Physics 224
The Interstellar Medium

Lecture #3

- Part I: Finish Collisional Processes
- Part II: Statistical Mechanics
- Part III: Quantum & Energy Levels
- Part IV (maybe): Radiative Transfer

Energy Levels of Atoms

n = principle quantum number

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

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

e- spin = -ħ/2 or +ħ/2

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

Energy Levels of Atoms

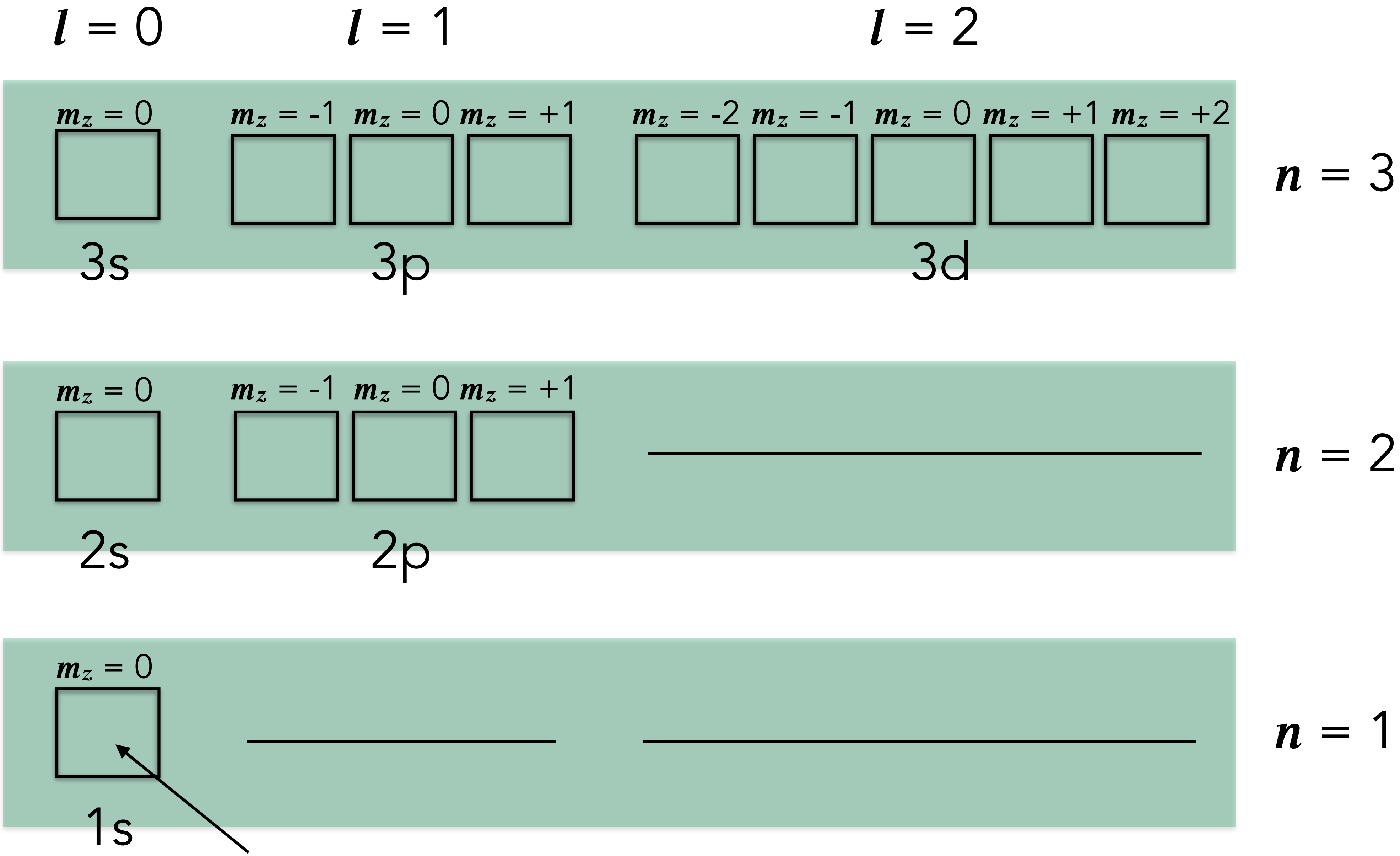
How do we arrange e- in a multi-electron atom?

Pauli exclusion principle says:

electrons can't share the same wavefunction (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

$n = 2$

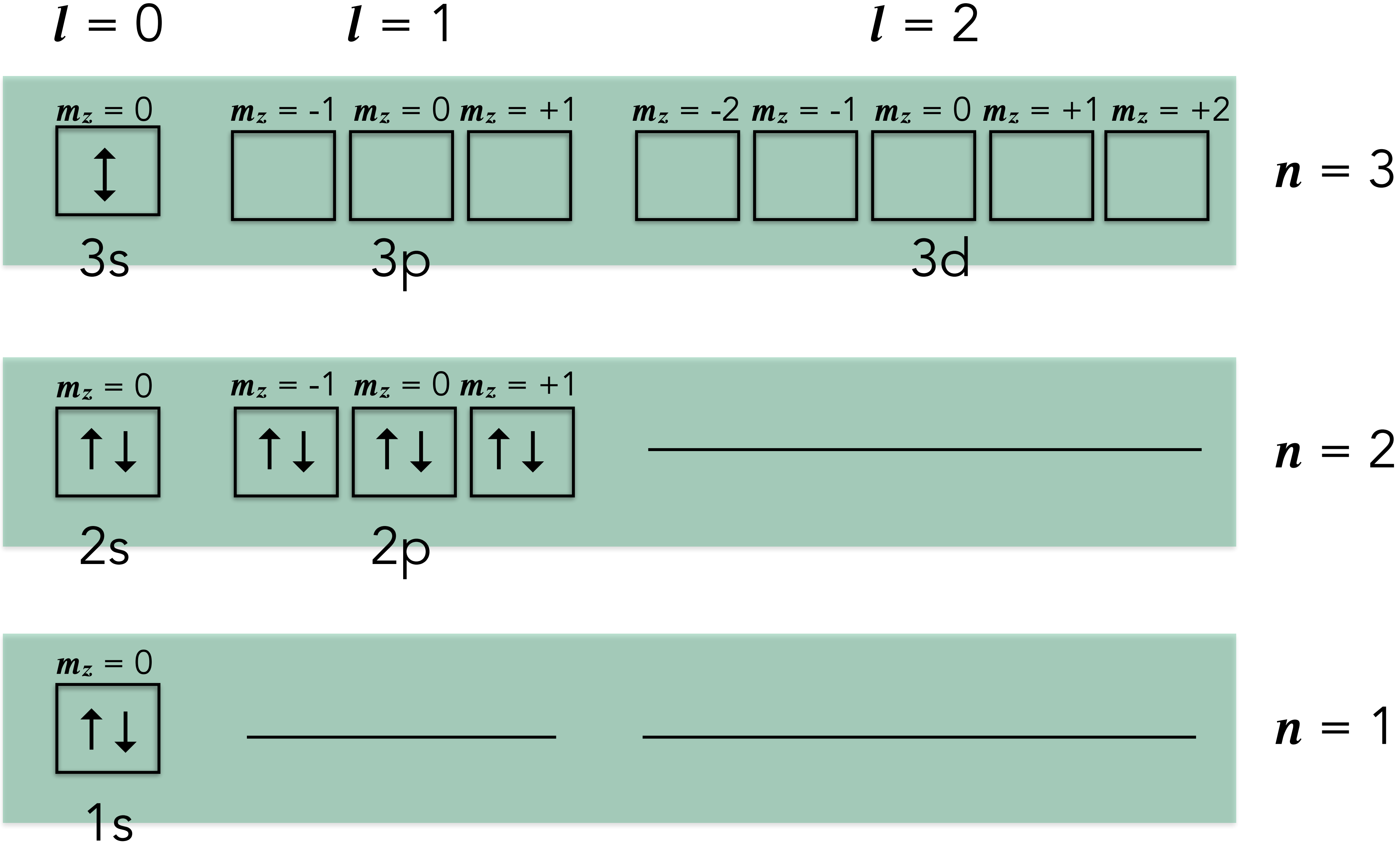
$m_z = 0$

1s

$n = 1$

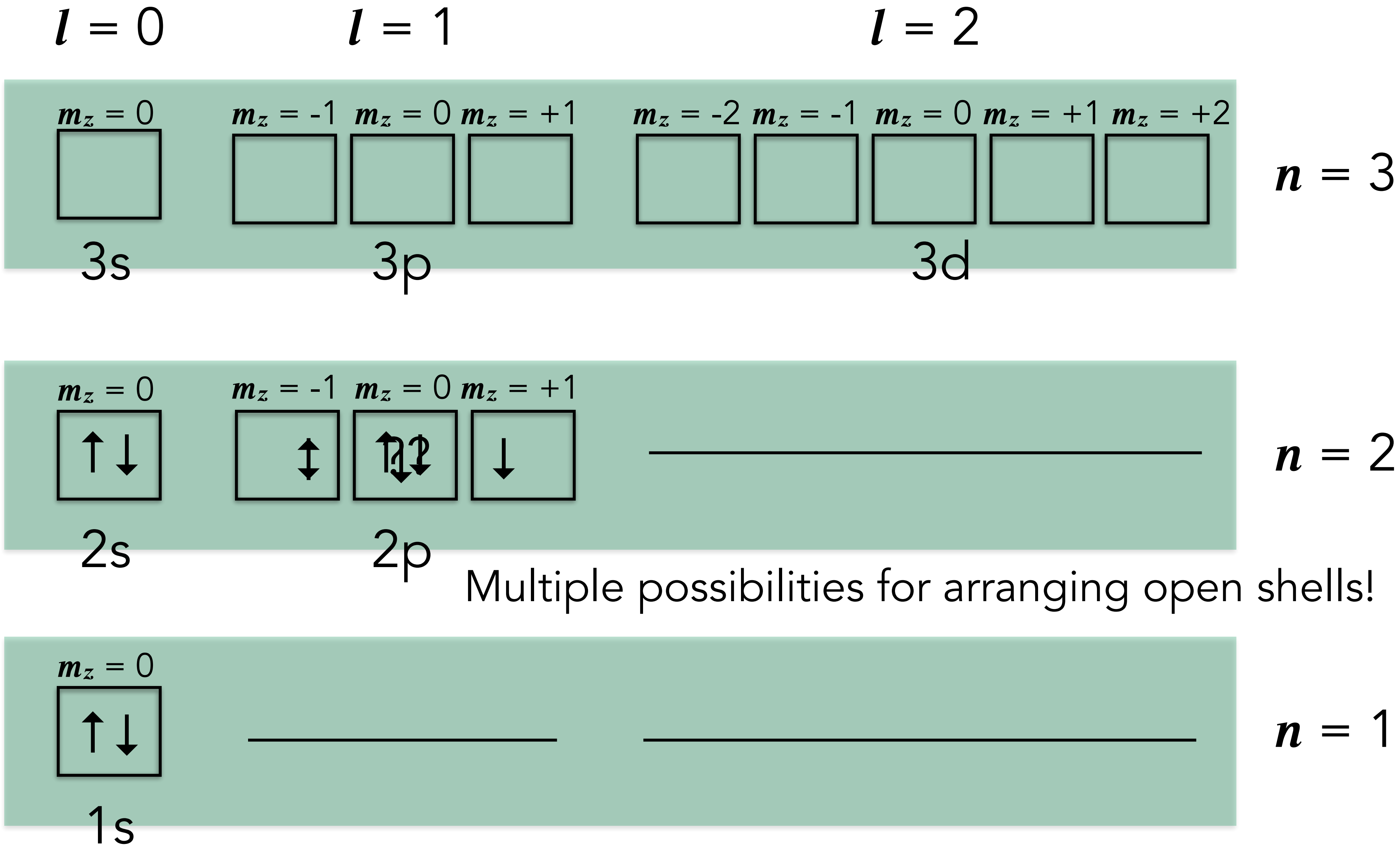
Can put 2 e- in each box: ↑↓

$\therefore$ degeneracy of subshell = $2(2l+1)$



Lets build the ground state of Na: 11 electrons

→$1s^2\ 2s^2\ 2p^6\ 3s$



Multiple possibilities for arranging open shells!

Lets build the ground state of C: 6 electrons

→$1s^2\ 2s^2\ 2p^2$

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

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

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

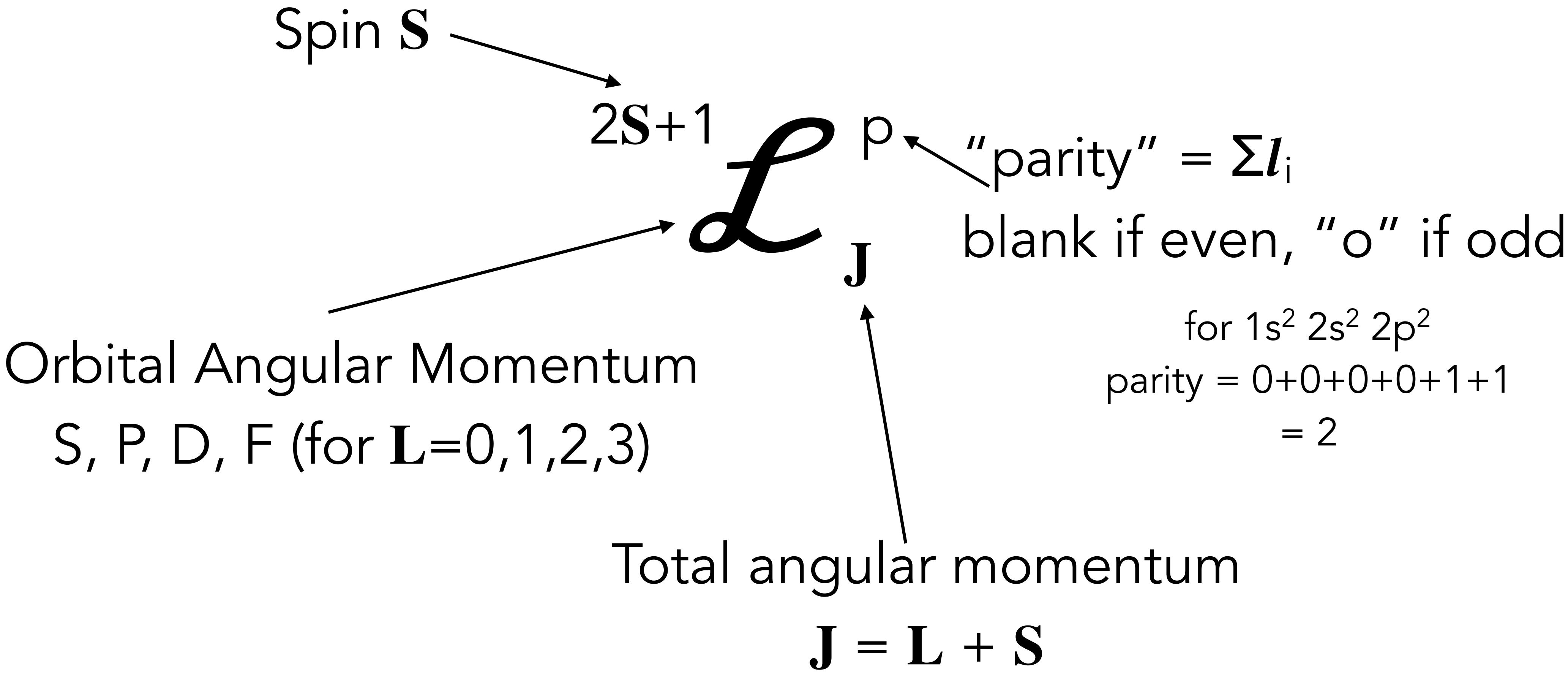
Different combinations of $\mathbf{L}$ and $\mathbf{S}$ have different energies.

- *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.

Spectroscopic Notation

The "Spectroscopic Term"



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

Orbital Angular Momentum

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

Total angular momentum

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

Possible Terms for 2 electrons in p

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

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

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

$$= 36 \text{ total}$$

Not all of these work - lets see why…

“Non-Equivalent” electrons (i.e. 2p3p, different *n*)

36 combinations 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)	+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 n)
only 15 combinations allowed (b.c. Pauli & some are identical)

(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 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)

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

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

= 36 total

Only 15 states allowed, so some terms don't work when electrons are equivalent - which ones?

Possible Terms for 2 electrons in p

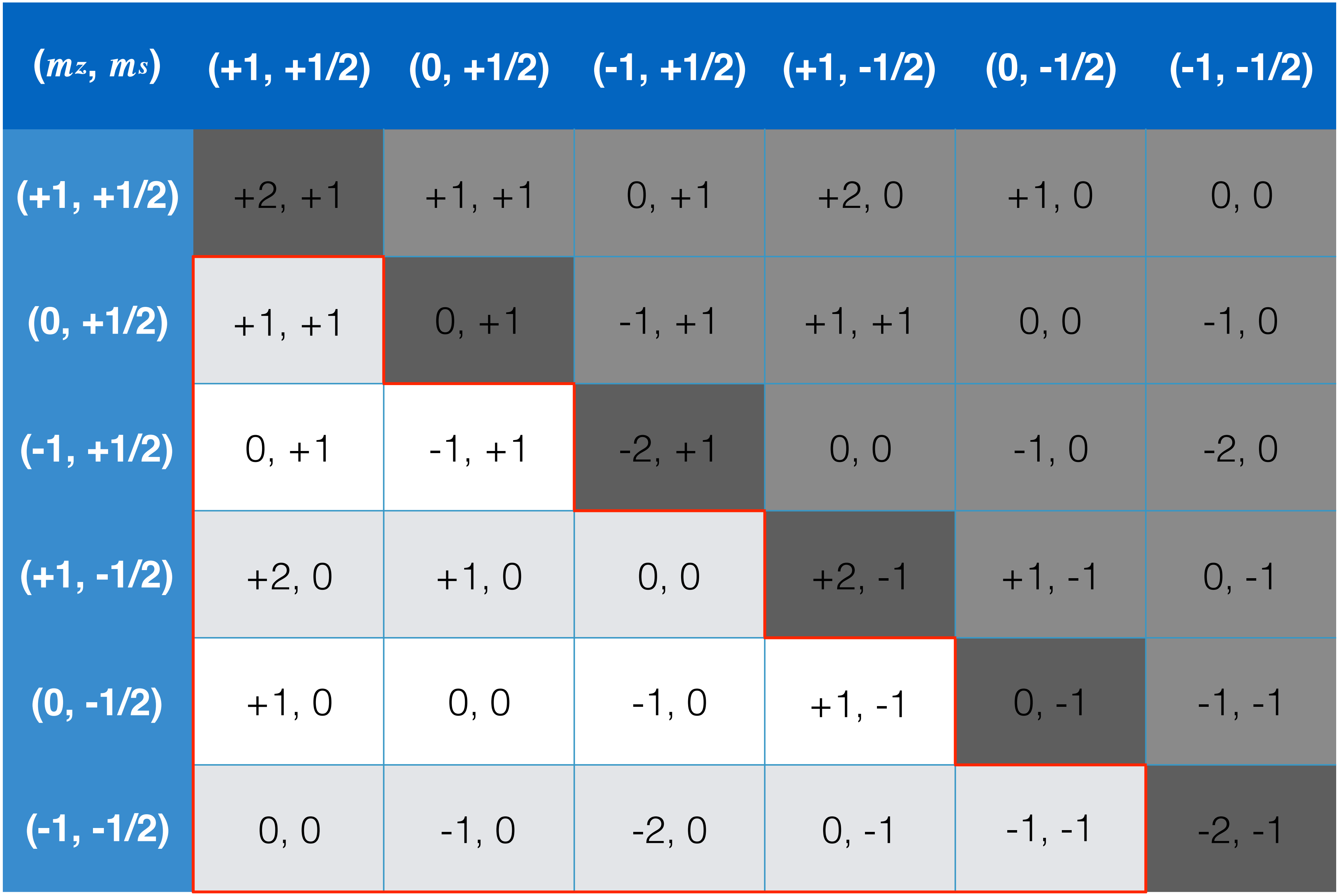
Term (deg.)	**L=0**	**L=1**	**L=2**
S=0	^{1}S (1)	^{1}P (3)	^{1}D (5)
S=1	^{3}S (3)	^{3}P (9)	~~^{3}D~~ ~~(15)~~

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

^{3}D has L = 2 (m_z = 2, 1, 0, -1, -2) and S=1 (m_s = 1, 0, -1)

$m_z = \pm 2$, $m_s = \pm 1$ not in the table so ^{3}D cannot be a valid term.

"Equivalent" electrons (i.e. $2p^2$, same $\boldsymbol{n}$)
only 15 combinations allowed (b.c. Pauli & some are identical)



(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 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)~~

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

= 21 remaining
still too many

^{1}S includes: m_z = 0 and m_s = 0

^{3}S includes: m_z = 0 and m_s = +1, 0, -1

^{1}P includes: m_z = +1, 0, -1 and m_s = 0

^{3}P includes: m_z = +1, 0, -1 and m_s = +1, 0, -1

^{1}D includes: m_z = +2, +1, 0, -1, -2 and m_s = 0

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

(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 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)~~

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

= 21 remaining

^{1}S includes: $m_z = 0$ and $m_s = 0$

^{3}S includes: $m_z = 0$ and $m_s = +1, 0, -1$

^{1}P includes: $m_z = +1, 0, -1$ and $m_s = 0$

^{3}P includes: $m_z = +1, 0, -1$ and $m_s = +1, 0, -1$

^{1}D includes: $m_z = +2, +1, 0, -1, -2$ and $m_s = 0$

must have
^{1}D

"Equivalent" electrons (i.e. 2p^2, same n)
only 15 combinations allowed (b.c. Pauli & symmetry)

(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 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)~~

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

= 5 accounted for
need 10 more,
16 remaining

^{1}S includes: m_z = 0 and m_s = 0

^{3}S includes: m_z = 0 and m_s = +1, 0, -1

^{1}P includes: m_z = +1, 0, -1 and m_s = 0

^{3}P includes: m_z = +1, 0, -1 and m_s = +1, 0, -1

Possible Terms for 2 electrons in p

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

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

= 5 accounted for
need 10 more,
16 remaining

^1S includes: $m_z = 0$ and $m_s = 0$

^3S includes: $m_z = 0$ and $m_s = +1, 0, -1$

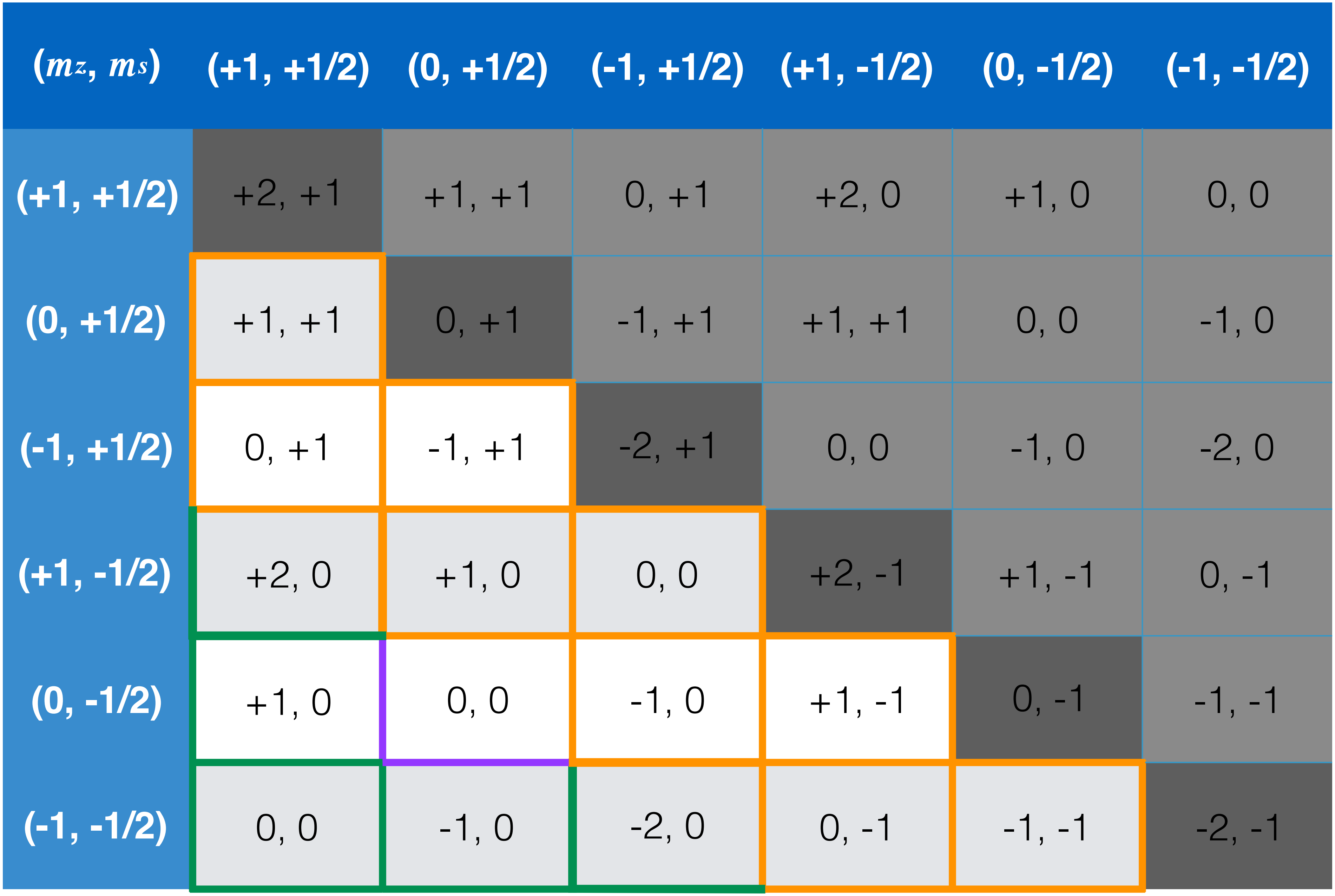
^1P includes: $m_z = +1, 0, -1$ and $m_s = 0$

^3P includes: $m_z = +1, 0, -1$ and $m_s = +1, 0, -1$

Only one way
to get 9 states

“Equivalent” electrons (i.e. $2p^2$, same $\boldsymbol{n}$)

only 15 combinations allowed (b.c. Pauli & symmetry)



(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

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

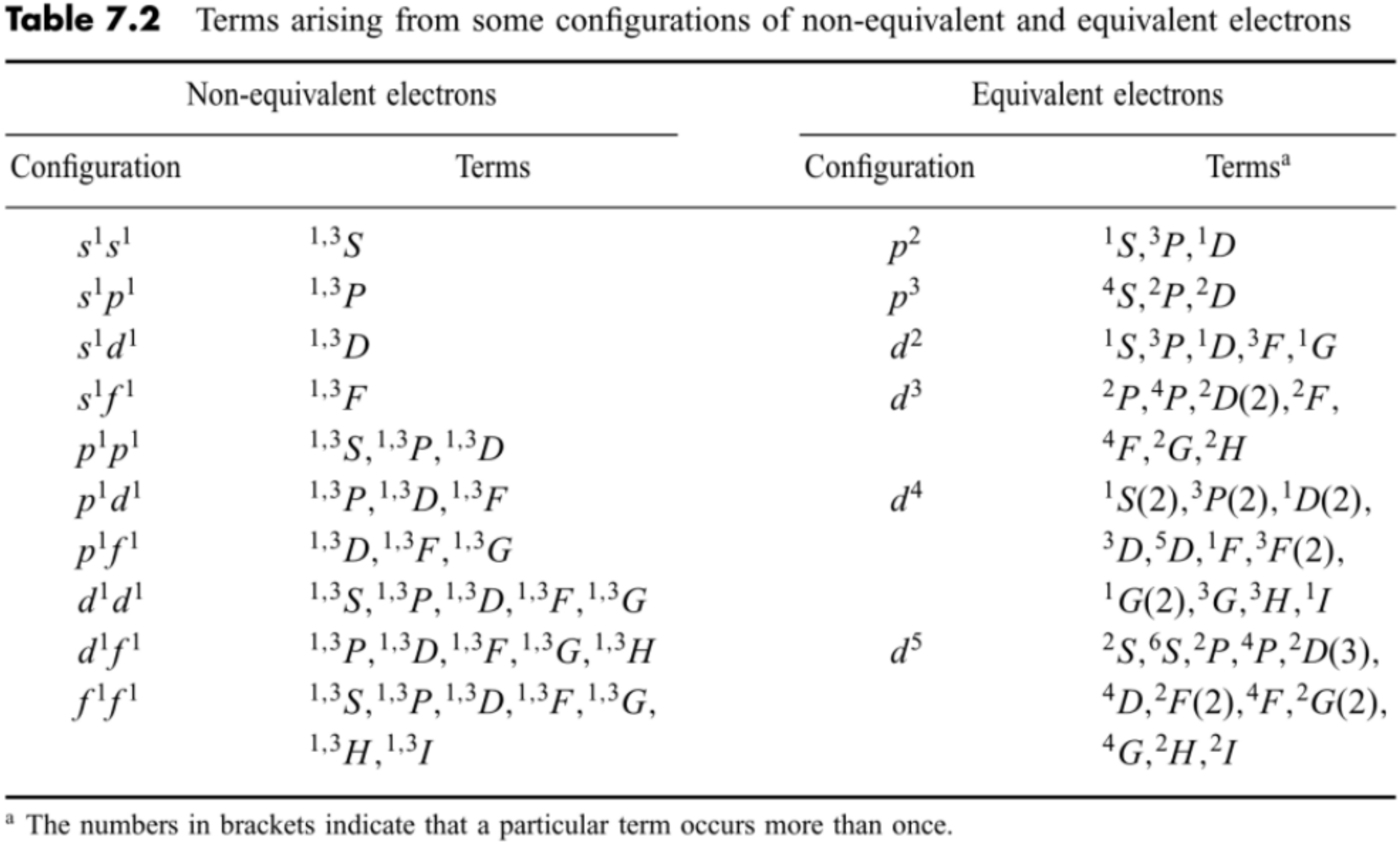


Table 7.2 Terms arising from some configurations of non-equivalent and equivalent electrons

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	$^{1,3}S, ^{1,3}P, ^{1,3}D, ^{1,3}F, ^{1,3}G,$		$^4D, ^2F(2), ^4F, ^2G(2),$
	$^{1,3}H, ^{1,3}I$		$^4G, ^2H, ^2I$

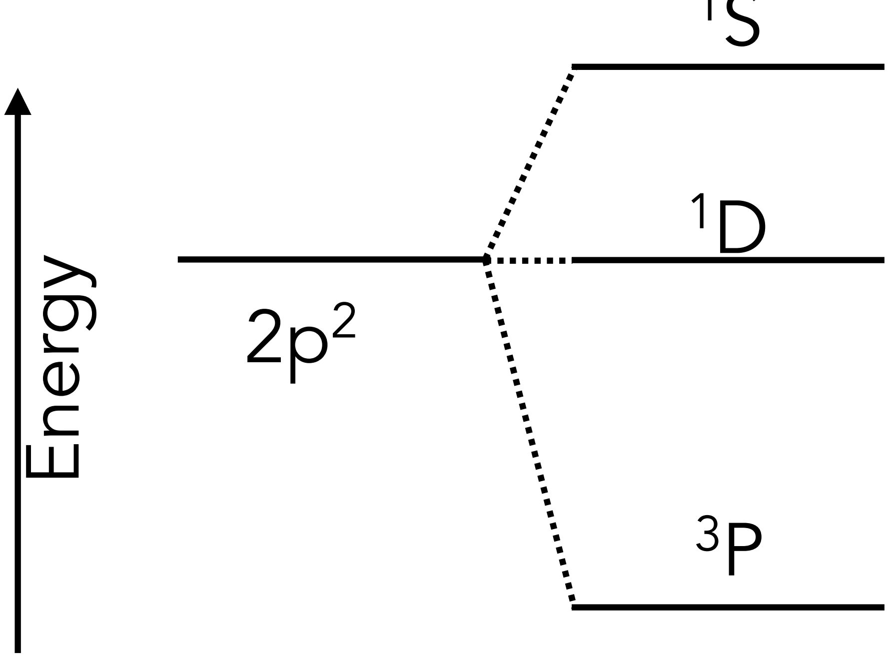
[a] The numbers in brackets indicate that a particular term occurs more than once.

from *Modern Spectroscopy* by Hollas

Energy Levels ⟷ Terms

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

Carbon:



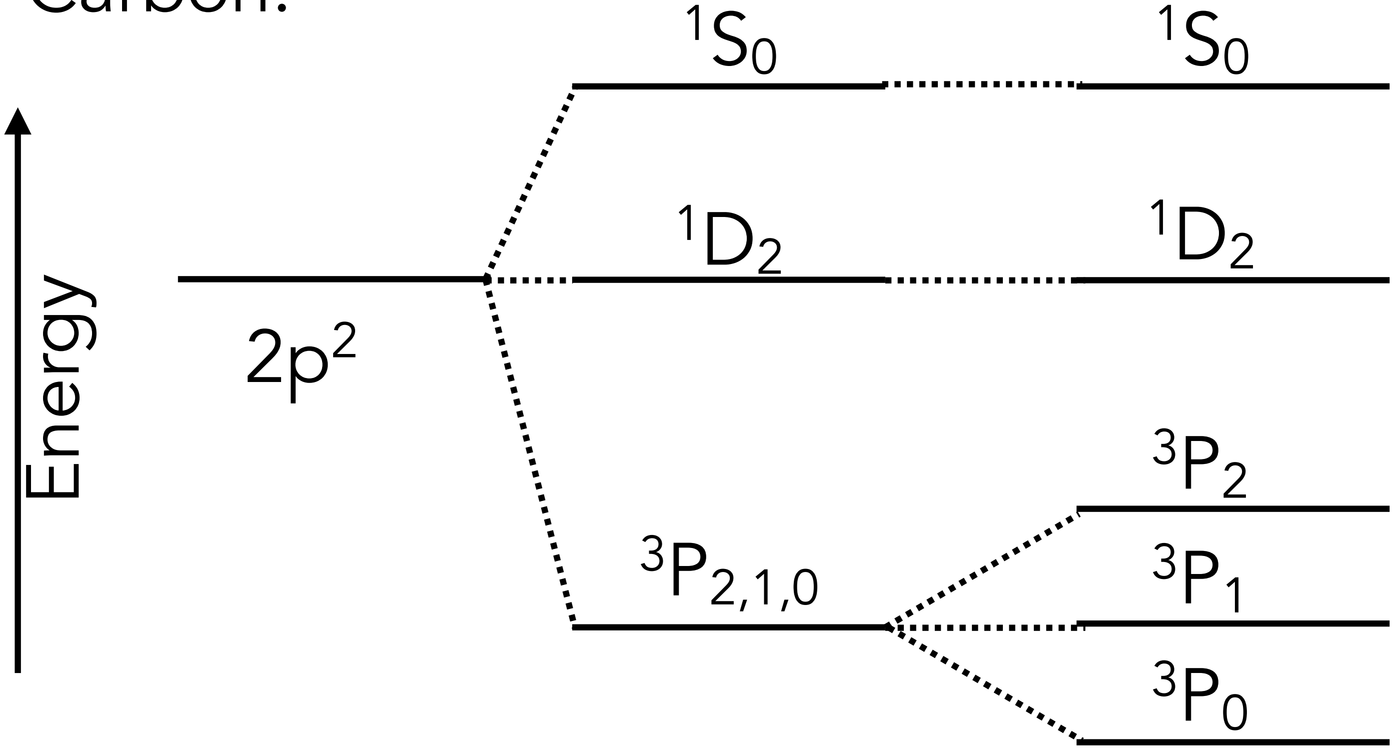
“Hund’s Rules”

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).

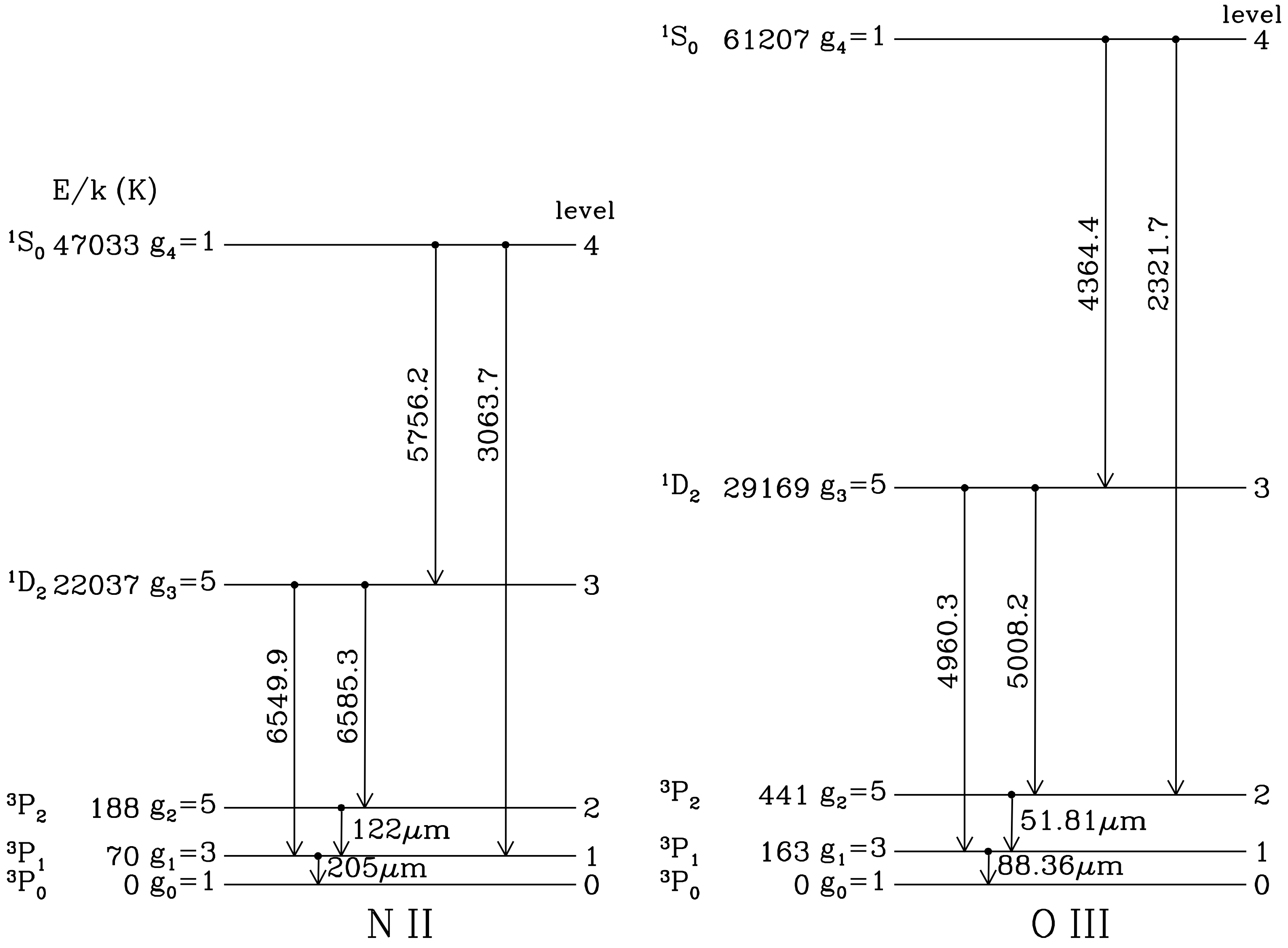
Energy Levels ⟷ Terms

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

Carbon:



Other examples of np^2 ground state configurations



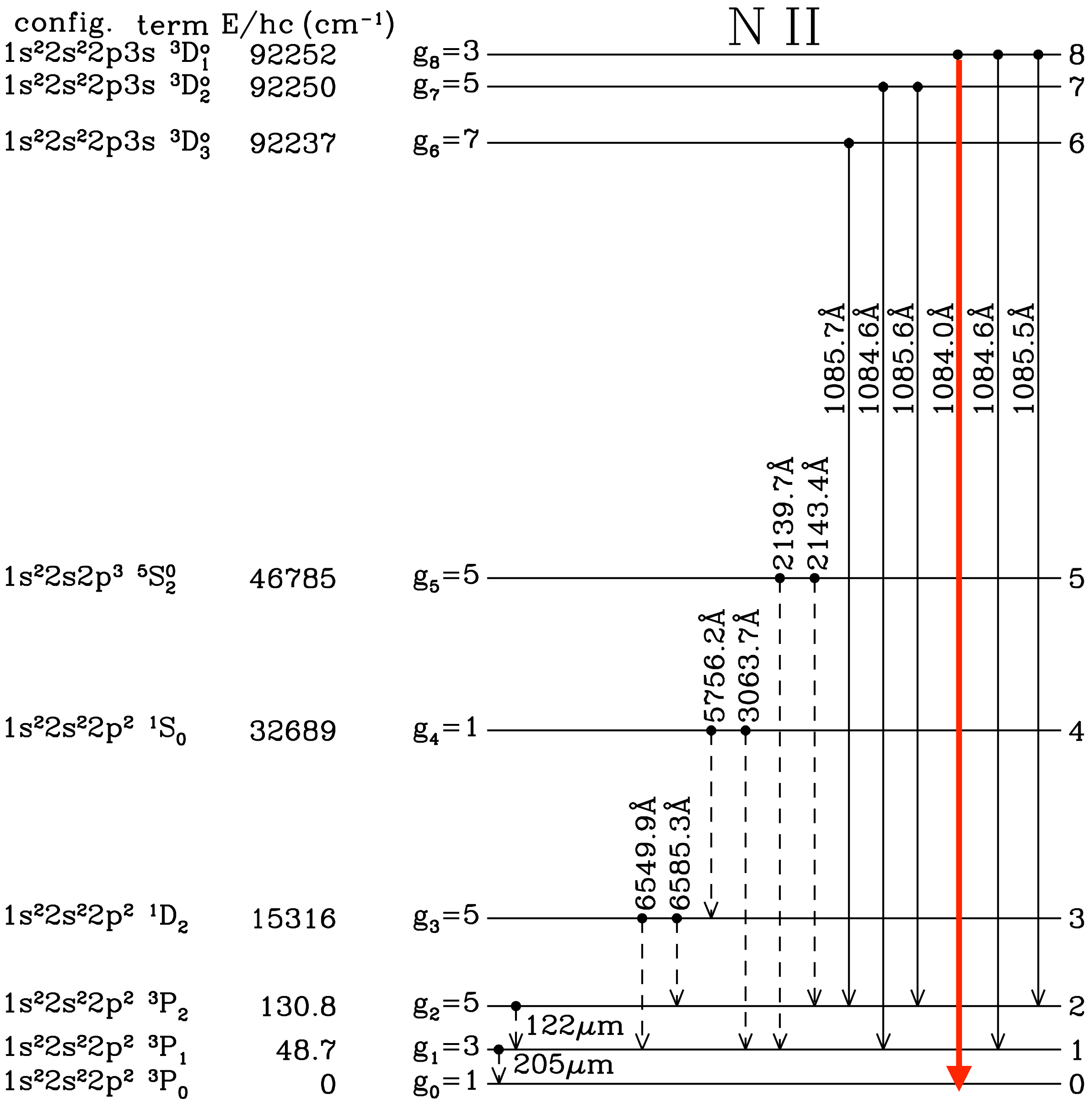
Selection Rules for Transitions

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

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 $\Delta l = 0$

All rules satisfied: "allowed" electric dipole transition

NII 1084.0 Å $^3P_0$ - $^3D_1^o$



✓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

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

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

Selection Rules for Transitions

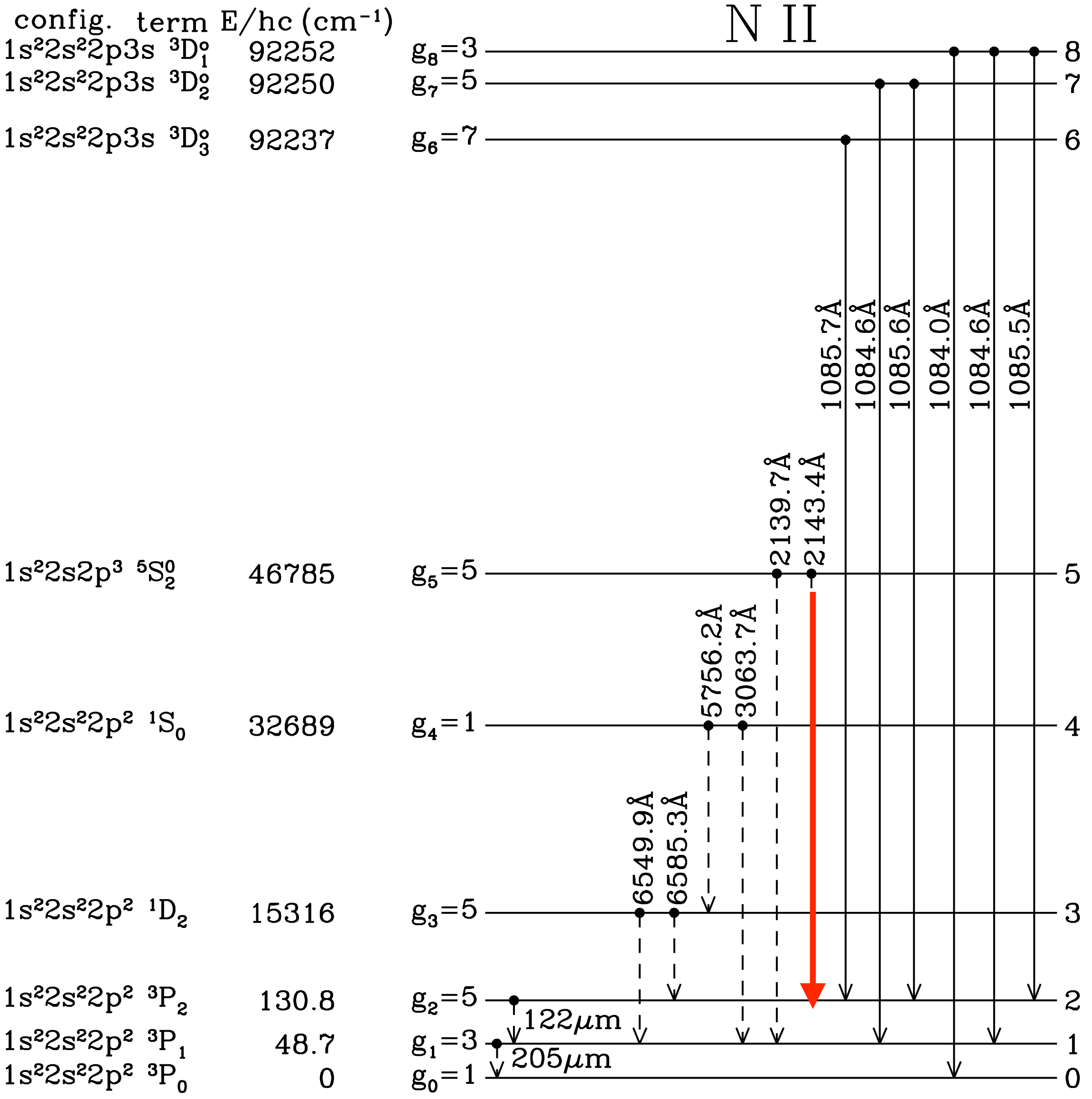
We can now figure out the energy levels, what about the transitions between them?

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 $\Delta \boldsymbol{l} = 0$

All rules except $\Delta S = 0$: "semi-forbidden" or "intercombination" or "intersystem" electric dipole transition

N II] 2143.4 Å $^5S_2^o$ - $^3P_2$

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 Δ*l* = 0

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

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

Selection Rules for Transitions

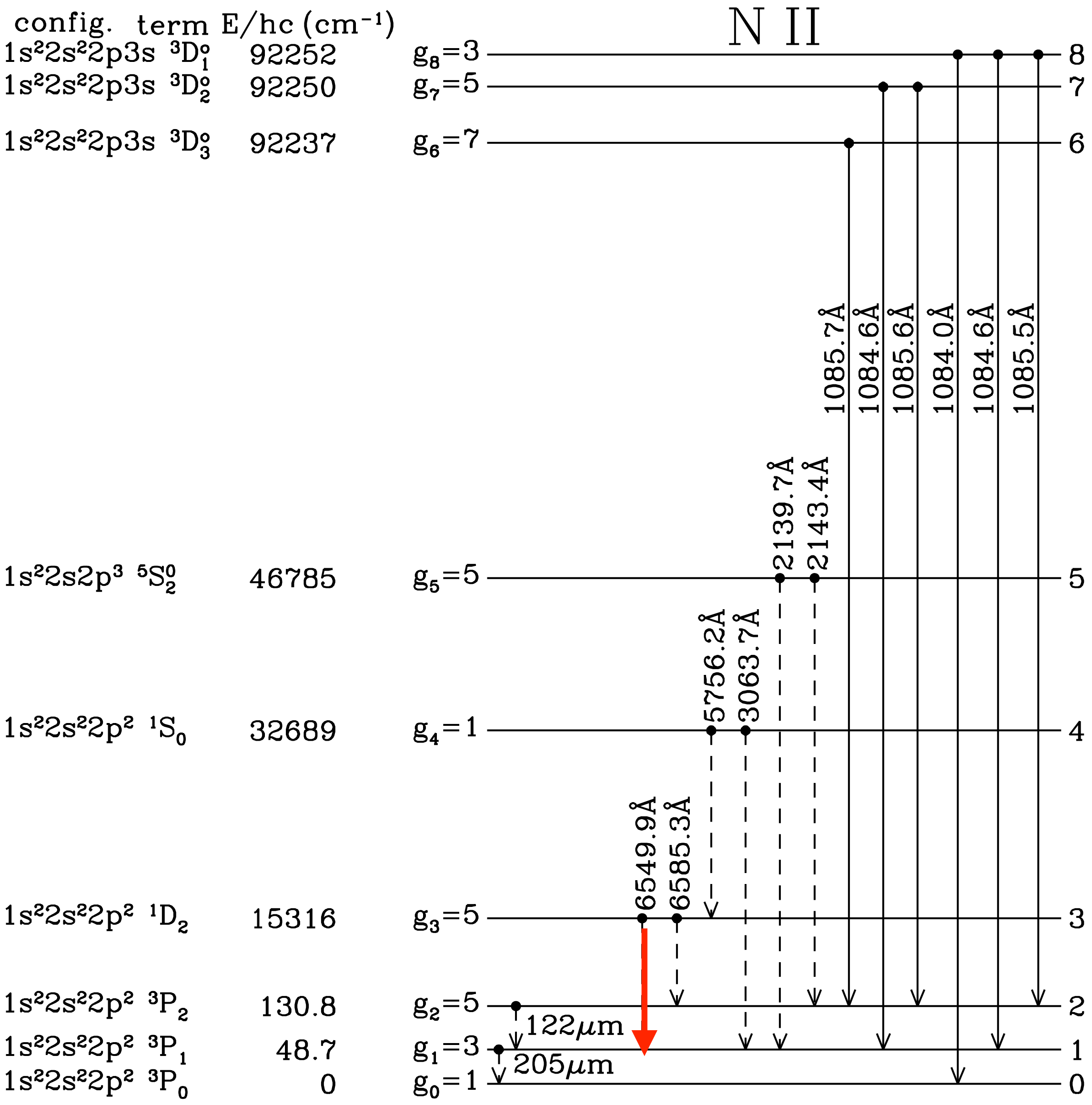
We can now figure out the energy levels, what about the transitions between them?

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 $\Delta \boldsymbol{l} = 0$

<u>More rules broken: “forbidden” transition, either magnetic dipole or electric quadrupole usually</u>

[N II] 6549.9 Å $^1D_2$ - $^3P_1$

double bracket for "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 $\Delta l = 0$

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

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

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!