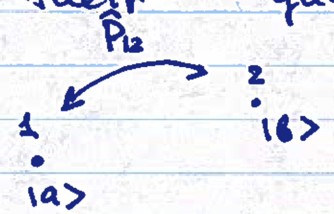
Pauli exclusion principle

If we have two (or more) non-distinguishable particles, this must be reflected in their quantum state



Exchange operator $\hat{P}_{12}$

$$\hat{P}_{12}\left[\,|a\rangle_1 \otimes |b\rangle_2\,\right] = |a\rangle_2 \otimes |b\rangle_1$$

$$\hat{P}_{12}\,|a,b\rangle = |b,a\rangle$$

$\cancel{\lambda^2 = 1}$ $\cancel{\lambda = \pm 1}$

$$\hat{P}_{12}\left[\hat{P}_{12}\,|a,b\rangle\right] = \hat{P}_{12}\,|b,a\rangle = |a,b\rangle \quad \text{identical}$$

if $\hat{P}_{12}\,|\psi_{12}\rangle = \lambda\,|\psi_{12}\rangle$ $\quad \hat{P}_{12}^2\,|\psi_{12}\rangle = \lambda^2|\psi_{12}\rangle = |\psi_{12}\rangle$

$\lambda = \pm 1$

$\lambda = 1$ the wavefunction is symmetric under exchange

Bosons $\quad \hat{P}_{12}\,|\psi\rangle = |\psi\rangle$ ← case for integer-spin particles

$S = 0, 1, \ldots$ photons, ~~[illegible]~~

or $\lambda = -1$ the wave function is anty-symmetric under exchange

Fermions $\quad \hat{P}_{12}\,|\psi\rangle = -|\psi\rangle$ ← case for half-integer particles

$S = 1/2$ electrons, protons, neutrons

Pauli exclusion principle: no two fermions can occupy the same quantum state.

Quantum state of an electron in an atom

$$\underbrace{|n, \ell, m_\ell\rangle}_{\text{orbital quantum numbers}} \otimes \underbrace{|s, m_s\rangle}_{\text{spin quantum number}} \quad (s = 1/2)$$

Each energy state $|n\rangle$ has massive degeneracy

$$\left.\begin{array}{l} n \rightarrow \ell = 0, 1, \ldots\ n-1 \\ \quad\ \hookrightarrow m_\ell = 0, \pm 1, \ldots\ \pm \ell \end{array}\right\} n^2$$

$$+\ m_s = \pm 1/2 \qquad\qquad 2$$

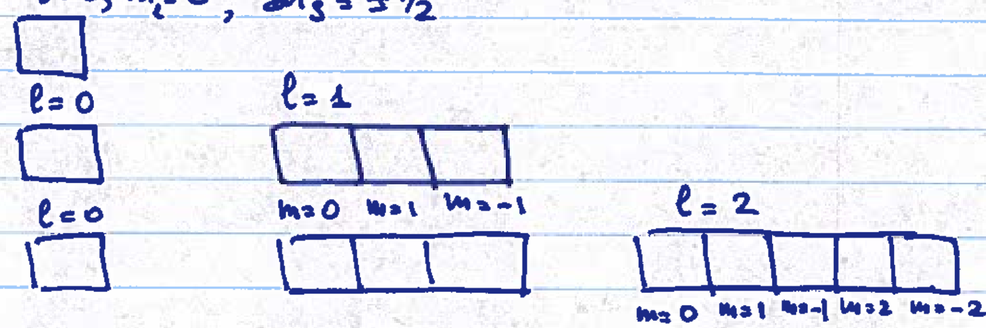
Total # of electron state options $\quad 2n^2$

$\ell = 0,\ m_\ell = 0,\ m_s = \pm 1/2$

$n = 1$
(2 states)

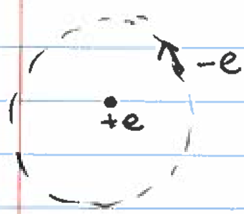
$n = 2$
(8 states)

$n = 3$
(18 states)

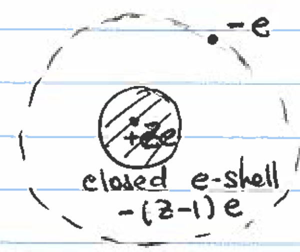


The rest of the periodic table

H



Alkali metals (Li, Na, K, Rb, Cs)



Hydrogen-like energy structure

Transitions $\underset{\text{ground}}{nS} \rightarrow nP$ states

~~Because~~

are in visible (Li, Na) or near-IR (K, Rb, Cs) range

Electro-magnetic waves interact much more easily with one outer (valence) electron, making alkali metal atoms very similar to hydrogen in terms of their absorption spectrum

Hydrogen energies

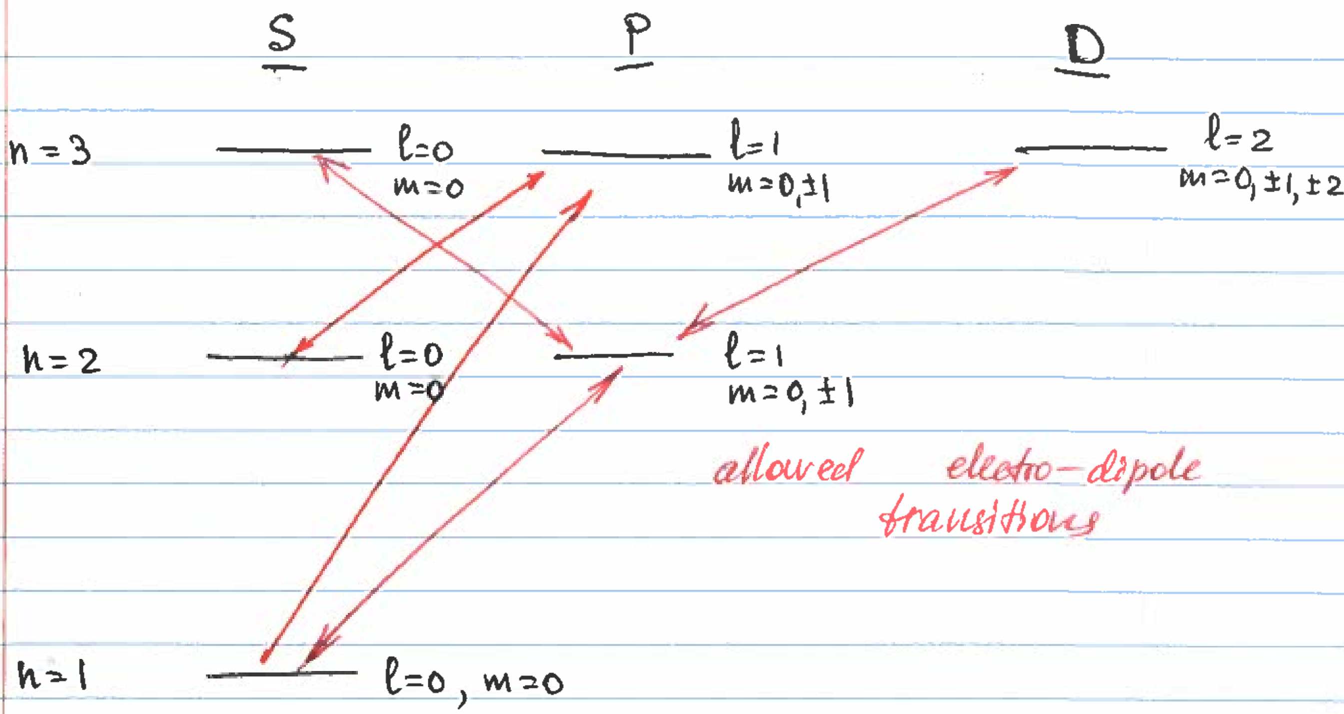
$$E_n = -\frac{E_R}{n^2}$$

Alkali metals energies

$$E_n = -\frac{E_R}{(n-\delta_e)^2}$$

quantum defect

A correction to the enery value due to the effect of (Z-1) electrons around the core

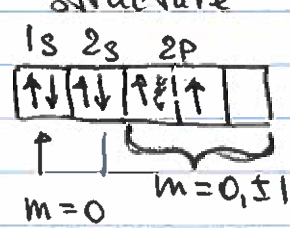


Spectroscopic names for orbitals

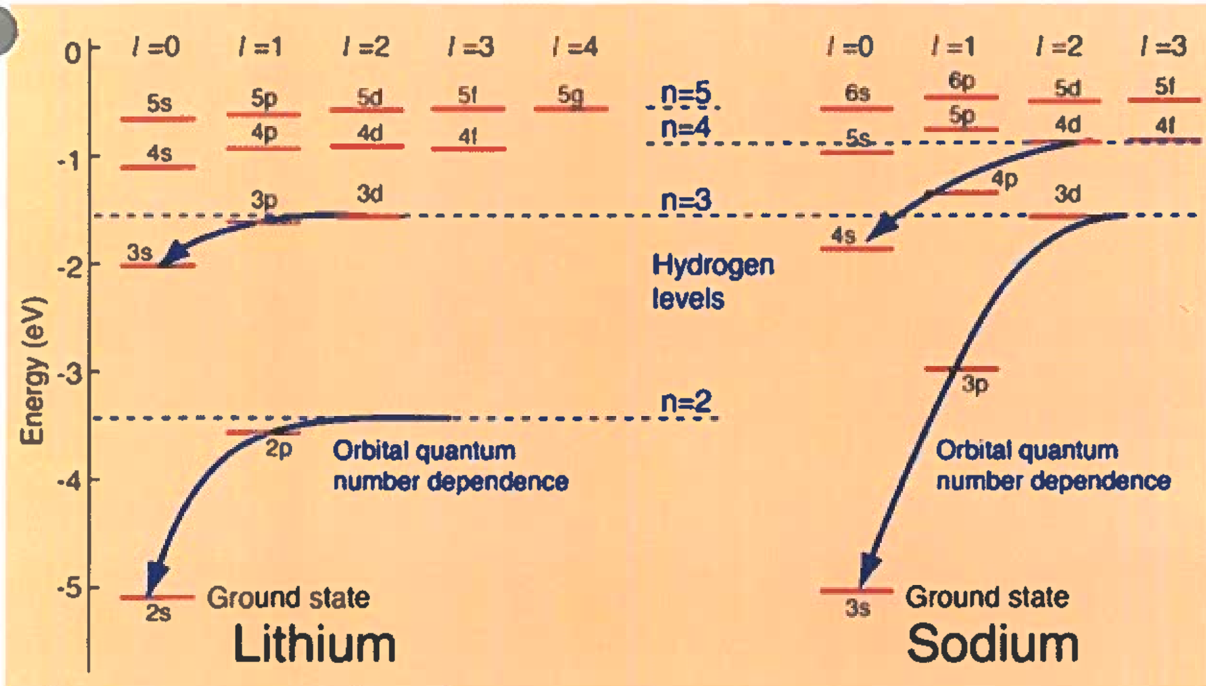
$l=0 \longrightarrow S$ (Sharp)
$l=1 \longrightarrow P$ (principal)
$l=2 \longrightarrow D$ (diffuse)
$l=3 \longrightarrow F$ (fundamental)
for higher $l \longrightarrow$ alphabetic G, H, ...

This energy structure is used universally for atomic structure

^{12}C



Pauli exclusion principle: no two electrons can occupy the same quantum state, so each orbital can fit only 2 electrons (spin orientations ↑ & ↓)



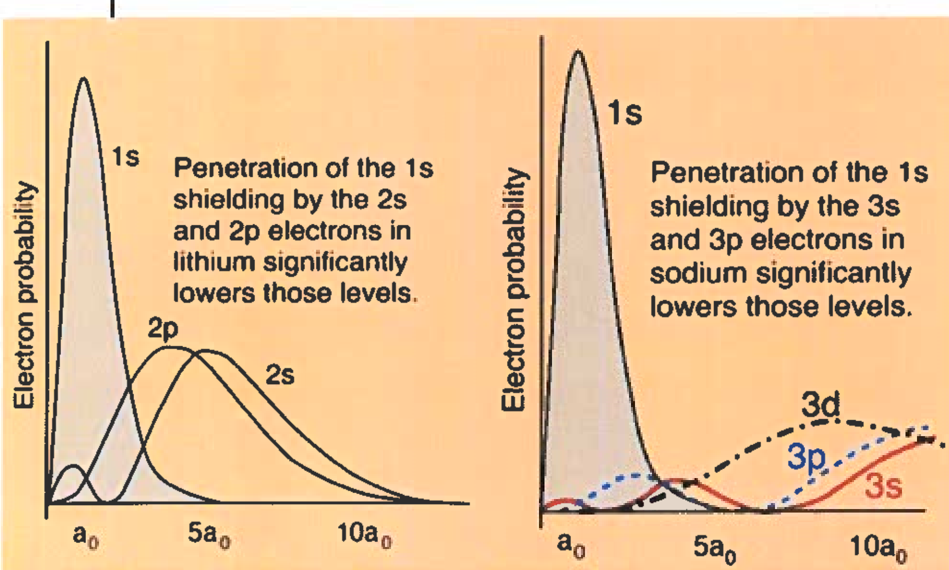
Quantum defect values

Atom	$l=$ 0	1	2	3
Li	0.40	0.04	0.00	0.00
Na	1.35	0.85	0.01	0.00
K	2.19	1.71	0.25	0.00
Rb	3.13	2.66	1.34	0.01
Cs	4.06	3.59	2.46	0.02

Hydrogen $E_n = -\frac{E_R}{n^2}$

Alkali $E_n = -\frac{E_R}{(n-\delta_\ell)^2}$

δ_ℓ - quantum defect



The rest of the spectrum ... it is complicated

Electron-electron interactions become very important, and ~~dominate~~ ~~the~~ strongly affect energy spectrum.

Example – He 2 electrons

Pauli exclusion principle becomes very important

	spin	energy level
electron 1	$\uparrow$	$n=1,\ \ell=0$
electron 2	$\downarrow$	$n=1,\ \ell=0$
or	$\uparrow$	$n=2,\ \ell=0,1$

Spins $\uparrow\downarrow$, total spin $S=0$ – para helium

$\uparrow\uparrow$, total spin $S=1$ – ortho helium

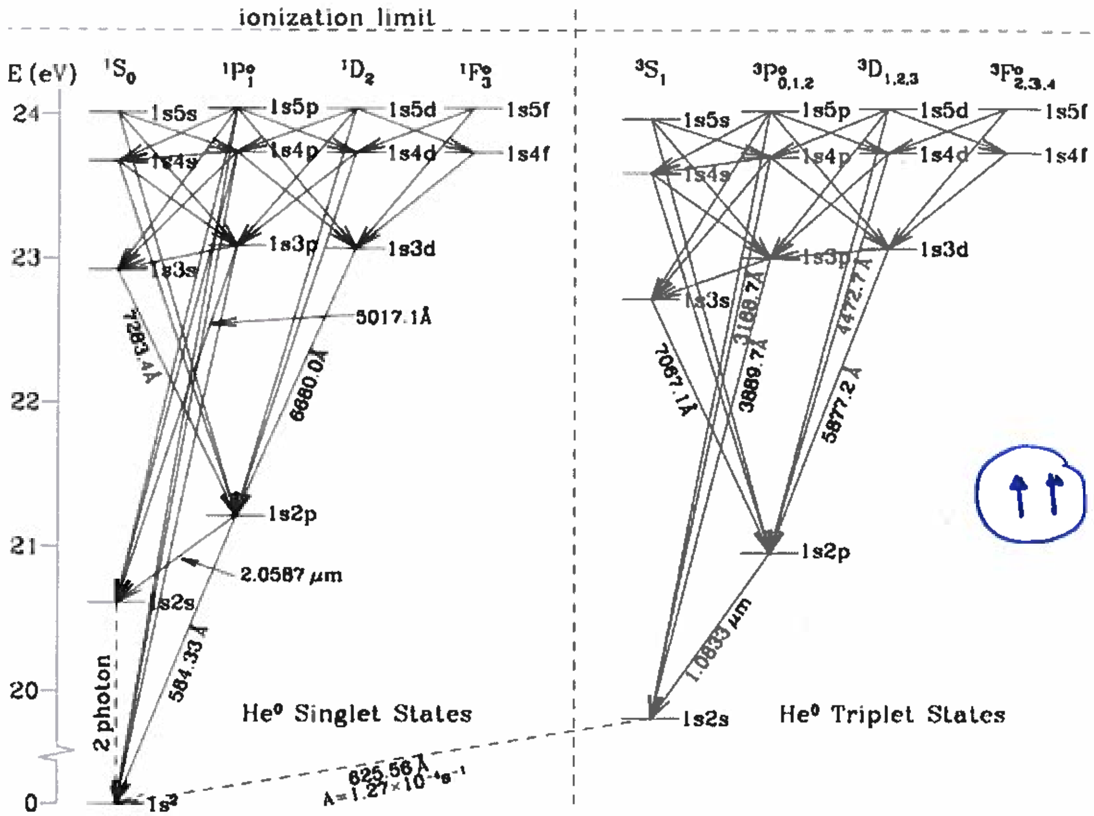


Figure 14.3 Radiative decay pathways for He^0 (see text). Selected lines are labeled by vacuum wavelength.

Figure 1: Grotrian diagram for Helium atom along with prominent lines.