

Chapter 35

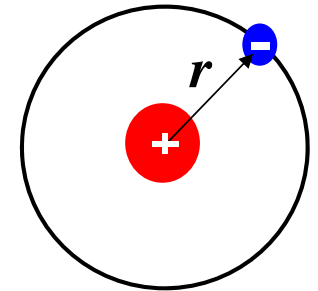
Quantum Mechanics of Atoms

- Schrödinger Equation for Hydrogen Atom
- Quantum Numbers
- Wave Function for Hydrogen Atom
- Complex Atoms
- *Lasers

§ 31-1 Schrödinger Equation for Hydrogen Atom

The atom is at rest, and the potential energy of the electron:

$$U(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

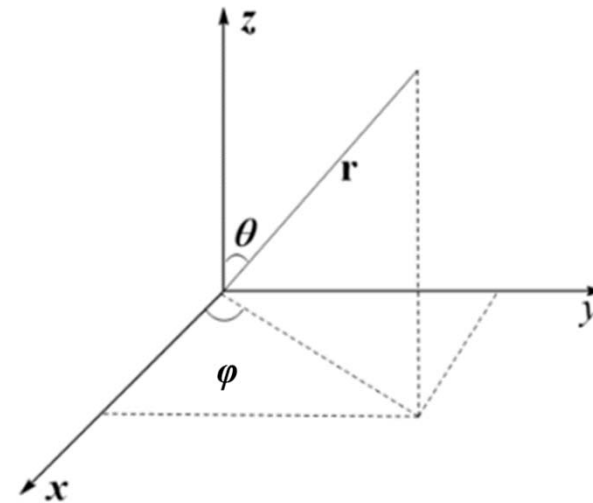


Time-independent Schrödinger equation for hydrogen atom:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi - \frac{e^2}{4\pi\epsilon_0 r} \psi = E\psi$$

In terms of spherical coordinate:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2}$$



$$\begin{aligned} x &= r \sin \theta \cos \varphi \\ y &= r \sin \theta \sin \varphi \\ z &= r \cos \theta \\ r^2 &= x^2 + y^2 + z^2 \\ \cos \theta &= \frac{z}{r} \\ \operatorname{tg} \varphi &= \frac{y}{x} \end{aligned}$$

Note: the following process of solving the Schrödinger equation is not required for you to master.

Separate variables: $\psi(r, \theta, \varphi) = R(r)Y(\theta, \varphi)$

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} r^2 \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) = -\frac{1}{Y} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \varphi^2} \right]$$
$$= \Lambda \text{ (constant)}$$

The squared angular momentum operator in spherical coordinate:

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right]$$

The angular momentum of the electron:

$$L = \sqrt{\Lambda} \hbar$$

Separate variables in Y : $Y(\theta, \varphi) = \Theta(\theta)\Phi(\varphi)$

$$\frac{1}{\Theta} \left[\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \right] + \Lambda \sin^2 \theta = -\frac{1}{\Phi} \frac{d^2 \Phi}{d\varphi^2} = \Gamma \text{ (constant)}$$

The z-component operator
of the angular momentum:

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi}, \quad \hat{L}_z^2 = -\hbar^2 \frac{\partial^2}{\partial \varphi^2}$$

The z-component (arbitrary)
angular momentum of the electron:

$$L_z = \sqrt{\Gamma} \hbar$$

Three differential equations to be solved:

$$\begin{cases} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2m}{\hbar^2} r^2 \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) - \Lambda \right] R = 0 \\ \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + (\Lambda \sin^2 \theta - \Gamma) \Theta = 0, & \frac{d^2 \Phi}{d\varphi^2} + \Gamma \Phi = 0 \end{cases}$$

Calculating results:

$$\begin{cases} E_n = -\frac{13.6eV}{n^2}, & (n = 1, 2, \dots) \\ \Lambda = l(l+1), & l = 0, 1, \dots, n-1 \\ \Gamma = m_l^2, & m_l = 0, \pm 1, \dots, \pm l \end{cases}$$

Angular momentum and its z-component:

$$\begin{cases} L = \sqrt{l(l+1)} \hbar, & l = 0, 1, \dots, n-1 \\ L_z = m_l \hbar, & m_l = 0, \pm 1, \dots, \pm l \end{cases}$$

§ 31-2 Quantum Numbers

1. Three quantum numbers

Solutions of the Schrödinger equation for hydrogen atom can be labeled by **3 quantum numbers**.

(1) Principal quantum number n

$$E_n = \frac{-13.6eV}{n^2}, \quad n = 1, 2, \dots$$

Energy is quantized, and it is as same as Bohr theory.

(2) Orbital quantum number l

$$L = \sqrt{l(l+1)} \hbar, \quad l = 0, 1, \dots, n-1$$

The magnitude of the orbital angular momentum L is also quantized, but in a different form from Bohr theory.

(3) Magnetic quantum number m_l

$$L_z = m_l \hbar, \quad m_l = 0, \pm 1, \dots, \pm l$$

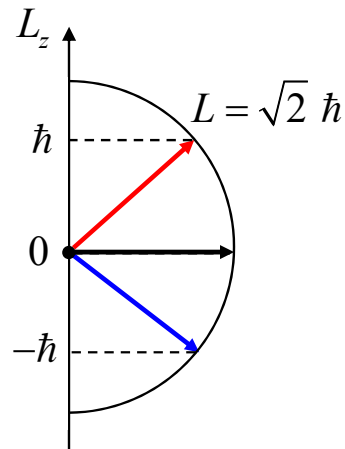
The direction of the orbital angular momentum L is quantized (Space quantization).

(a) $l=1$

$$m_l = 0, \pm 1$$

$$L = \sqrt{2}\hbar$$

$$L_z = 0, \pm \hbar$$

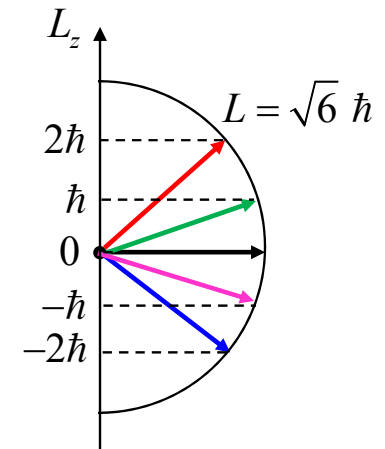


(b) $l=2$

$$m_l = 0, \pm 1, \pm 2$$

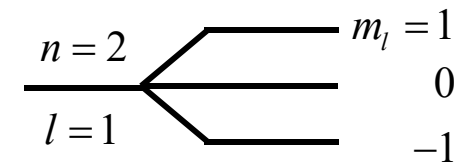
$$L = \sqrt{6}\hbar$$

$$L_z = 0, \pm \hbar, \pm 2\hbar$$

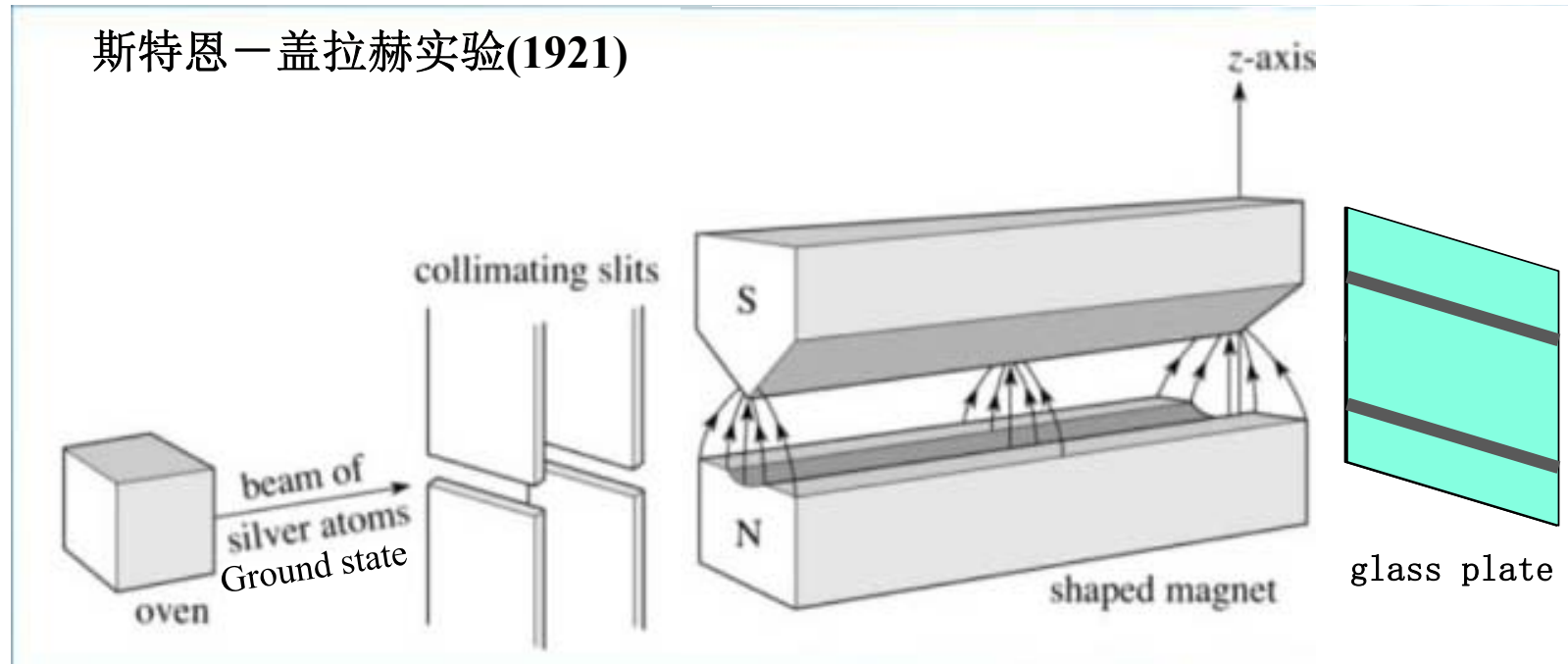


Magnetic quantum number m_l proved by experiment:

Zeeman effect: when a magnetic field applied, the spectral lines of gas were split into several very closely spaced lines. (eigen energy depends on m_l)



2. The 4th quantum number



Force applied on the atom:

$$F_z = \frac{\partial}{\partial z} (\vec{\mu} \cdot \vec{B}) \approx \mu_z \frac{\partial B}{\partial z} \quad (\mu: \text{Magnetic dipole moment of the atom})$$

Ground state $\rightarrow l = 0 \rightarrow$ magnetic moment due to orbital effect: $\mu = 0$.₈

G. E. Uhlenbeck and Goudsmit (1924): Except the orbital motion, the electron also has a spin and the spin angular momentum.

Dirac: Spin is a relativistic effect.

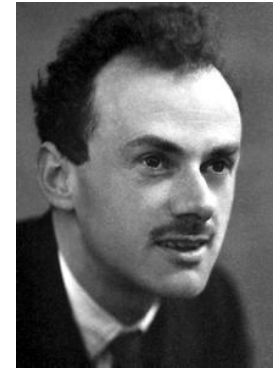
Every elementary particle has a spin, and the **spin quantum number** can be:

(1) Integers \rightarrow **boson**, such as photon;

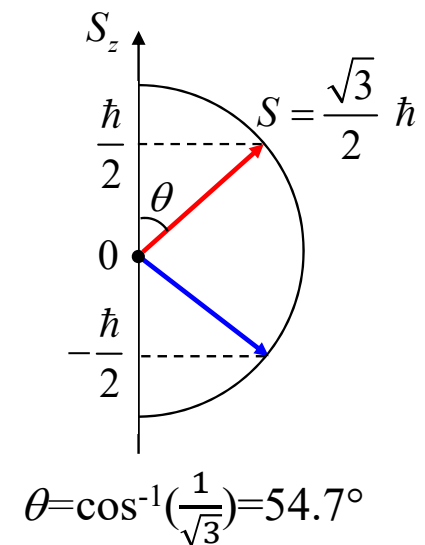
(2) Half-integers \rightarrow **fermion**, such as electron:

$$s = \frac{1}{2}, \quad S = \sqrt{s(s+1)} \cdot \hbar = \frac{\sqrt{3}}{2} \hbar, \quad S_z = m_s \hbar$$

Spin magnetic quantum number: $m_s = \pm \frac{1}{2}$



Paul Dirac
Nobel 1933



Possible states

Example1: How many different states are possible for an electron whose principal quantum number is $n = 2$? List all of them.

Solution: Remember rules of quantum numbers

n	l	m_l	m_s	n	l	m_l	m_s
2	0	0	1/2	2	0	0	-1/2
2	1	1	1/2	2	1	1	-1/2
2	1	0	1/2	2	1	0	-1/2
2	1	-1	1/2	2	1	-1	-1/2

Energy and angular momentum

Example2: Determine (a) the energy and (b) the orbital angular momentum for each state in Example1.

Solution: (a) $n = 2$, all states have same energy

$$E_2 = -\frac{13.6eV}{4} = -3.4eV$$

(b) For $l = 0$: $L = \sqrt{l(l+1)} \cdot \hbar = 0$

For $l = 1$: $L = \sqrt{l(l+1)} \cdot \hbar = \sqrt{2}\hbar = 1.5 \times 10^{-34} J \cdot s$

Macroscopic $L \rightarrow$ continuous

§ 31-3 Wave Function for Hydrogen Atom

The wave function for ground state:

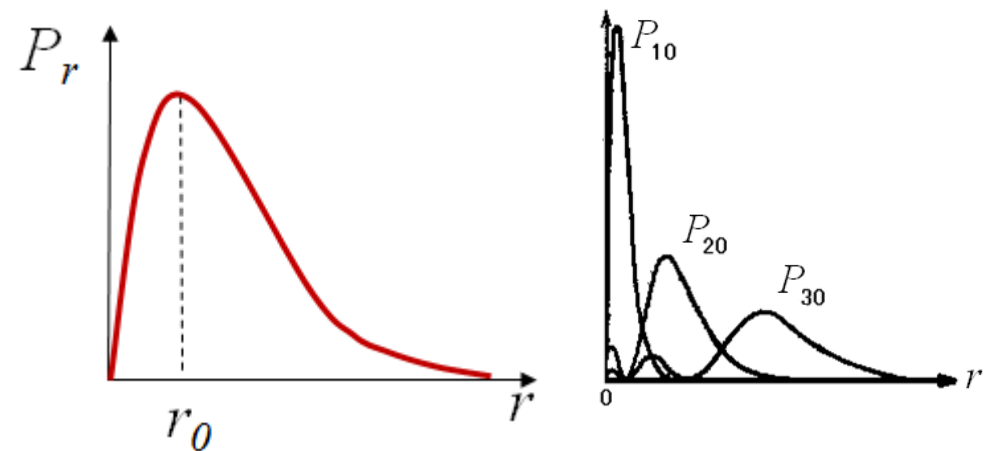
$$\psi_{100} = \frac{1}{\sqrt{\pi r_0^3}} e^{-\frac{r}{r_0}} \quad \text{Bohr radius: } r_0 = \frac{h^2 \epsilon_0}{\pi m e^2} \approx 5.29 \times 10^{-11} \text{ m}$$

The probability density is: $|\psi_{100}|^2$

Radial probability distribution:

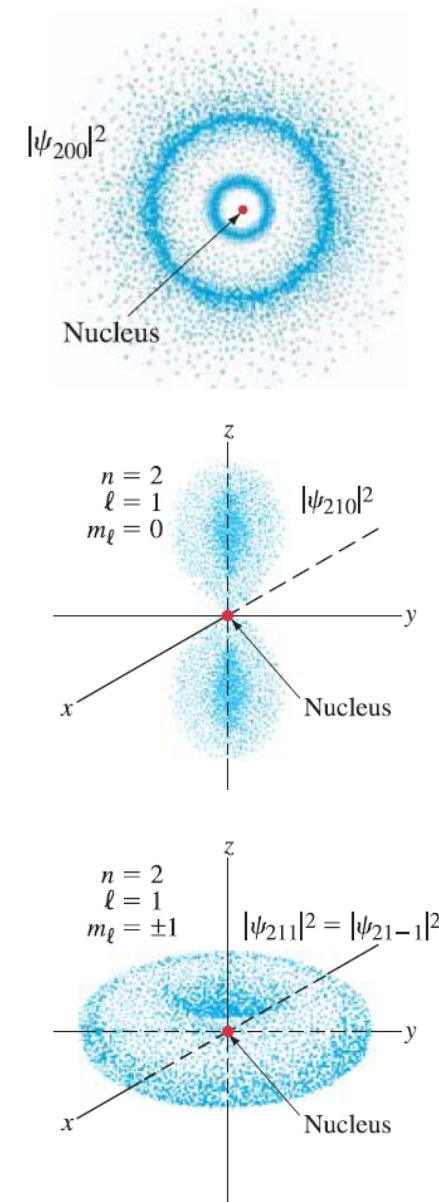
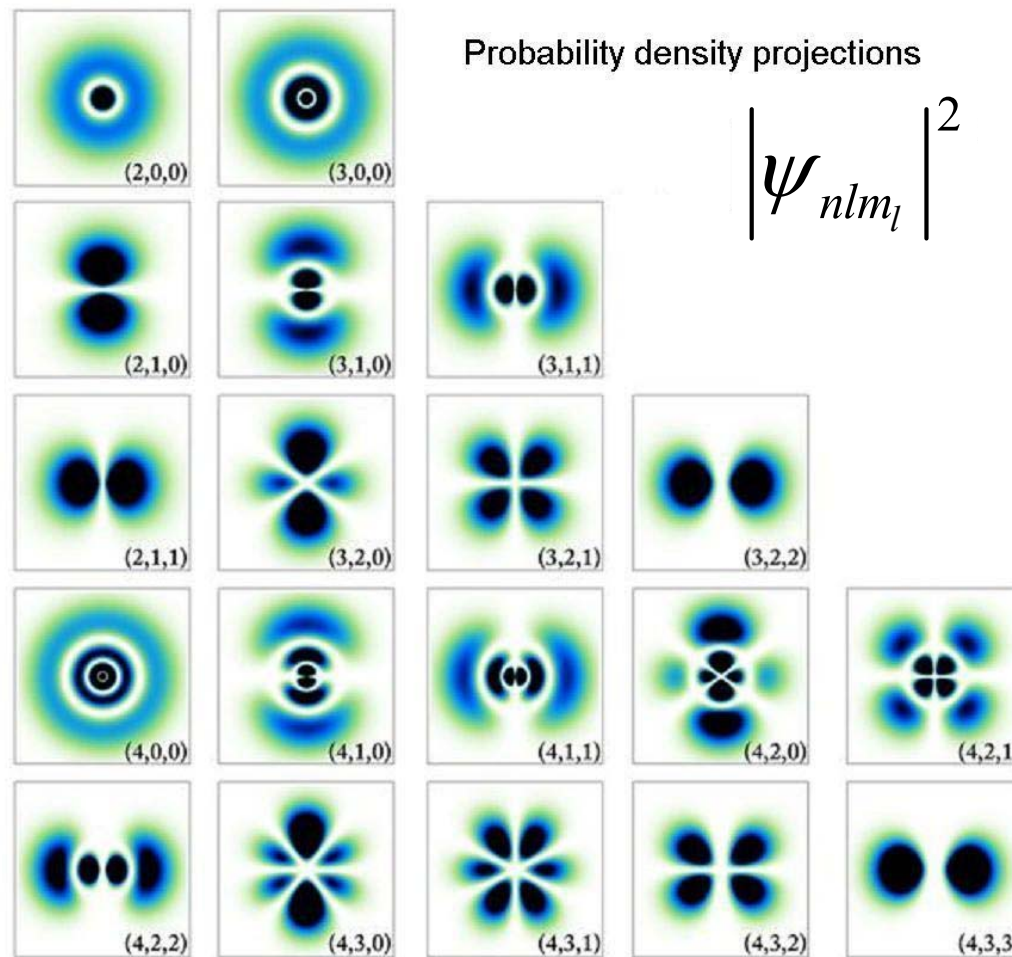
$$|\psi|^2 dV = |\psi|^2 \cdot 4\pi r^2 dr = P_r dr$$

$$\Rightarrow P_r = 4\pi r^2 |\psi|^2 = \frac{4r^2}{r_0^3} e^{-\frac{2r}{r_0}}$$



The peak of the curve is the “**most probable**” value of r and occurs for $r = r_0$, the Bohr radius.

- ◆ Probability distribution → “electron cloud”;
- ◆ There is no “orbit” for the electron in atom.



§ 31-4 Complex Atoms

For complex atoms (**atomic number $Z > 1$**) contain more than one electron, solving the Schrödinger equation to derive the wave function and energy levels that describe the motion of electrons is very complex and difficult.

In quantum mechanics, the state of electrons in complex atoms is still determined by four quantum numbers (n, l, m_l, m_s):

Each (n, l, m_l, m_s) \longleftrightarrow a state of electron

1. Two principles for the arrangements of electrons

(1) **Lowest energy principle \rightarrow ground state**

When an atomic system is in the ground state, each electron always occupies the lowest possible energy level.

(2) Pauli exclusion principle

No two electrons in an atom can occupy the same quantum state.

This principle is **valid for all fermions**.

Conclusion: in an atom, no two electrons can share the same four quantum numbers (n, l, m_l, m_s).

or, for all electrons in an atom, there is **at least one quantum number** that is different between them.

Question:

How many electrons can be in state $l = 0, 1, 2$?

How many electrons can be in state $n = 1, 2, 3$?



Wolfgang Pauli
Nobel 1945

2. Shell structure of electrons

- ◆ Electrons with same $n \rightarrow$ in the same **shell**;
- ◆ Electrons with same n and $l \rightarrow$ **same subshell**.

$$\begin{array}{cccccc} n = & 1, & 2, & 3, & 4, & 5, & 6 \\ & K, & L, & M, & N, & O, & P \end{array}$$

$$\begin{array}{cccccc} l = & 0, & 1, & 2, & 3, & 4 \\ & s, & p, & d, & f, & g \end{array}$$

Maximum number of electrons each shell (subshell) can contain:

$$N_{sub} = 2(2l+1)$$

$$N_{shell} = 2 \sum_{l=0}^{n-1} (2l+1) = 2n^2$$

$$\begin{array}{cccccc} l = & 0, & 1, & 2, & 3, & 4 \\ & s & p & d & f & g \\ & 2 & 6 & 10 & 14 & 18 \end{array}$$

$$\begin{array}{cccccc} n = & 1, & 2, & 3, & 4, & 5 \\ & K & L & M & N & O \\ & 2 & 8 & 18 & 32 & 50 \end{array}$$

- ❑ Smaller $n \rightarrow$ shell with lower energy level (for smaller atomic number);
- ❑ Smaller $l \rightarrow$ subshell with lower energy level;
- ❑ Electrons fill the shells and subshells in “ $n+l$ ” order.

Electrons fill the shells and subshells from left to right:

$n \backslash l$	s	p	d	f	g
	0	1	2	3	4
1	1s ²				
2	2s ²	2p ⁶			
3	3s ²	3p ⁶	3d ¹⁰		
4	4s ²	4p ⁶	4d ¹⁰	4f ¹⁴	
5	5s ²	5p ⁶	5d ¹⁰	5f ¹⁴	5g ¹⁸

<p>26 ⁵D₄</p> <p>Fe</p> <p>Iron</p> <p>55.845</p> <p>[Ar]3d⁶4s²</p> <p>7.9025</p>	<p>27 ⁴F_{9/2}</p> <p>Co</p> <p>Cobalt</p> <p>58.933</p> <p>[Ar]3d⁷4s²</p> <p>7.8810</p>
--	--

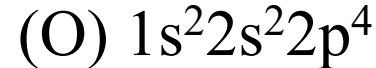
For the most precise values and uncertainties visit ciaaw.org and pml.nist.gov/data.
NIST SP 966 (July 2019)

Electron configurations

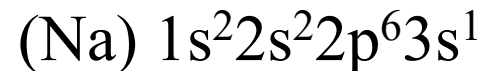
Example3: Which of the following electron configurations are possible, and which forbidden? (a) $1s^2 2s^3 2p^3$; (b) $1s^2 2s^2 2p^5 3s^2$; (c) $1s^2 2s^2 2p^6 2d^2$.

Solution: (a) Forbidden, only 2 allowed states in 2s

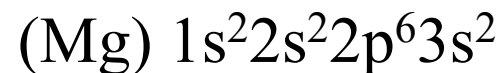
Allowed configurations?



(b) Allowed, but excited state.



(c) Forbidden, no 2d subshell.



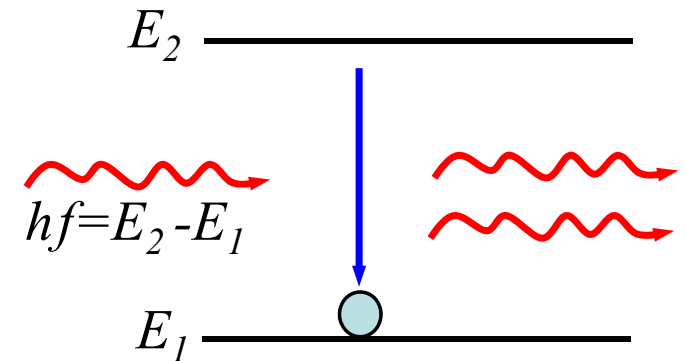
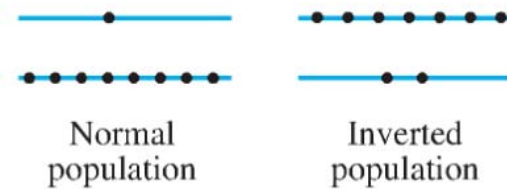
§ 31-5 *Lasers

Laser: “Light Amplification by Stimulated Emission of Radiation”.

(1) Stimulated emission

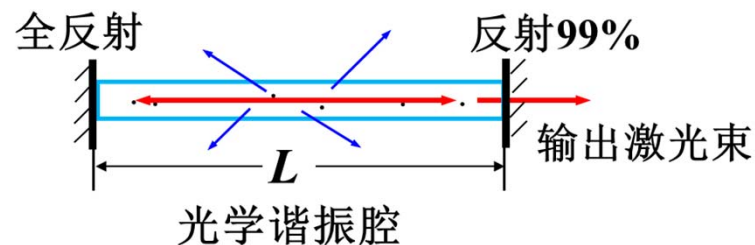
(2) Inverted population

$$N_{high} > N_{low}$$



- Metastable state (longer lifetime of higher energy level) ;
- Pumping (input energy to excite the electron).

(3) Optical resonator



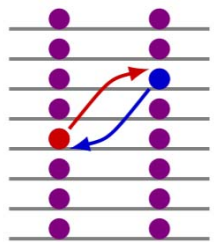
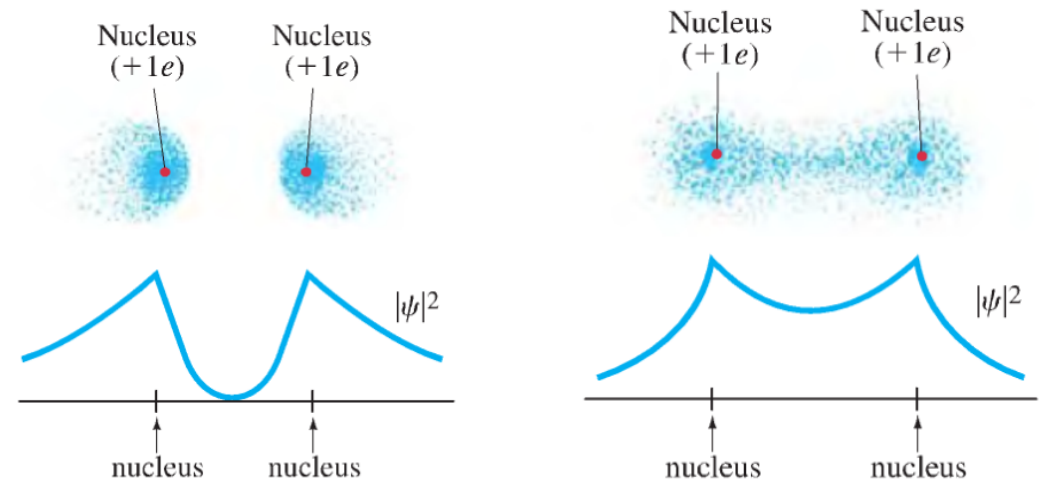
*Chapter 36 Molecules and Solids

Bonding in Molecules

Molecular spectra

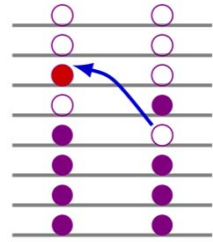
Band theory of solids

Semiconductors & diodes



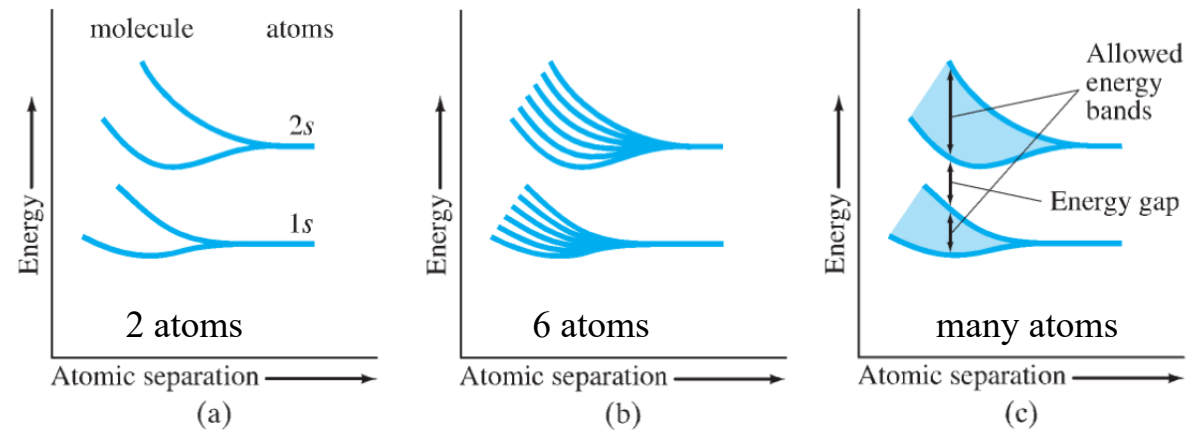
满带中电子迁移

Valence / Filled Band



导带中电子迁移

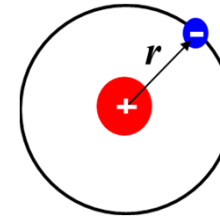
Conduction Band



Summary

1. Time-independent Schrödinger equation for hydrogen atom

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{e^2}{4\pi\epsilon_0 r}\psi = E\psi$$



2. Principal quantum number n

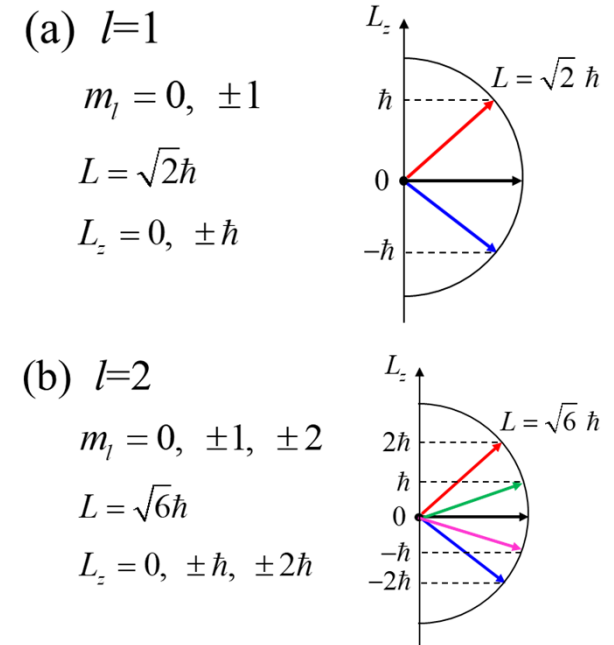
$$E_n = \frac{-13.6eV}{n^2}, \quad n = 1, 2, \dots$$

3. Orbital quantum number l

$$L = \sqrt{l(l+1)} \hbar, \quad l = 0, 1, \dots, n-1$$

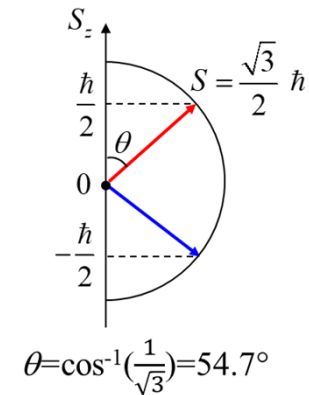
4. Magnetic quantum number m_l

$$L_z = m_l \hbar, \quad m_l = 0, \pm 1, \dots, \pm l$$



5. Spin magnetic quantum number m_s

$$s = \frac{1}{2}, \quad S = \sqrt{s(s+1)} \cdot \hbar = \frac{\sqrt{3}}{2} \hbar, \quad S_z = m_s \hbar, \quad m_s = \pm \frac{1}{2}$$



6. Radial probability distribution

$$\psi_{100} = \frac{1}{\sqrt{\pi r_0^3}} e^{-\frac{r}{r_0}} \quad \text{Bohr radius: } r_0 = \frac{h^2 \epsilon_0}{\pi m e^2} \approx 5.29 \times 10^{-11} \text{ m}$$

$$|\psi|^2 dV = |\psi|^2 \cdot 4\pi r^2 dr = P_r dr \quad \Rightarrow \quad P_r = 4\pi r^2 |\psi|^2 = \frac{4r^2}{r_0^3} e^{-\frac{2r}{r_0}}$$

7. Two principles for the arrangements of electrons

- (1) Lowest energy principle \rightarrow ground state
- (2) Pauli exclusion principle

8. Shell structure of electrons

$n = 1, 2, 3, 4, 5, 6$
K, L, M, N, O, P

$l = 0, 1, 2, 3, 4$
s, p, d, f, g

9. Maximum number of electrons contained in each shells and subshells

$$N_{sub} = (2l+1)$$

$$N_{shell} = 2 \sum_{l=0}^{n-1} (2l+1) = 2n^2$$

$l = 0, 1, 2, 3, 4$
$s \quad p \quad d \quad f \quad g$
$2 \quad 6 \quad 10 \quad 14 \quad 18$

$n = 1, 2, 3, 4, 5$
$K \quad L \quad M \quad N \quad O$
$2 \quad 8 \quad 18 \quad 32 \quad 50$

10. Electrons fill the shells and subshells from left to right

$n \backslash l$	s	p	d	f	g
	0	1	2	3	4
1	1s²				
2	2s²	2p⁶			
3	3s²	3p⁶	3d¹⁰		
4	4s²	4p⁶	4d¹⁰	4f¹⁴	
5	5s²	5p⁶	5d¹⁰	5f¹⁴	5g¹⁸

Thank You

Wishing you all the best results!