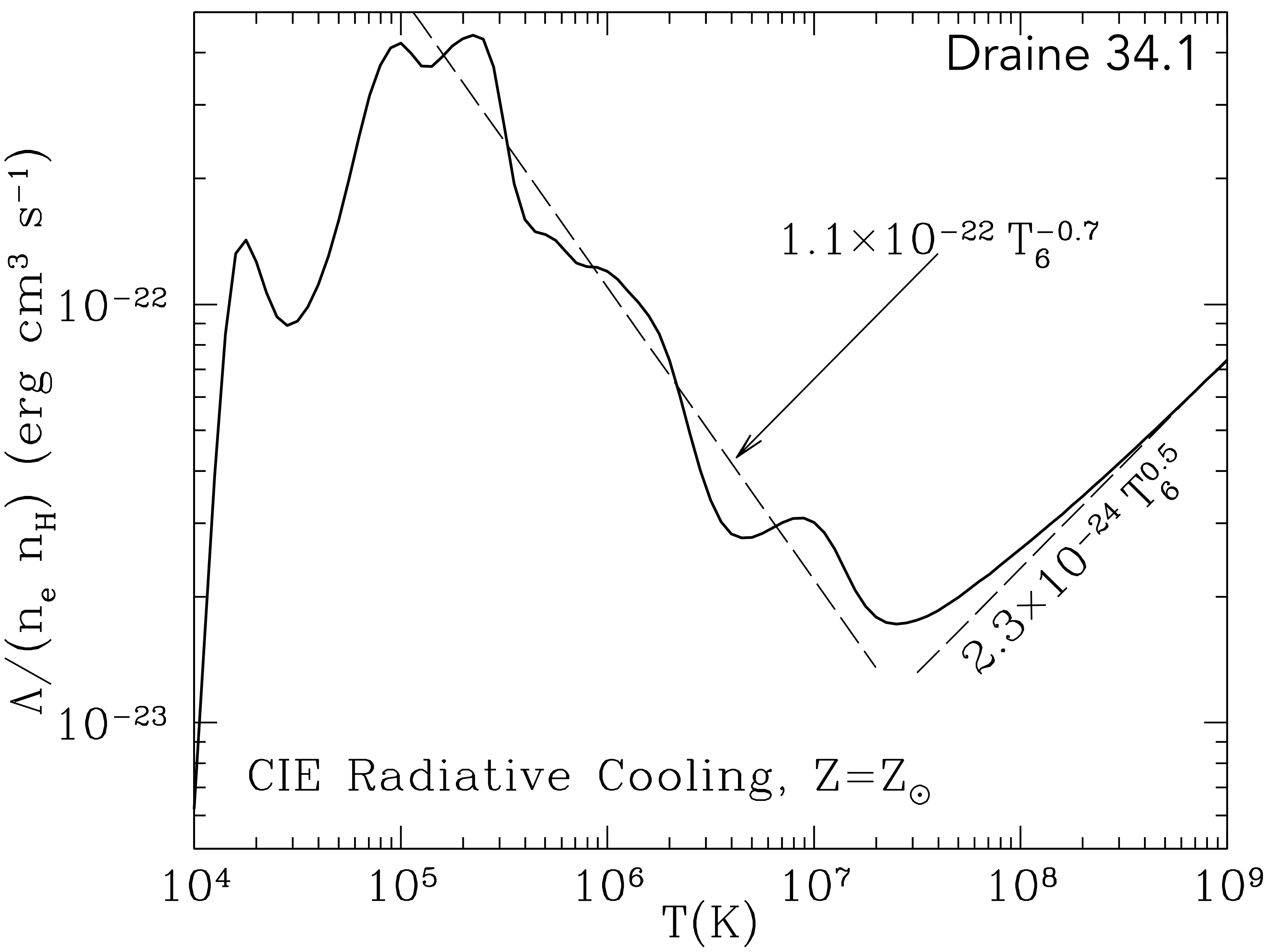
Physics 224
The Interstellar Medium

Lecture #4

- Part I: Energy Levels & Transitions in Atoms
- Part II: Order of Magnitude Energy Levels
- Next: Radiative Transfer

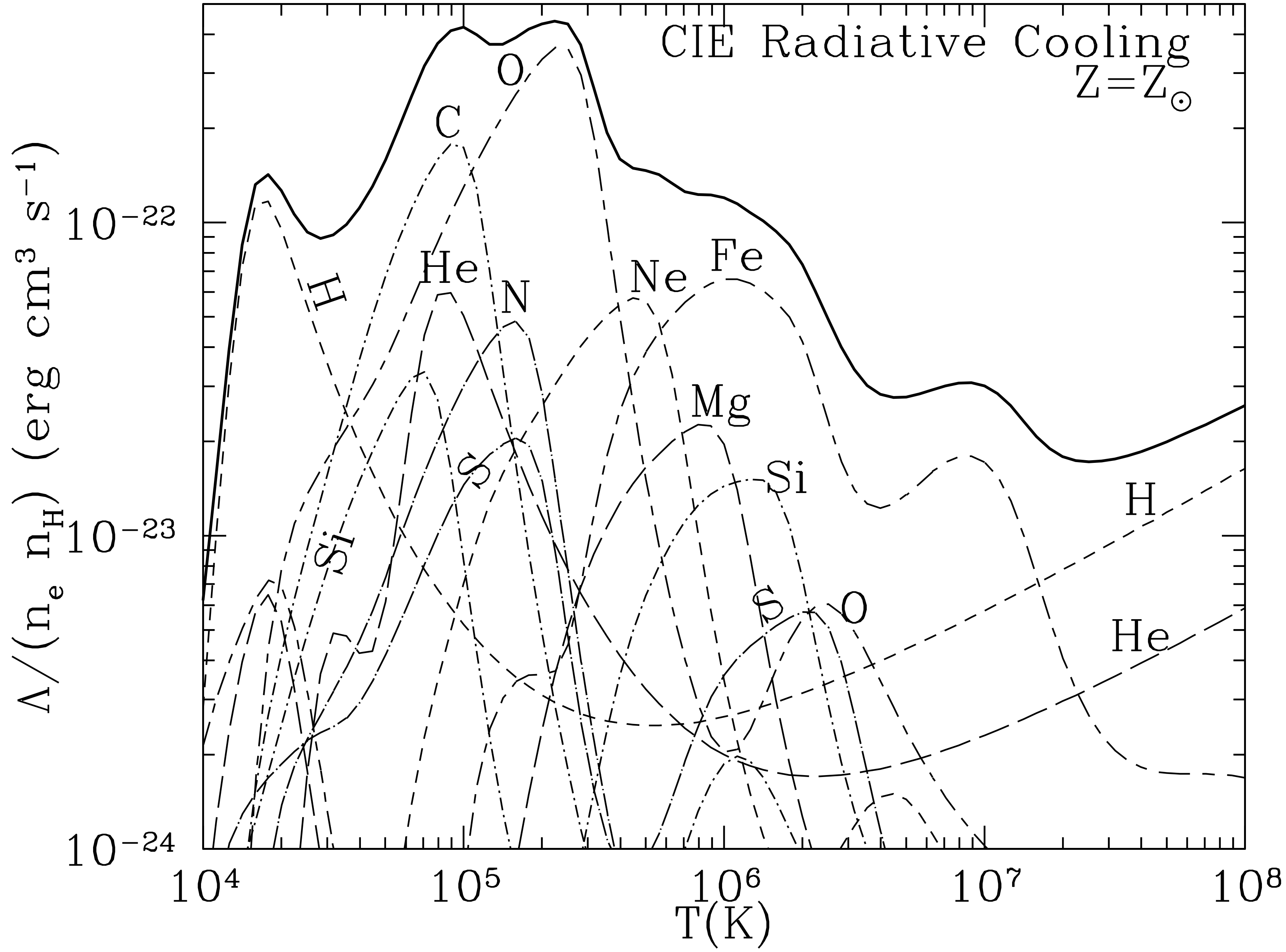
Emission lines from ions, atoms & molecules are critical for cooling ISM gas



Ionized Gas

Emission lines from ions, atoms & molecules are critical for cooling ISM gas

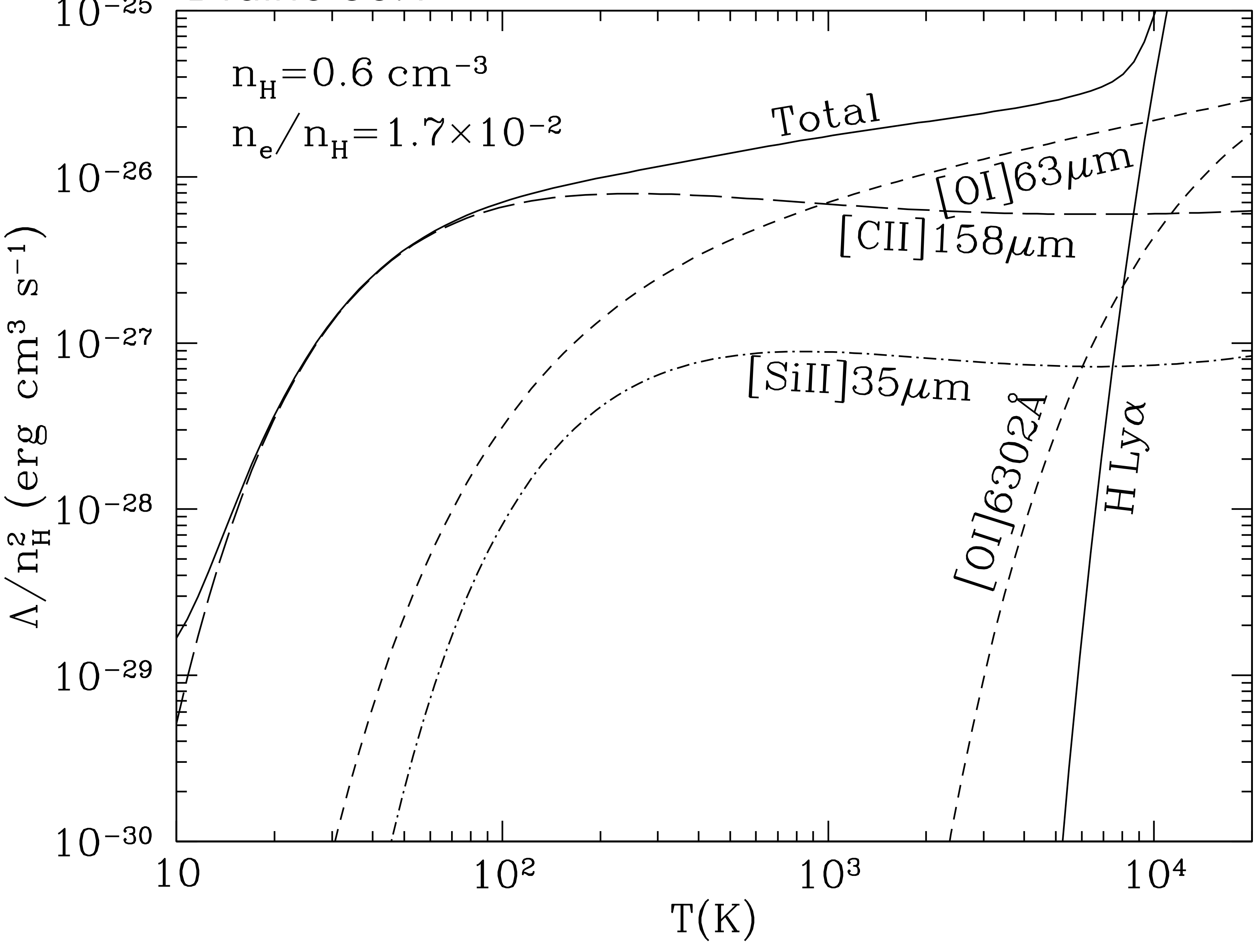
Draine 34.3



Ionized Gas

Emission lines from ions, atoms & molecules are critical for cooling ISM gas

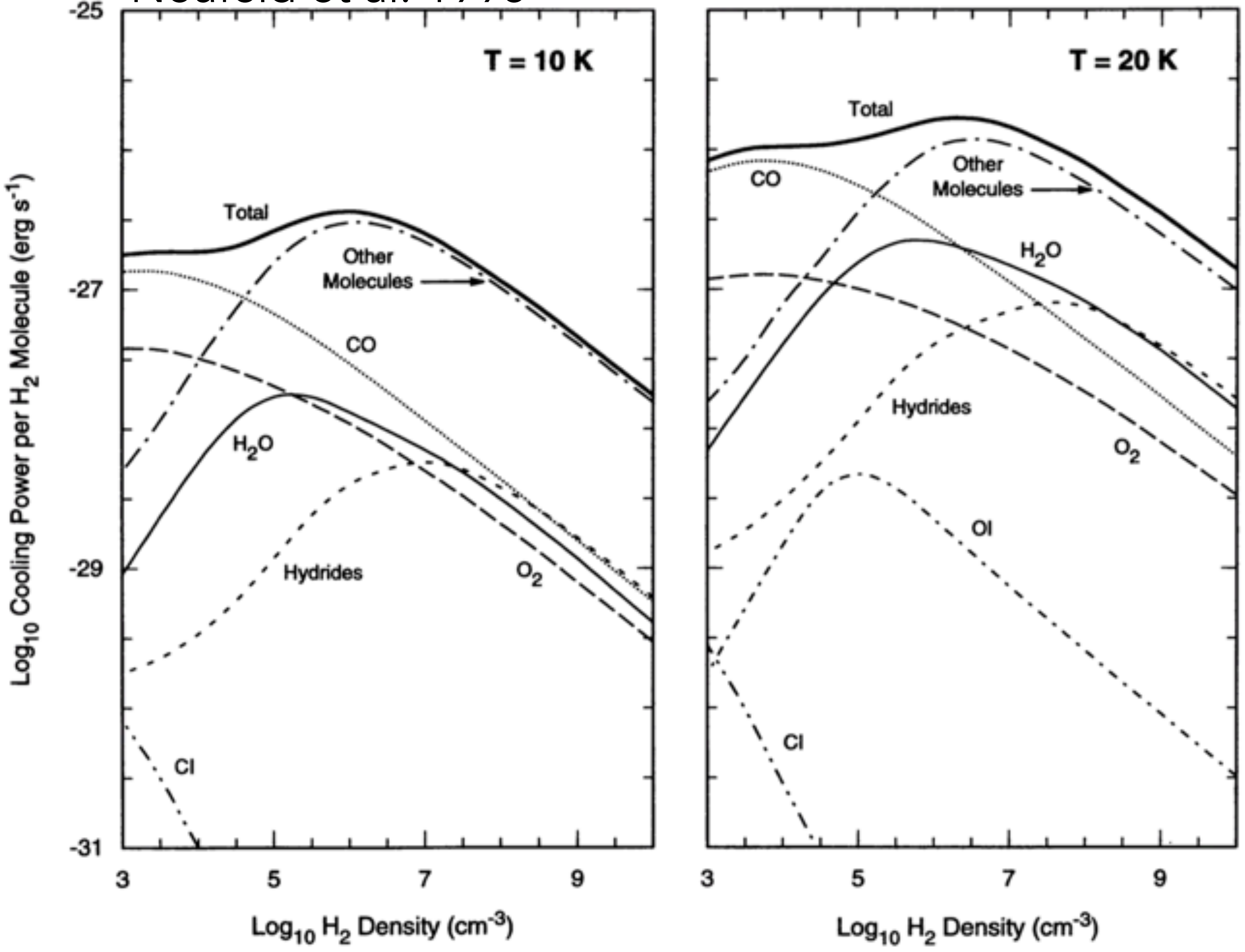
Draine 30.1



Neutral Gas

Emission lines from ions, atoms & molecules are critical for cooling ISM gas

Neufeld et al. 1995



Molecular Gas

Emission lines from ions, atoms & molecules are critical for cooling ISM gas

- Given some ion, atom or molecule - what sets the spacing between energy levels?
- How likely (or how frequently) do transitions between the various levels occur?

Energy Levels of Atoms & Ions

First need to know how electrons are configured in atom/ion:

Set by the quantum numbers that describe the wave-function

n = principle quantum number

l = orbital angular momentum in units of ħ ($0 \le l < n$)

m_z = proj. of angular mom. on z axis ($-l \le m_z \le l$)

e- spin = -ħ/2 or +ħ/2

degenerate (same energy) w/o applied B-field

Energy Levels of Atoms & Ions

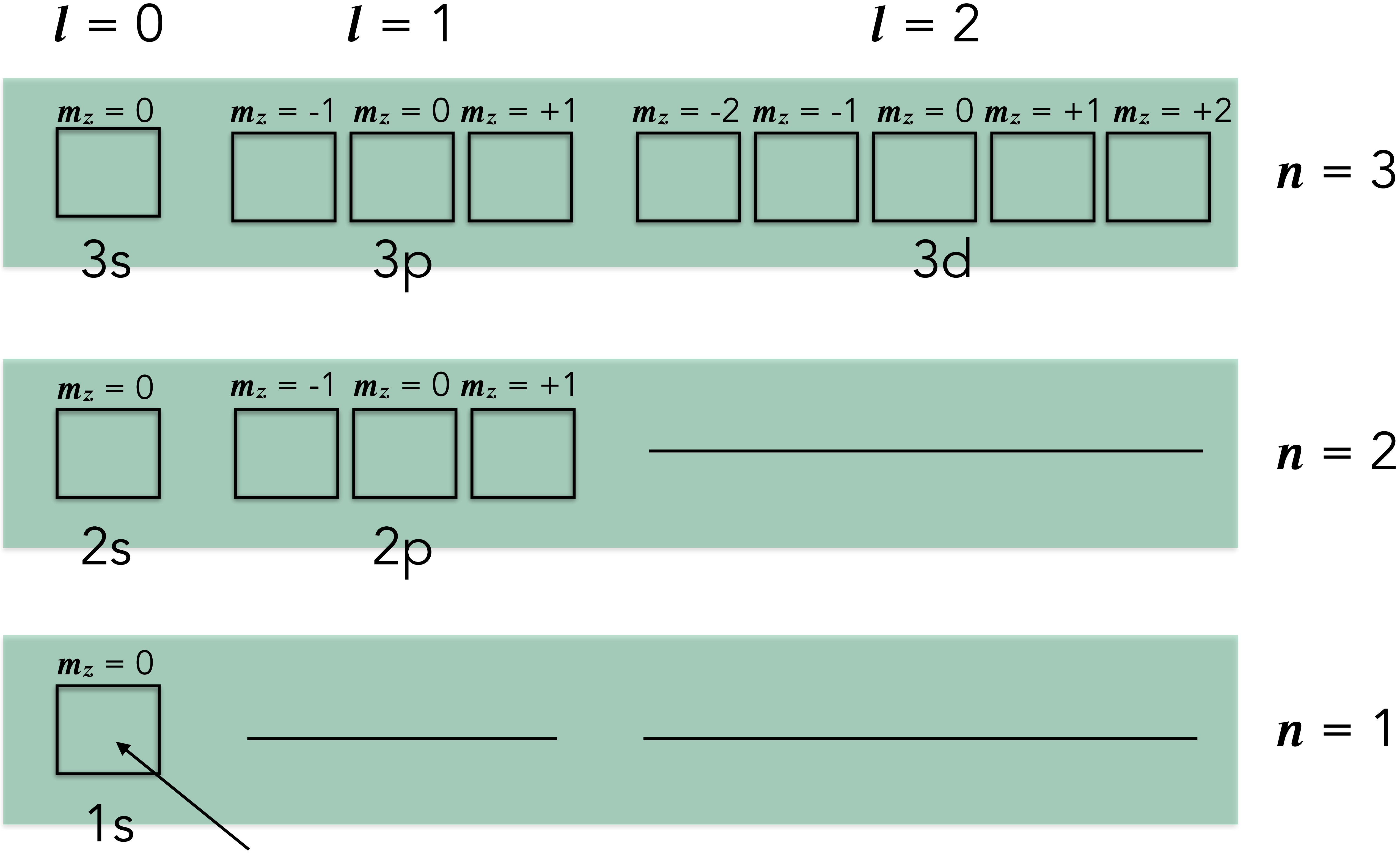
How do we arrange e- in a multi-electron atom?

Pauli exclusion principle says:

electrons can't share the same wave-function (n, l, m_z, spin)

For ground state configuration: fill up "subshells" from lowest energy up

subshell = combination of nl designated by number n and letter for l (0=s, 1=p, 2=d, 3=f, …)



$l = 0$ $l = 1$ $l = 2$

$m_z = 0$ $m_z = -1$ $m_z = 0$ $m_z = +1$ $m_z = -2$ $m_z = -1$ $m_z = 0$ $m_z = +1$ $m_z = +2$

3s 3p 3d

$n = 3$

$m_z = 0$ $m_z = -1$ $m_z = 0$ $m_z = +1$

2s 2p

$n = 2$

$m_z = 0$

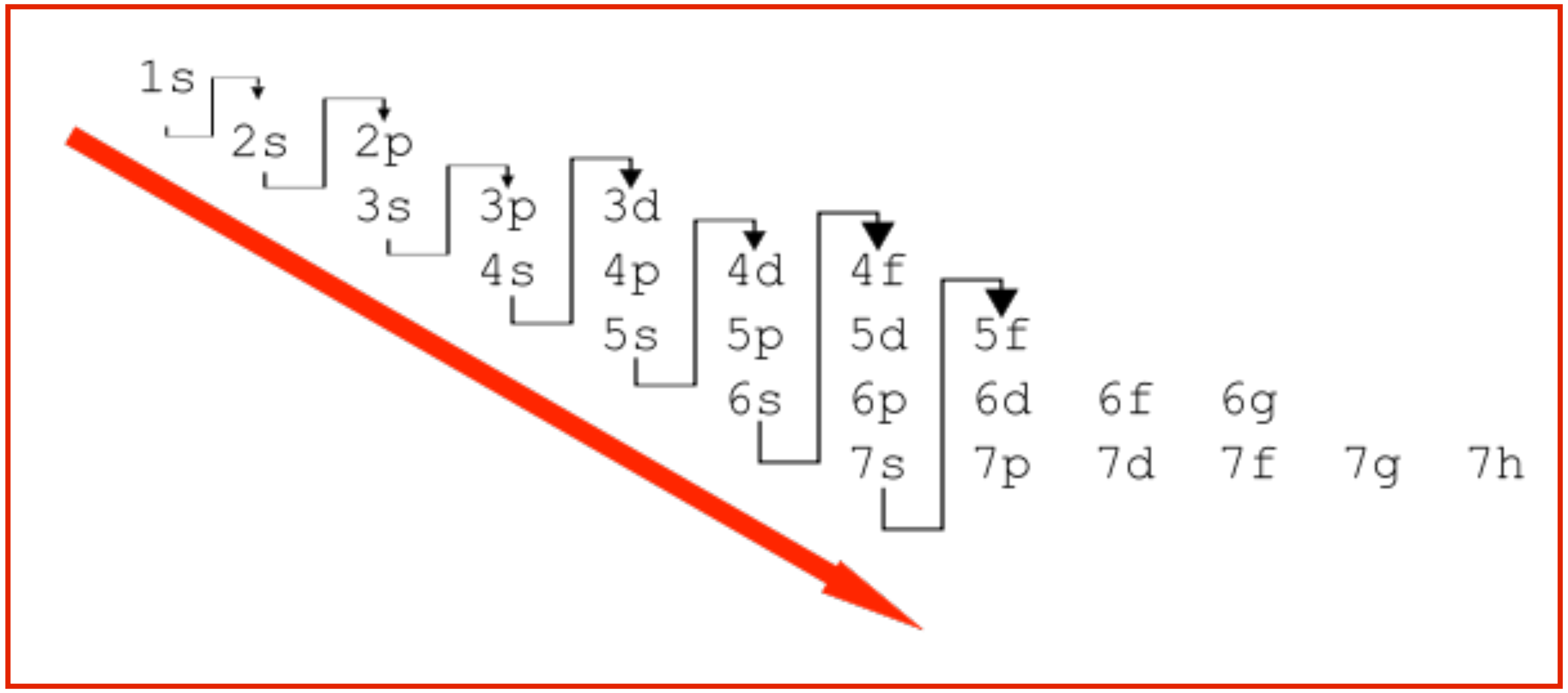
1s

$n = 1$

Can put 2 e- in each box: ↑↓

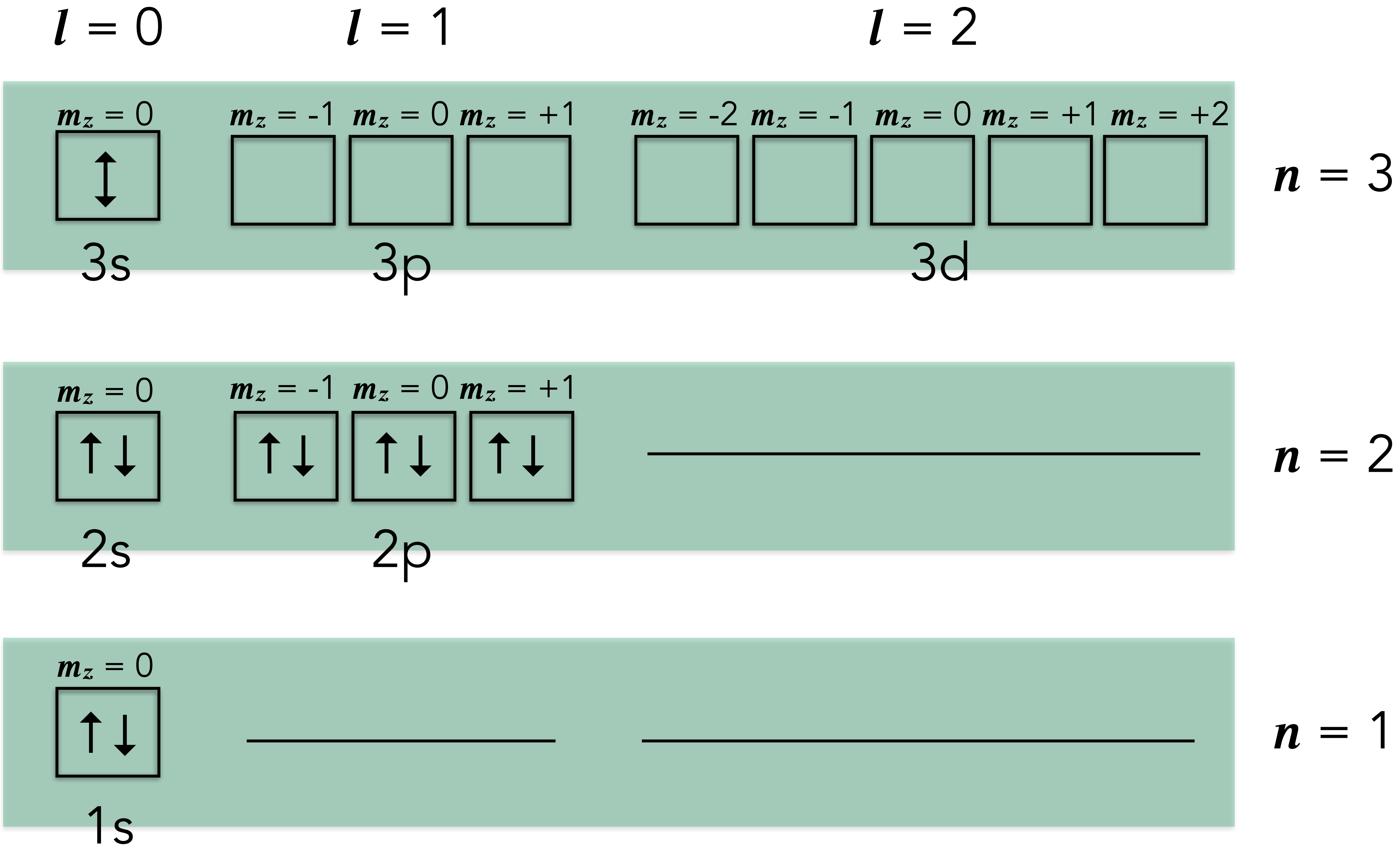
∴ degeneracy of subshell = $2(2l+1)$

For ground state (lowest energy):
Subshells are filled in order of increasing $\boldsymbol{n+l}$,
and then in order of increasing $\boldsymbol{n}$.



Number of electrons in each subshell listed with

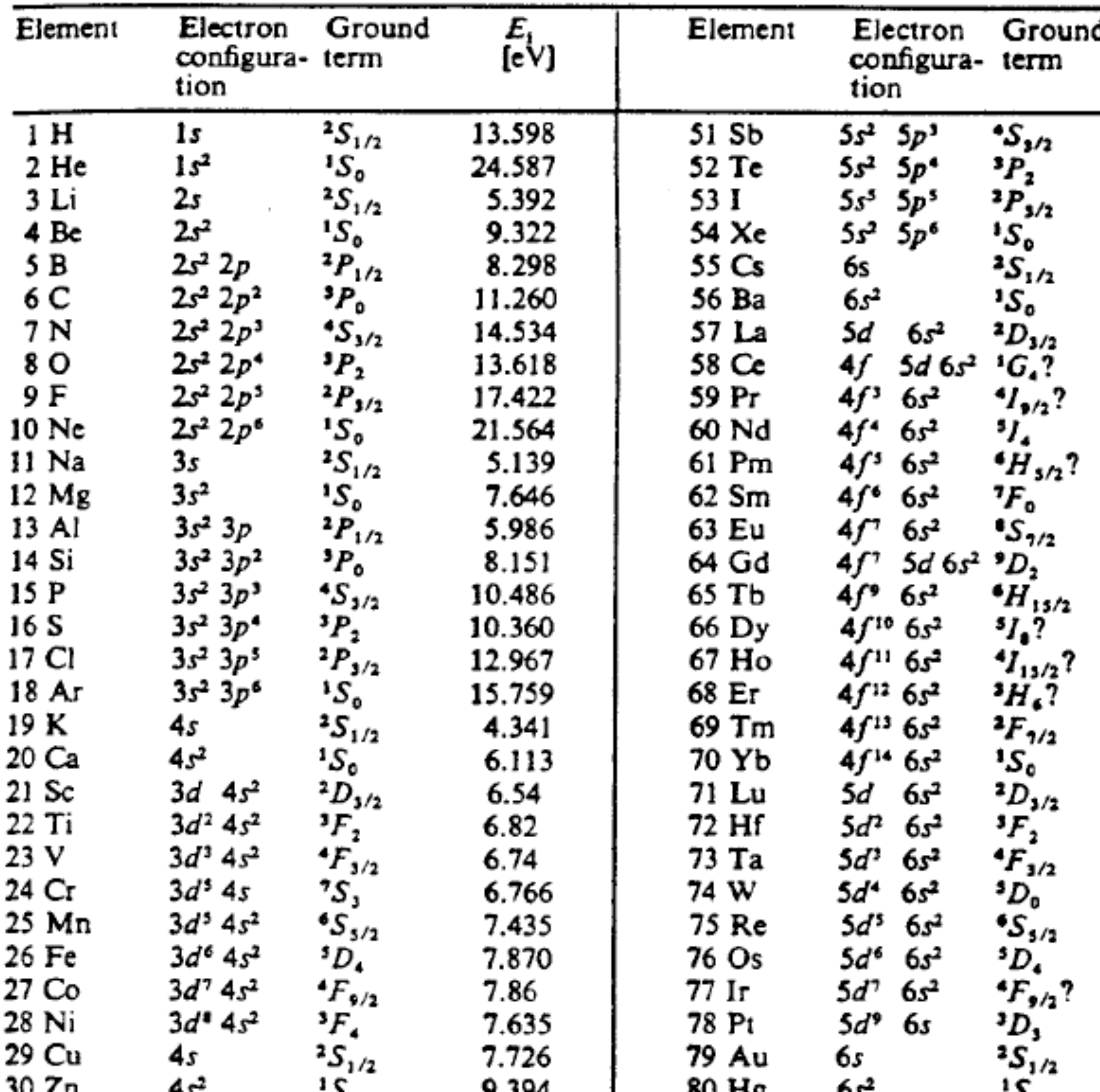
$2p^2$



Lets build the ground state of Na: 11 electrons

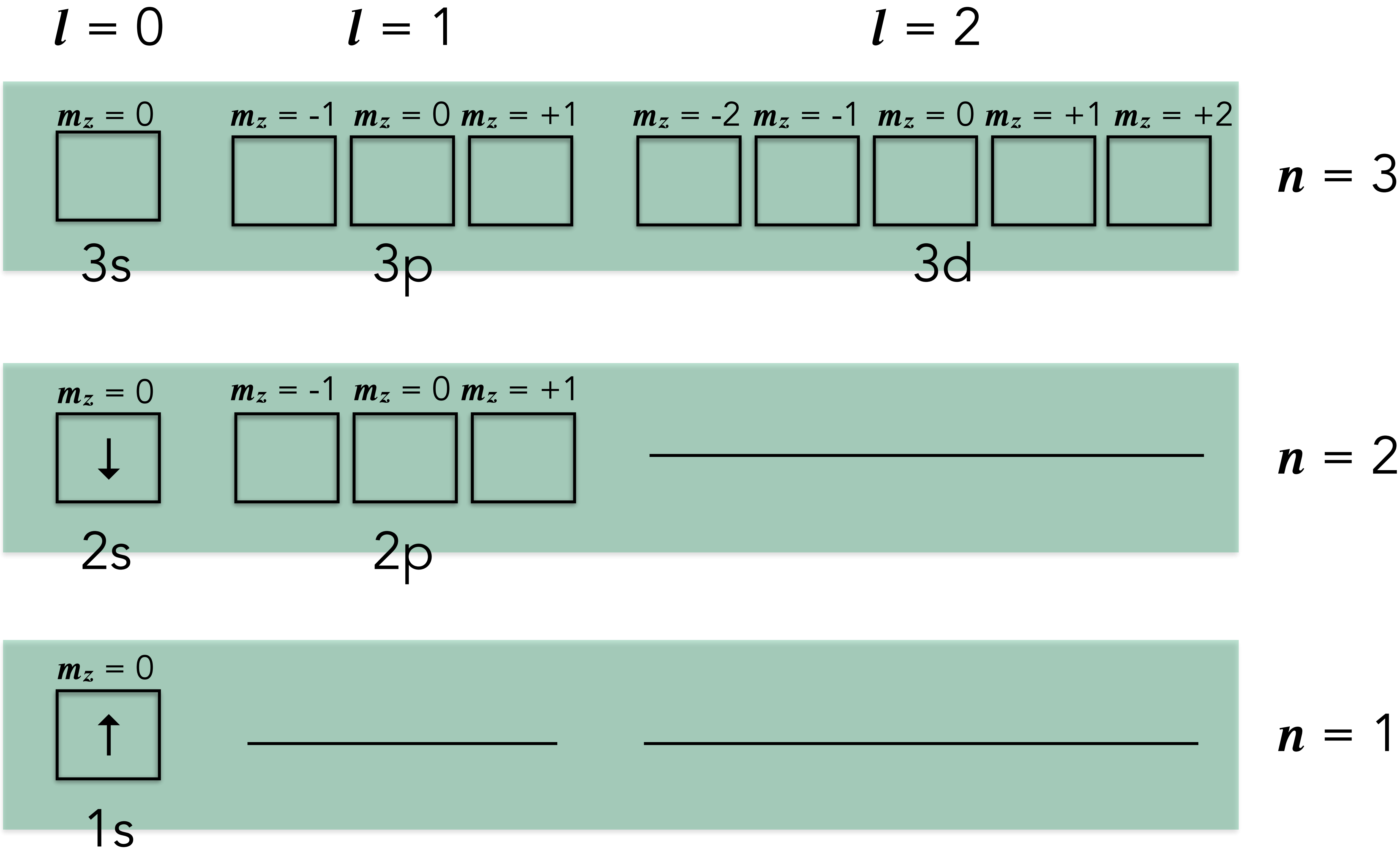
→ $1s^2\ 2s^2\ 2p^6\ 3s$

Table 2.1 – Electron configuration of atoms



Element	Electron configuration	Ground term	E_i [eV]	Element	Electron configuration	Ground term
1 H	$1s$	$^2S_{1/2}$	13.598	51 Sb	$5s^2\ 5p^3$	$^4S_{3/2}$
2 He	$1s^2$	$^1S_0$	24.587	52 Te	$5s^2\ 5p^4$	$^3P_2$
3 Li	$2s$	$^2S_{1/2}$	5.392	53 I	$5s^5\ 5p^5$	$^2P_{3/2}$
4 Be	$2s^2$	$^1S_0$	9.322	54 Xe	$5s^2\ 5p^6$	$^1S_0$
5 B	$2s^2\ 2p$	$^2P_{1/2}$	8.298	55 Cs	6s	$^2S_{1/2}$
6 C	$2s^2\ 2p^2$	$^3P_0$	11.260	56 Ba	$6s^2$	$^1S_0$
7 N	$2s^2\ 2p^3$	$^4S_{3/2}$	14.534	57 La	$5d\ 6s^2$	$^2D_{3/2}$
8 O	$2s^2\ 2p^4$	$^3P_2$	13.618	58 Ce	$4f\ 5d\ 6s^2$	$^1G_4$?
9 F	$2s^2\ 2p^5$	$^2P_{3/2}$	17.422	59 Pr	$4f^3\ 6s^2$	$^4I_{9/2}$?
10 Ne	$2s^2\ 2p^6$	$^1S_0$	21.564	60 Nd	$4f^4\ 6s^2$	$^5I_4$
11 Na	$3s$	$^2S_{1/2}$	5.139	61 Pm	$4f^5\ 6s^2$	$^6H_{5/2}$?
12 Mg	$3s^2$	$^1S_0$	7.646	62 Sm	$4f^6\ 6s^2$	$^7F_0$
13 Al	$3s^2\ 3p$	$^2P_{1/2}$	5.986	63 Eu	$4f^7\ 6s^2$	$^8S_{7/2}$
14 Si	$3s^2\ 3p^2$	$^3P_0$	8.151	64 Gd	$4f^7\ 5d\ 6s^2$	$^9D_2$
15 P	$3s^2\ 3p^3$	$^4S_{3/2}$	10.486	65 Tb	$4f^9\ 6s^2$	$^6H_{15/2}$
16 S	$3s^2\ 3p^4$	$^3P_2$	10.360	66 Dy	$4f^{10}\ 6s^2$	$^5I_8$?
17 Cl	$3s^2\ 3p^5$	$^2P_{3/2}$	12.967	67 Ho	$4f^{11}\ 6s^2$	$^4I_{15/2}$?
18 Ar	$3s^2\ 3p^6$	$^1S_0$	15.759	68 Er	$4f^{12}\ 6s^2$	$^3H_6$?
19 K	$4s$	$^2S_{1/2}$	4.341	69 Tm	$4f^{13}\ 6s^2$	$^2F_{7/2}$
20 Ca	$4s^2$	$^1S_0$	6.113	70 Yb	$4f^{14}\ 6s^2$	$^1S_0$
21 Sc	$3d\ 4s^2$	$^2D_{3/2}$	6.54	71 Lu	$5d\ 6s^2$	$^2D_{3/2}$
22 Ti	$3d^2\ 4s^2$	$^3F_2$	6.82	72 Hf	$5d^2\ 6s^2$	$^3F_2$
23 V	$3d^3\ 4s^2$	$^4F_{3/2}$	6.74	73 Ta	$5d^3\ 6s^2$	$^4F_{3/2}$
24 Cr	$3d^5\ 4s$	$^7S_3$	6.766	74 W	$5d^4\ 6s^2$	$^5D_0$
25 Mn	$3d^5\ 4s^2$	$^6S_{5/2}$	7.435	75 Re	$5d^5\ 6s^2$	$^6S_{5/2}$
26 Fe	$3d^6\ 4s^2$	$^5D_4$	7.870	76 Os	$5d^6\ 6s^2$	$^5D_4$
27 Co	$3d^7\ 4s^2$	$^4F_{9/2}$	7.86	77 Ir	$5d^7\ 6s^2$	$^4F_{9/2}$?
28 Ni	$3d^8\ 4s^2$	$^3F_4$	7.635	78 Pt	$5d^9\ 6s$	$^3D_3$
29 Cu	$4s$	$^2S_{1/2}$	7.726	79 Au	$6s$	$^2S_{1/2}$
30 Zn	$4s^2$	^1S	9.394	80 Hg	$6s^2$	^1S

Note that in many tables "closed" shells aren't listed, e.g. $1s^2$ $2s^2\ 2p^6$



$l = 0$ $l = 1$ $l = 2$

$n = 3$

$m_z = 0$ $m_z = -1$ $m_z = 0$ $m_z = +1$ $m_z = -2$ $m_z = -1$ $m_z = 0$ $m_z = +1$ $m_z = +2$

3s 3p 3d

$n = 2$

$m_z = 0$ $m_z = -1$ $m_z = 0$ $m_z = +1$

↓

2s 2p

$n = 1$

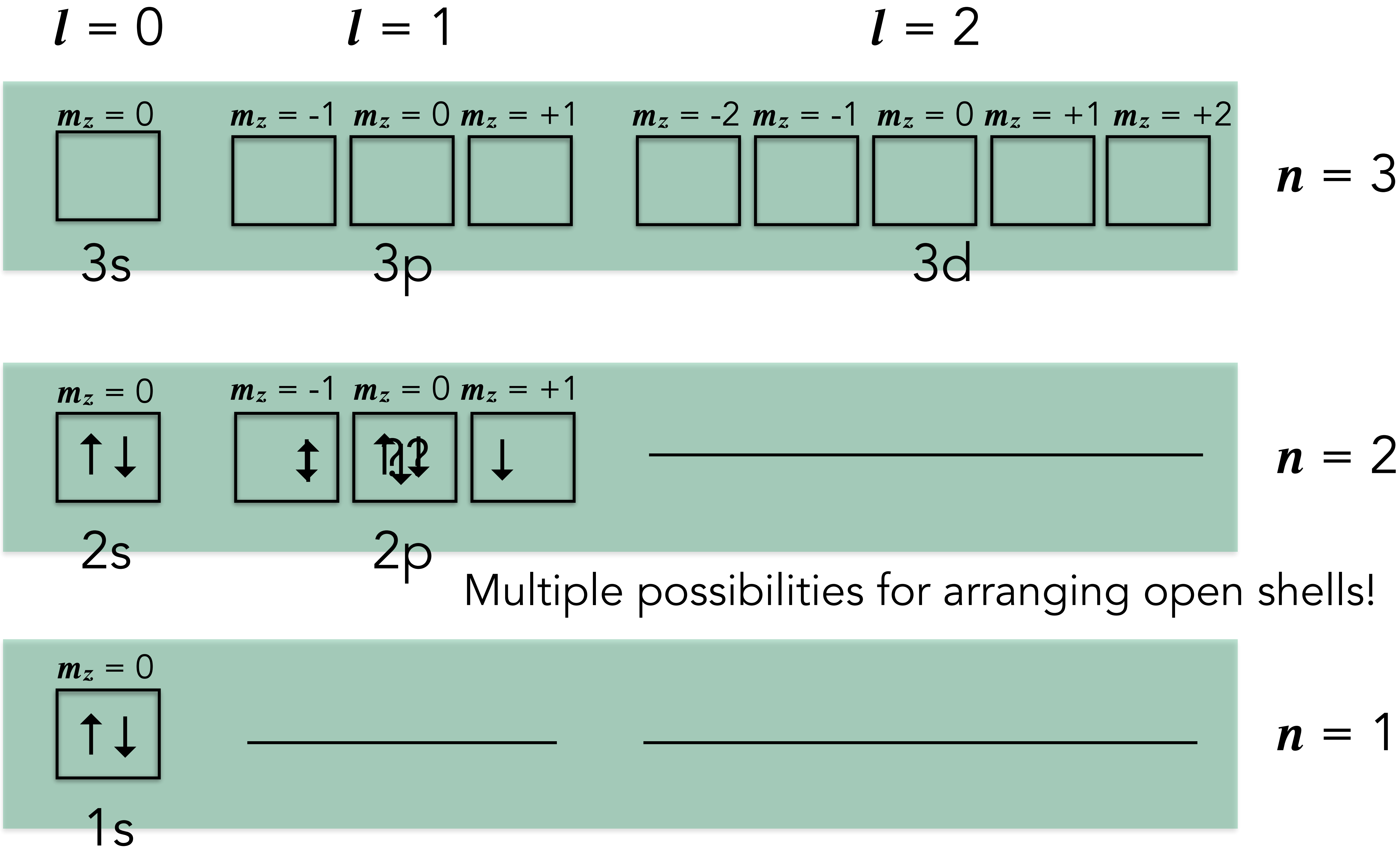
$m_z = 0$

↑

1s

Excited state of He

→1s 2s



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3s 3p 3d $n = 3$

$m_z = 0$ $m_z = -1$ $m_z = 0$ $m_z = +1$

2s 2p $n = 2$

Multiple possibilities for arranging open shells!

$m_z = 0$

1s $n = 1$

Lets build the ground state of C: 6 electrons

$\rightarrow 1s^2\ 2s^2\ 2p^2$

Multiple possibilities for distributing e- in unfilled subshell, lead to different overall angular momentum

$\mathbf{L}$ = vector sum of angular momentum

$\mathbf{S}$ = vector sum of spin angular momentum

$\mathbf{J} = \mathbf{L} + \mathbf{S}$ = total angular momentum

$$\mathbf{L} = \sum_{\mathrm{i}} \mathbf{l}_{\mathrm{i}}$$

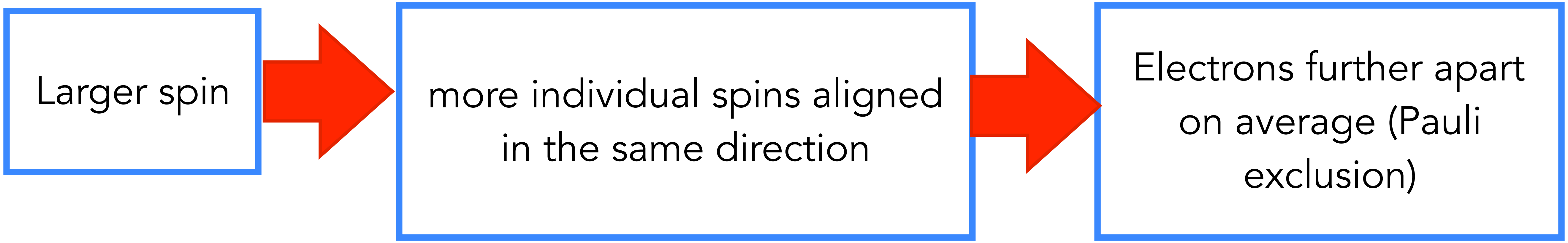
$$\mathbf{S} = \sum_{\mathrm{i}} \mathbf{s}_{\mathrm{i}}$$

Note that full shells and subshells do not contribute to the angular momentum: $\mathbf{J} = \mathbf{L} = \mathbf{S} = 0$

Why is this important:

Different combinations of **L** and **S** have different energies.

L-S Coupling: Total spin **S** interacts with total angular momentum **L** (“spin-orbit coupling”)



Larger spin

more individual spins aligned in the same direction

Electrons further apart on average (Pauli exclusion)

Larger Spin has Lower energy (usually)

Spectroscopic Notation

The "Spectroscopic Term"

helps to keep track of the configuration of the electrons

Spin $\mathbf{S}$

$$^{2\mathbf{S}+1}\mathcal{L}^{p}_{\mathbf{J}}$$

"parity" = $\Sigma \boldsymbol{l}_i$

blank if even, "o" if odd

for $1s^2\ 2s^2\ 2p^2$
parity = 0+0+0+0+1+1
= 2 (even)

Orbital Angular Momentum

S, P, D, F (for $\mathbf{L}$=0,1,2,3)

Total angular momentum

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

$\mathbf{L}$ = vector sum of angular momentum

$\mathbf{S}$ = vector sum of spin angular momentum

$\mathbf{J} = \mathbf{L} + \mathbf{S}$ = total angular momentum

- *z* component of the total angular momentum can have values between $-\mathbf{L}$ and $\mathbf{L}$, i.e. $(2\mathbf{L}+1)$ degenerate levels
- *z* component of the total spin can have values between $-\mathbf{S}$ and $\mathbf{S}$, i.e. $(2\mathbf{S}+1)$ degenerate levels

Each $\mathbf{L}$ and $\mathbf{S}$ has $(2\mathbf{L}+1)(2\mathbf{S}+1)$ possible $\boldsymbol{m_z}$ & spin combinations.

Calculating Spectroscopic Terms:

$$^{2\mathbf{S}+1}\mathcal{L}^{\mathrm{p}}_{\mathbf{J}}$$

$$\mathbf{L} = \sum_{\mathrm{i}} \mathbf{l}_{\mathrm{i}} \qquad \mathbf{S} = \sum_{\mathrm{i}} \mathbf{s}_{\mathrm{i}} \qquad \mathbf{J} = \mathbf{L} + \mathbf{S}$$

Configuration of 2 electrons: 1s2s

$m_{l1}=0,\ m_{l2}=0,\ \mathbf{L}=0$ → $^{1}\mathbf{S}_{0}$

$m_{s1}=\pm½,\ m_{s2}=\pm½,\ \mathbf{S}=0,1$ → $^{3}\mathbf{S}_{1}$

$\mathbf{J} = \mathbf{L} + \mathbf{S}$ so $\mathbf{J} = 0,1$ → $^{3}\mathbf{S}_{1}$

Possible Terms: $^{1}S_{0}$, $^{3}S_{1}$

Calculating Spectroscopic Terms: $^{2\mathbf{S}+1}\mathcal{L}_{\mathbf{J}}^{p}$

Possible Spectroscopic Terms for 2 electrons in p
(for p, recall $\boldsymbol{l}$ = 1, so $\mathbf{L}$ can be 0,1,2)

	L=0	**L=1**	**L=2**
S=0	^{1}S (1)	^{1}P (3)	^{1}D (5)
S=1	^{3}S (3)	^{3}P (9)	^{3}D (15)

$(2\mathbf{L}+1)(2\mathbf{S}+1)$

= 1+3+5+3+9+15
= 36 total terms

However, not all of these work - lets see why…

"Non-Equivalent" electrons (i.e. 2p3p, different ***n***)
all 36 combinations are allowed:

(m_z, m_s)	(+1, +1/2)	(0, +1/2)	(-1, +1/2)	(+1, -1/2)	(0, -1/2)	(-1, -1/2)
(+1, +1/2)	**L, S** = +2, +1	+1, +1	0, +1	+2, 0	+1, 0	0, 0
(0, +1/2)	+1, +1	0, +1	-1, +1	+1, +1	0, 0	-1, 0
(-1, +1/2)	0, +1	-1, +1	-2, +1	0, 0	-1, 0	-2, 0
(+1, -1/2)	+2, 0	+1, 0	0, 0	+2, -1	+1, -1	0, -1
(0, -1/2)	+1, 0	0, 0	-1, 0	+1, -1	0, -1	-1, -1
(-1, -1/2)	0, 0	-1, 0	-2, 0	0, -1	-1, -1	-2, -1

"Equivalent" electrons (i.e. $2p^2$, same $\boldsymbol{n}$)
only 15 combinations allowed (b.c. exclusion principle)

(m_z, m_s)	**(+1, +1/2)**	**(0, +1/2)**	**(-1, +1/2)**	**(+1, -1/2)**	**(0, -1/2)**	**(-1, -1/2)**
(+1, +1/2)	+2, +1	+1, +1	0, +1	+2, 0	+1, 0	0, 0
(0, +1/2)	+1, +1	0, +1	-1, +1	+1, +1	0, 0	-1, 0
(-1, +1/2)	0, +1	-1, +1	-2, +1	0, 0	-1, 0	-2, 0
(+1, -1/2)	+2, 0	+1, 0	0, 0	+2, -1	+1, -1	0, -1
(0, -1/2)	+1, 0	0, 0	-1, 0	+1, -1	0, -1	-1, -1
(-1, -1/2)	0, 0	-1, 0	-2, 0	0, -1	-1, -1	-2, -1

Possible Terms for 2 equivalent electrons in p

Term (deg.)	**L=0**	**L=1**	**L=2**
S=0	^{1}S (1)	^{1}P (3)	^{1}D (5)
S=1	^{3}S (3)	^{3}P (9)	^{3}D (15)

$$^{2\mathbf{S}+1}\mathcal{L}$$

$$(2\mathbf{L}+1)(2\mathbf{S}+1)$$

Only 15 combinations allowed - some terms don't work when electrons are equivalent

For 2 electrons in p, possible terms are ^{1}S, ^{3}P, ^{1}D

It gets complicated & tedious to do this for more electrons or for excited states. Just look it up!

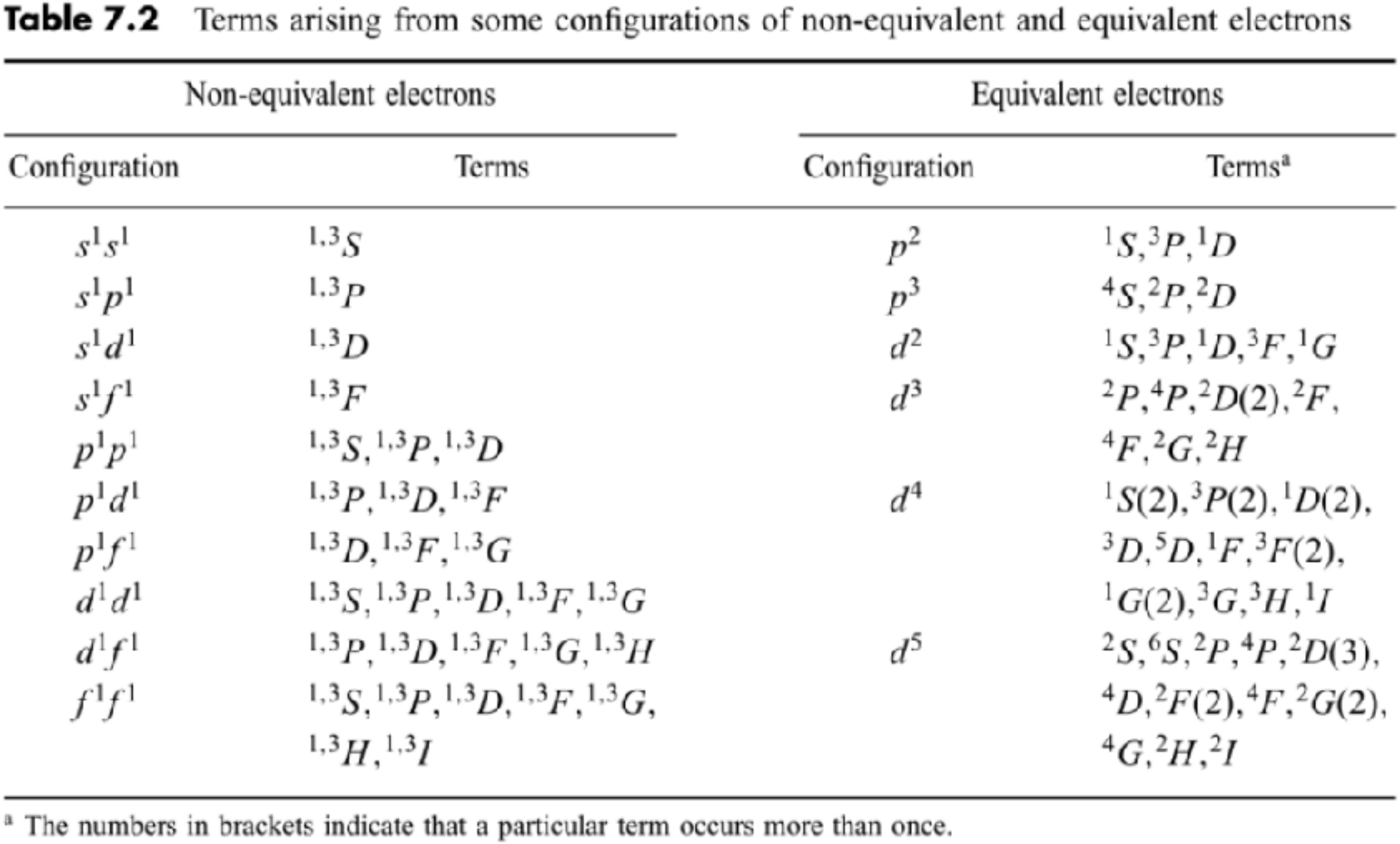


Table 7.2 Terms arising from some configurations of non-equivalent and equivalent electrons

Non-equivalent electrons		Equivalent electrons	
Configuration	Terms	Configuration	Terms[a]
s^1s^1	$^{1,3}S$	p^2	$^1S, ^3P, ^1D$
s^1p^1	$^{1,3}P$	p^3	$^4S, ^2P, ^2D$
s^1d^1	$^{1,3}D$	d^2	$^1S, ^3P, ^1D, ^3F, ^1G$
s^1f^1	$^{1,3}F$	d^3	$^2P, ^4P, ^2D(2), ^2F,$
p^1p^1	$^{1,3}S, ^{1,3}P, ^{1,3}D$		$^4F, ^2G, ^2H$
p^1d^1	$^{1,3}P, ^{1,3}D, ^{1,3}F$	d^4	$^1S(2), ^3P(2), ^1D(2),$
p^1f^1	$^{1,3}D, ^{1,3}F, ^{1,3}G$		$^3D, ^5D, ^1F, ^3F(2),$
d^1d^1	$^{1,3}S, ^{1,3}P, ^{1,3}D, ^{1,3}F, ^{1,3}G$		$^1G(2), ^3G, ^3H, ^1I$
d^1f^1	$^{1,3}P, ^{1,3}D, ^{1,3}F, ^{1,3}G, ^{1,3}H$	d^5	$^2S, ^6S, ^2P, ^4P, ^2D(3),$
f^1f^1	$^{1,3}S, ^{1,3}P, ^{1,3}D, ^{1,3}F, ^{1,3}G,$		$^4D, ^2F(2), ^4F, ^2G(2),$
	$^{1,3}H, ^{1,3}I$		$^4G, ^2H, ^2I$

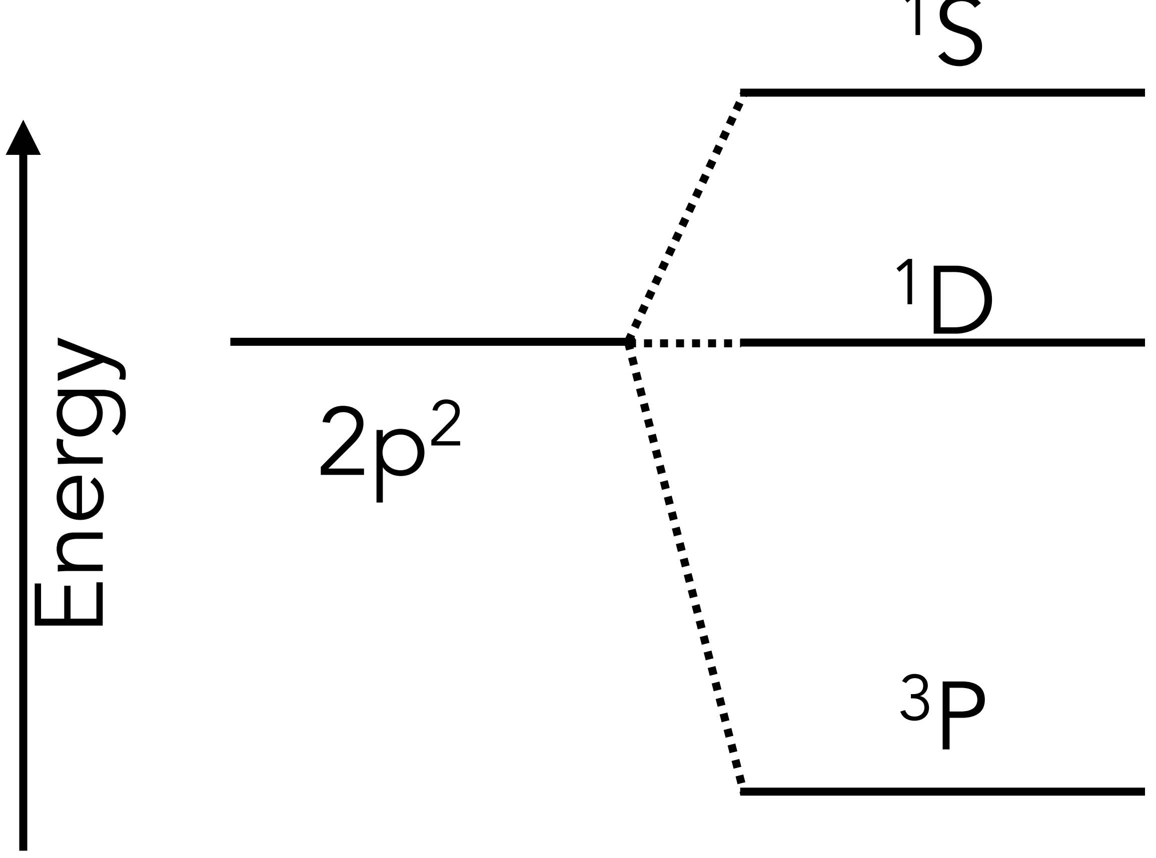
[a] The numbers in brackets indicate that a particular term occurs more than once.

from *Modern Spectroscopy* by Hollas

Energy Levels ⟷ Terms

$$^{2\mathbf{S}+1}\mathcal{L}^{p}_{\mathbf{J}}$$

Carbon:



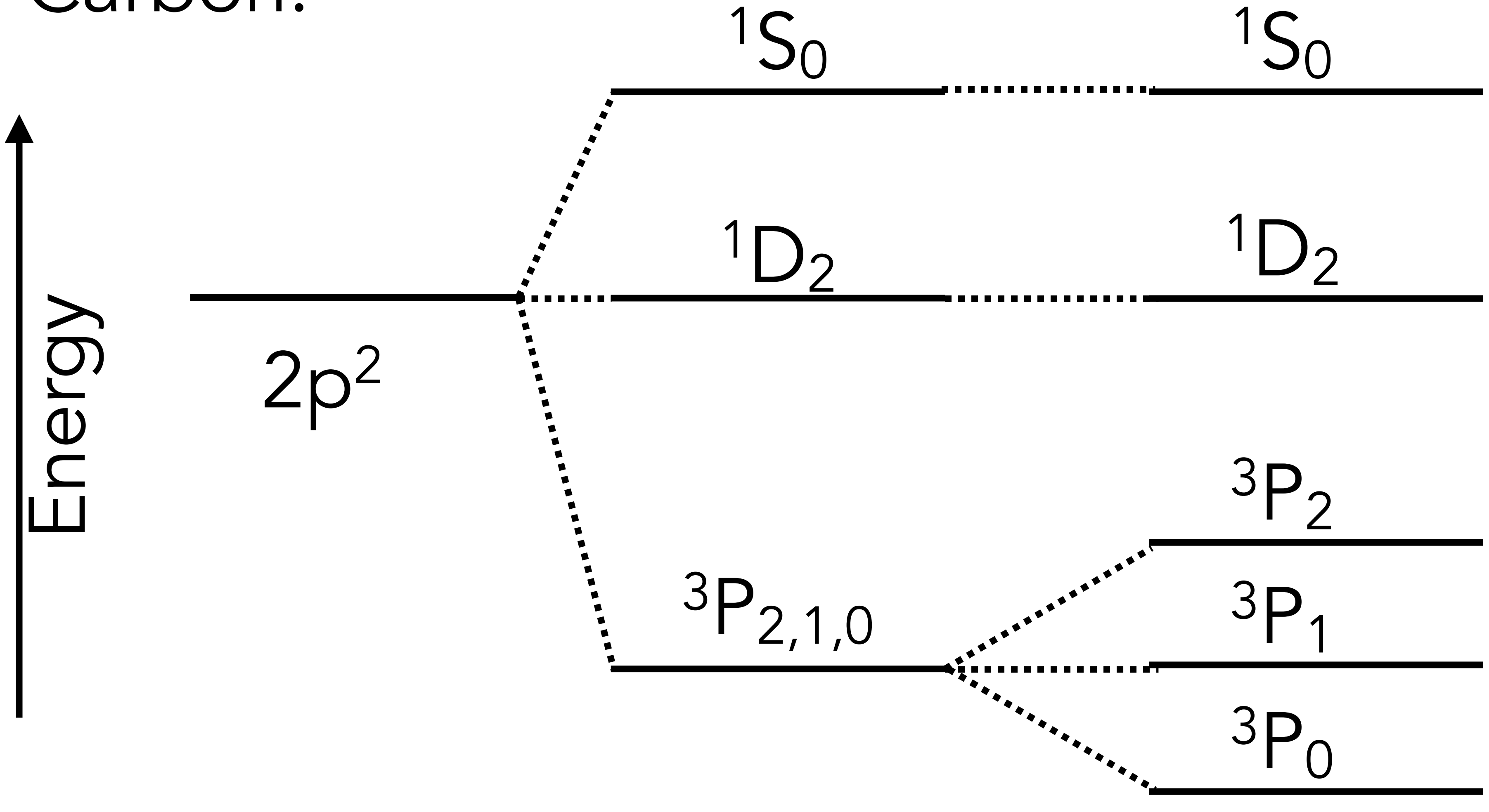
"Hund's Rules"

1) Terms w/larger spin generally have lower energy.
2) For terms with given configuration and spin, larger L has lower energy.
3) Higher J = higher energy if shell is less than half full (opposite otherwise).

Energy Levels ⟷ Terms

$$^{2\mathbf{S}+1}\mathcal{L}^{\mathrm{p}}_{\mathbf{J}}$$

Carbon:



Energy

$2p^2$

$^1S_0$

$^1D_2$

$^3P_{2,1,0}$

$^1S_0$

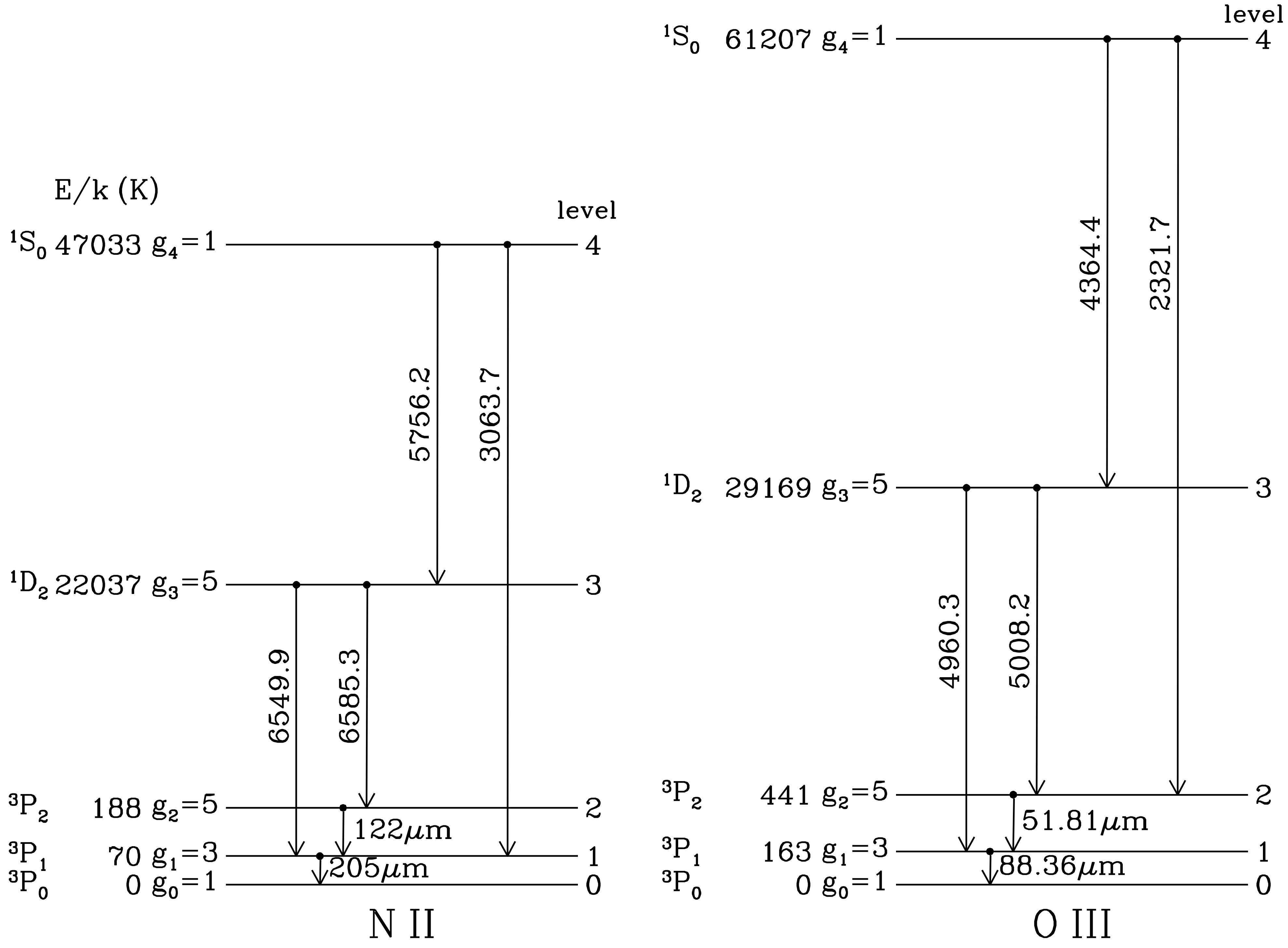
$^1D_2$

$^3P_2$

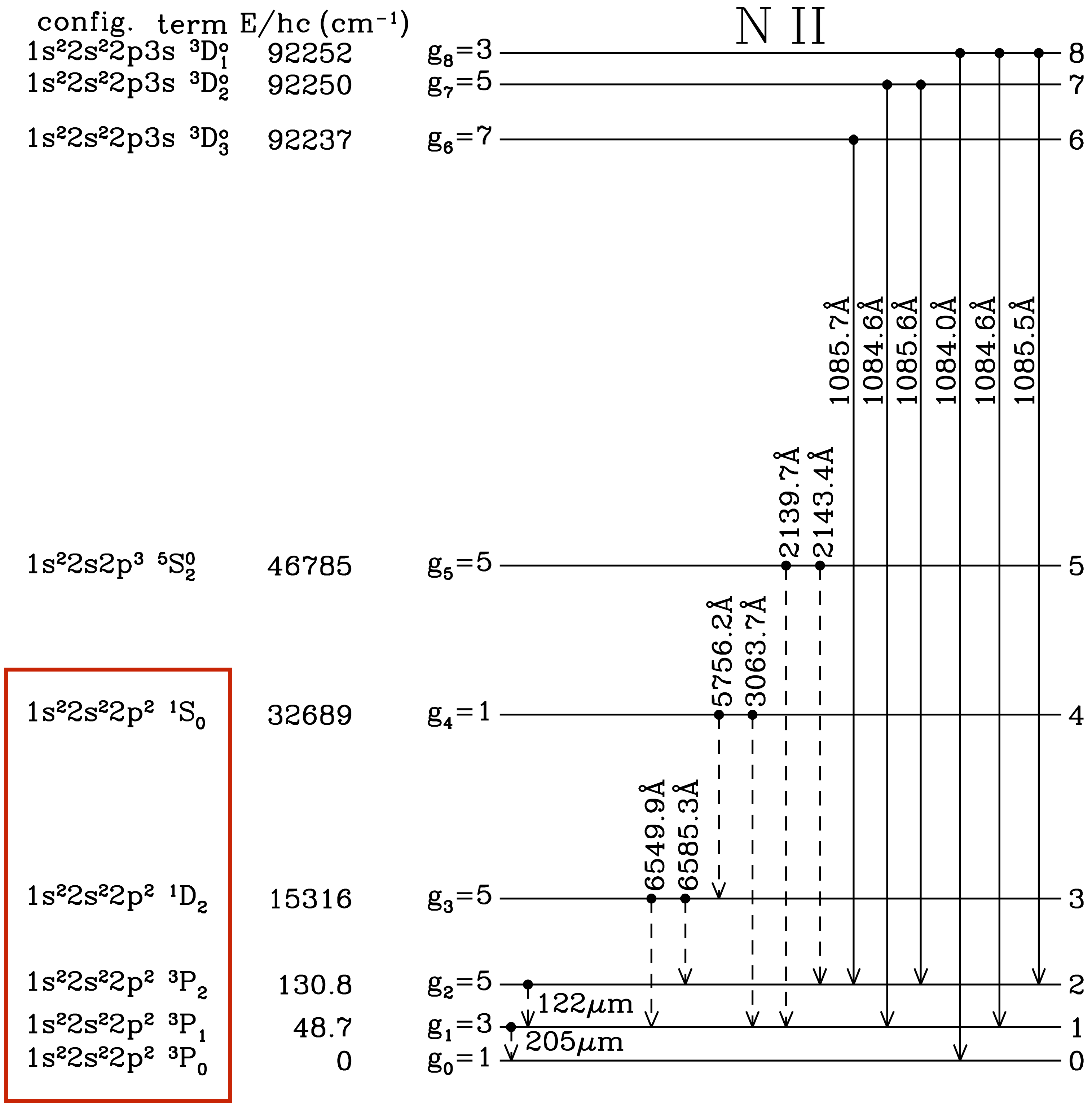
$^3P_1$

$^3P_0$

Other examples of np^2 ground state configurations



First nine energy levels for 6 electron config, eg NII



ground

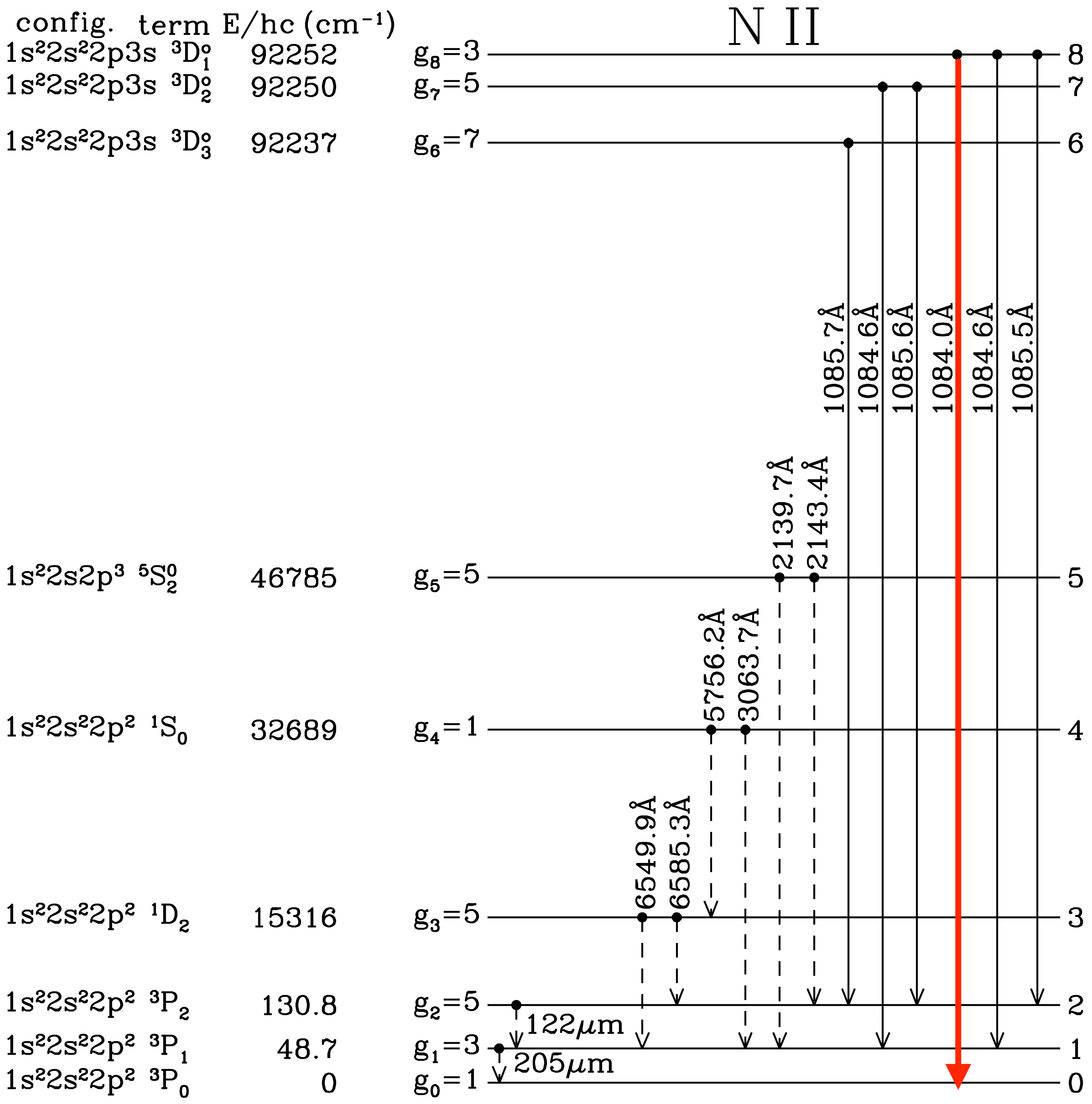
Selection Rules for Transitions

We can now figure out the energy levels, what about the transitions between them?

Type of Transition	Mechanism	Selection Rules
“allowed"	electric dipole	1) Parity must change 2) ΔL = 0, ±1 3) ΔJ = 0, ±1 but not J=0→0 4) only one e- wavefunction ***nl*** changes with Δ***l*** = ±1 5) ΔS = 0
“semi-forbidden” or “intersystem”	electric dipole but with ΔS ≠ 0 from configuration mixing due to relativistic effects	same as “allowed” except violates #5
“forbidden"	magnetic dipole or electric quadrupole	violates at least one other selection rule other than #5

NII 1084.0 Å $^3P_0$ - $^3D_1^{\circ}$

$$^{2S+1}\mathcal{L}_{J}^{p}$$



✓1) Parity must change

✓2) ΔJ = 0, ±1, but J=0→0 is forbidden

✓3) ΔS = 0

✓4) ΔL = 0, ±1, but L=0→0 is forbidden

✓5) if one e- then Δ***l*** = 0

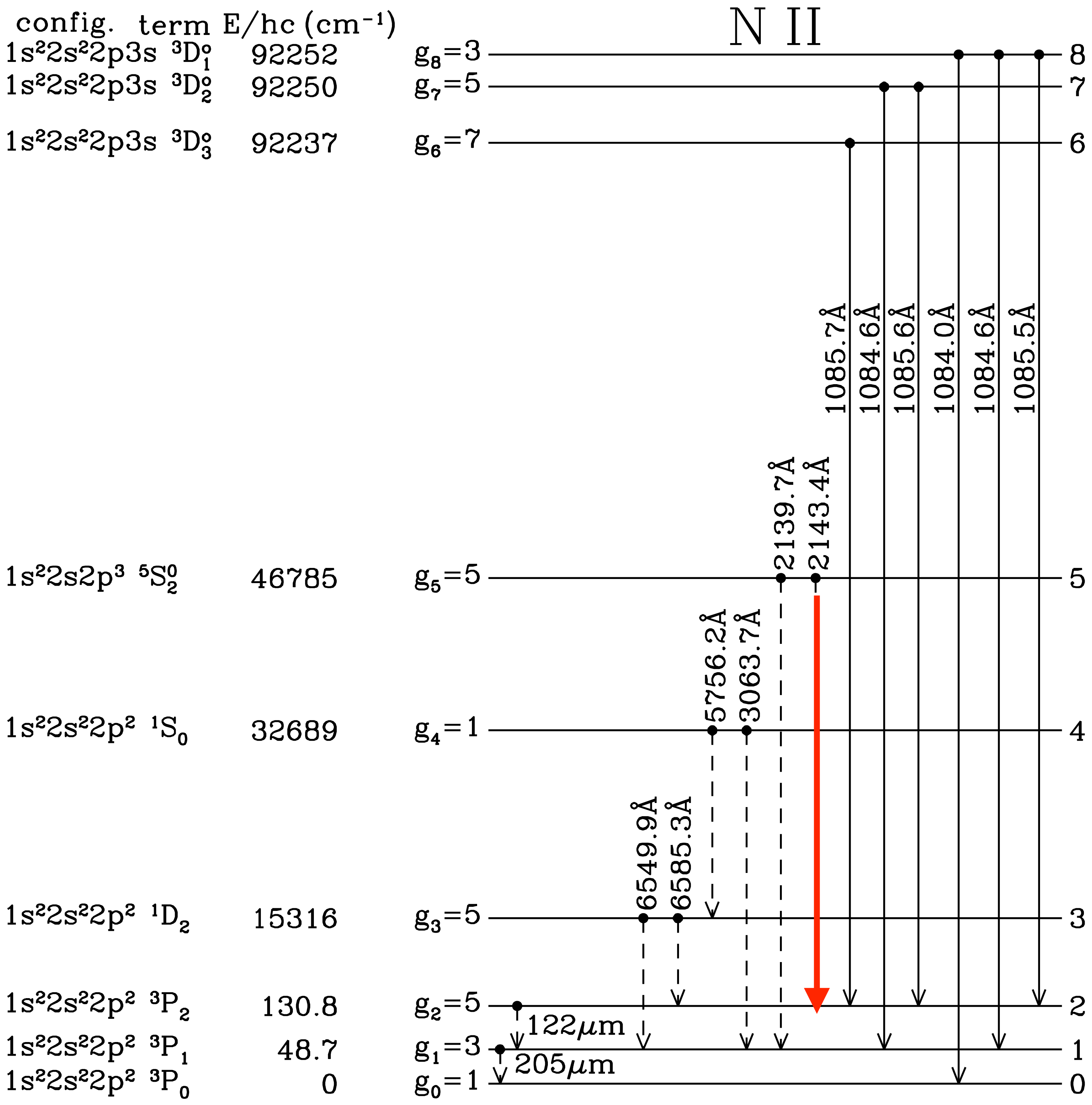
$$A_{ul} = 2.18 \times 10^{8}\ \mathrm{s}^{-1}$$

$$1/A_{ul} = 4.6\ \mathrm{ns}$$

N II] 2143.4 Å $^5S_2^o$ - $^3P_2$

$$^{2S+1}\mathcal{L}^{p}_{J}$$

single bracket for "semi-forbidden"



- ✓ 1) Parity must change
- ✓ 2) ΔJ = 0, ±1, but J=0→0 is forbidden
- ✗ 3) ΔS = 0
- ✓ 4) ΔL = 0, ±1, but L=0→0 is forbidden
- ✓ 5) if one e- then $\Delta l = 0$

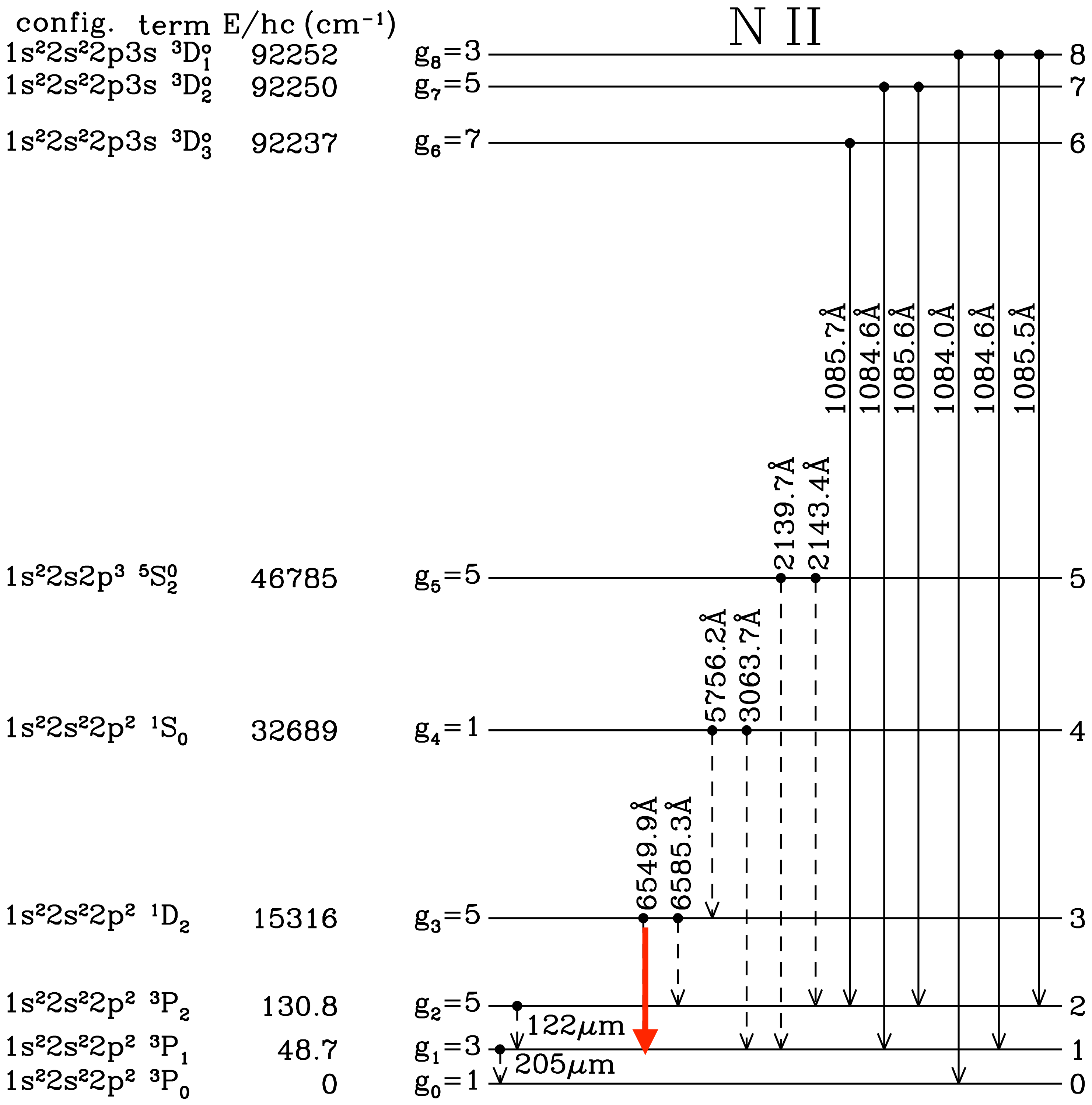
$$A_{ul} = 1.27 \times 10^2 \ s^{-1}$$

$$1/A_{ul} = 7.9 \ \text{ms}$$

[N II] 6549.9 Å $^1D_2$ - $^3P_1$

$^{2S+1}\mathcal{L}^{p}_{\mathbf{J}}$

double bracket for "forbidden"



- ✗ 1) Parity must change
- ✓ 2) $\Delta J = 0, \pm 1$, but $J=0 \rightarrow 0$ is forbidden
- ✗ 3) $\Delta S = 0$
- ✓ 4) $\Delta L = 0, \pm 1$, but $L=0 \rightarrow 0$ is forbidden
- ✗ 5) if one e- then $\Delta \boldsymbol{l} = 0$

$$A_{ul} = 9.2 \times 10^{-4}\ s^{-1}$$

$$1/A_{ul} \sim 20\ min$$

Reminder: if we know the Einstein A value,
we know all of the other Einstein B values too,
including the rate coefficient for absorption (B_{lu})

$$B_{lu} = (g_u/g_l)B_{ul}$$

$$B_{lu} \propto A_{ul}$$

$$B_{ul} = (c^3/(8\pi h\nu^3))\ A_{ul}$$

When Einstein A value is very small,
low coefficient for absorption.

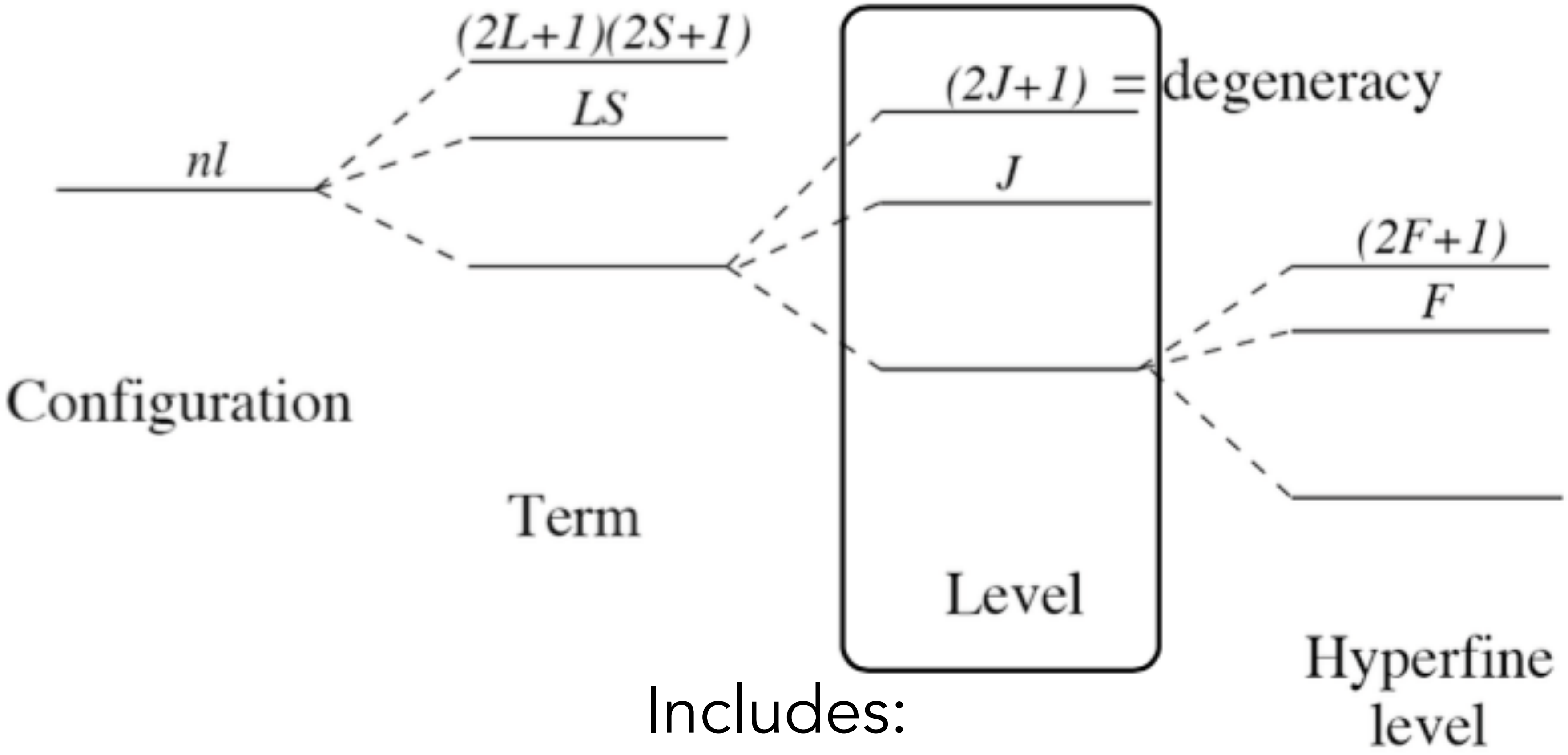
Forbidden transitions are very important in astronomy!

Collisions populate the levels of the ground state

There is a low probability for transitions
so the line is generally optically thin

When there is a radiative transition, that energy
escapes! Very important for cooling!

Fine and Hyperfine Structure Transitions



Fine & Hyperfine
are "forbidden"
parity doesn't change
$\Delta S \neq 0$

Includes:

-fine structure transitions (transitions within a term, e.g. $^2P_{1/2}$ - $^2P_{3/2}$ 158μm line of [CII] within ^2P term)

-hyperfine structure transitions (transitions within a given level of a term caused by splitting due to interaction of electron & nuclear spin, e.g. HI 21 cm spin-flip transition)