Atomic Structure

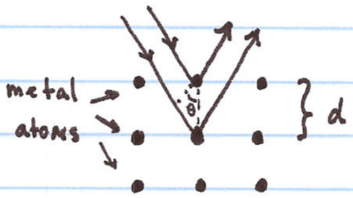
Wave-Particle Duality

- Wave-like phenomena (e.g. light) can behave like particles
- Particle-like phenomena (e.g. electrons) can behave like waves

Photoelectric Effect shows particle nature of light

Davisson-Germer Experiment shows wave nature of electrons.

↳ • Sent beam of electrons at surface of a metal
- Electrons diffracted according Bragg's Law
- Electron wavelength $\lambda = \frac{h}{p}$ (DeBroglie wavelength)



$2d\sin\theta = m\lambda$ $m = 1, 2, 3, \ldots$

⇒ electrons (normally considered a particle) behave like X-rays (normally considered waves)

Q. When do electrons behave like waves?

A. When their DeBroglie λ satisfies

$$\lambda \gtrsim \text{size of system of interest}$$

e.g. Davisson-Germer Experiment: size of system = d (lattice spacing)

eg. atom: size of system = size of atom

Electrons behave like waves in atoms $\left(\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} \sim \text{size of atom} \right)$

In physics, wave phenomena described by a "wave equation".
e.g. a vibrating violin string

Facts about wave equations

- Solution is a function that describes a wave ("wave function")
- Infinite number of solutions
- Boundary conditions (e.g. ends of violin string cannot move) limit solutions to a discrete set, members of which are labelled by an integer ($\psi_0(x,t)$, $\psi_1(x,t)$, $\psi_2(x,t)$ . . .)
- Each integer corresponds to a frequeny of vibration (e.g harmonics)
- Number of integers needed to label solution = number of independent degrees of freedom (e.g. string needs 1 integer, drumhead needs 2 integers, vibrating block of jello needs 3 integer)

Wave equation for electron in atom: <u>Schrödinger Equation</u>

- Solution labeled by 3 integers.
- These integers are called "quantum numbers"
- A 4th quantum number associated with the spin of the electron
- $|\psi(x,y,z,t)|^2 \Delta x \Delta y \Delta z$ = probability of finding the electron in box of volume $\Delta x \Delta y \Delta z$ centered at (x,y,z) at the time t.

Atomic Quantum Numbers

label	name	meaning	Values	Use
n	principal	Determines electron energy	$1, 2, \ldots, \infty$	$E_n = \frac{E_1}{n^2}$
l	angular momentum	Determines electron angular momentum	$0, \ldots, n-1$	$L = \sqrt{l(l+1)}\,\hbar$
m_l	magnetic	Determines z-component of angular momentum	$-l, \ldots, l$	$L_z = m_l \hbar$
s	spin	Determines z-component of spin angular momentum of electron	$\pm \frac{1}{2}$	$S_z = S\hbar$

$\hbar = \frac{h}{2\pi}$, $E_1 = -13.6\,\text{eV}$

Connection to chemistry notation

n	Symbol
1	K shell
2	L shell
3	M shell
4	N shell
5	O shell

l	Symbol
0	s orbital
1	p orbital
2	d orbital
3	f orbital
4	g orbital

Eg. $n = 2$ (L shell)

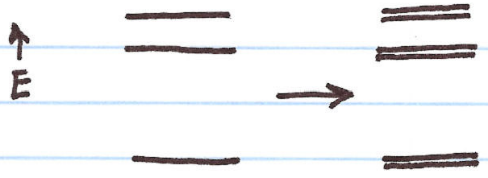
$$l = \begin{cases} 0 & \text{(s orbital)} \\ 1 & \text{(p orbital)} \end{cases}$$

Eg $n = 3$ (M shell)

$$l = \begin{cases} 0 & \text{(s orbital)} \\ 1 & \text{(p orbital)} \\ 2 & \text{(d orbital)} \end{cases}$$

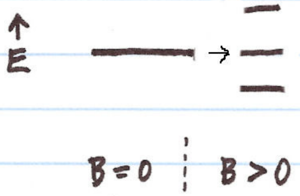
Corrections to Electron energy

Energy levels slightly depend on spin quantum number



spin-orbit effect – interaction of spin magnetic moment of electron with electric field of nucleus

When atom in a magnetic field, Energy levels also depend on magnetic quantum number m_ℓ



Zeeman effect – interaction of orbital magnetic moment of electron with an external magnetic field

Pauli Exclusion Principle

No two electrons in an atom can have the same values for all 4 of its quantum numbers.

Working out Atomic Structure

Central-field approximation – electric potential function of complex atoms about the same as for Hydrogen atom (except for value of the charge).

→ So complex atom has same quantum numbers as hydrogen atom.

Occupation of orbital

orbital	max occupancy	ℓ	rule : $2(2\ell+1)$
s	2	0	$2(2\cdot0+1)=2$
p	6	1	$2(2\cdot1+1)=6$
d	10	2	$2(2\cdot2+1)=10$
f	14	3	$2(2\cdot3+1)=14$
g	18	4	$2(2\cdot4+1)=18$

Spectroscopic Notation

- For atomic structure
- $\underset{\text{principal q number}}{n}\,\underbrace{\Theta^i\Theta^j\ldots\Theta^k}_{\text{orbital symbol}}$ $\quad$ i, j, k : occupation of orbital

eg. Structure of Si ($Z=14$)

↑ atomic number = number of protons = number of electrons.

$$\underbrace{1s^2}_{2\;+}\;\underbrace{2s^2p^6}_{8\;+}\;\underbrace{3s^2p^2}_{4}\quad=14$$