Complex Atoms

Several quantum numbers: n, l, m_l, s, m_s

Lifting the l -degeneracy

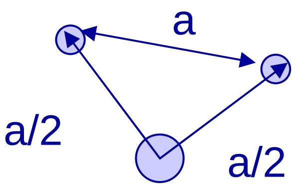
Magnetic effects

Pauli’s exclusion priciple

Shell strcuture and the

Periodic Table of the elements

The Helium atom; semi-classical approximation



Without repulsion:

$$E = 2E_1 = -2Z^2 E_0 = -8 \cdot (13.6)eV = -108.8eV$$

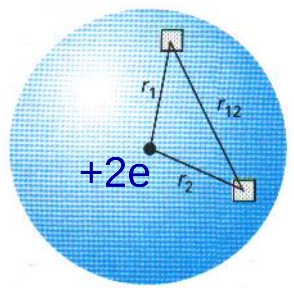
With repulsion; electrons at fixed distance ~a$_0$,
Repulsive energy:

$$\frac{e^2}{4\pi\varepsilon_0 a_0} = \alpha\hbar c \frac{\alpha m_e c}{\hbar} = 2E_0 = 27.2eV$$

Calculated: $E_{tot} = -81.6eV$

Experimental: $E_{tot} = -79eV$

Complex Atoms and the Schrödinger Equation



$$H = \underbrace{-\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right)}_{E_{kin}} \underbrace{- \frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_2}}_{\text{attraction}} + \underbrace{\frac{e^2}{4\pi\varepsilon_0 r_{12}}}_{\text{repulsion}}$$

NB:
A non-central force

Two-particle Schrödinger equation: $H\Psi(\vec{r}_1, \vec{r}_2) = E\Psi(\vec{r}_1, \vec{r}_2)$

First approximation: unperturbed system (no repulsion) $H^{(0)} = H_1 + H_2$

Each: $H_i = -\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{2e^2}{4\pi\varepsilon_0 r_1}$ has solution $E_i = -R\frac{Z^2}{n_1^2} = -R\frac{4}{n_1^2}$

Wave function: $\Psi(\vec{r}_1, \vec{r}_2) = \psi_{nlm}(\vec{r}_1)\psi_{nlm}(\vec{r}_2) = \psi_1\psi_2$

$$H^{(0)}\Psi(\vec{r}_1, \vec{r}_2) = (H_1 + H_2)\psi_1\psi_2 = (H_1\psi_1)\psi_2 + \psi_1(H_2\psi_2)$$
$$= E_1\psi_1\psi_2 + E_2\psi_1\psi_2 = E\psi_1\psi_2$$

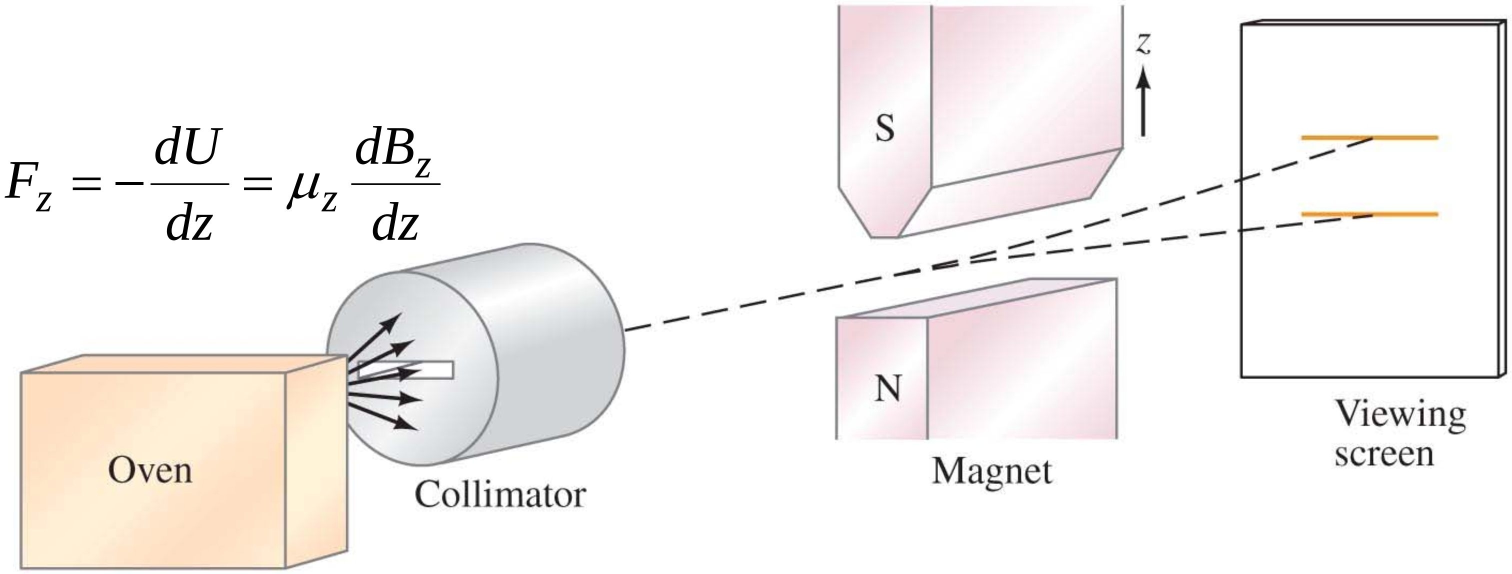
Hence: $\boxed{E = -8R\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)}$

General rule: complex atoms → Product wave functions of hydrogen orbitals

Magnetic Dipole Moments; Total Angular Momentum

Stern-Gerlach experiment
-nonuniform magnetic field
-classically a continuum of deflection angles is expected
Instead, the angles were quantized, corresponding to the quantized values of the magnetic moment.

$$F_z = -\frac{dU}{dz} = \mu_z \frac{dB_z}{dz}$$



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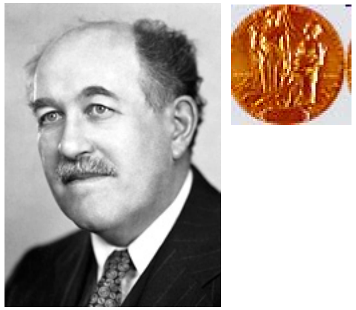
General for a magnetic dipole:
-Force on a dipole in a gradient
-Orientation of a dipole in a Homogeneous B-field



The Nobel Prize in Physics 1943
"for his contribution to the development of the molecular ray method and his discovery of the magnetic moment of the proton"

Magnetic Dipoles

Potential Energy of a magnetic dipole $U = -\vec{\mu} \cdot \vec{B}$

Choose the magnetic field along z; $U = -\mu_z B_z$

Force = gradient of the potential:

$$F_z = -\frac{dU}{dz} = \frac{d\mu_z B_z}{dz} = \mu_z \frac{dB_z}{dz}$$

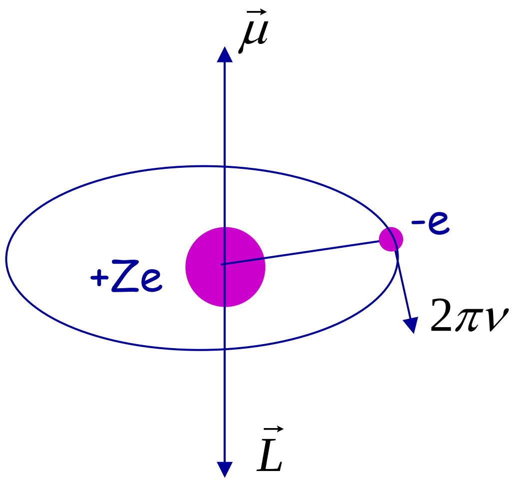
1. Only a force if there is a magnetic field gradient → Stern-Gerlach space quantisation

2. In a homogeneous magnetic field → Zeeman effect

Both effects related to quantisation of angular momentum

Intermezzo

Angular momentum and the unit of the Bohr magneton



Angular velocity $\omega = 2\pi\nu$

Magnetic moment

$$\mu = IA = \pi r^2 e\nu$$

Angular momentum

$$L = mvr = m\omega r^2 = 2\pi m\nu r^2$$

Hence $\vec{\mu} = -\frac{e}{2m_e}\vec{L}$

Define $\mu_B = \frac{e\hbar}{2m_e}$ Bohr magneton

We find a relation between the angular momentum and the magnetic moment of a classical point charge

$$\boxed{\vec{\mu} = -g_L \mu_B \frac{\vec{L}}{\hbar}}$$

For a classical particle $g_L = 1$

For a (relativistic) spin

$$\boxed{\vec{\mu}_S = -g_S \mu_B \frac{\vec{S}}{\hbar}}$$

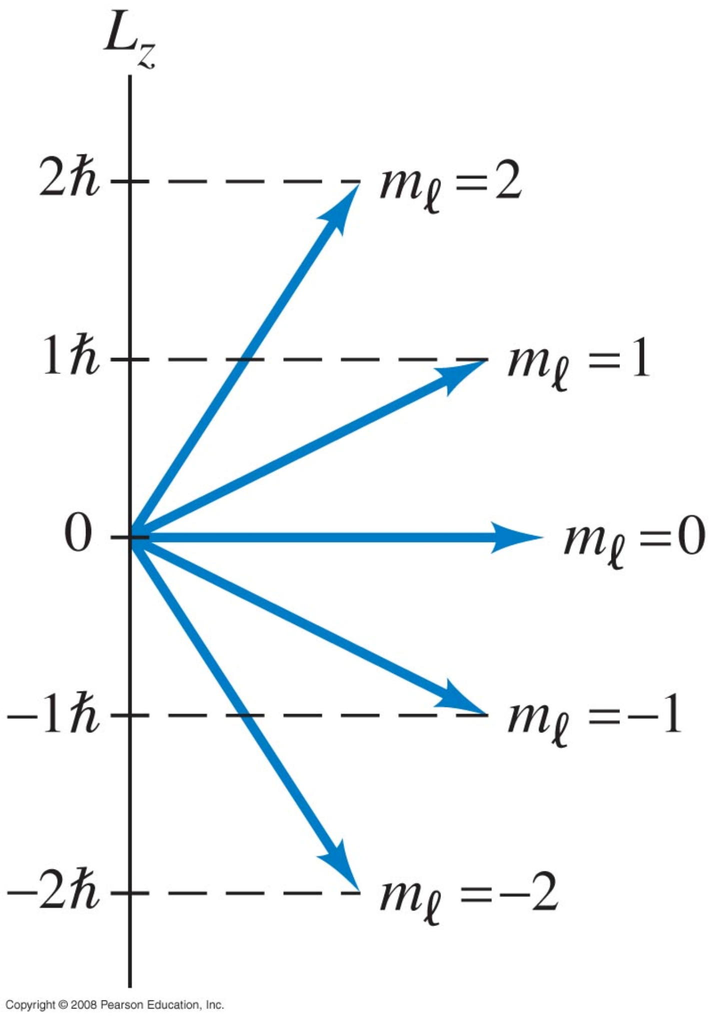
$g_S = 1/2$

This is peculiar !

Hydrogen Atom:
Schrödinger Equation and Quantum Numbers

If no magnetic field: energy does not depend on m

m_l degeneracy



In a magnetic field

$$U = -\vec{\mu} \cdot \vec{B} = -\mu_z B_z$$

$$\mu_z = -g_L \mu_B \frac{L_z}{\hbar}$$

For atomic wave functions;

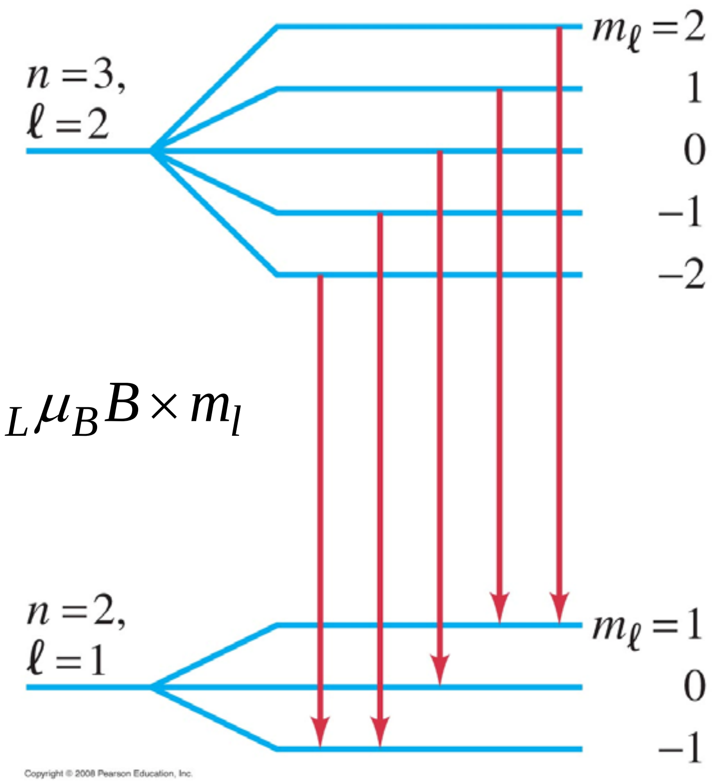
$$L_z \Psi = m\hbar\Psi$$

Hence splitting

$$U = g_L \mu_B m_l B$$

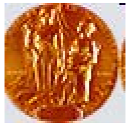
Hydrogen Atom: The Zeeman effect

In a magnetic field, the energy levels split depending on m_ℓ.



$$U = g_L \mu_B B \times m_l$$

Pieter Zeeman



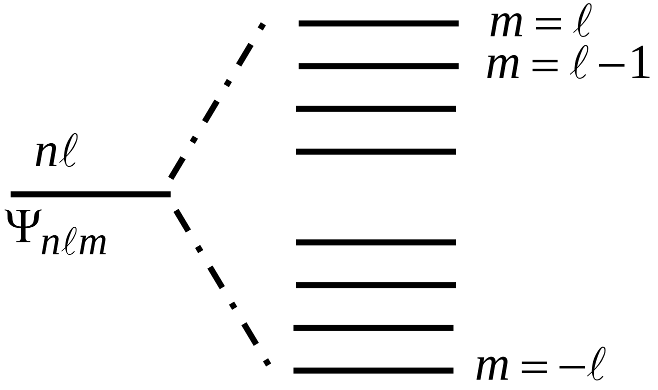
1902

Hendrik Lorentz

"in recognition of the extraordinary service
they rendered by their researches
into the influence of magnetism
upon radiation phenomena"

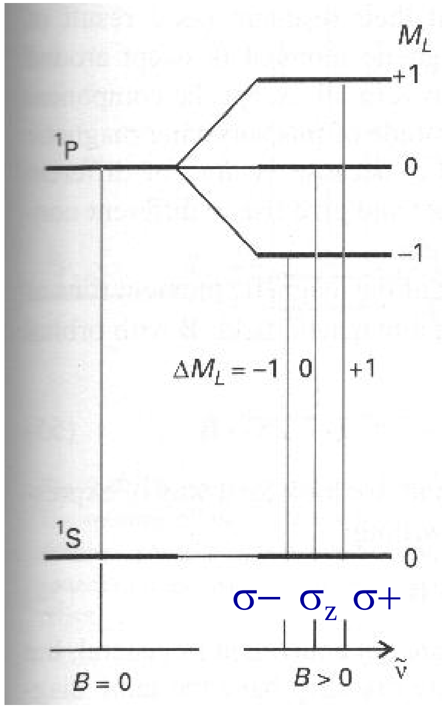
Normal Zeeman effect

Energy splitting for an *nl* state



Energy splitting: $\delta E_m = g\mu_B M$

For an $^1S \rightarrow {}^1P$-transition

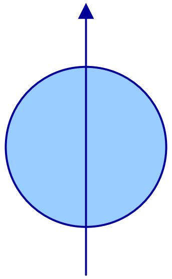


Recall selection rules for *m*
and polarization of light

Electron spin

No classical analogue for this phenomenon

$$s = \frac{1}{2}\hbar$$

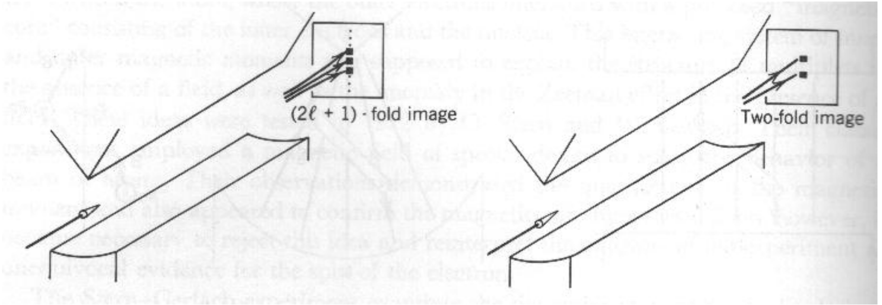


There is an additional “two-valuedness” in the spectra of atoms, behaving like an angular momentum

This may be interpreted/represented as an angular momentum

Origin of the spin-concept

-Stern-Gerlach experiment; space quantization



-Theory: the periodic system requires an **additional** two-valuedness

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For a (relativistic) spin

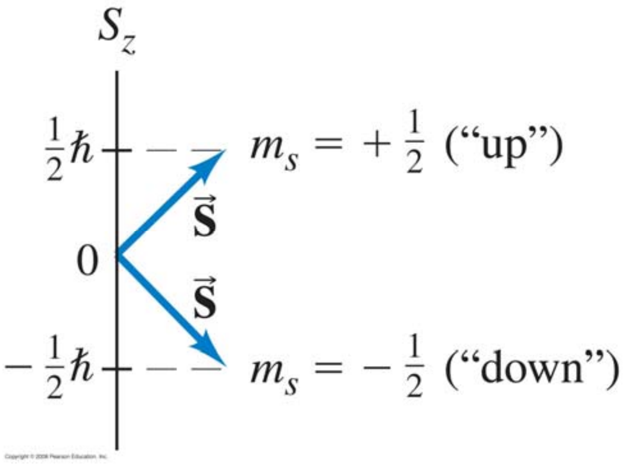
$$\vec{\mu}_S = -g_S \mu_B \frac{\vec{S}}{\hbar}$$

$$g_S = 1/2$$

This is peculiar !

Hydrogen Atom:
Schrödinger Equation and Quantum Numbers

4. The spin quantum number, m_s, for an electron can take on the values +½ and -½. The need for this quantum number was found by experiment; spin is an intrinsically quantum mechanical quantity, although it mathematically behaves as a form of angular momentum.



Hydrogen Atom:
Schrödinger Equation and Quantum Numbers

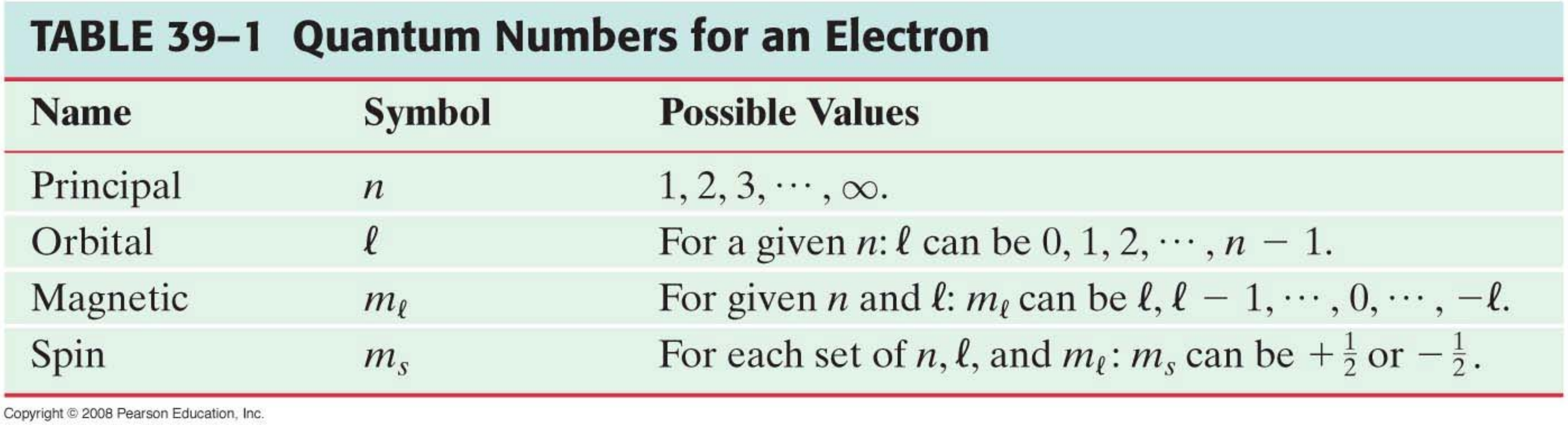


TABLE 39–1 Quantum Numbers for an Electron

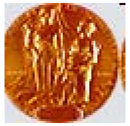
Name	Symbol	Possible Values
Principal	n	$1, 2, 3, \cdots, \infty$.
Orbital	ℓ	For a given n: ℓ can be $0, 1, 2, \cdots, n-1$.
Magnetic	m_ℓ	For given n and ℓ: m_ℓ can be $\ell, \ell-1, \cdots, 0, \cdots, -\ell$.
Spin	m_s	For each set of n, ℓ, and m_ℓ: m_s can be $+\frac{1}{2}$ or $-\frac{1}{2}$.

Complex Atoms; the Exclusion Principle

In order to understand the electron distributions in atoms, another principle is needed. This is the Pauli exclusion principle:

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

The quantum state is specified by the four quantum numbers; no two electrons can have the same set.



The Nobel Prize in Physics 1945
"for the discovery of the Exclusion Principle,
also called the Pauli Principle"

Intermezzo: the problem of “screening”

Question : why do *l*-values for the same *n* have differing energies

The potential energy in a multi-electron atom:

$$V = \underbrace{-\frac{Ze^2}{4\pi\varepsilon_0}\sum_{i=1}^{Z}\frac{1}{|\vec{r}_i|}}_{\text{attraction to nucleus}} + \underbrace{\frac{e^2}{4\pi\varepsilon_0}\sum_{i<j}\frac{1}{|\vec{r}_i - \vec{r}_j|}}_{\text{repulsion between electrons}}$$

V is a *non*-central potential

$$\begin{tikzcd}
 & -\dfrac{Ze^2}{4\pi\varepsilon_0 r} \quad \text{for} \quad r \to 0 \\
V_c(r) \arrow[ur] \arrow[dr] & \\
 & -\dfrac{e^2}{4\pi\varepsilon_0 r} \quad \text{for} \quad r \to \infty
\end{tikzcd}$$

Then V can be written in terms of an “effective screened nuclear charge”

$$V_{cfa}(r) = -\frac{Z_{eff}(r)e^2}{4\pi\varepsilon_0 r}$$

Central Field Approximation:

The overall effect of $V\left(\sum_i \vec{r}_i\right)$

is centrally directed toward the nucleus

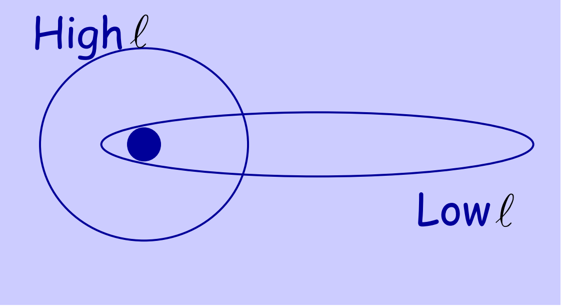
Intermezzo: the problem of “screening”

Radial part of the wave function

$$-\frac{\hbar^2}{2mr}\frac{d}{dr}rR_{nl}+\left[\frac{Z_{eff}(r)}{r}+\frac{\hbar^2\ell(\ell+1)}{2mr^2}\right]R_{nl}=E_{nl}R_{nl}$$

$\longrightarrow$ Energy E_{nl} depends on ℓ

Energy E_{nl} does *not* depend on *m*



For low ℓ values (and same n)
electron comes closer to the nucleus

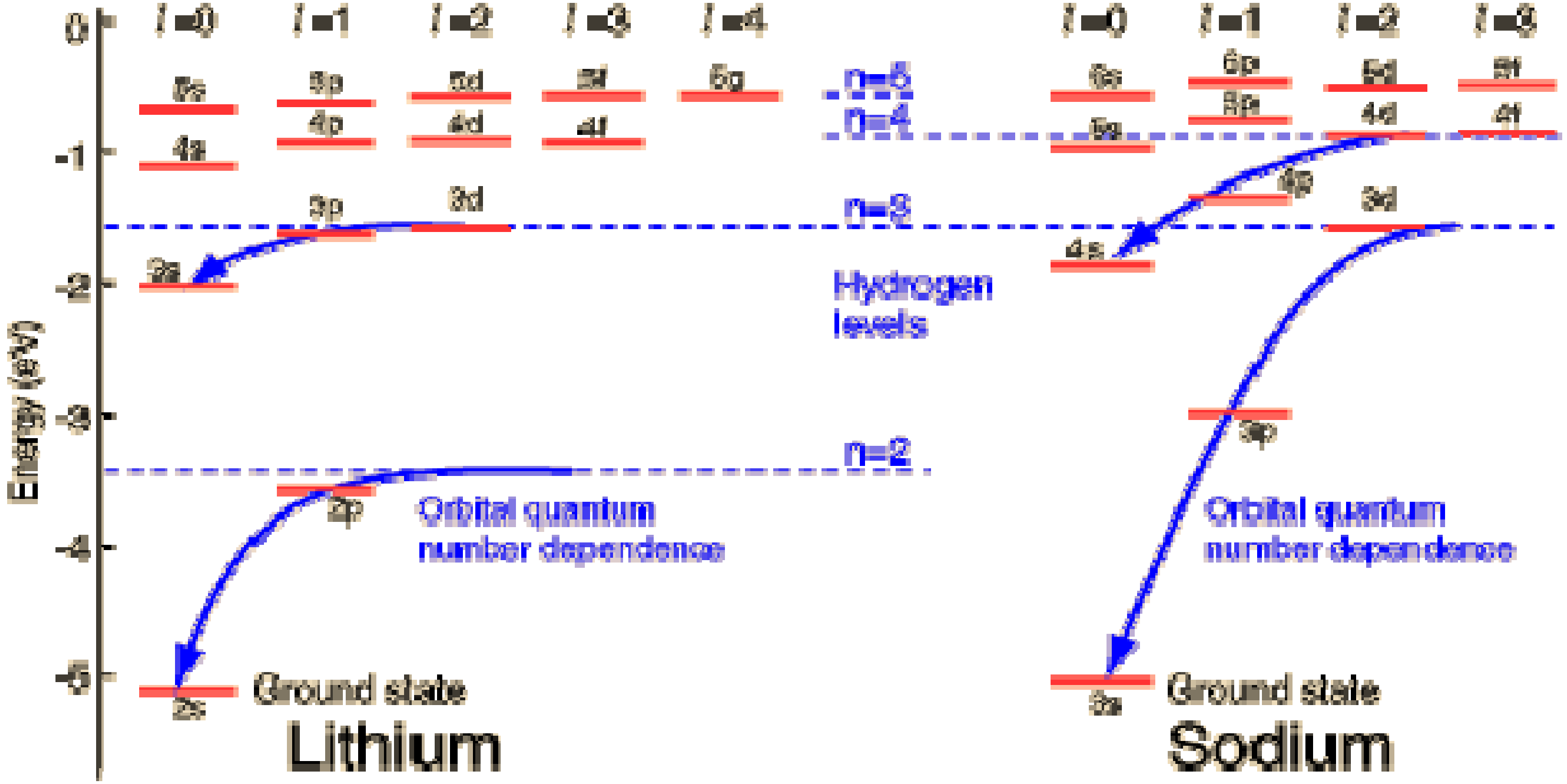
More Coulomb attraction

More binding energy

Lower ℓ states → lower energy

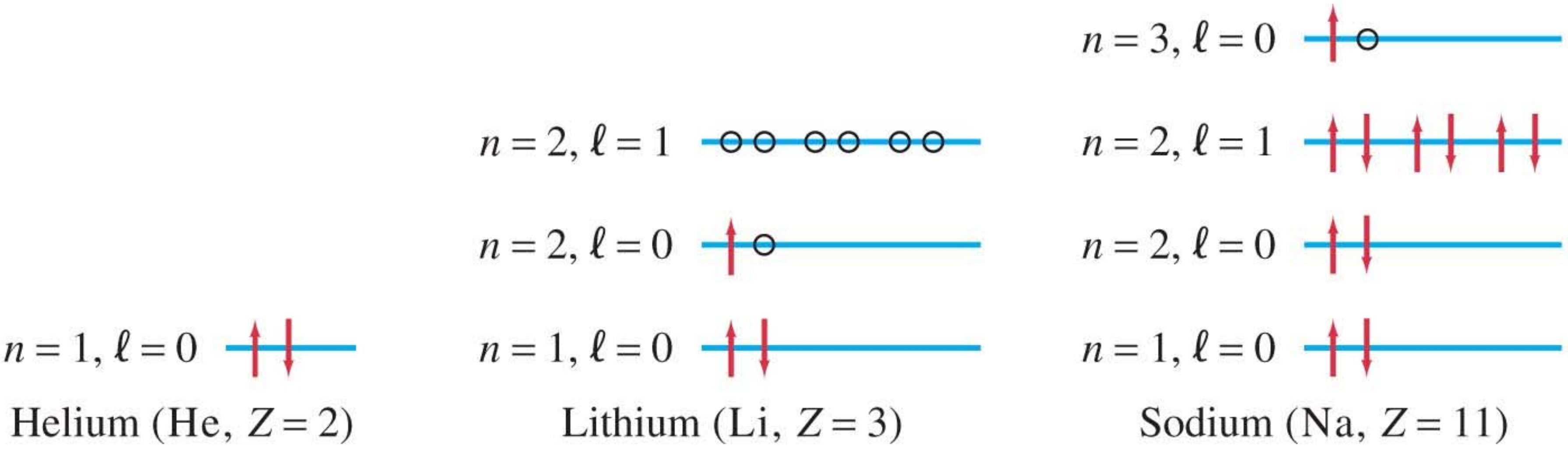
Intermezzo: the problem of “screening”

Lowering of low ℓ quantum states as an effect of screening



Complex Atoms; the Aufbau Principle

This chart shows the occupied – and some unoccupied – states in He, Li, and Na.



The Periodic Table of the Elements

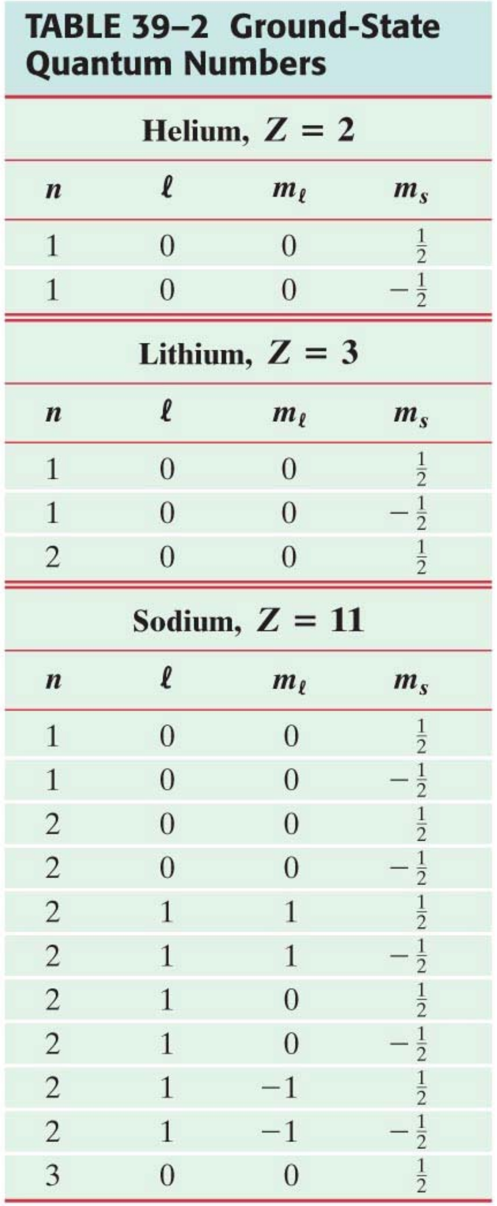


TABLE 39–2 Ground-State Quantum Numbers

Helium, $Z = 2$

n	ℓ	m_ℓ	m_s
1	0	0	$\frac{1}{2}$
1	0	0	$-\frac{1}{2}$

Lithium, $Z = 3$

n	ℓ	m_ℓ	m_s
1	0	0	$\frac{1}{2}$
1	0	0	$-\frac{1}{2}$
2	0	0	$\frac{1}{2}$

Sodium, $Z = 11$

n	ℓ	m_ℓ	m_s
1	0	0	$\frac{1}{2}$
1	0	0	$-\frac{1}{2}$
2	0	0	$\frac{1}{2}$
2	0	0	$-\frac{1}{2}$
2	1	1	$\frac{1}{2}$
2	1	1	$-\frac{1}{2}$
2	1	0	$\frac{1}{2}$
2	1	0	$-\frac{1}{2}$
2	1	−1	$\frac{1}{2}$
2	1	−1	$-\frac{1}{2}$
3	0	0	$\frac{1}{2}$

Each value of ℓ is given its own letter symbol.

Electron configurations are written by giving the value for n, the letter code for ℓ, and the number of electrons in the subshell as a superscript.

For example, here is the groundstate configuration of sodium:

$$1s^22s^22p^63s^1$$

The Periodic Table of the Elements

subshells

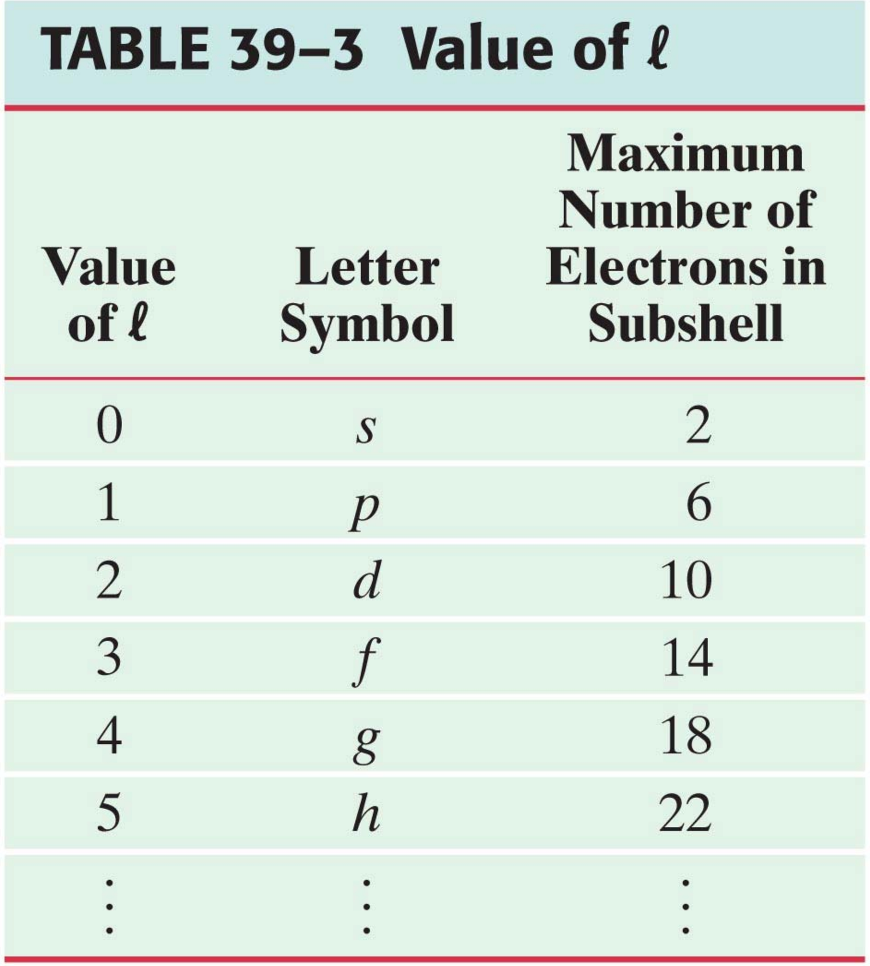
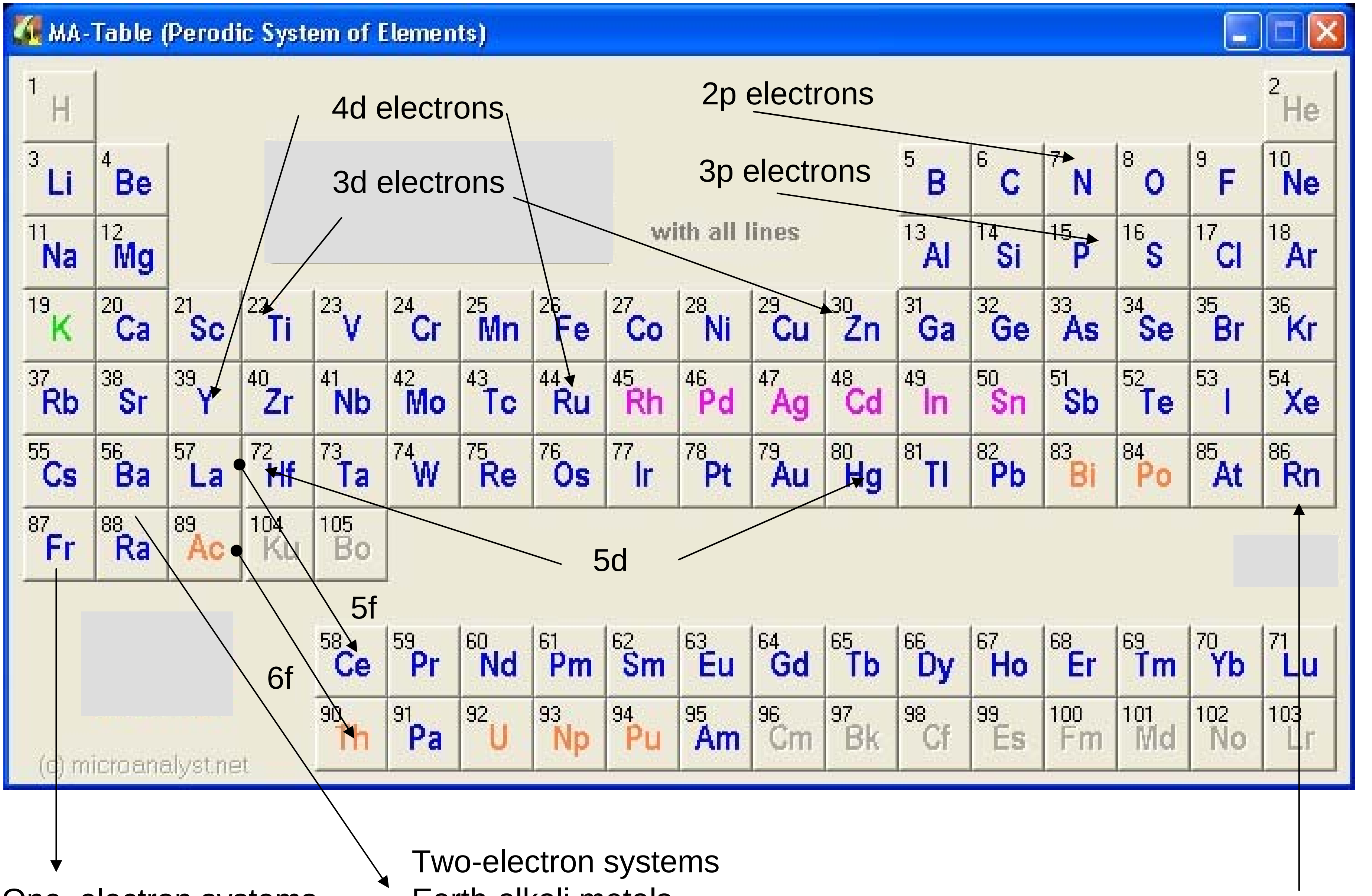


TABLE 39–3 Value of ℓ

Value of ℓ	Letter Symbol	Maximum Number of Electrons in Subshell
0	*s*	2
1	*p*	6
2	*d*	10
3	*f*	14
4	*g*	18
5	*h*	22
⋮	⋮	⋮



MA-Table (Perodic System of Elements)

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Ku	105 Bo													
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

with all lines

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4d electrons

2p electrons

3d electrons

3p electrons

5d

5f

6f

One–electron systems
Alkali metals
Li(2s), Na(3s),K(4s), Rb (5s)

Two-electron systems
Earth-alkali metals

Filled shells
He(1s^2), Ne(2p^6)
Noble gases