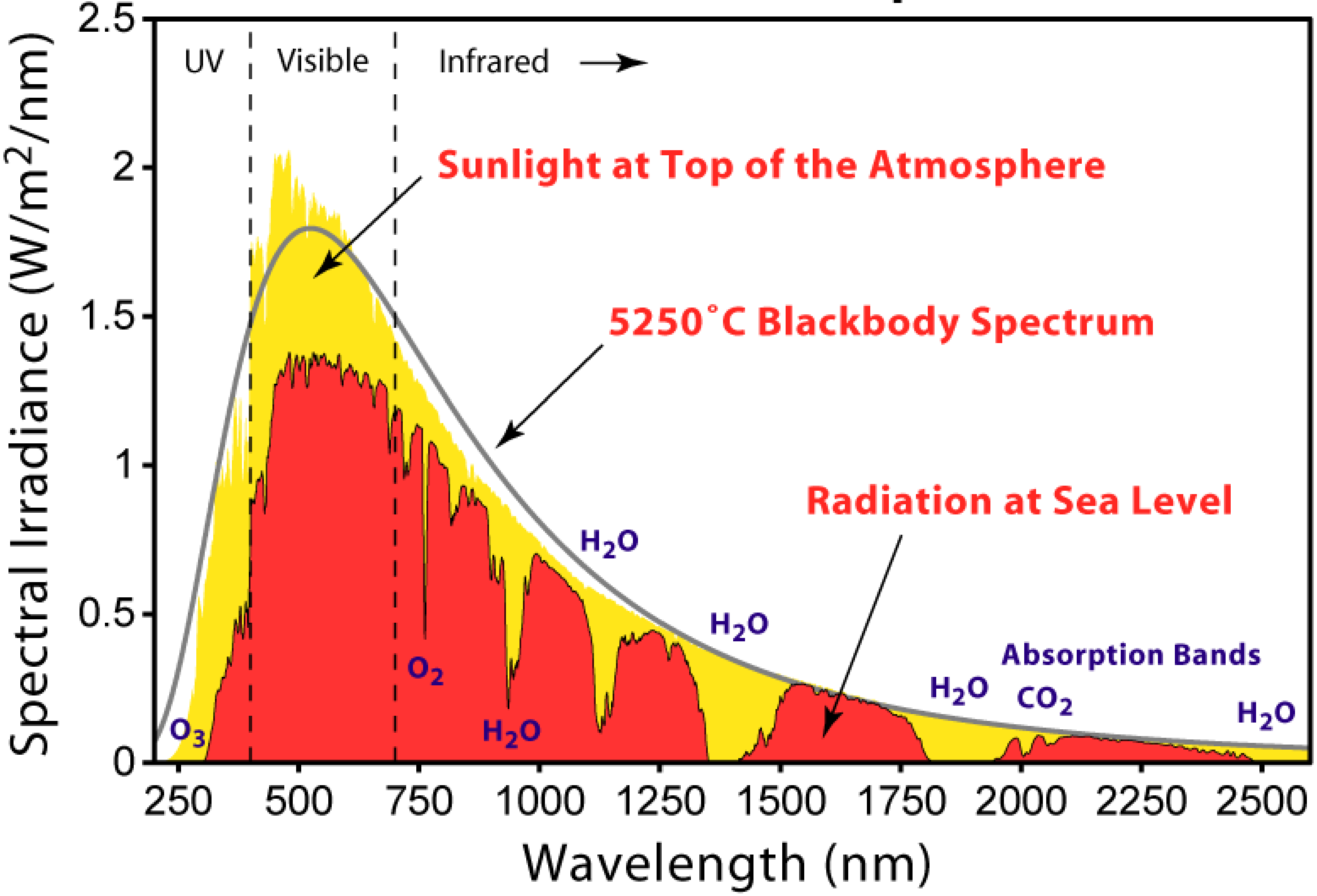




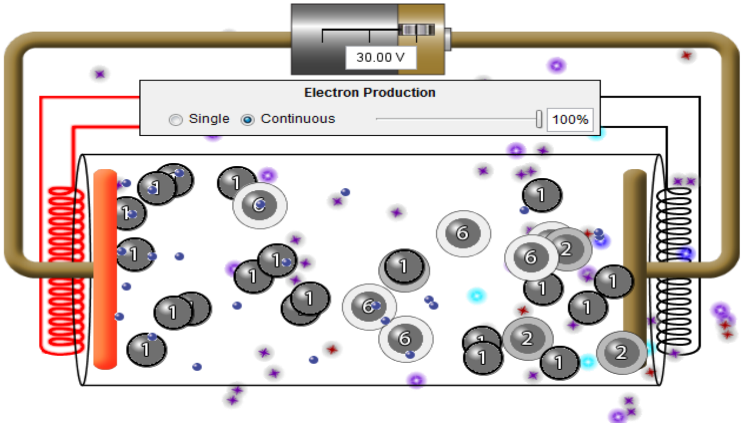
Excite an atom by collision



Solar Radiation Spectrum



Neon light (gas discharging)



《湖口望庐山瀑布水》

唐 张九龄

万丈红泉落，迢迢半紫氛。

奔流下杂树，洒落出云天。

日照虹霓似，天清风雨闻。

灵山多秀色，空水共氤氲。

The Nobel Prize in Physics 1922
Niels Bohr

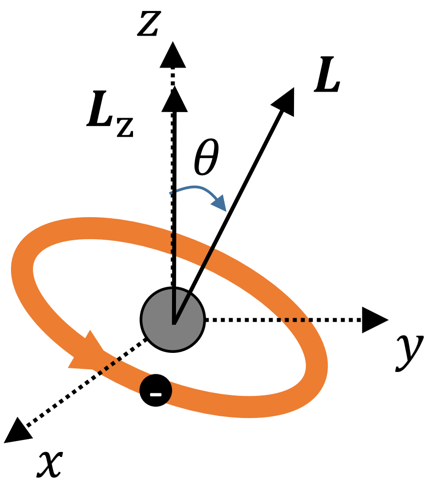
The Nobel Prize in Physics 1922

Niels Henrik David Bohr

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

3.5 Orbital angular momentum and space quantization

Electron in the atom has an orbital angular momentum $\boldsymbol{L}$.

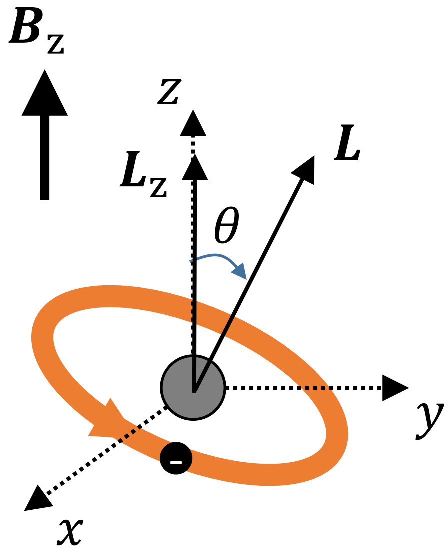


Quantized orbital angular momentum:

$$L = \hbar\sqrt{\ell(\ell+1)}$$

Where $\ell = 0, 1, 2, \ldots n-1.$

What's the significance of m_ℓ?



In the presence of an magnetic field $\boldsymbol{B}_\mathrm{z}$,

$\boldsymbol{L}_\mathrm{z}$ is also quantized.

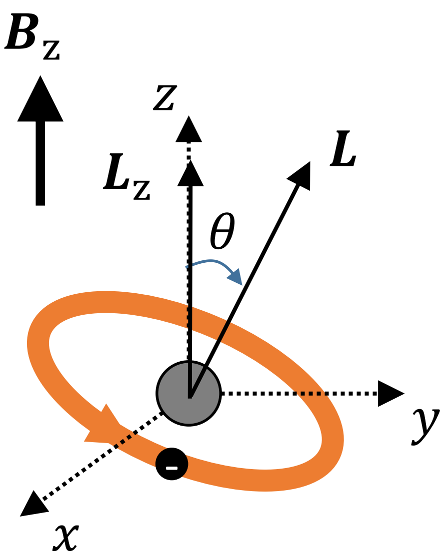
$$L_\mathrm{z} = m_\ell \hbar$$

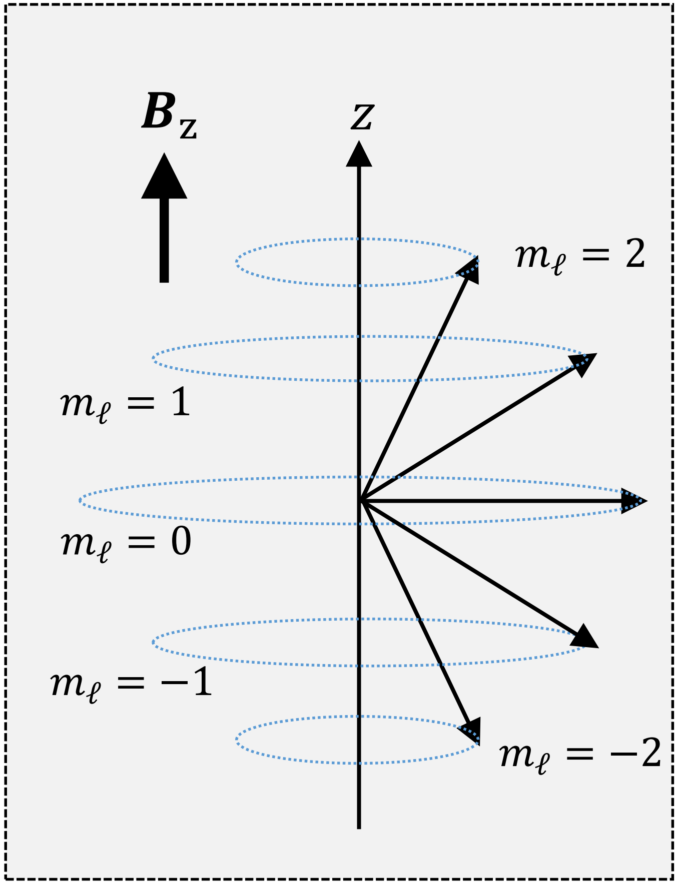
Therefore, m_ℓ is called the **magnetic quantum number**.

$$\because \ |L_\mathrm{z}| < |L|$$

$$\therefore \ |m_\ell| \leq \ell$$

Space distribution of $\boldsymbol{L}$ ($\ell = 2$)?





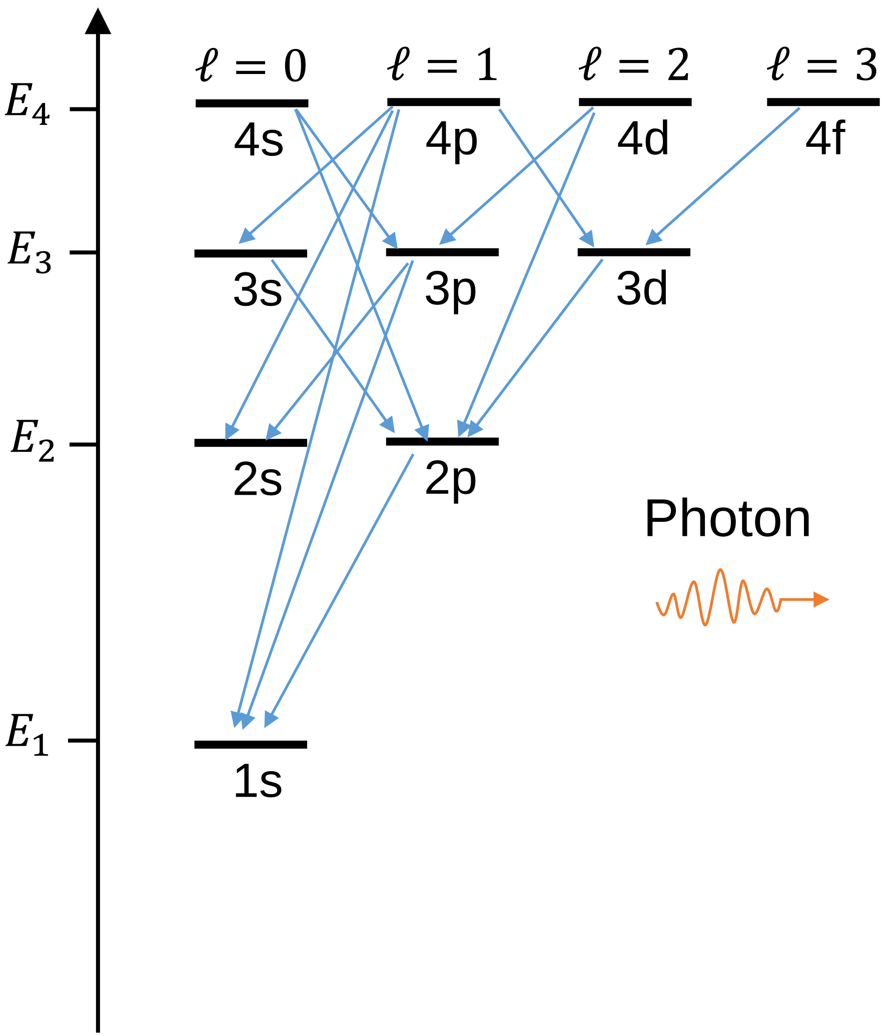
$$L = \hbar[\ell(\ell+1)]^{1/2}$$

$$L_z = m_\ell \hbar$$

$$\cos\theta = \frac{m_\ell}{\sqrt{\ell(\ell+1)}}$$

Hence, we say L is **space quantized**!

Photon emission/absorption selection rules



Energy conservation!

n change!

Angular momentum conservation!

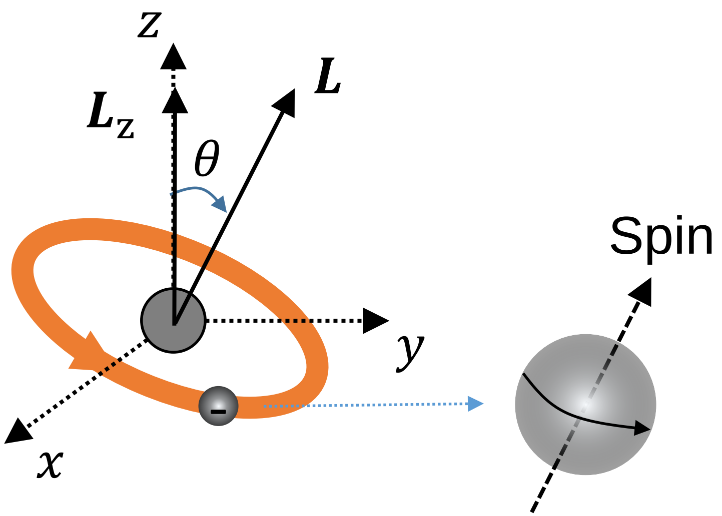
ℓ change!

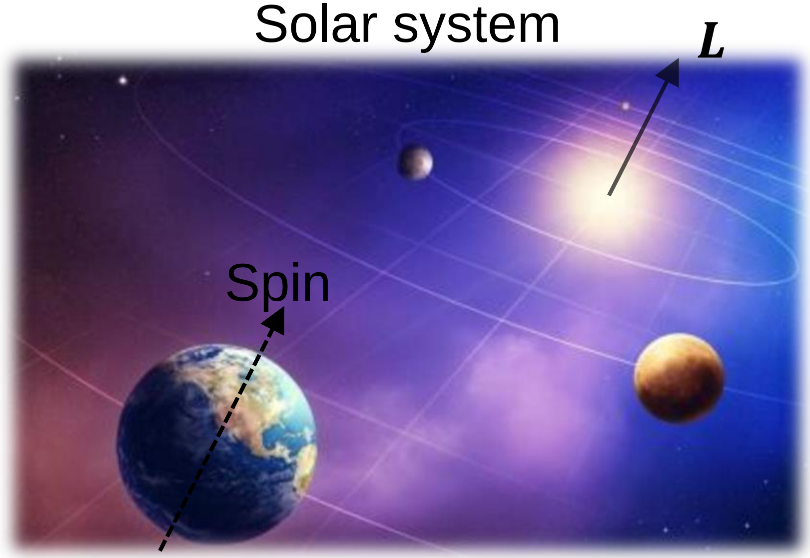
Selection rules:

$$\Delta\ell = \pm 1$$

$$m_\ell = 0, \pm 1$$

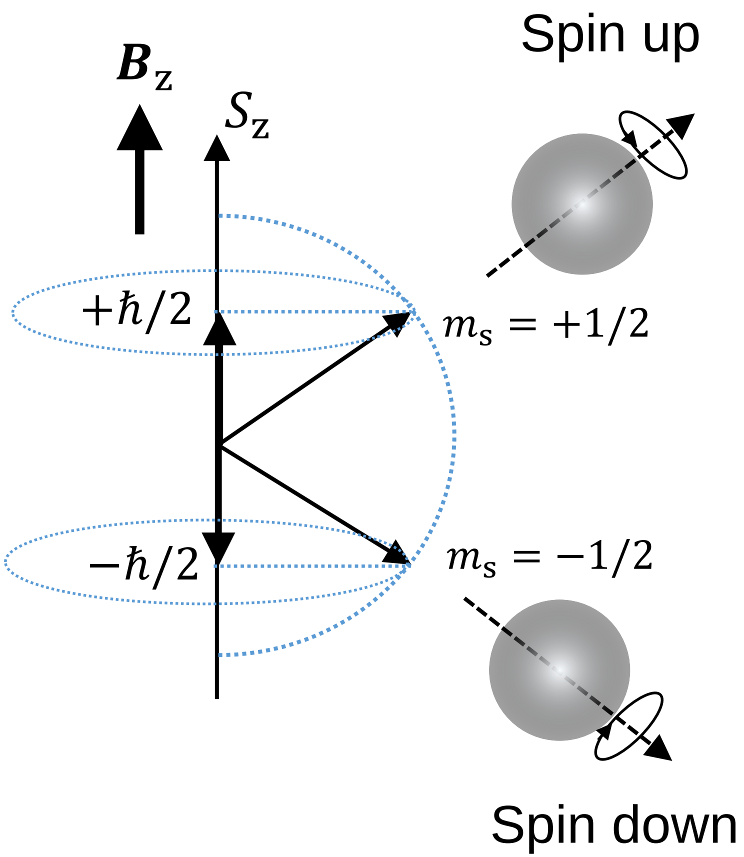
3.6 Electron spin S and total angular momentum J





Spin or intrinsic angular momentum:

$$S = \hbar\sqrt{s(s+1)},\ s = 1/2.$$



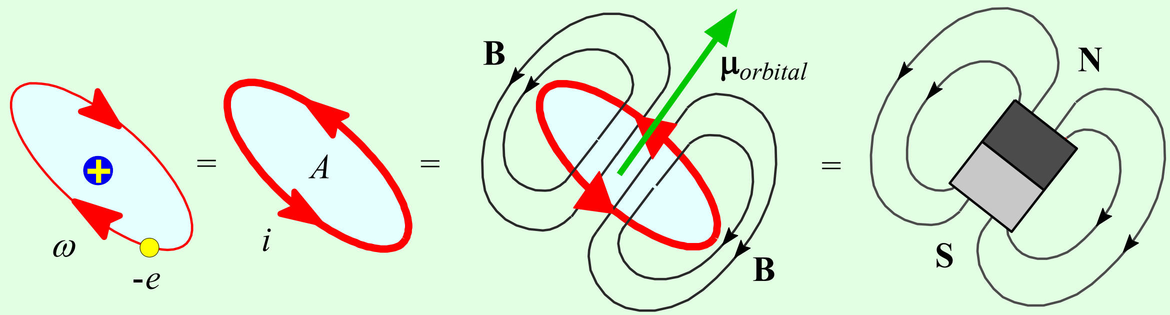
Spin: $S = \hbar\sqrt{s(s+1)}$, $s = 1/2$.

$$S_z = m_s\hbar$$

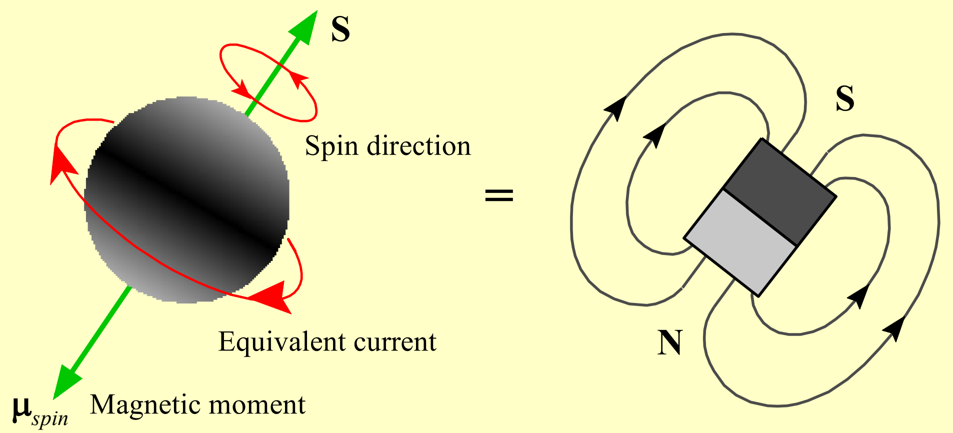
$m_s = \pm 1/2$: Spin magnetic quantum numbers

Spin is also space quantized.

$$\cos\theta = \pm\frac{1}{\sqrt{3}}$$

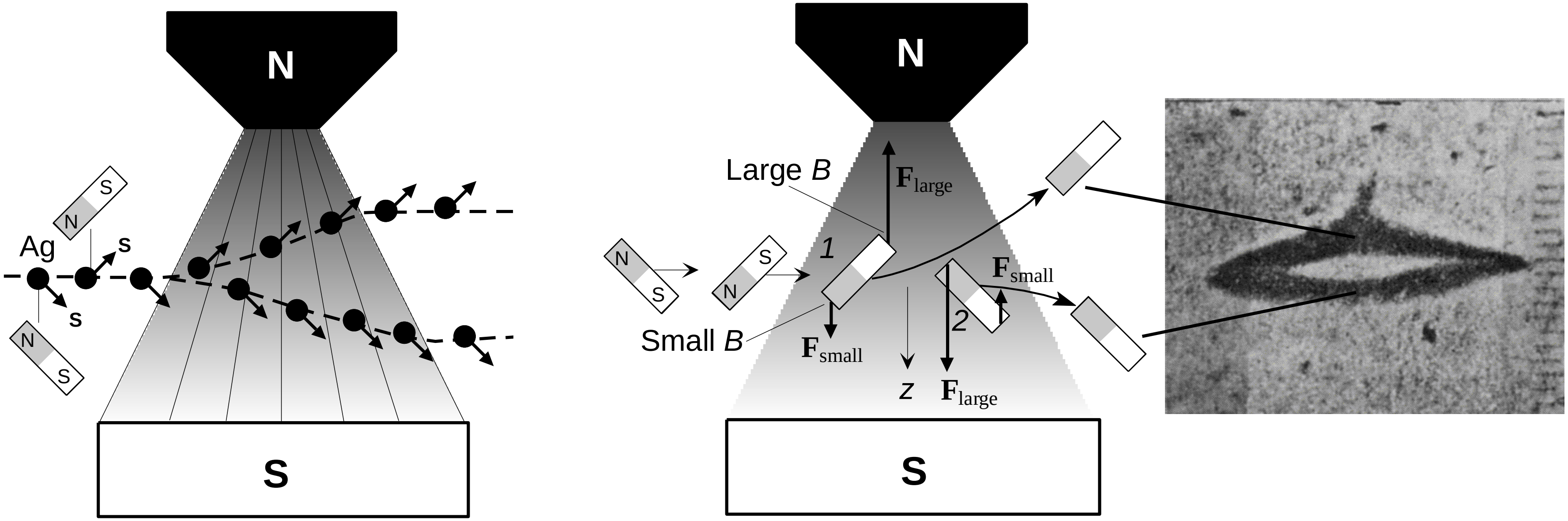


(a) The orbitting electron is equivalent to a current loop which behaves like a bar of magnet.

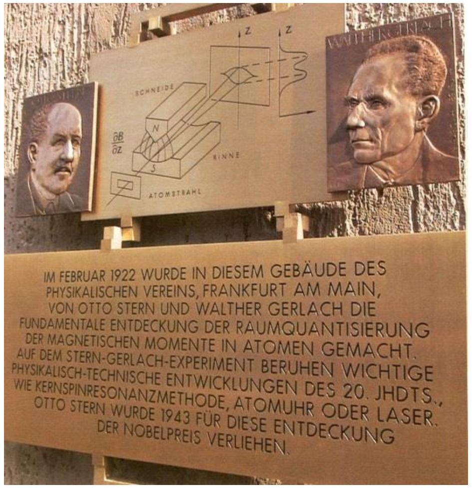


(b) The spinning electron ican be imagined to be equivalent to a current loop as shown. This current loop behaves like a bar of magnet just as in orbital case.

Stern-Gerlach experiment



(a) (b) (c)



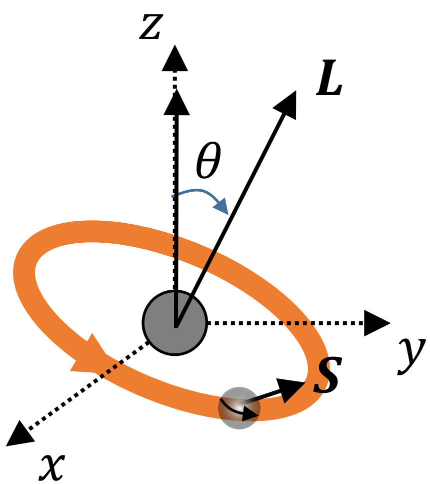
The Nobel Prize in Physics 1943
Otto Stern

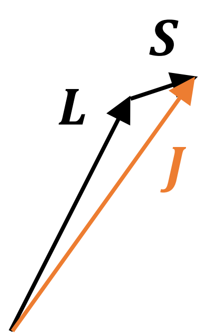
The Nobel Prize in Physics 1943

Otto Stern

The Nobel Prize in Physics 1943 was awarded to Otto Stern *"for his contribution to the development of the molecular ray method and his discovery of the magnetic moment of the proton"*.

Total angular momentum $\boldsymbol{J}$





$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$$

$$J = \hbar\sqrt{j(j+1)}$$

$$J_{\mathrm{z}} = m_{\mathrm{j}}\hbar$$

$$\begin{cases} j = \ell + s \text{ and } j = \ell - s \text{ for } \ell > 0 \\ j = s \text{ for } \ell = 0 \end{cases}$$

$$m_{\mathrm{j}} = -j, -(j-1), \ldots, 0, \ldots, j-1, j$$

3.7 Pauli exclusion principle 泡利不相容原理

Pauli exclusion principle is based on experimental observations

No two electrons with in a given system may have all four identical quantum numbers: n, ℓ, m_ℓ, m_s

In Chinese: 一山不容二虎

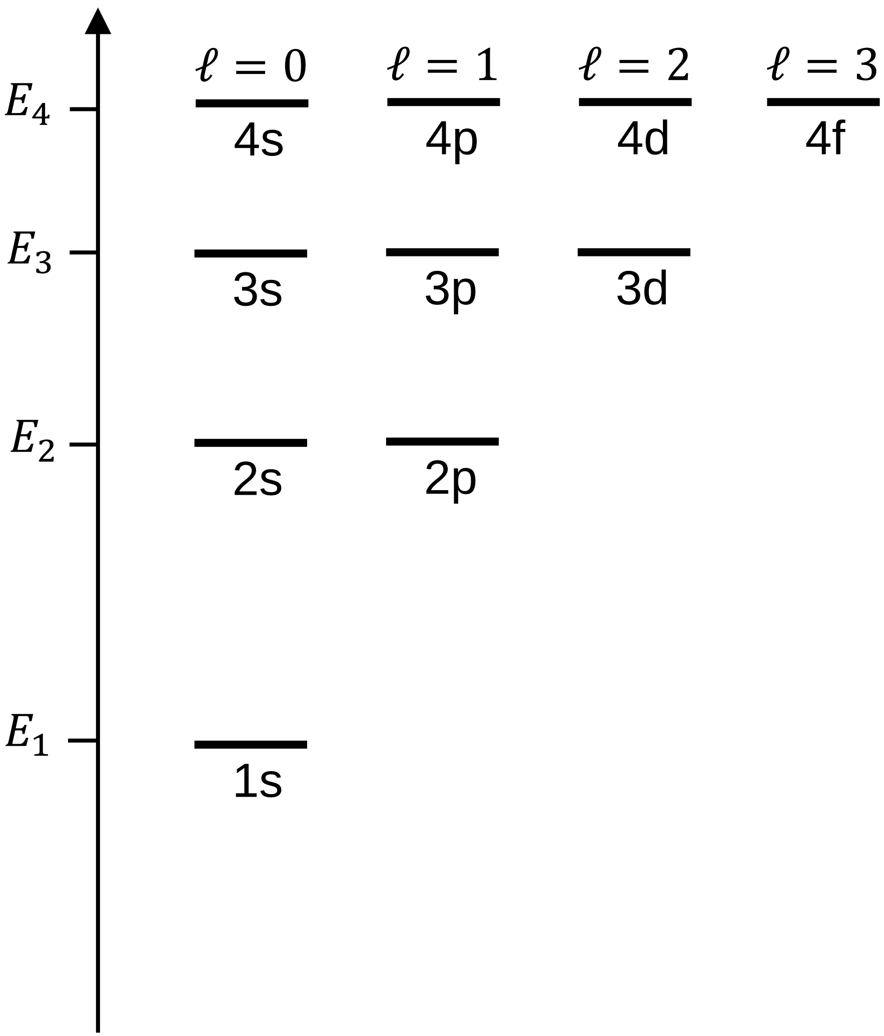
The Nobel Prize in Physics 1945
Wolfgang Pauli

The Nobel Prize in Physics 1945

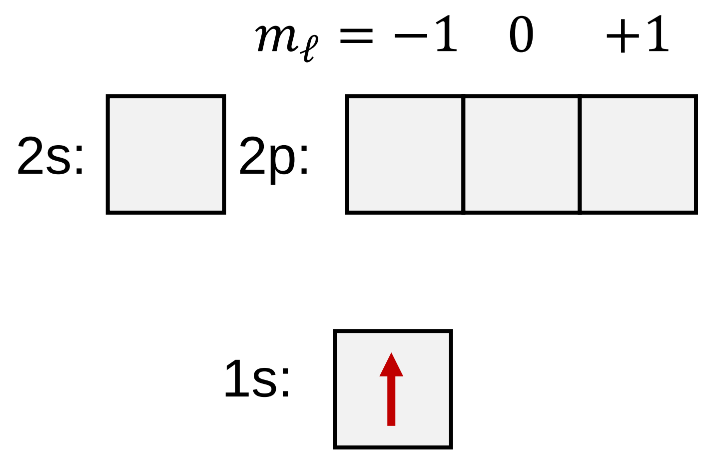
Wolfgang Pauli

The Nobel Prize in Physics 1945 was awarded to Wolfgang Pauli *"for the discovery of the Exclusion Principle, also called the Pauli Principle"*.

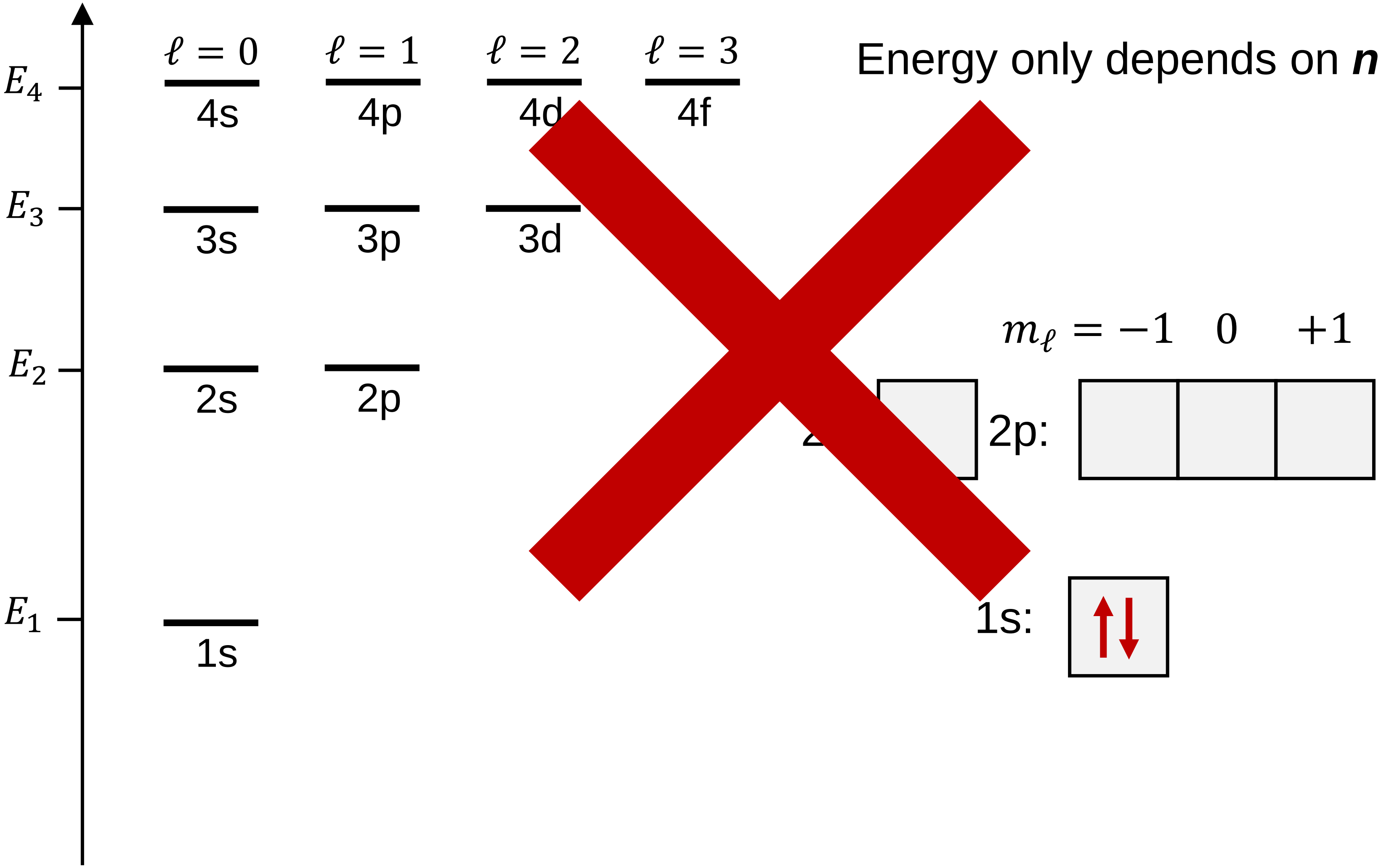
Hydrogen atom



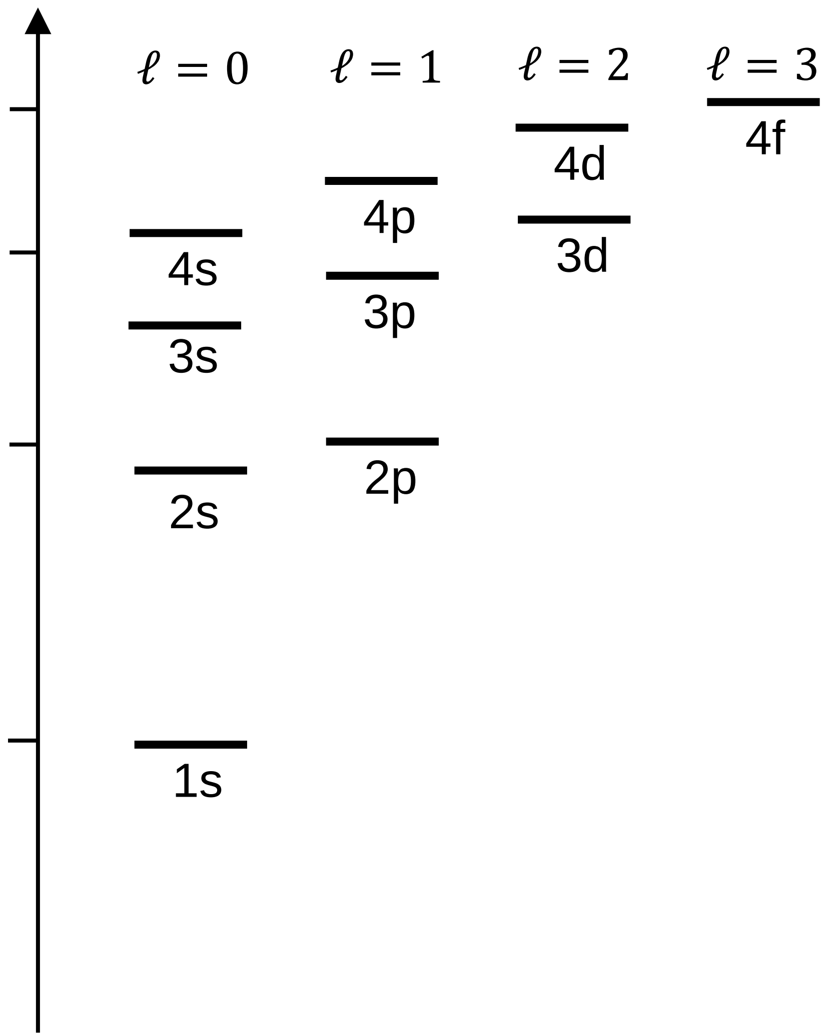
Energy only depends on ***n***



He atom

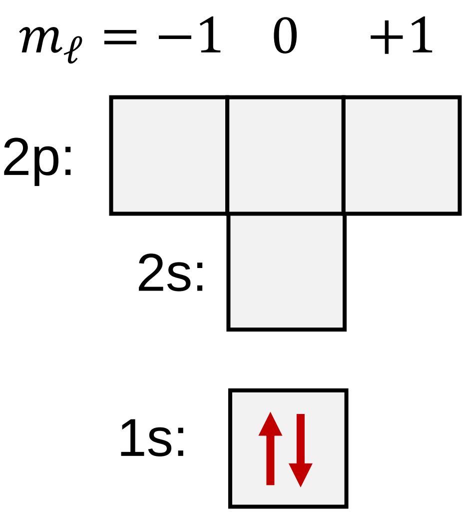

$\ell = 0$
$\ell = 1$
$\ell = 2$
$\ell = 3$
Energy only depends on ***n***
E_4
4s
4p
4d
4f
E_3
3s
3p
3d
E_2
2s
2p
$m_\ell = -1 \quad 0 \quad +1$
2p:
E_1
1s
1s:

He atom

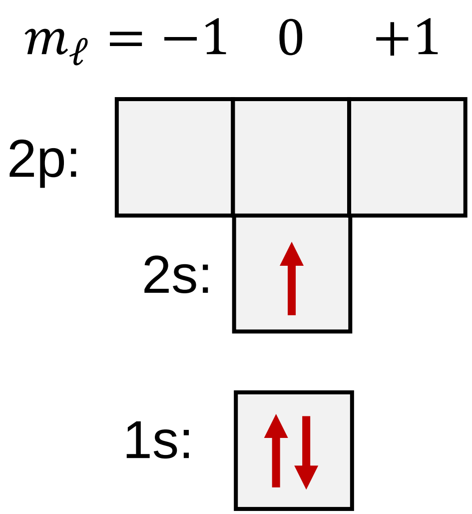


Interactions of two electrons

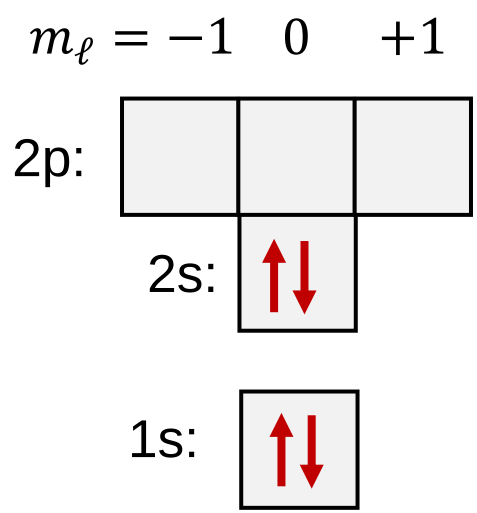
Energy depends on both ***n*** and ℓ



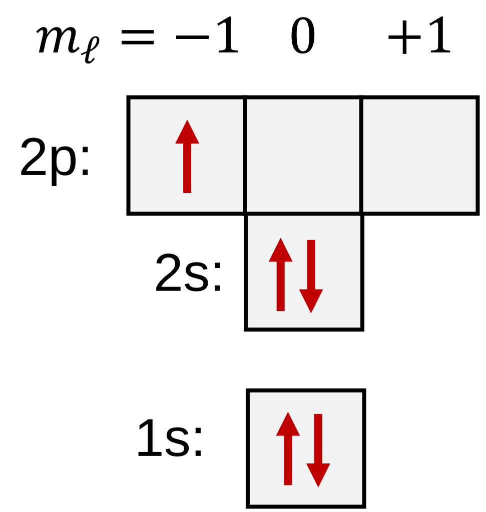
Li atom



Be atom



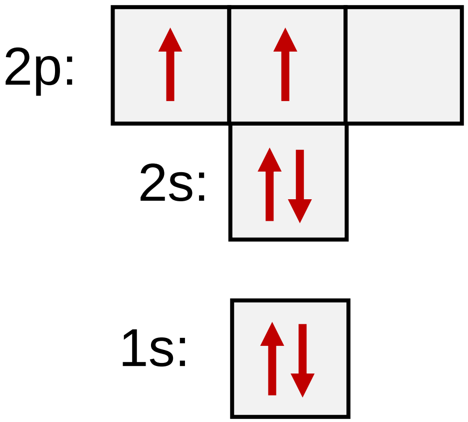
B atom



Hund's rule

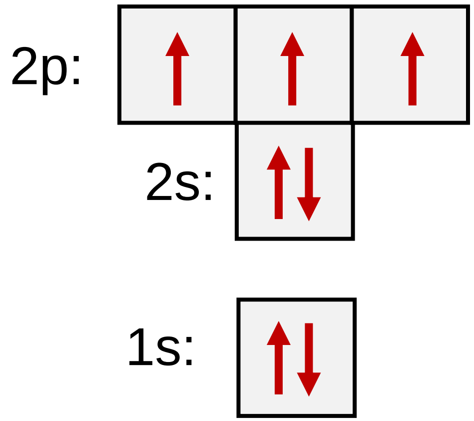
C atom

$$m_\ell = -1 \quad 0 \quad +1$$



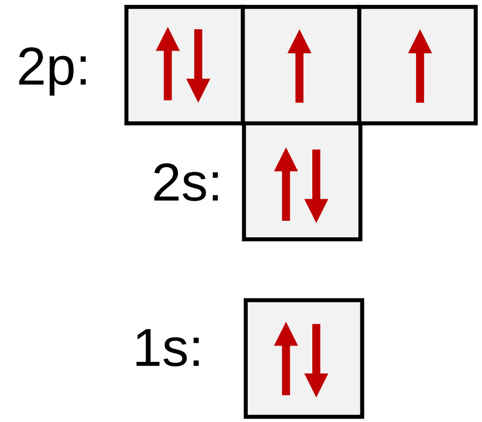
N atom

$$m_\ell = -1 \quad 0 \quad +1$$



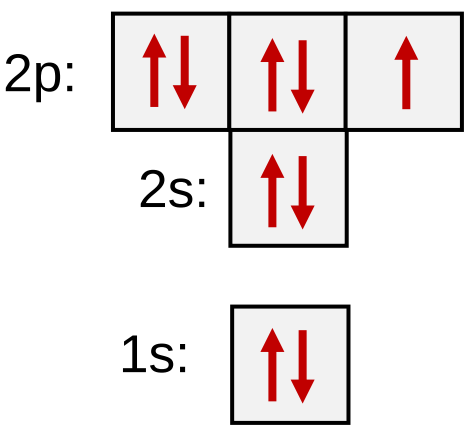
O atom

$$m_\ell = -1 \quad 0 \quad +1$$



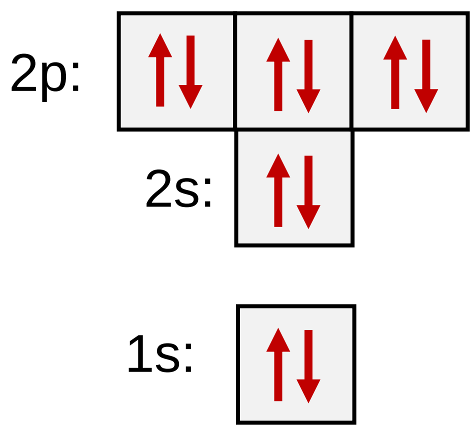
F atom

$$m_\ell = -1 \quad 0 \quad +1$$



Ne atom

$$m_\ell = -1 \quad 0 \quad +1$$



Solvay conference 1927

SOLVAY CONFERENCE 1927

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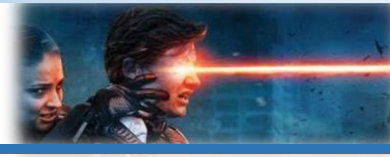
A. PICARD E. HENRIOT P. EHRENFEST Ed. HERSEN Th. DE DONDER E. SCHRÖDINGER E. VERSCHAFFELT W.PAULI W. HEISENBERG R.H FOWLER L. BRILLOUIN

P. DEBYE M. KNUDSEN W.L. BRAGG H.A. KRAMERS P.A.M. DIRAC A.H. COMPTON L. de BROGLIE M. BORN N. BOHR

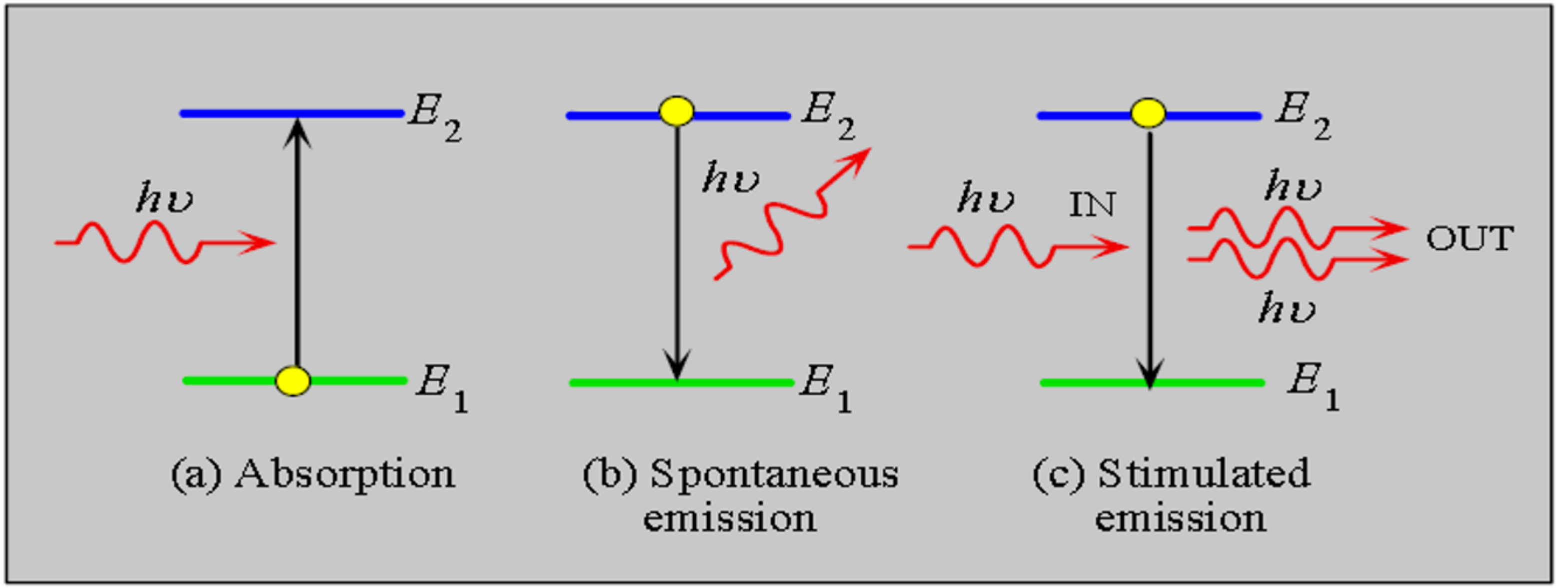
I. LANGMUIR M, PLANCK Mme CURIE H.A.LORENTZ A. EINSTEIN P. LANGEVIN Ch.E. GUYE C.T.R. WILSON O.W. RICHARDSON

Absents : Sir W.H. BRAGG, H. DESLANDRES et E. VAN AUBEL

3.5 LASER



Light Amplification by Stimulated Emission of Radiation

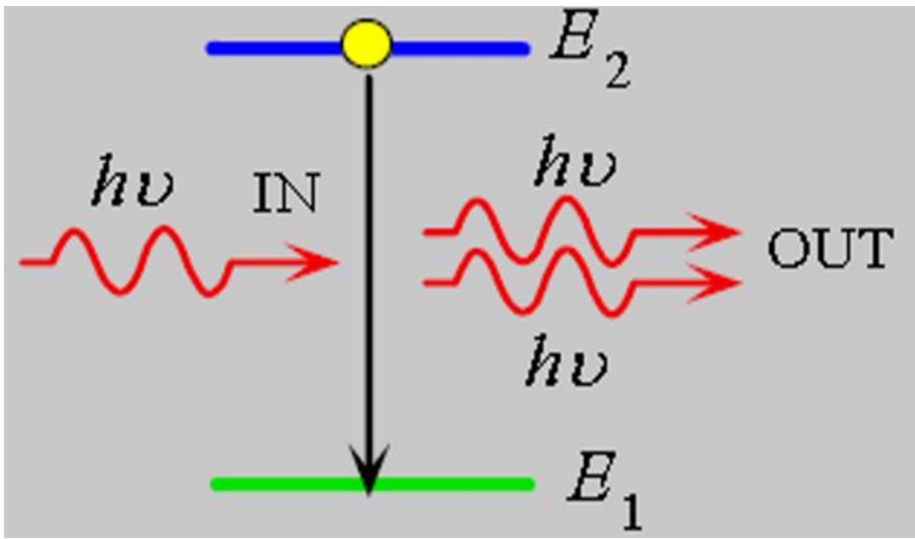


Spontaneous emission: Once an atom is in an excited state, there is a constant probability that it will jump back to a lower state by emitting a photon

Stimulated emission: An atom is in an excited state and a photon is incident on it. The incoming photon increases the probability that the excited atom will return to the ground.

Stimulated emission 受激辐射

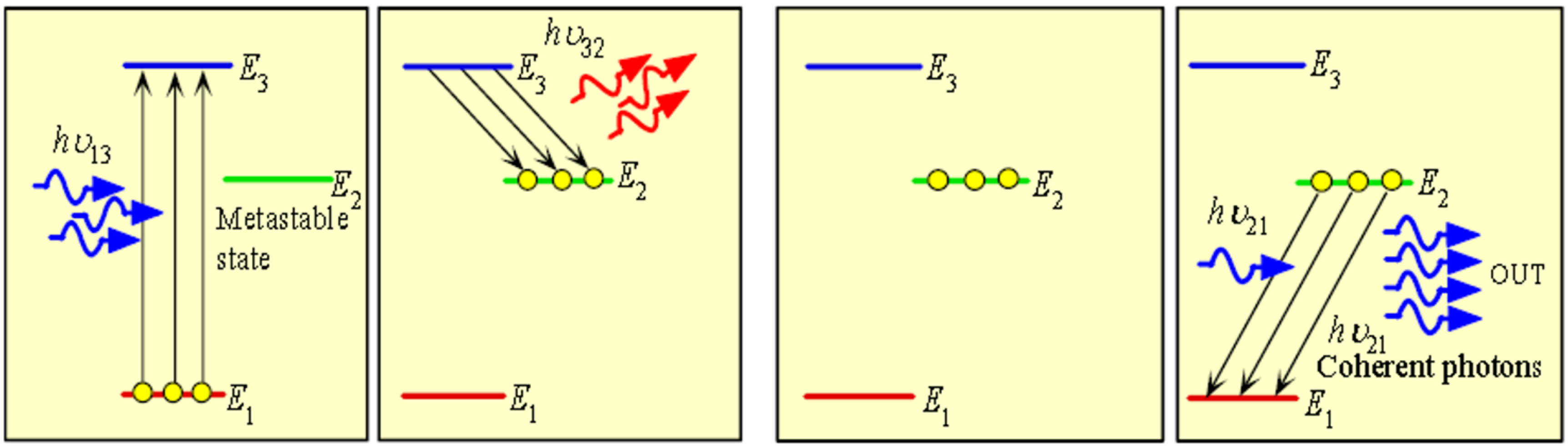
An atom is in an excited state and a photon is incident on it. The incoming photon increases the probability that the excited atom will return to the ground.



Population inversion 粒子数反转

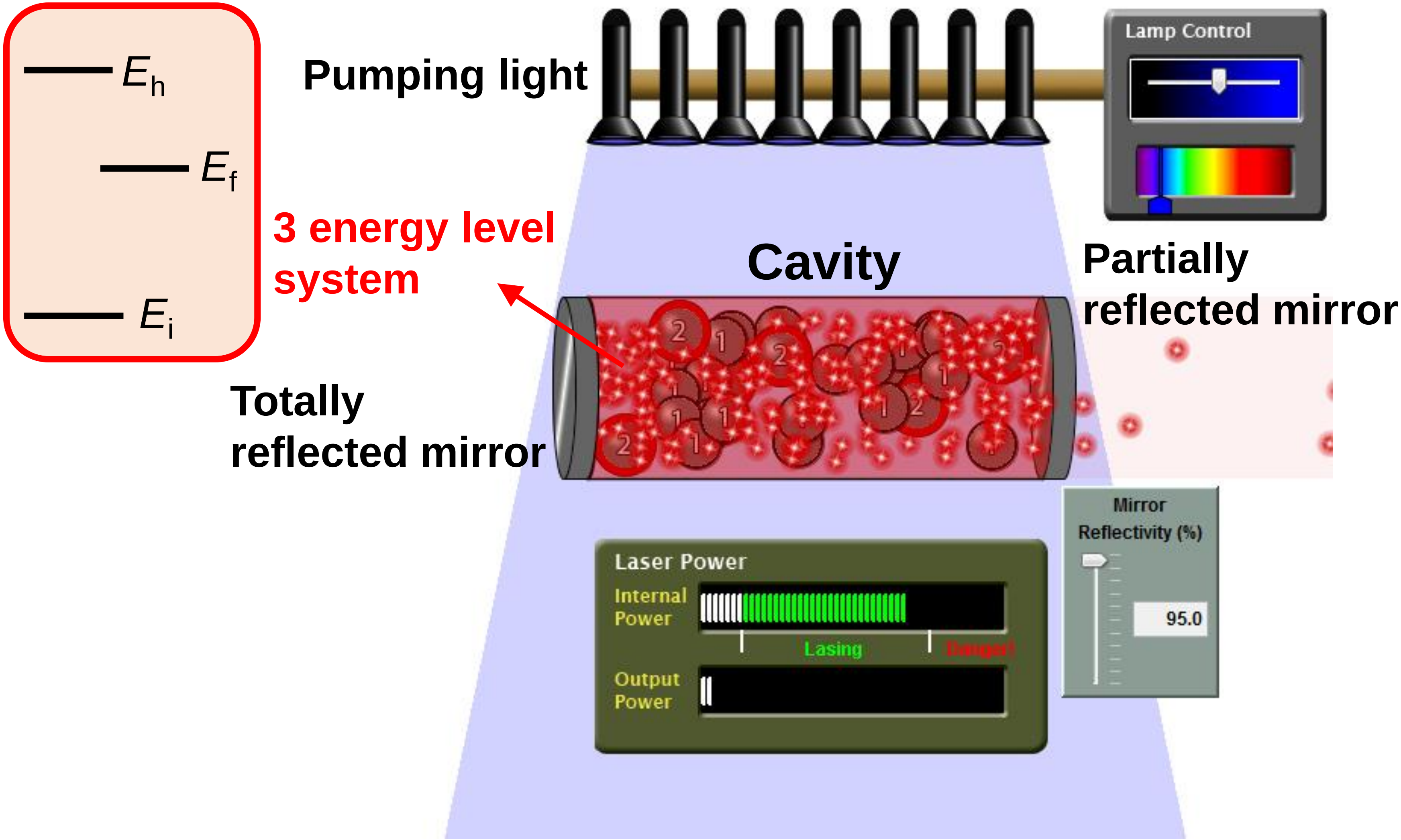
- When light is incident on a system of atoms, both stimulated absorption and stimulated emission are equally probable.

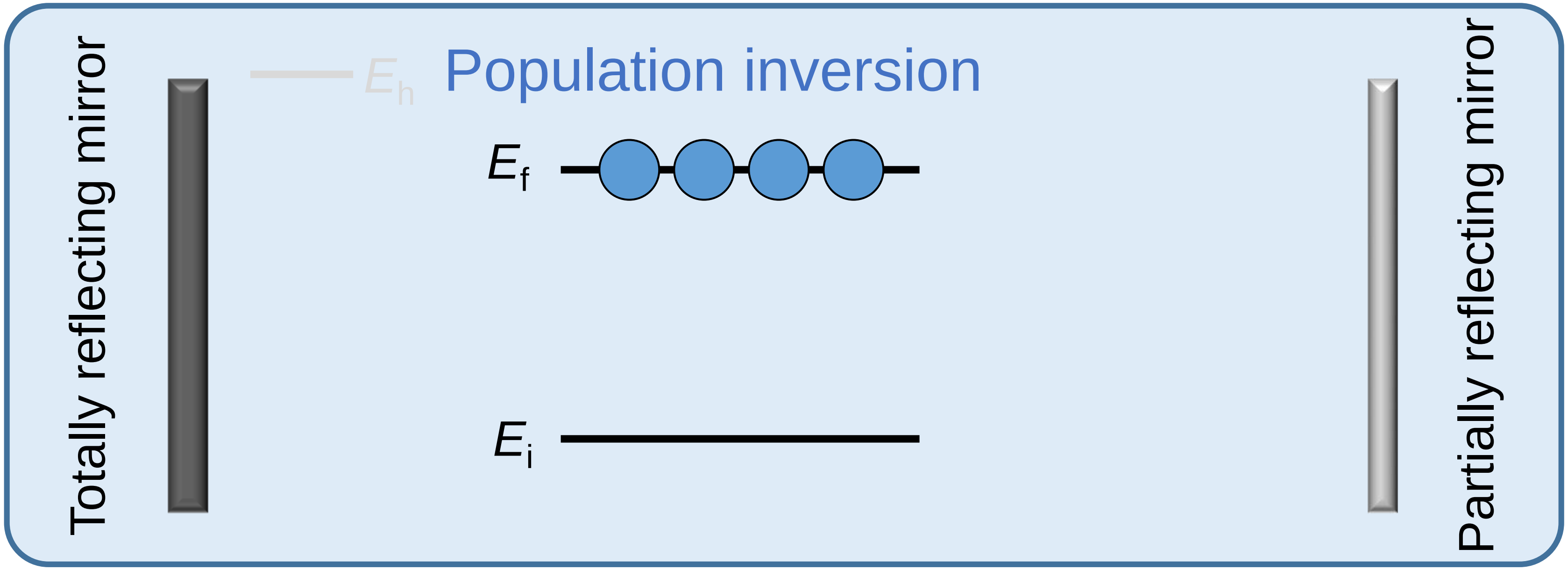
- Generally, a net absorption occurs since most atoms are in the ground states. If you can cause more atoms to be in excited states, a net emission of photons can result.



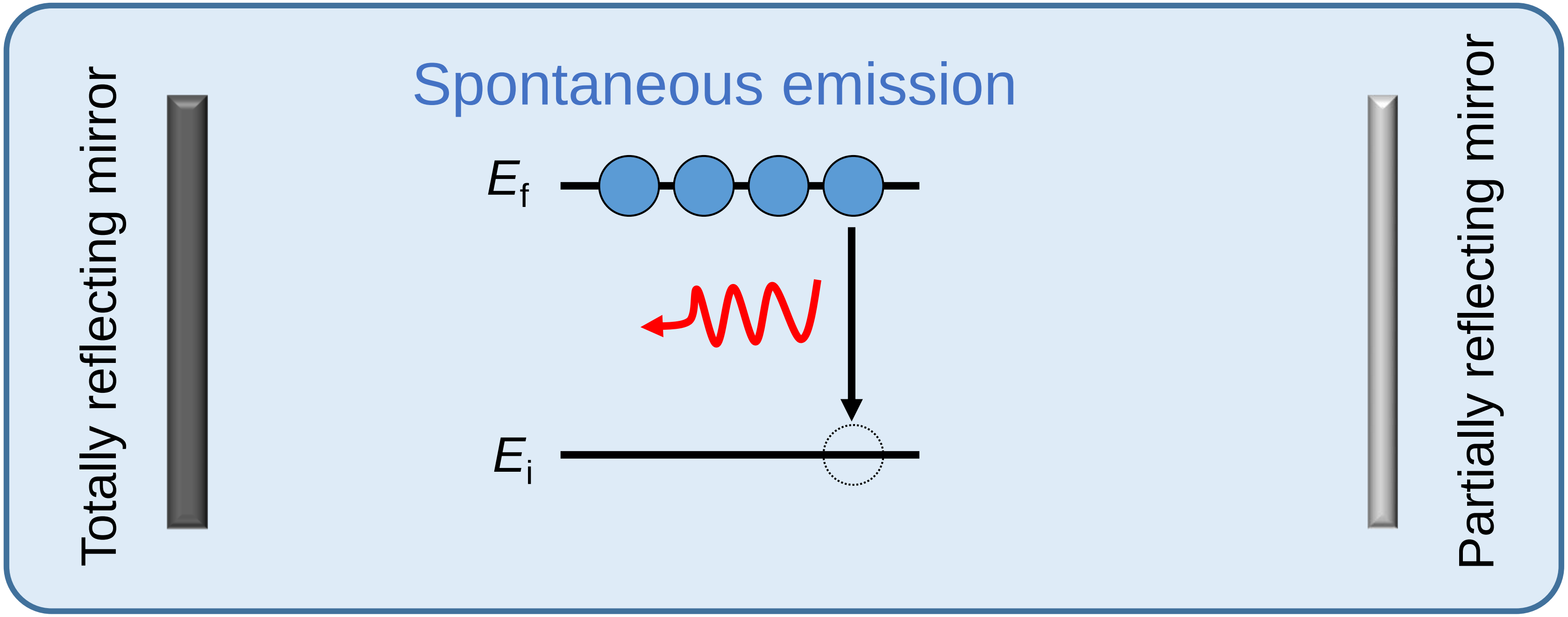
- A three energy level system can realize the population inversion.

LASER working principle

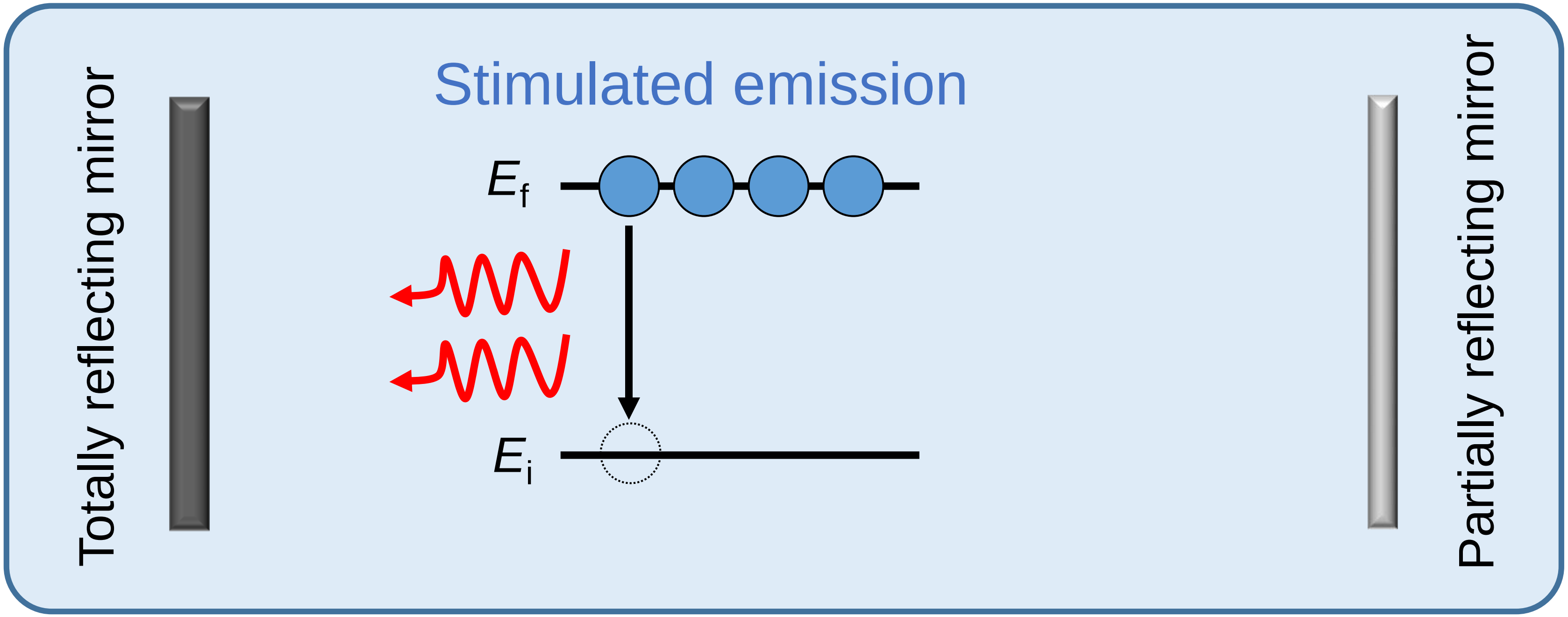




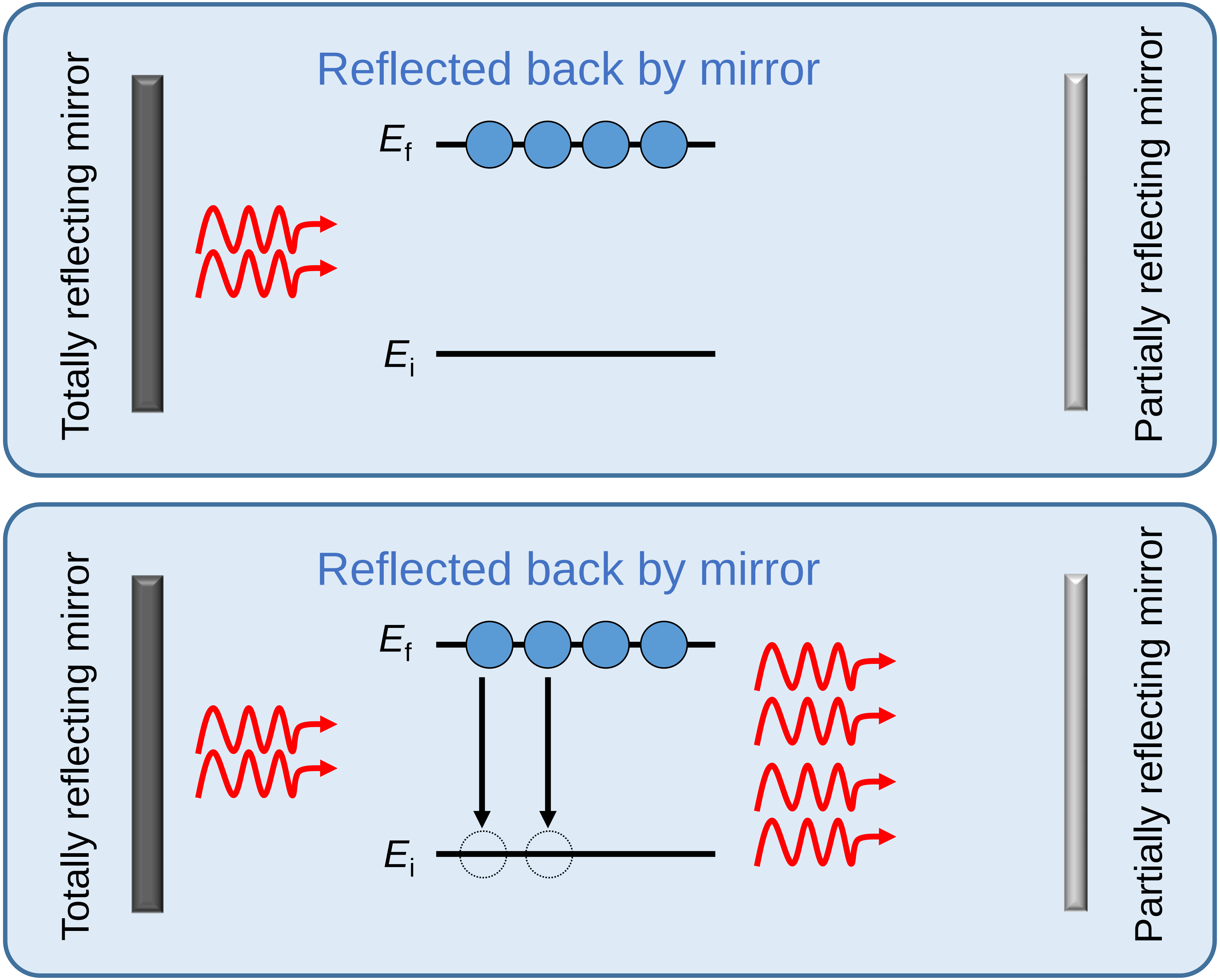
Length of resonant cavity： $L = n\dfrac{\lambda}{2} \quad (n = 1, 2, 3, \cdots)$

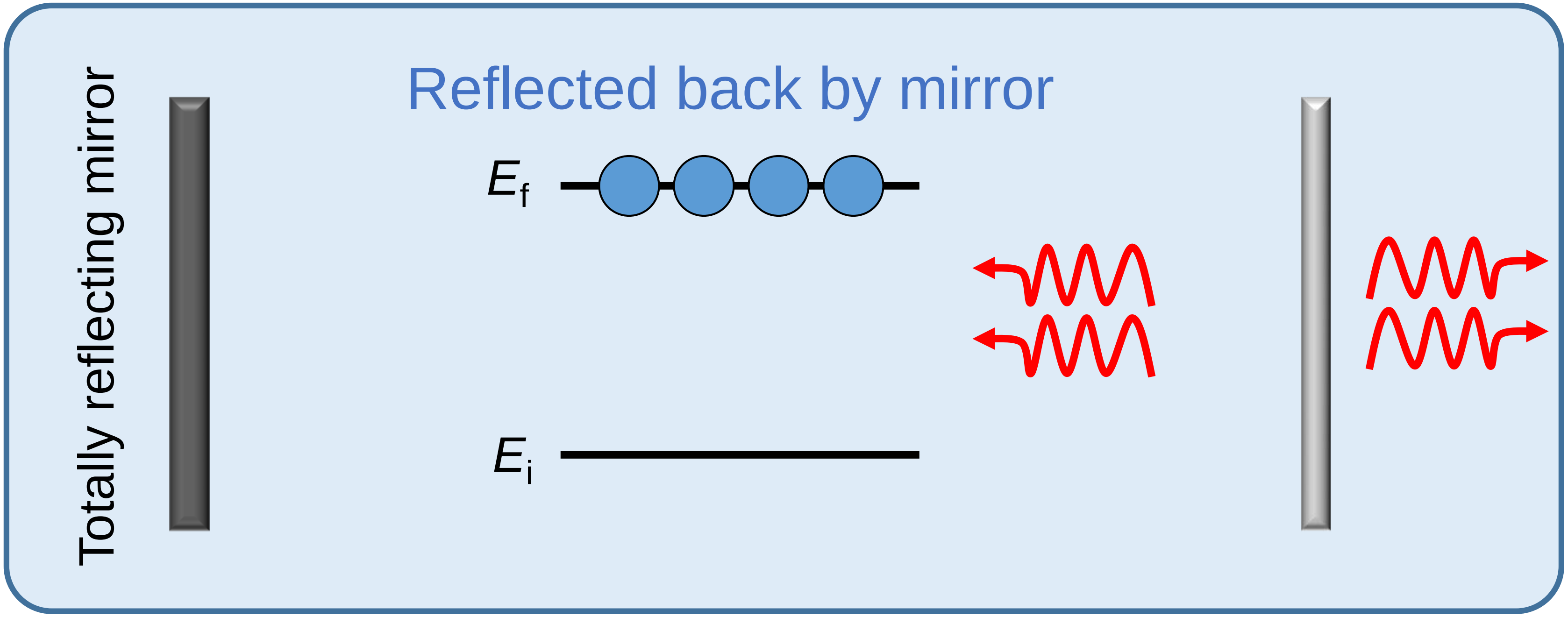
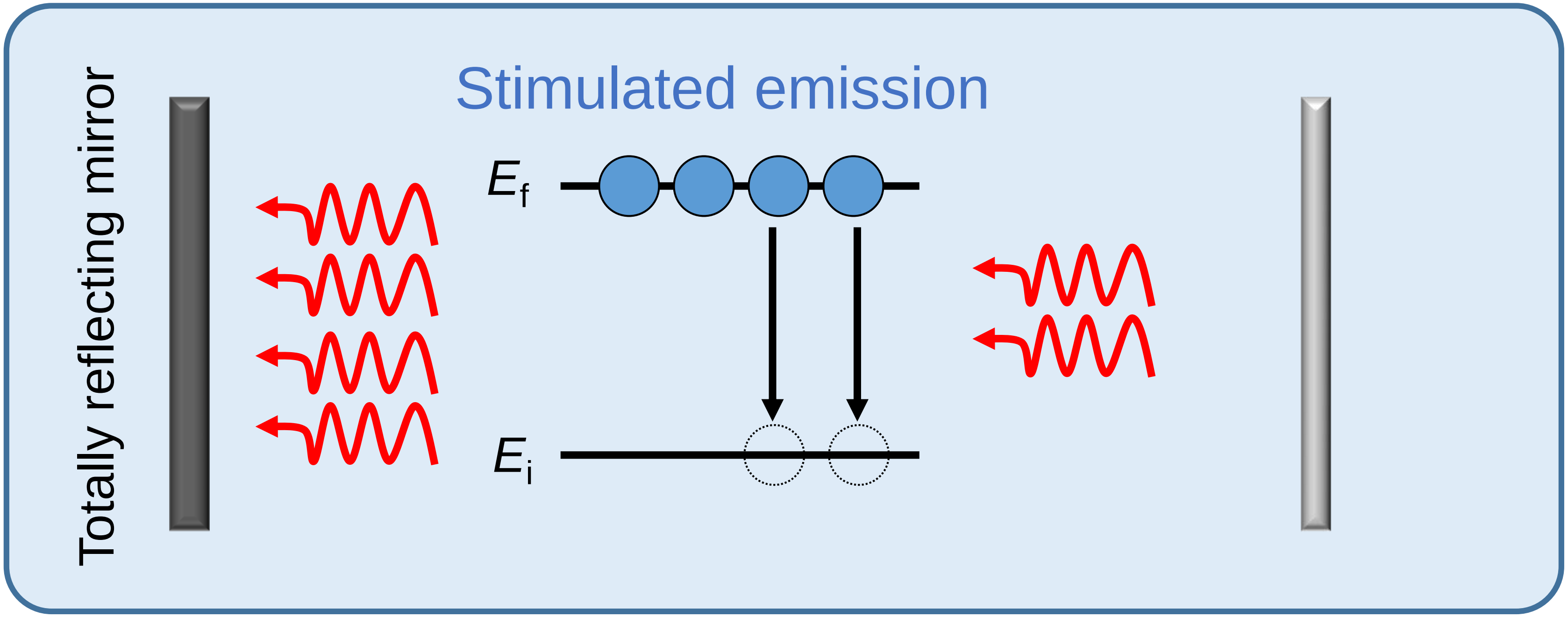


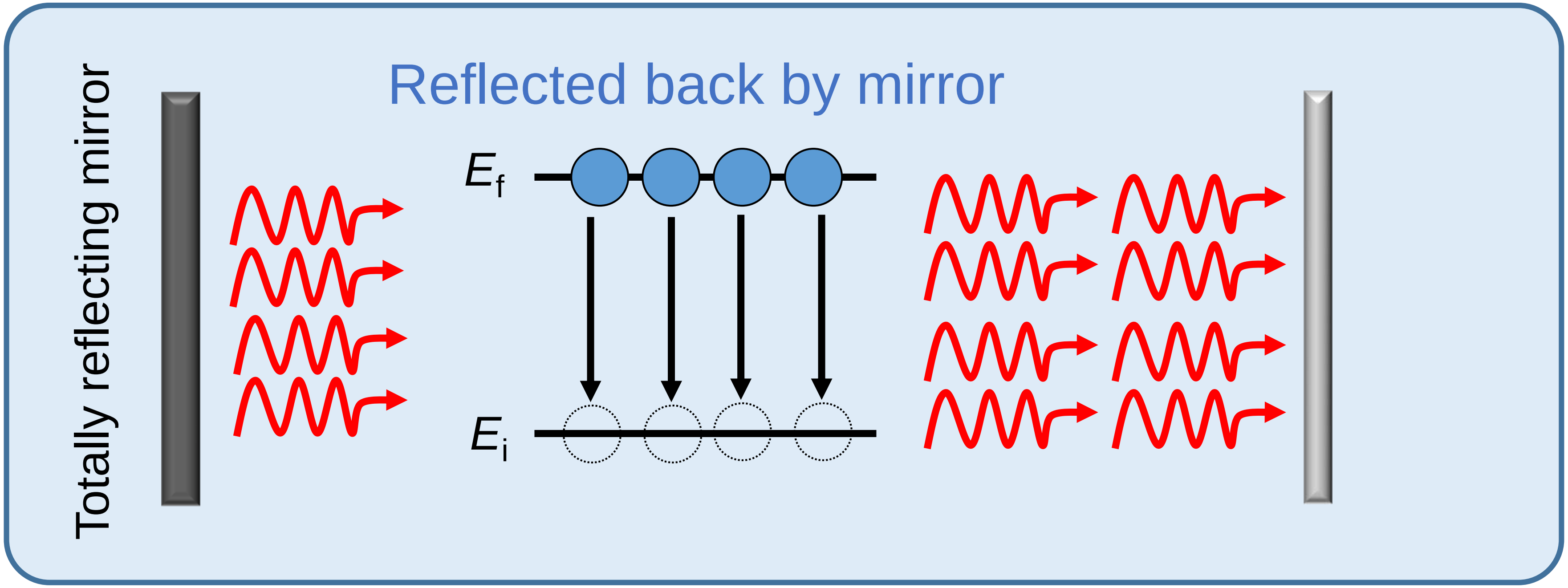
Spontaneous emission
Totally reflecting mirror
Partially reflecting mirror
E_f
E_i

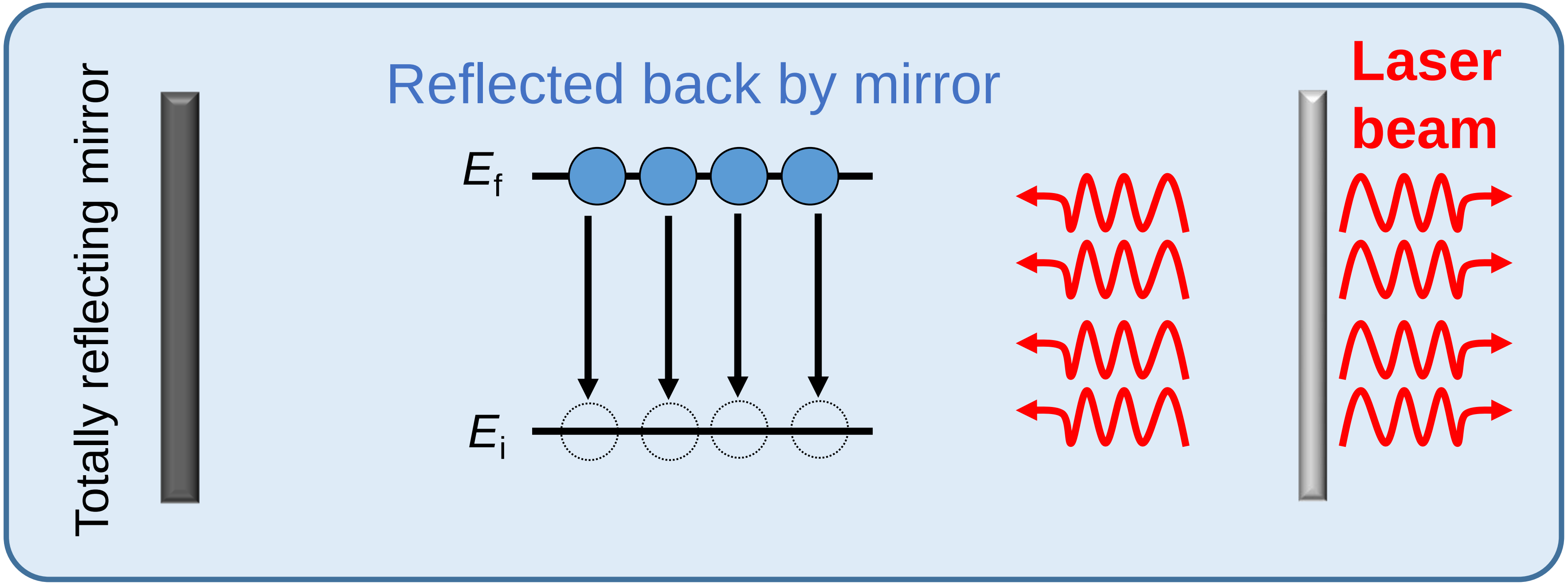


Stimulated emission
Totally reflecting mirror
Partially reflecting mirror
E_f
E_i

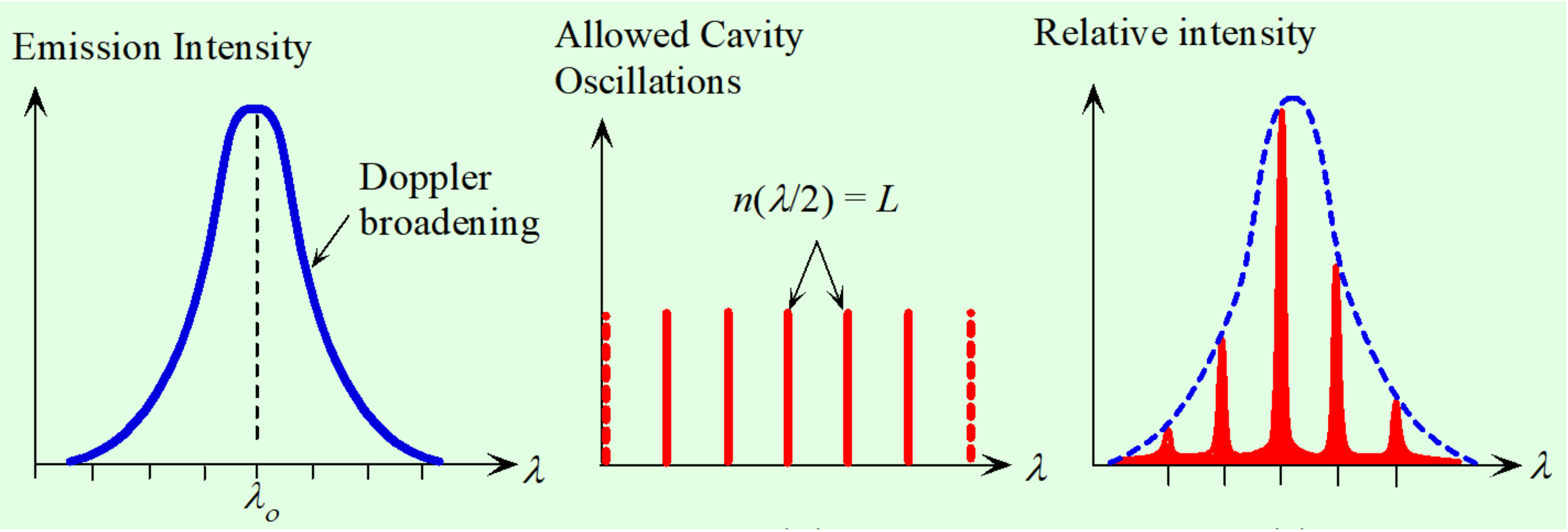

Totally reflecting mirror
Reflected back by mirror
E_f
E_i
Partially reflecting mirror
Totally reflecting mirror
Reflected back by mirror
E_f
E_i
Partially reflecting mirror


Totally reflecting mirror
Reflected back by mirror
E_f
E_i

Totally reflecting mirror
Stimulated emission
E_f
E_i


Totally reflecting mirror
Reflected back by mirror
E_f
E_i


Totally reflecting mirror
Reflected back by mirror
E_f
E_i
Laser beam

Doppler broadened emission

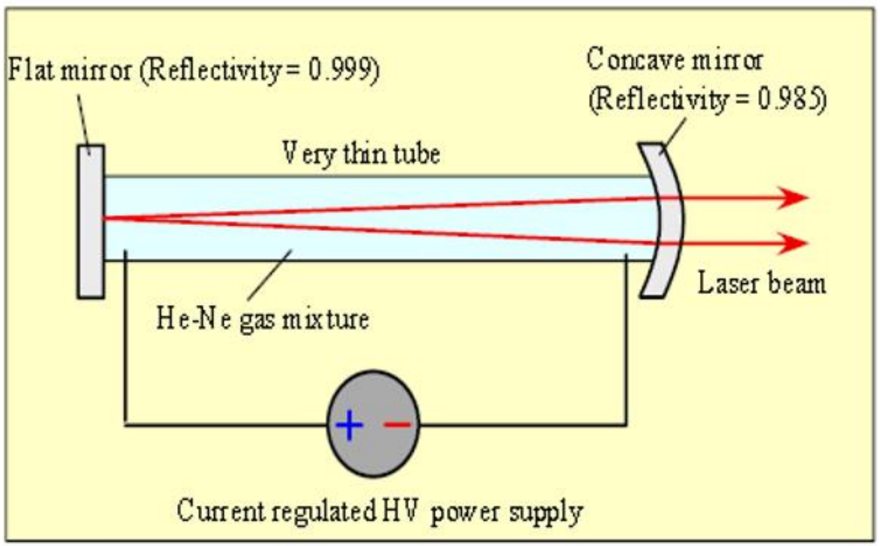


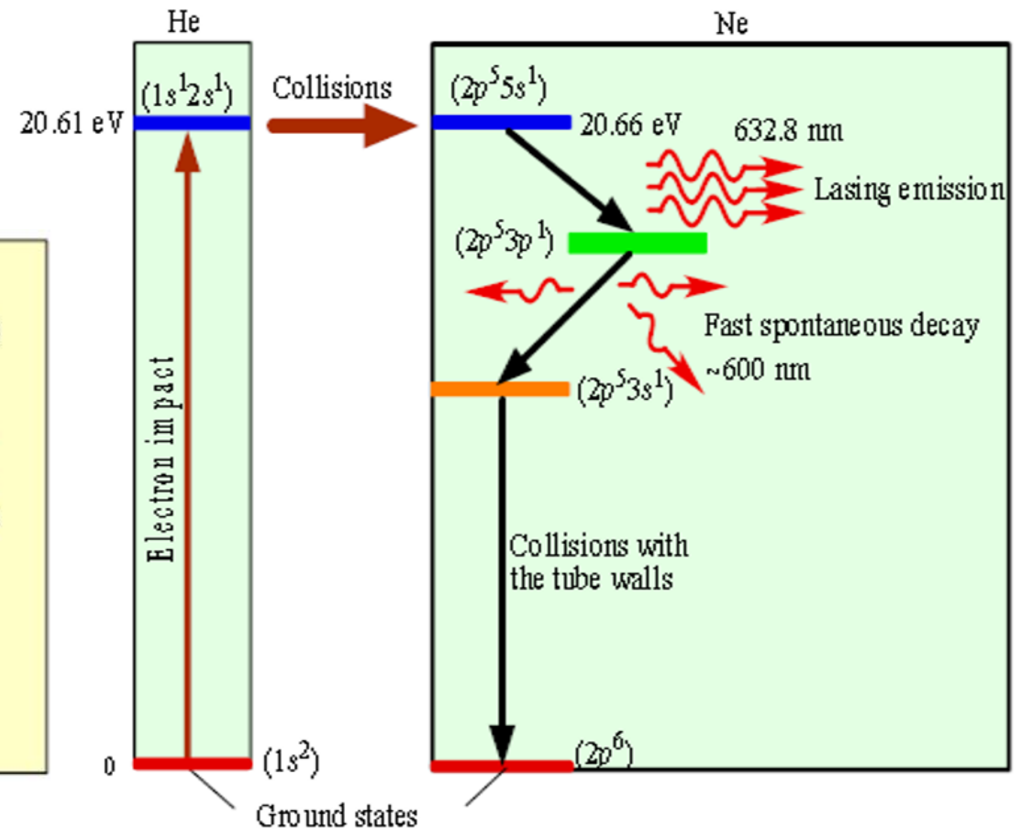
He-Ne laser

$$\mathrm{He} + e^- \rightarrow \mathrm{He}^* + e^-$$

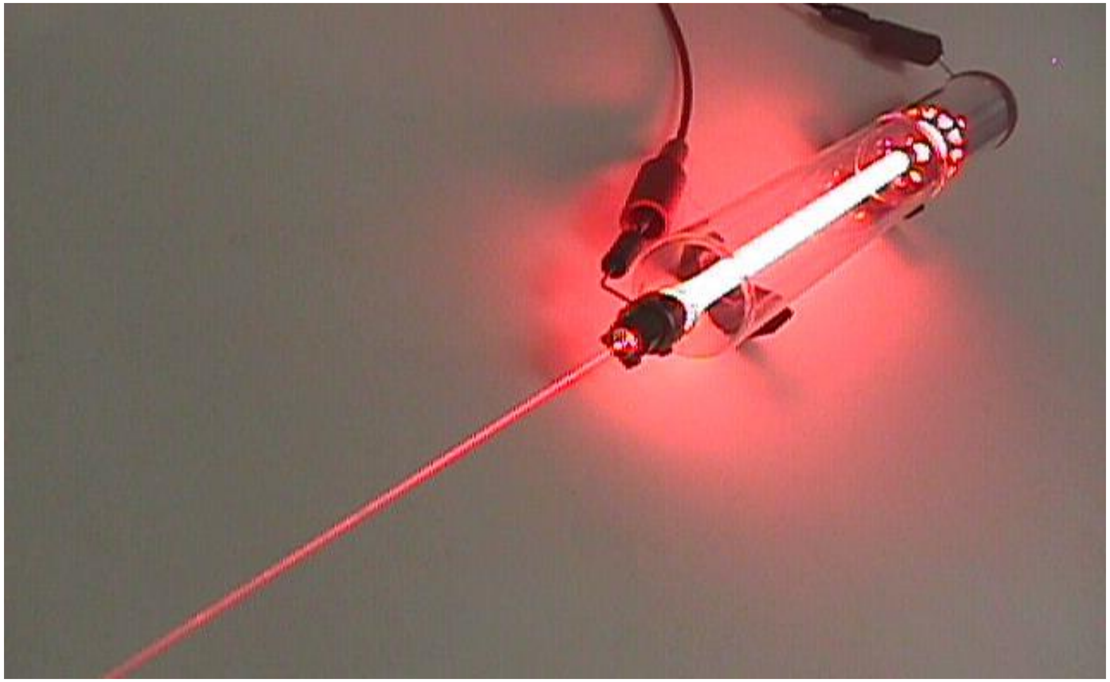
$$\mathrm{He}^* + \mathrm{Ne} \rightarrow \mathrm{He} + \mathrm{Ne}^*$$

$$\mathrm{Ne}^* \rightarrow \mathrm{Ne} + h\nu$$

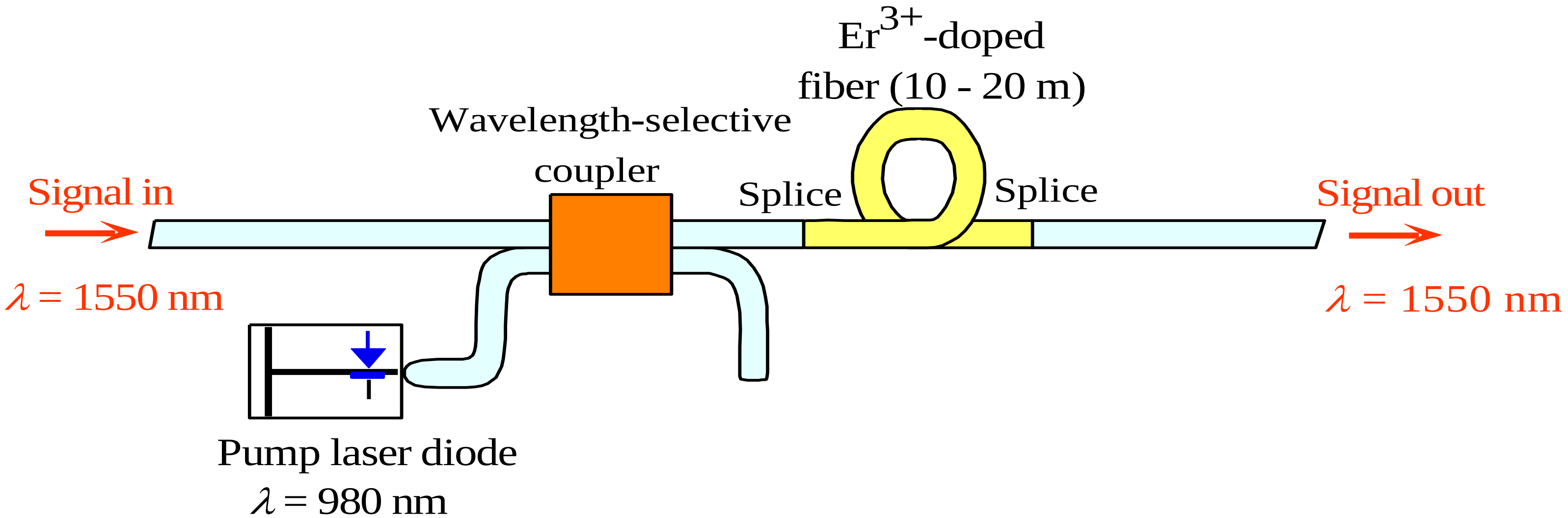


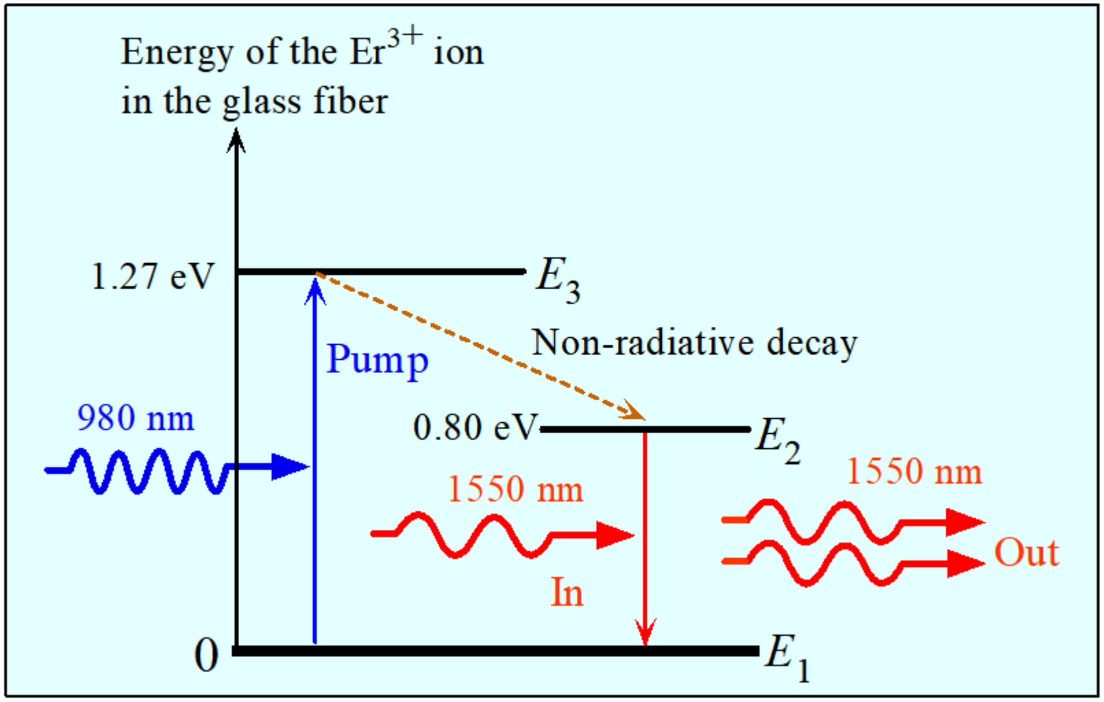


He-Ne laser



Er^{3+} doped fiber amplifier (EDFA)





Application of laser

- Science – precise measurement, spectroscopy
- Medicine – laser scalpel, eye surgery
- Industry – cutting and welding, guidance systems
- Arts – etching
- Telecommunications (fiber optics)
- Radars
- Precise measurement of long distances (e.g. Moon)
- Consumer – CDs, DVDs, laser lights

The detection of the binary data stored in the form of pits on the compact disc is done with the use of a **semiconductor laser.** The laser is focused to a diameter of about 0.8 mm at the bottom of the disc, but is further focused to about 1.7 micrometers as it passes through the clear plastic substrate to strike the reflective layer. The reflected laser will be detected by a photodiode. Moral of the story: without optoelectronics there will no CD player!