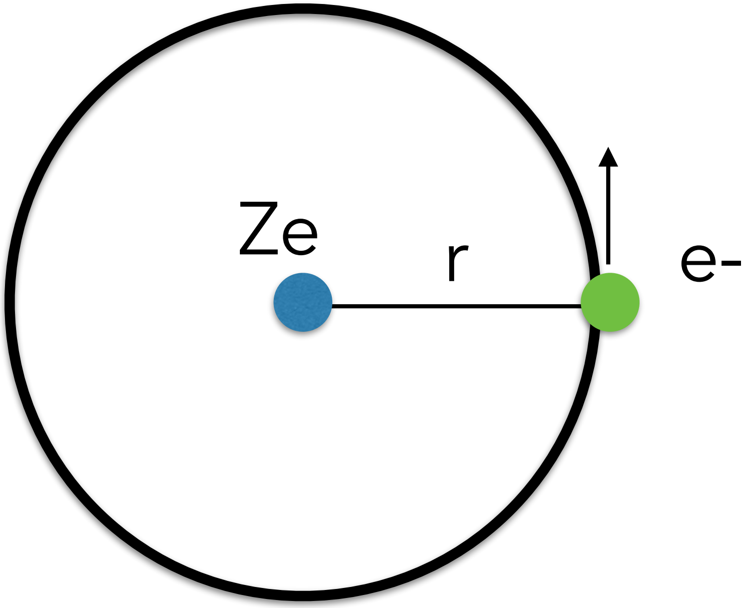
Physics 224
The Interstellar Medium

Lecture #4

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

Order of Magnitude Energy Levels

Classical non-relativistic atom

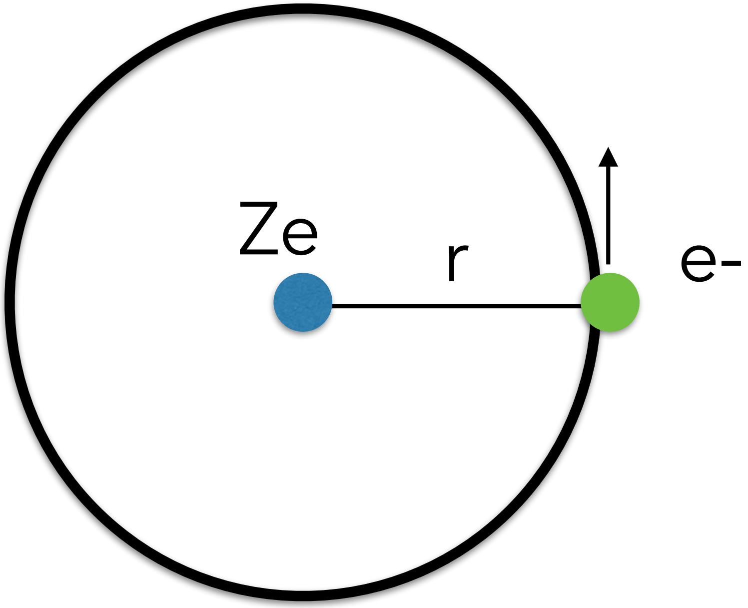


First
"allowed transitions"

Coulomb interactions
between e- and nucleus

Order of Magnitude Energy Levels

Classical non-relativistic atom



First

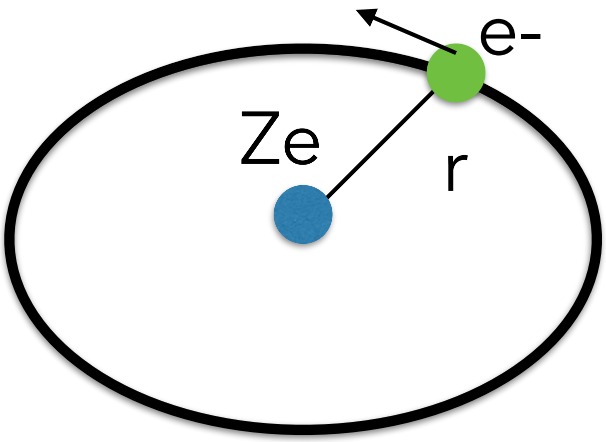
"allowed transitions"

Coulomb interactions between e- and nucleus

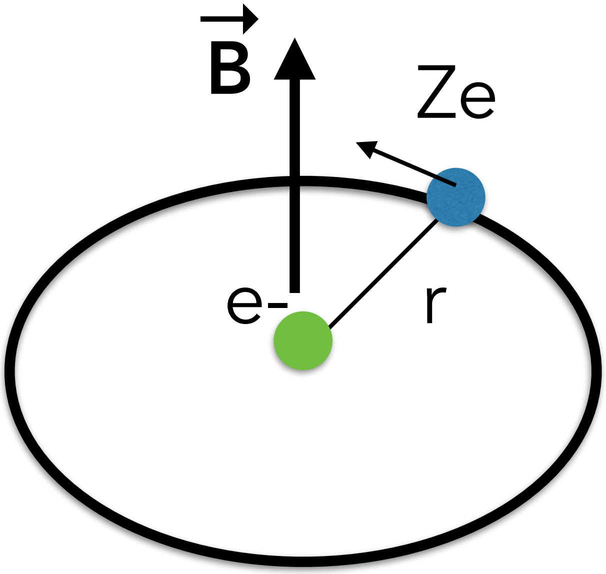
$E \sim 13.6\ \text{eV}\ (Z^2/n^2)$

Order of Magnitude Energy Levels

Classical non-relativistic atom



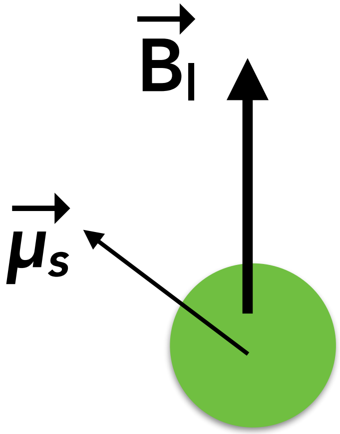
from nucleus's point of view



from e- point of view
orbiting proton generates B-field

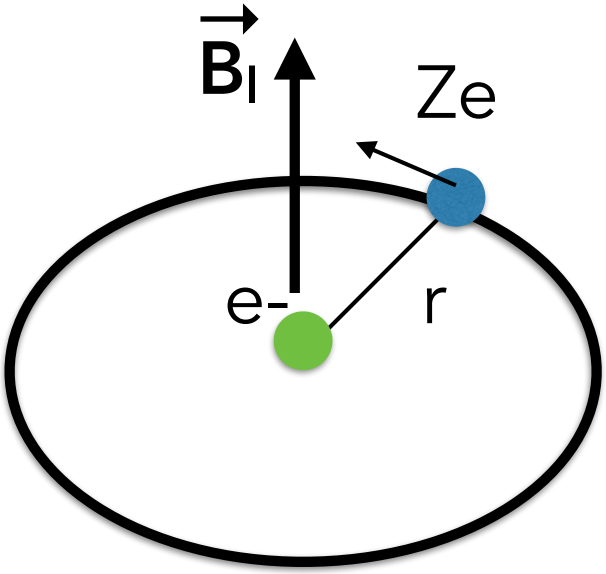
Order of Magnitude Energy Levels

Classical non-relativistic atom



spin magnetic moment
of electron interacts
with orbit B-field

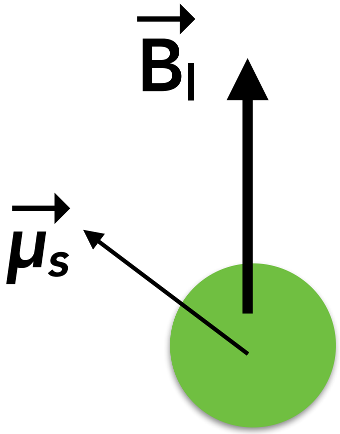
Spin-Orbit
coupling!



from e- point of view
orbiting proton generates B-field

Order of Magnitude Energy Levels

Classical non-relativistic atom



spin magnetic moment
of electron interacts
with orbit B-field

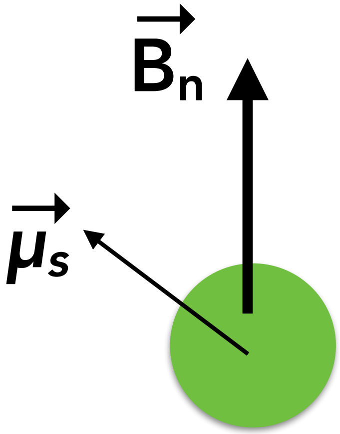
"fine structure" transitions

interaction between spin and angular momentum of e-

$E \sim 13.6 \text{ eV } (\alpha^2 Z^4/n^5)$

Order of Magnitude Energy Levels

Classical non-relativistic atom



spin magnetic moment of electron interacts with B-field from nuclear spin

"hyperfine structure" transitions

interaction between magnetic moments of nucleus and e-

$$E \sim 13.6 \text{ eV } (m_e/m_n)(\alpha^2 Z^4/n^5)$$

Order of Magnitude Energy Levels

"Allowed" Electric Dipole	$E \sim 13.6\ \mathrm{eV}\ (Z^2/n^2)$
"Forbidden" Fine Structure	$E \sim 13.6\ \mathrm{eV}\ (\alpha^2 Z^4/n^5)$
"Forbidden" Hyperfine Structure	$E \sim 13.6\ \mathrm{eV}\ (m_e/m_n)(\alpha^2 Z^4/n^5)$

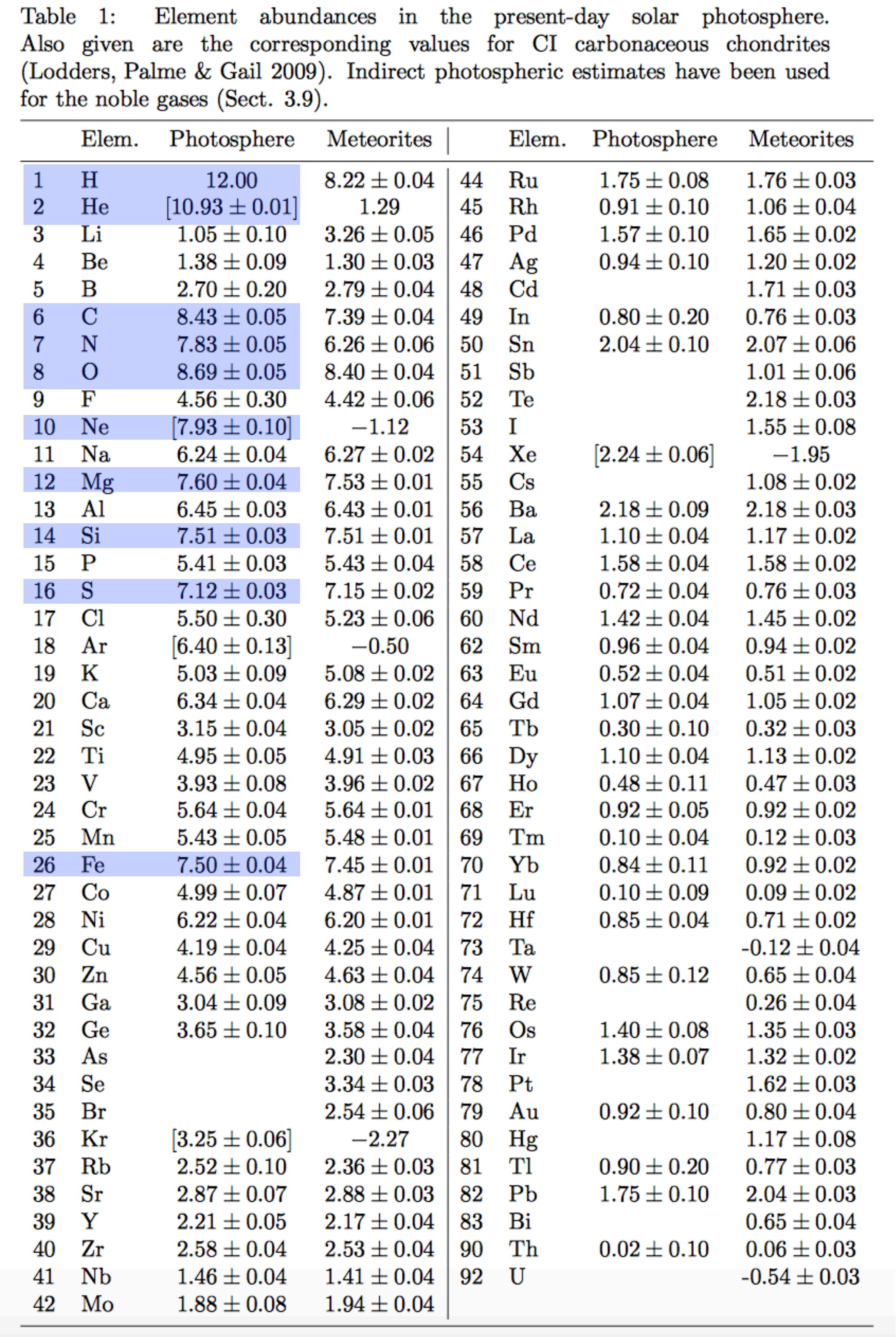


Table 1: Element abundances in the present-day solar photosphere. Also given are the corresponding values for CI carbonaceous chondrites (Lodders, Palme & Gail 2009). Indirect photospheric estimates have been used for the noble gases (Sect. 3.9).

	Elem.	Photosphere	Meteorites		Elem.	Photosphere	Meteorites
1	H	12.00	8.22 ± 0.04	44	Ru	1.75 ± 0.08	1.76 ± 0.03
2	He	[10.93 ± 0.01]	1.29	45	Rh	0.91 ± 0.10	1.06 ± 0.04
3	Li	1.05 ± 0.10	3.26 ± 0.05	46	Pd	1.57 ± 0.10	1.65 ± 0.02
4	Be	1.38 ± 0.09	1.30 ± 0.03	47	Ag	0.94 ± 0.10	1.20 ± 0.02
5	B	2.70 ± 0.20	2.79 ± 0.04	48	Cd		1.71 ± 0.03
6	C	8.43 ± 0.05	7.39 ± 0.04	49	In	0.80 ± 0.20	0.76 ± 0.03
7	N	7.83 ± 0.05	6.26 ± 0.06	50	Sn	2.04 ± 0.10	2.07 ± 0.06
8	O	8.69 ± 0.05	8.40 ± 0.04	51	Sb		1.01 ± 0.06
9	F	4.56 ± 0.30	4.42 ± 0.06	52	Te		2.18 ± 0.03
10	Ne	[7.93 ± 0.10]	−1.12	53	I		1.55 ± 0.08
11	Na	6.24 ± 0.04	6.27 ± 0.02	54	Xe	[2.24 ± 0.06]	−1.95
12	Mg	7.60 ± 0.04	7.53 ± 0.01	55	Cs		1.08 ± 0.02
13	Al	6.45 ± 0.03	6.43 ± 0.01	56	Ba	2.18 ± 0.09	2.18 ± 0.03
14	Si	7.51 ± 0.03	7.51 ± 0.01	57	La	1.10 ± 0.04	1.17 ± 0.02
15	P	5.41 ± 0.03	5.43 ± 0.04	58	Ce	1.58 ± 0.04	1.58 ± 0.02
16	S	7.12 ± 0.03	7.15 ± 0.02	59	Pr	0.72 ± 0.04	0.76 ± 0.03
17	Cl	5.50 ± 0.30	5.23 ± 0.06	60	Nd	1.42 ± 0.04	1.45 ± 0.02
18	Ar	[6.40 ± 0.13]	−0.50	62	Sm	0.96 ± 0.04	0.94 ± 0.02
19	K	5.03 ± 0.09	5.08 ± 0.02	63	Eu	0.52 ± 0.04	0.51 ± 0.02
20	Ca	6.34 ± 0.04	6.29 ± 0.02	64	Gd	1.07 ± 0.04	1.05 ± 0.02
21	Sc	3.15 ± 0.04	3.05 ± 0.02	65	Tb	0.30 ± 0.10	0.32 ± 0.03
22	Ti	4.95 ± 0.05	4.91 ± 0.03	66	Dy	1.10 ± 0.04	1.13 ± 0.02
23	V	3.93 ± 0.08	3.96 ± 0.02	67	Ho	0.48 ± 0.11	0.47 ± 0.03
24	Cr	5.64 ± 0.04	5.64 ± 0.01	68	Er	0.92 ± 0.05	0.92 ± 0.02
25	Mn	5.43 ± 0.05	5.48 ± 0.01	69	Tm	0.10 ± 0.04	0.12 ± 0.03
26	Fe	7.50 ± 0.04	7.45 ± 0.01	70	Yb	0.84 ± 0.11	0.92 ± 0.02
27	Co	4.99 ± 0.07	4.87 ± 0.01	71	Lu	0.10 ± 0.09	0.09 ± 0.02
28	Ni	6.22 ± 0.04	6.20 ± 0.01	72	Hf	0.85 ± 0.04	0.71 ± 0.02
29	Cu	4.19 ± 0.04	4.25 ± 0.04	73	Ta		-0.12 ± 0.04
30	Zn	4.56 ± 0.05	4.63 ± 0.04	74	W	0.85 ± 0.12	0.65 ± 0.04
31	Ga	3.04 ± 0.09	3.08 ± 0.02	75	Re		0.26 ± 0.04
32	Ge	3.65 ± 0.10	3.58 ± 0.04	76	Os	1.40 ± 0.08	1.35 ± 0.03
33	As		2.30 ± 0.04	77	Ir	1.38 ± 0.07	1.32 ± 0.02
34	Se		3.34 ± 0.03	78	Pt		1.62 ± 0.03
35	Br		2.54 ± 0.06	79	Au	0.92 ± 0.10	0.80 ± 0.04
36	Kr	[3.25 ± 0.06]	−2.27	80	Hg		1.17 ± 0.08
37	Rb	2.52 ± 0.10	2.36 ± 0.03	81	Tl	0.90 ± 0.20	0.77 ± 0.03
38	Sr	2.87 ± 0.07	2.88 ± 0.03	82	Pb	1.75 ± 0.10	2.04 ± 0.03
39	Y	2.21 ± 0.05	2.17 ± 0.04	83	Bi		0.65 ± 0.04
40	Zr	2.58 ± 0.04	2.53 ± 0.04	90	Th	0.02 ± 0.10	0.06 ± 0.03
41	Nb	1.46 ± 0.04	1.41 ± 0.04	92	U		-0.54 ± 0.03
42	Mo	1.88 ± 0.08	1.94 ± 0.04				

Asplund et al. 2009
Solar Abundances

$= 12 + \log_{10}(X/H)$

Elements with 12+log(X/H) > 7:
H, He, C, N, O, Ne, Mg, Si, S, Fe

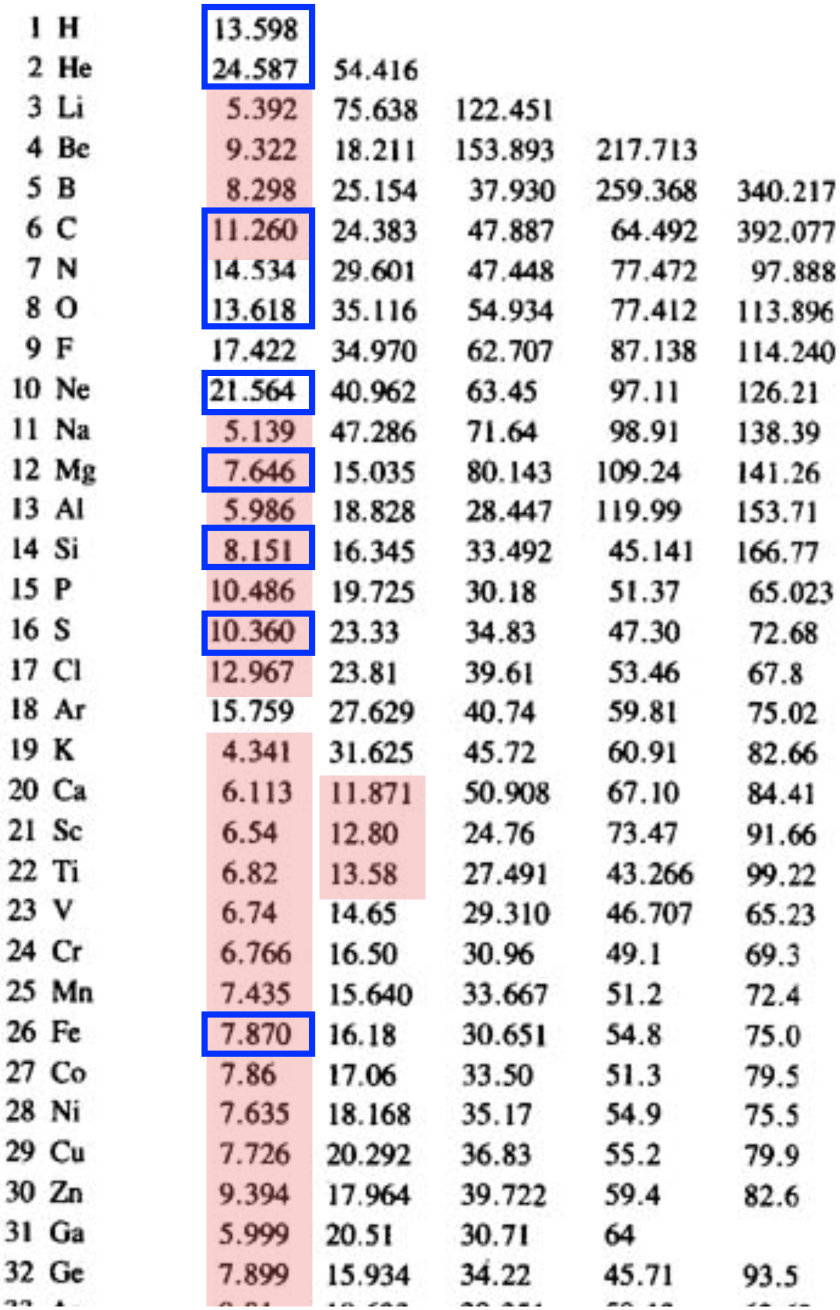
Important for ISM processes

Some notation:

neutral: H I
singly ionized: H II

e.g. triply ionized oxygen (O^{3+}) = O IV

Ionization Potentials

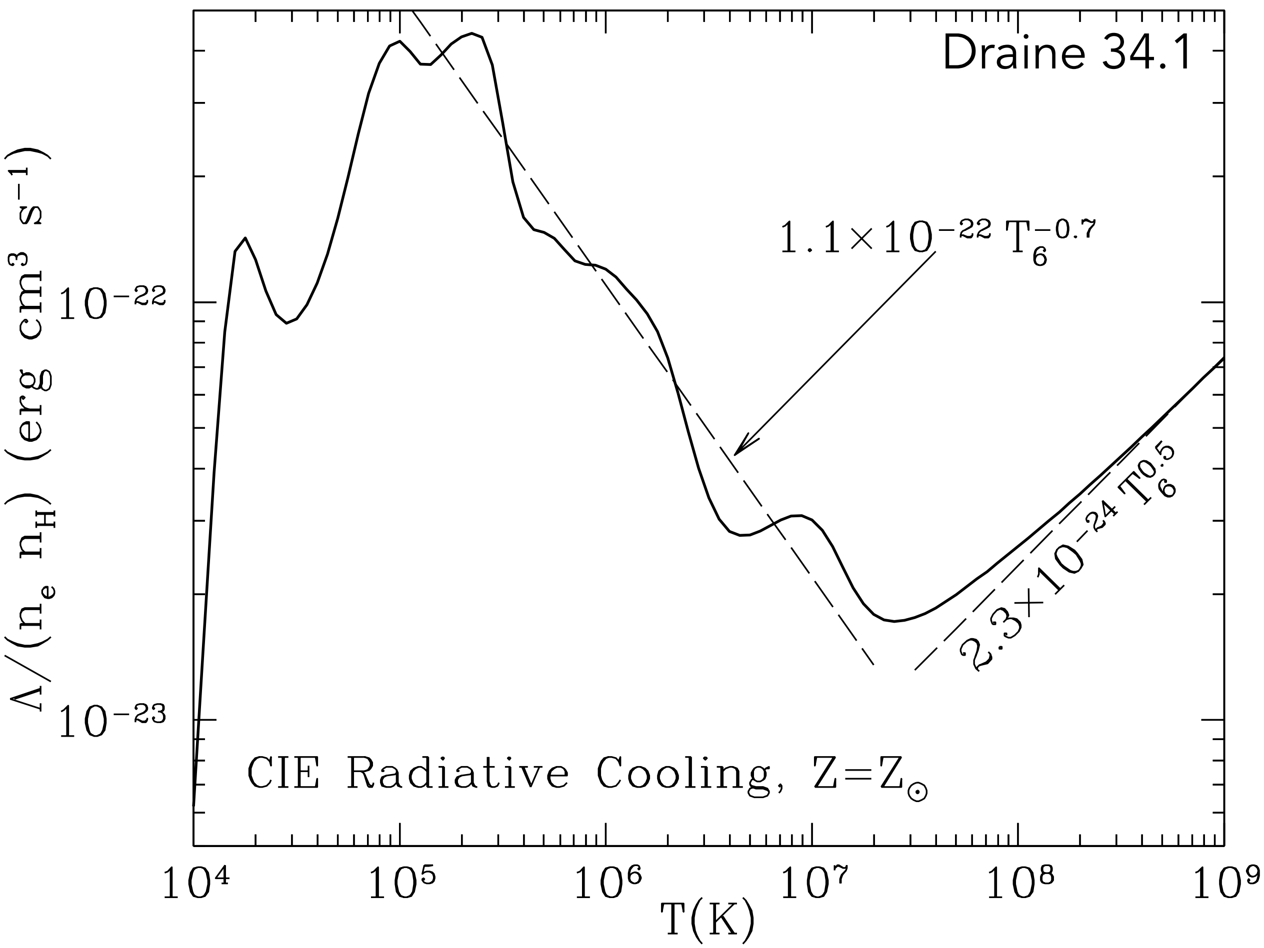


	I→II	II→III	III→IV	IV→V	V→VI
1 H	13.598				
2 He	24.587	54.416			
3 Li	5.392	75.638	122.451		
4 Be	9.322	18.211	153.893	217.713	
5 B	8.298	25.154	37.930	259.368	340.217
6 C	11.260	24.383	47.887	64.492	392.077
7 N	14.534	29.601	47.448	77.472	97.888
8 O	13.618	35.116	54.934	77.412	113.896
9 F	17.422	34.970	62.707	87.138	114.240
10 Ne	21.564	40.962	63.45	97.11	126.21
11 Na	5.139	47.286	71.64	98.91	138.39
12 Mg	7.646	15.035	80.143	109.24	141.26
13 Al	5.986	18.828	28.447	119.99	153.71
14 Si	8.151	16.345	33.492	45.141	166.77
15 P	10.486	19.725	30.18	51.37	65.023
16 S	10.360	23.33	34.83	47.30	72.68
17 Cl	12.967	23.81	39.61	53.46	67.8
18 Ar	15.759	27.629	40.74	59.81	75.02
19 K	4.341	31.625	45.72	60.91	82.66
20 Ca	6.113	11.871	50.908	67.10	84.41
21 Sc	6.54	12.80	24.76	73.47	91.66
22 Ti	6.82	13.58	27.491	43.266	99.22
23 V	6.74	14.65	29.310	46.707	65.23
24 Cr	6.766	16.50	30.96	49.1	69.3
25 Mn	7.435	15.640	33.667	51.2	72.4
26 Fe	7.870	16.18	30.651	54.8	75.0
27 Co	7.86	17.06	33.50	51.3	79.5
28 Ni	7.635	18.168	35.17	54.9	75.5
29 Cu	7.726	20.292	36.83	55.2	79.9
30 Zn	9.394	17.964	39.722	59.4	82.6
31 Ga	5.999	20.51	30.71	64	
32 Ge	7.899	15.934	34.22	45.71	93.5

Can be ionized when H is neutral.

Carbon is the most abundant element that can be ionized when H is neutral.

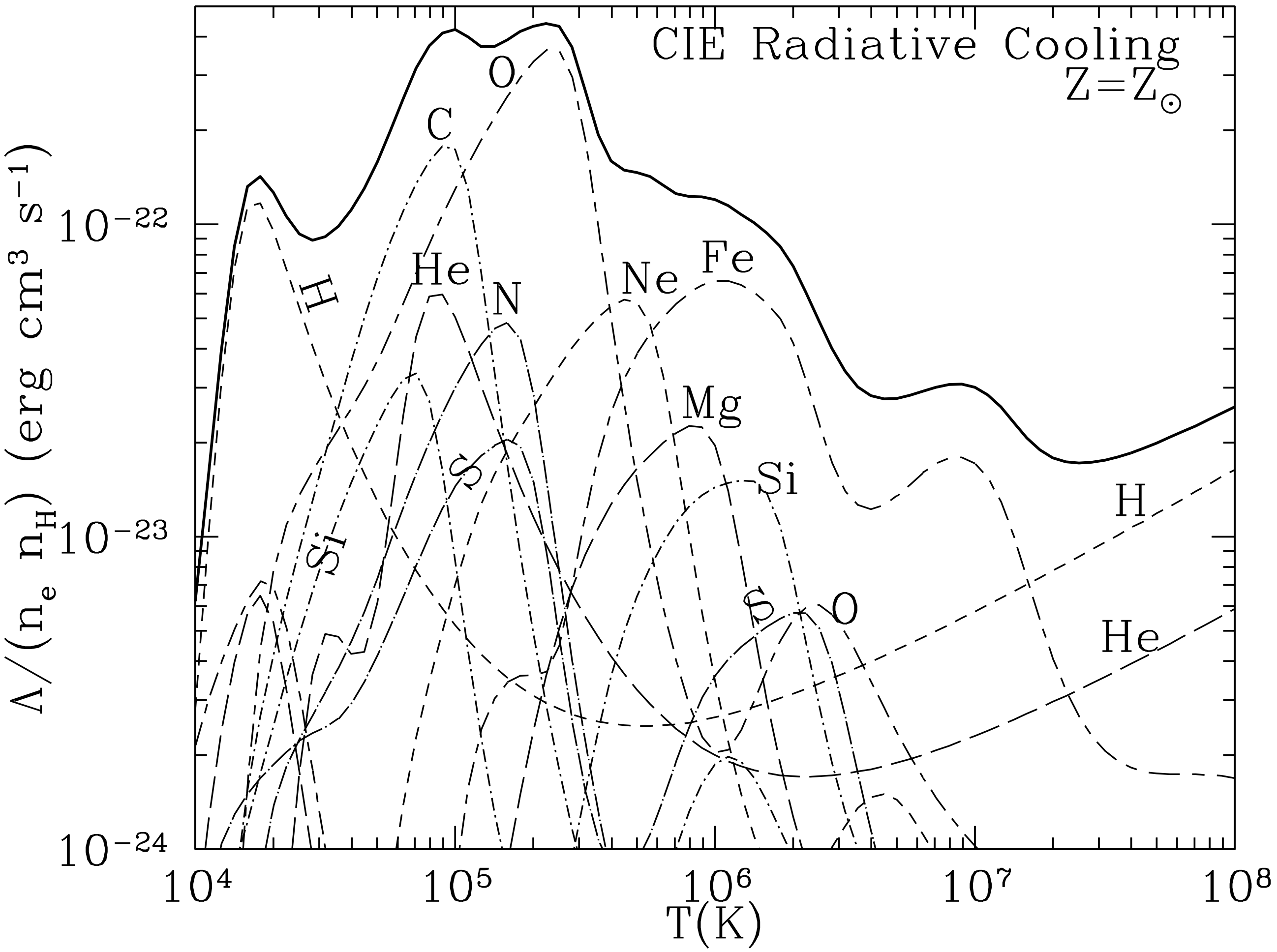
Emission lines from ions, atoms & molecules are critical for cooling ISM gas



Ionized Gas

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

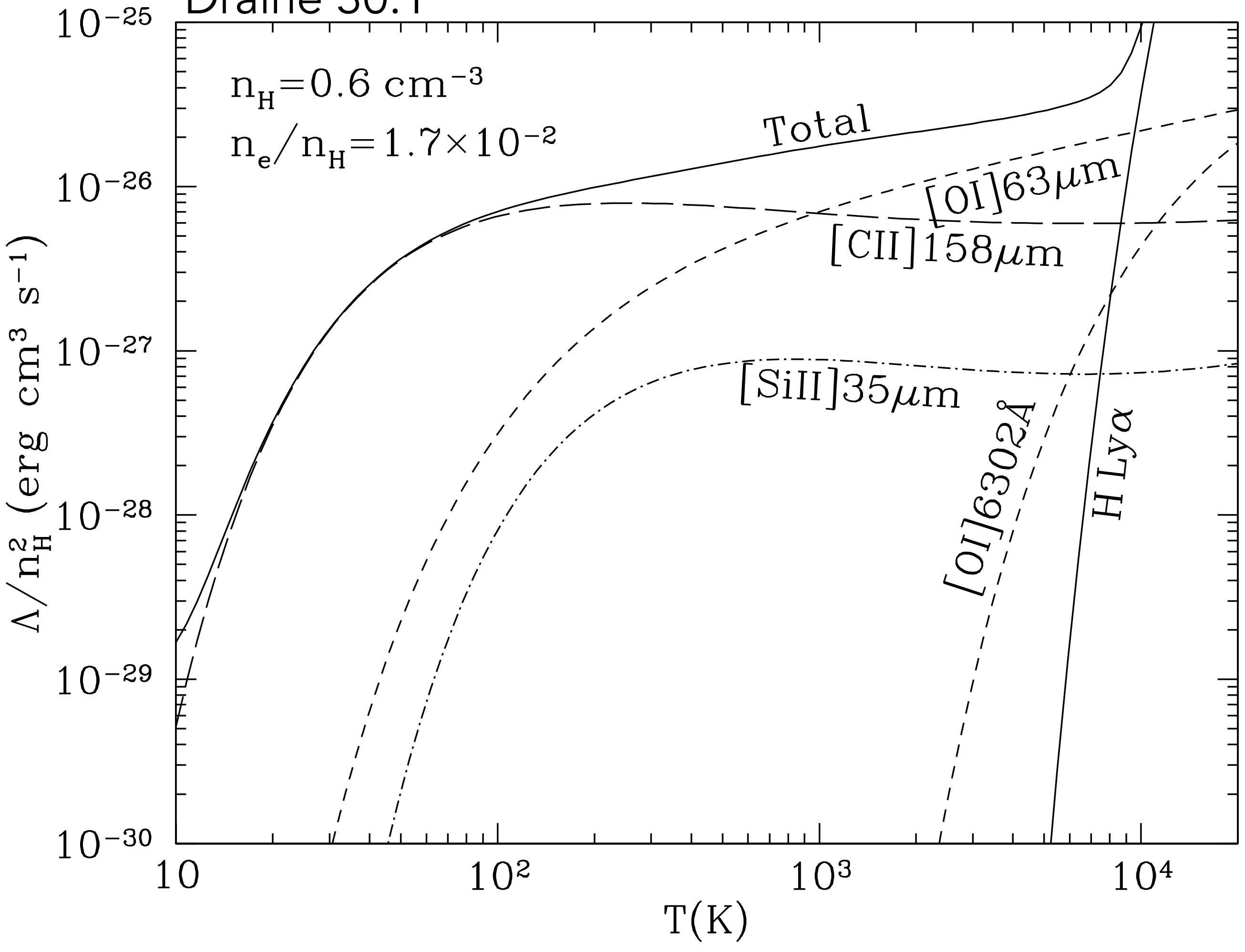
Draine 34.3



Ionized Gas

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

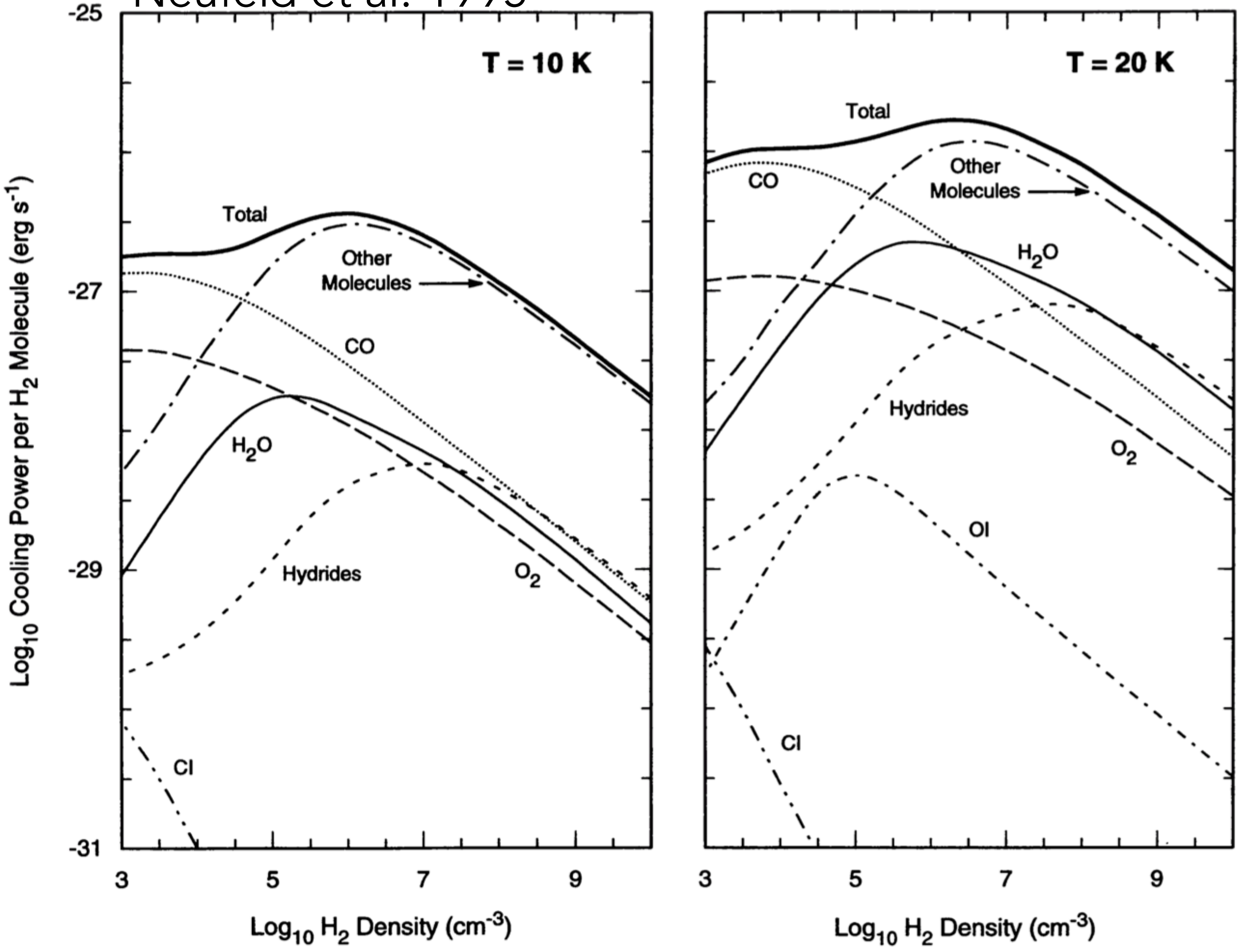
Draine 30.1



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 ($0 \leq l < n$)

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 & Ions

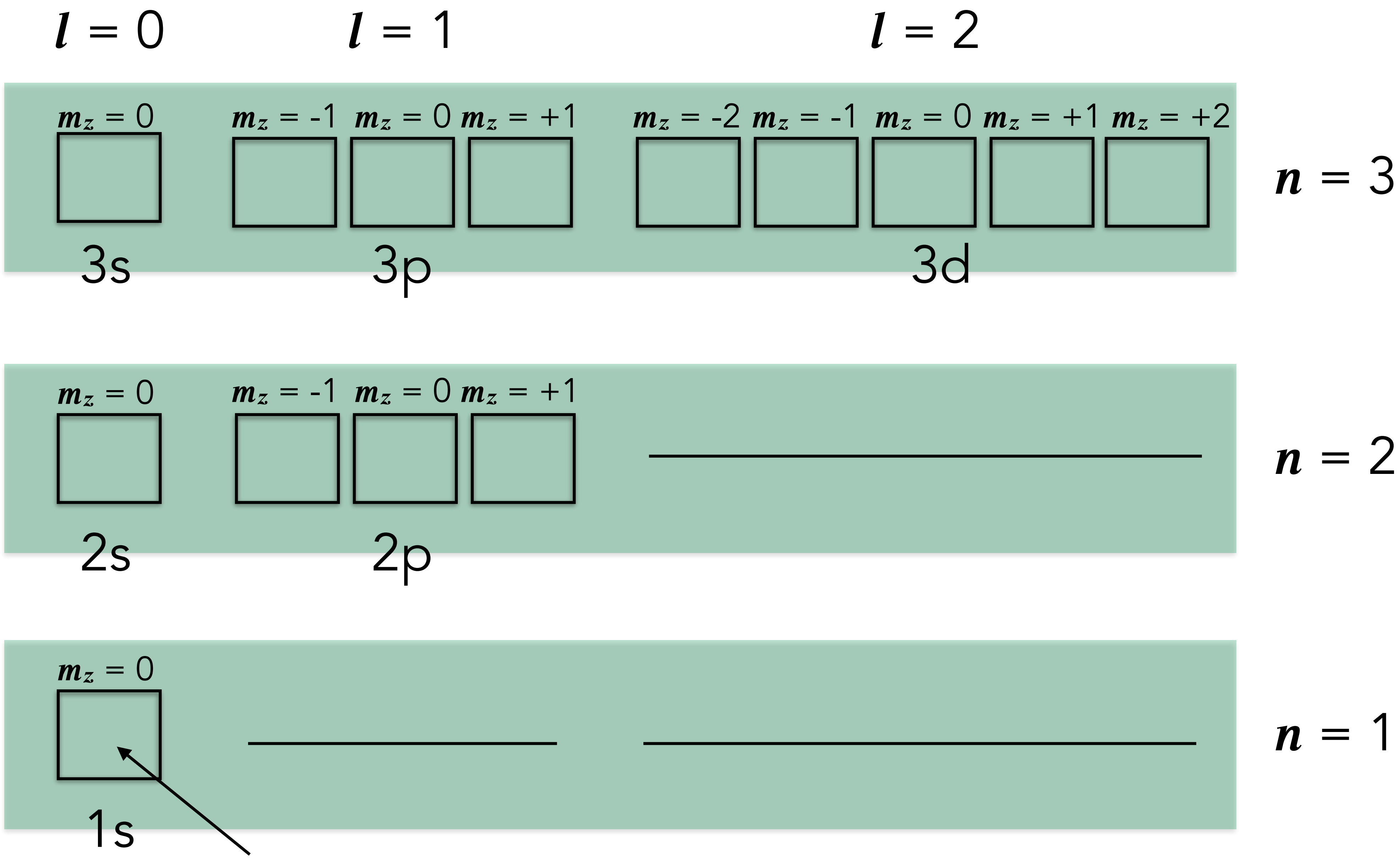
How do we arrange e- in a multi-electron atom?

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, …)



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

$n = 3$

$m_z = 0$

3s

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

3p

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

3d

$n = 2$

$m_z = 0$

2s

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

2p

$n = 1$

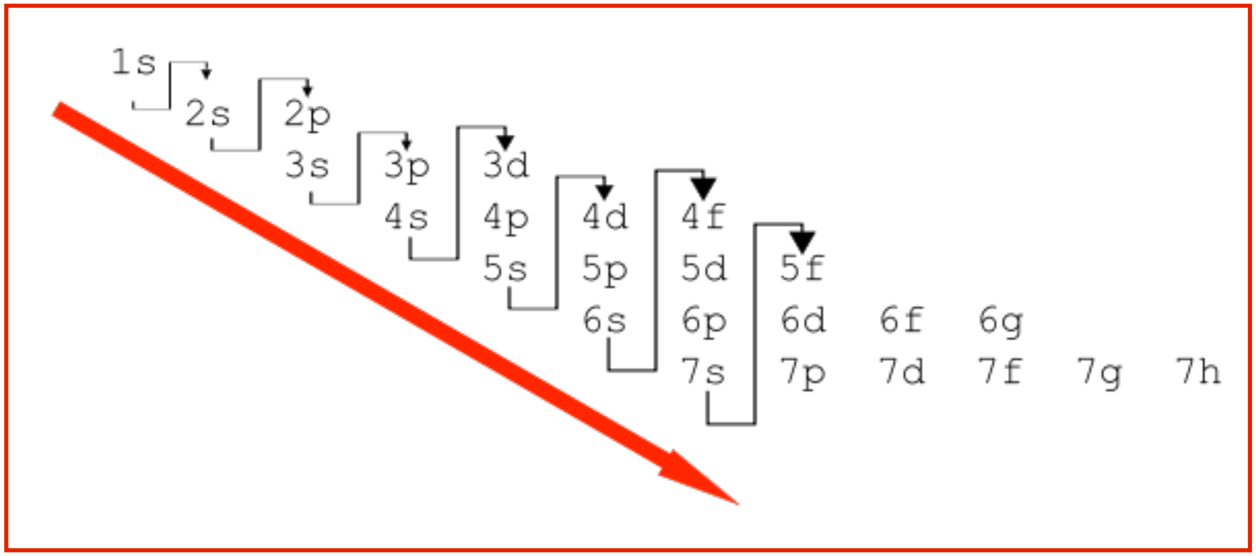
$m_z = 0$

1s

Can put 2 e- in each box: ↑↓

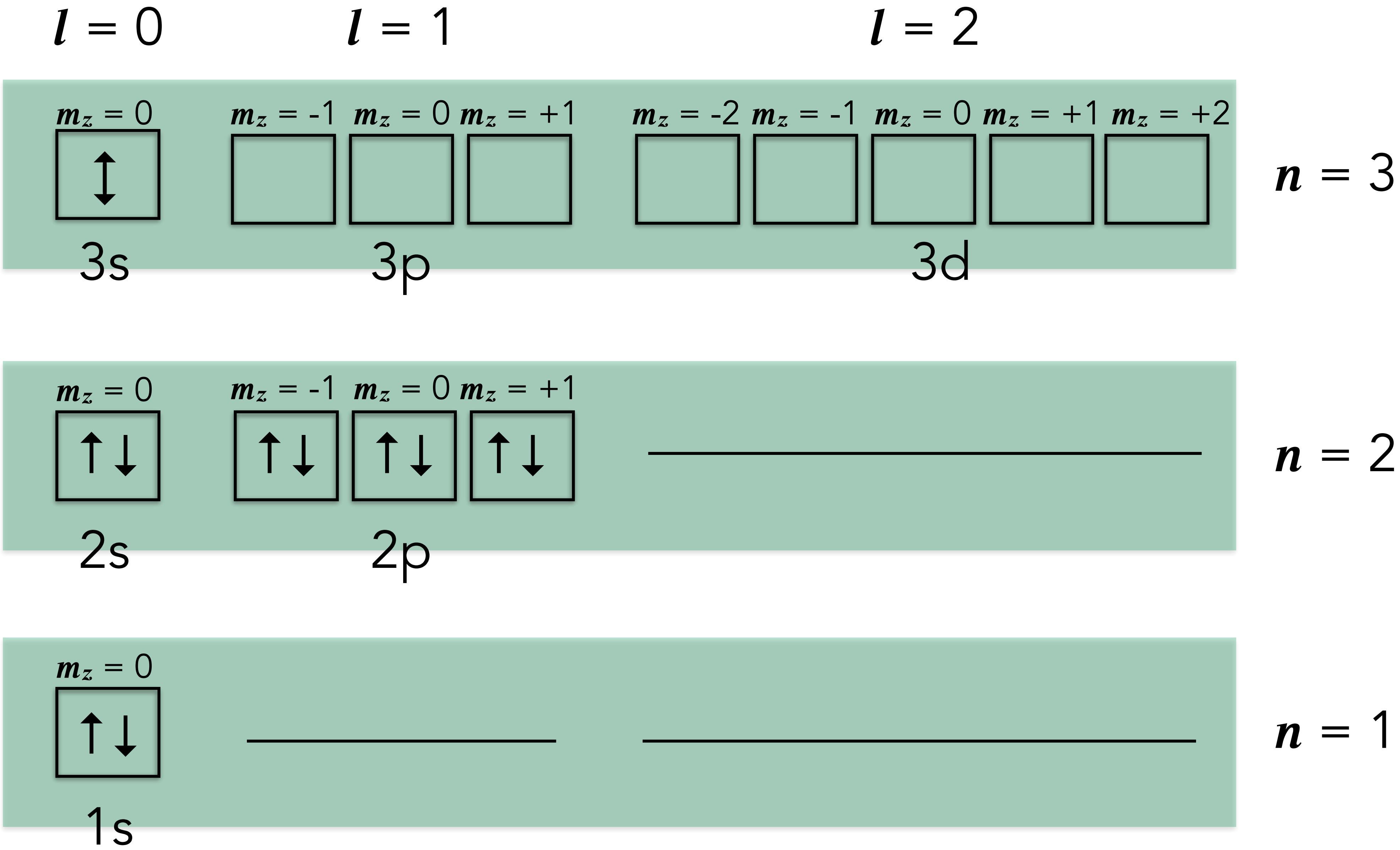
∴ degeneracy of subshell = $2(2l+1)$

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



Number of electrons in each subshell listed with

$2p^2$



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

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

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 $n = 1$

Lets build the ground state of Na: 11 electrons

→ $1s^2\ 2s^2\ 2p^6\ 3s$

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

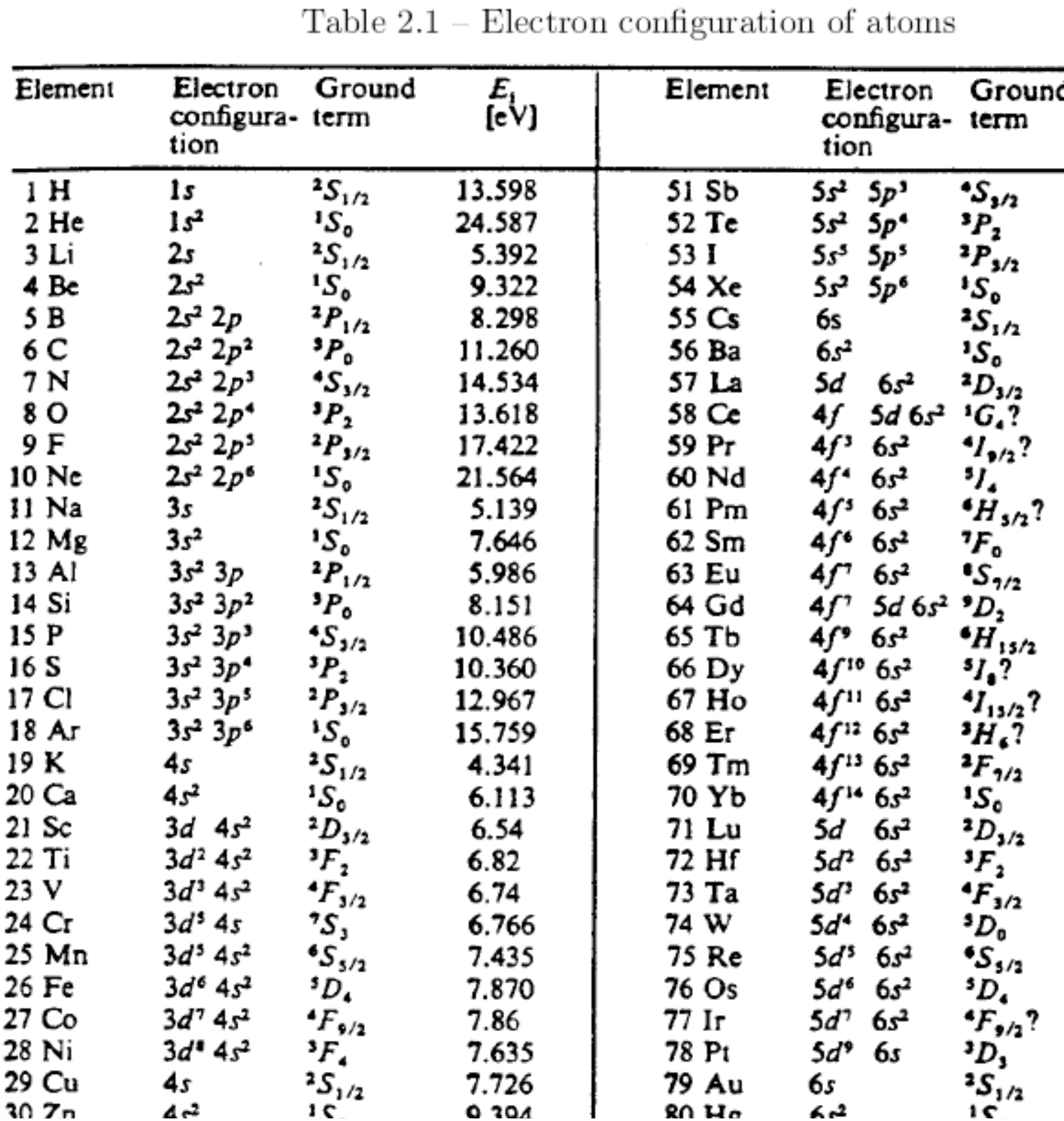
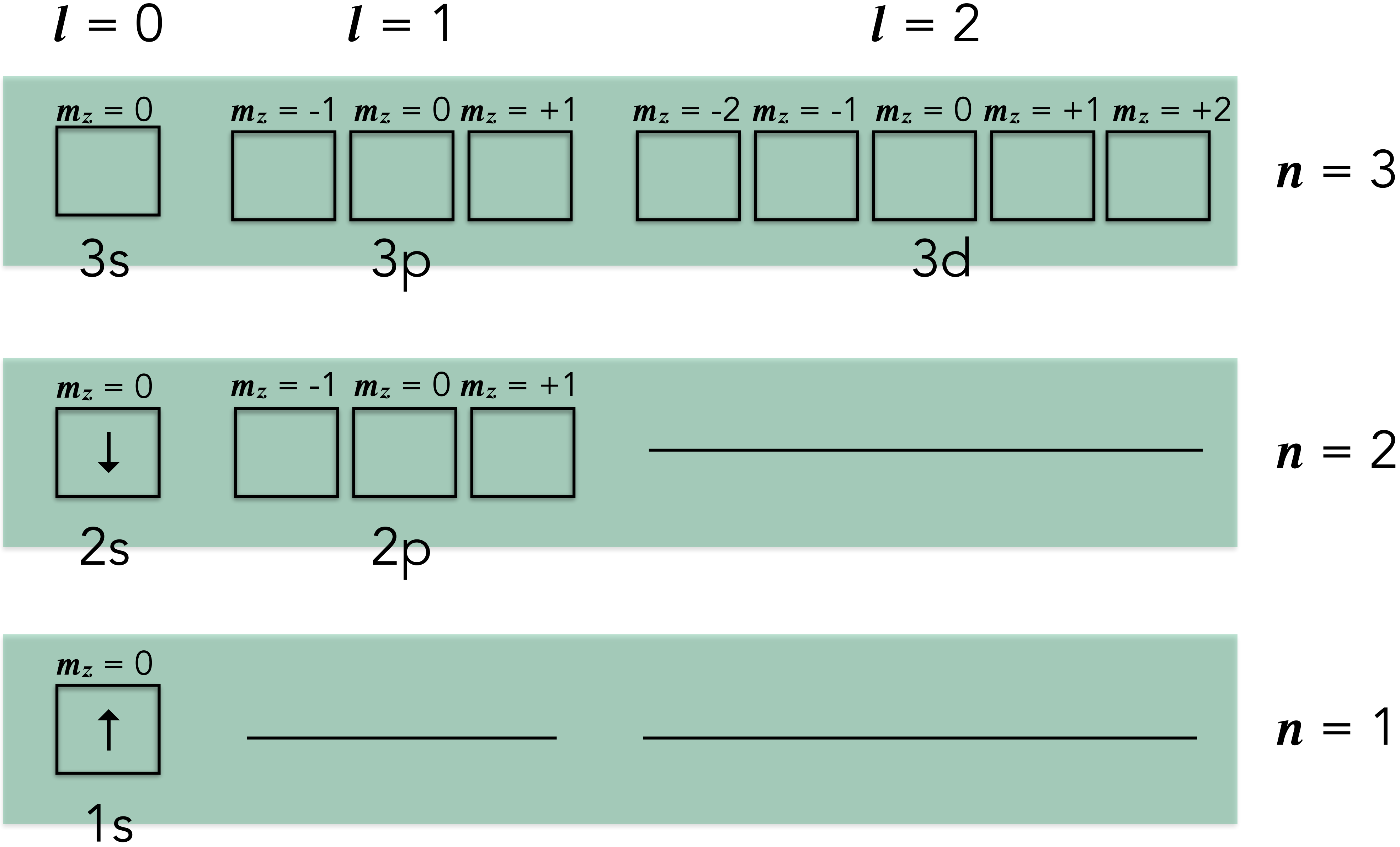


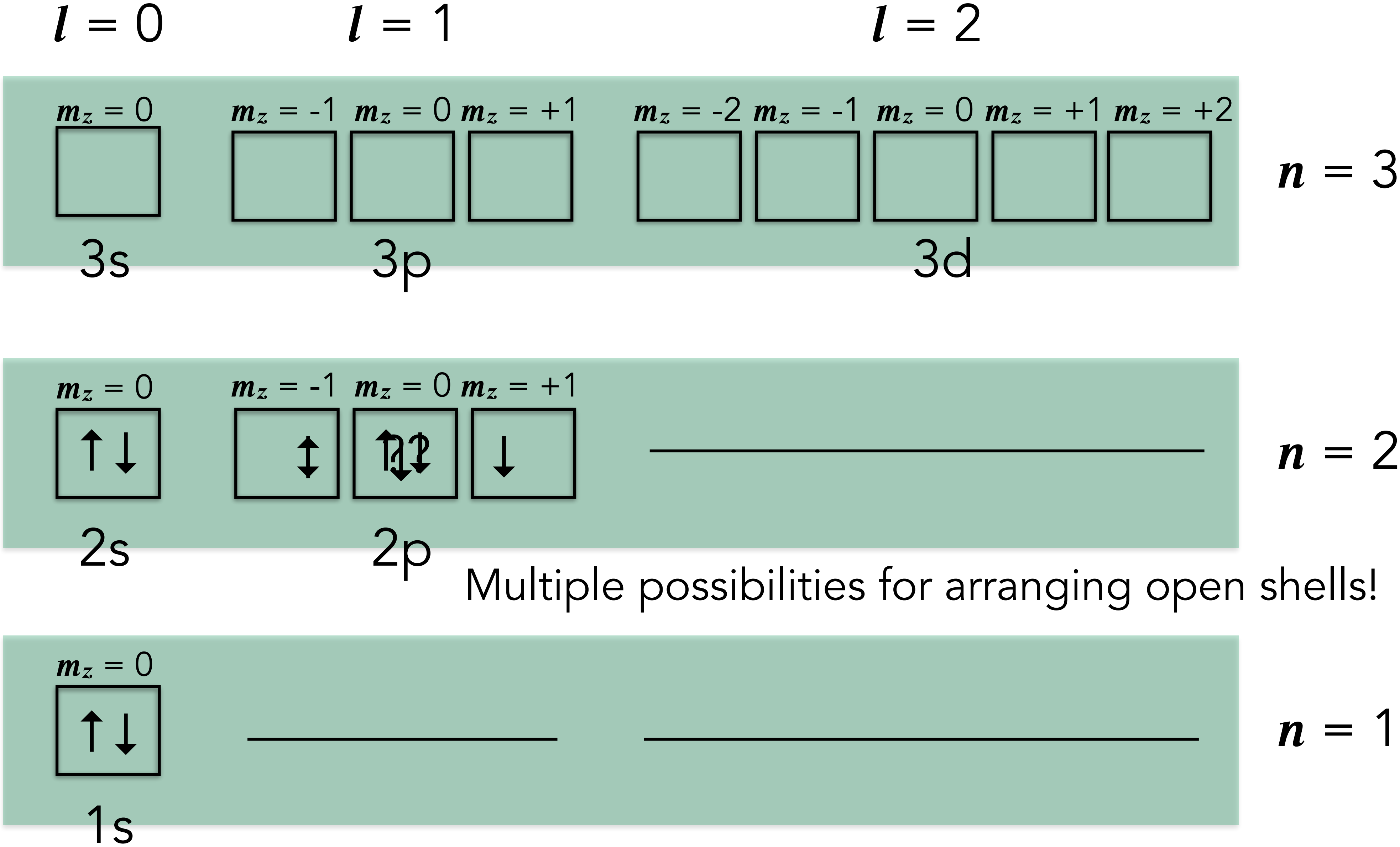
Table 2.1 – Electron configuration of atoms

Element	Electron configuration	Ground term	E_i [eV]	Element	Electron configuration	Groun
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



Excited state of He

→1s 2s



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

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

3s 3p 3d $n = 3$

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

2s 2p $n = 2$

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

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

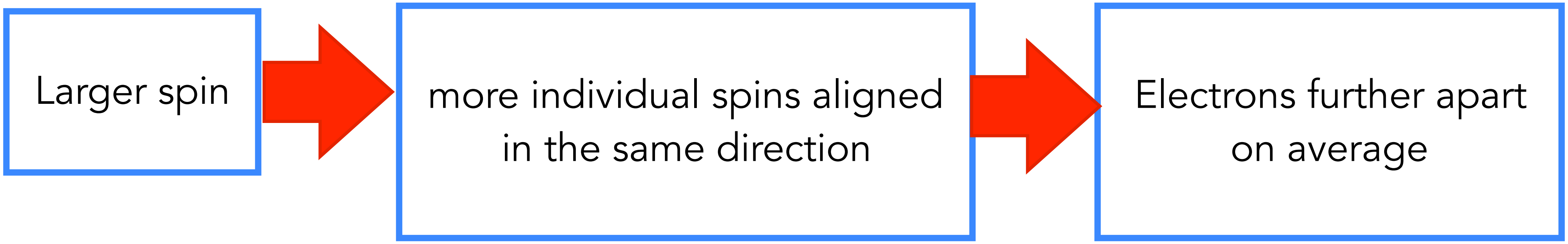
$$\mathbf{S} = \sum_{\mathrm{i}} \mathbf{s}_{\mathrm{i}}$$

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

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 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

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

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

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

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

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

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:

3p e-

2p e-

(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 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 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)~~

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

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

^{3}D has L = 2 ($\boldsymbol{m_z}$ = 2, 1, 0, -1, -2) and S=1 ($\boldsymbol{m}_s$ = 1, 0, -1)

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

Possible Terms for 2 equivalent 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)

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

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

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

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

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

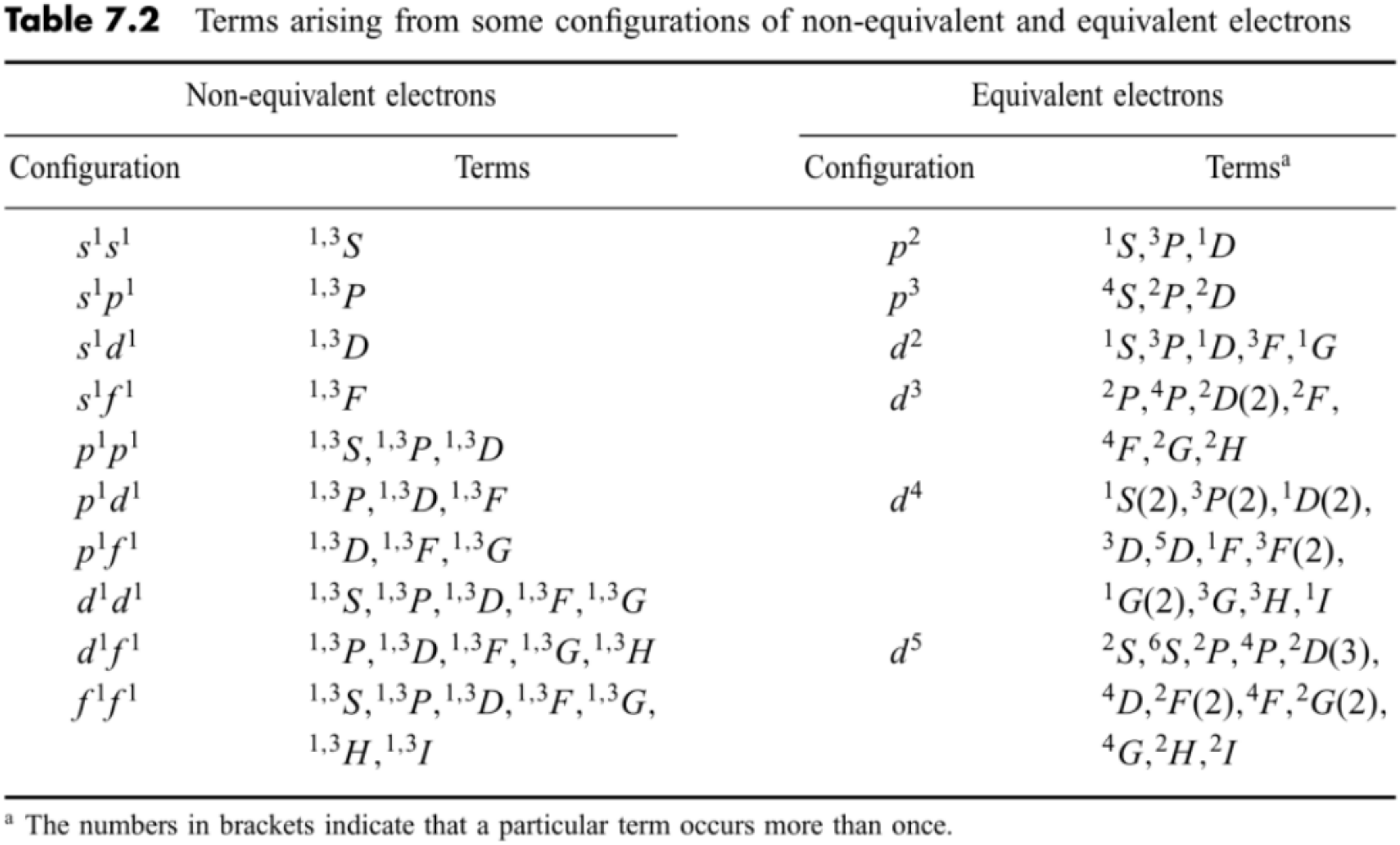


Table 7.2 Terms arising from some configurations of non-equivalent and equivalent electrons

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

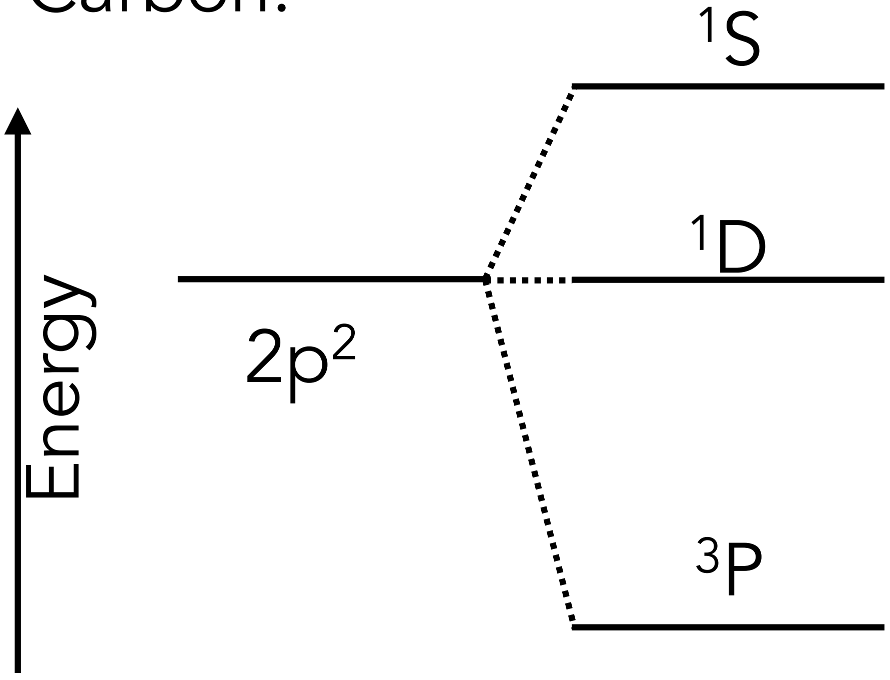
[a] The numbers in brackets indicate that a particular term occurs more than once.

from *Modern Spectroscopy* by Hollas

Energy Levels ⟷ Terms

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

Carbon:



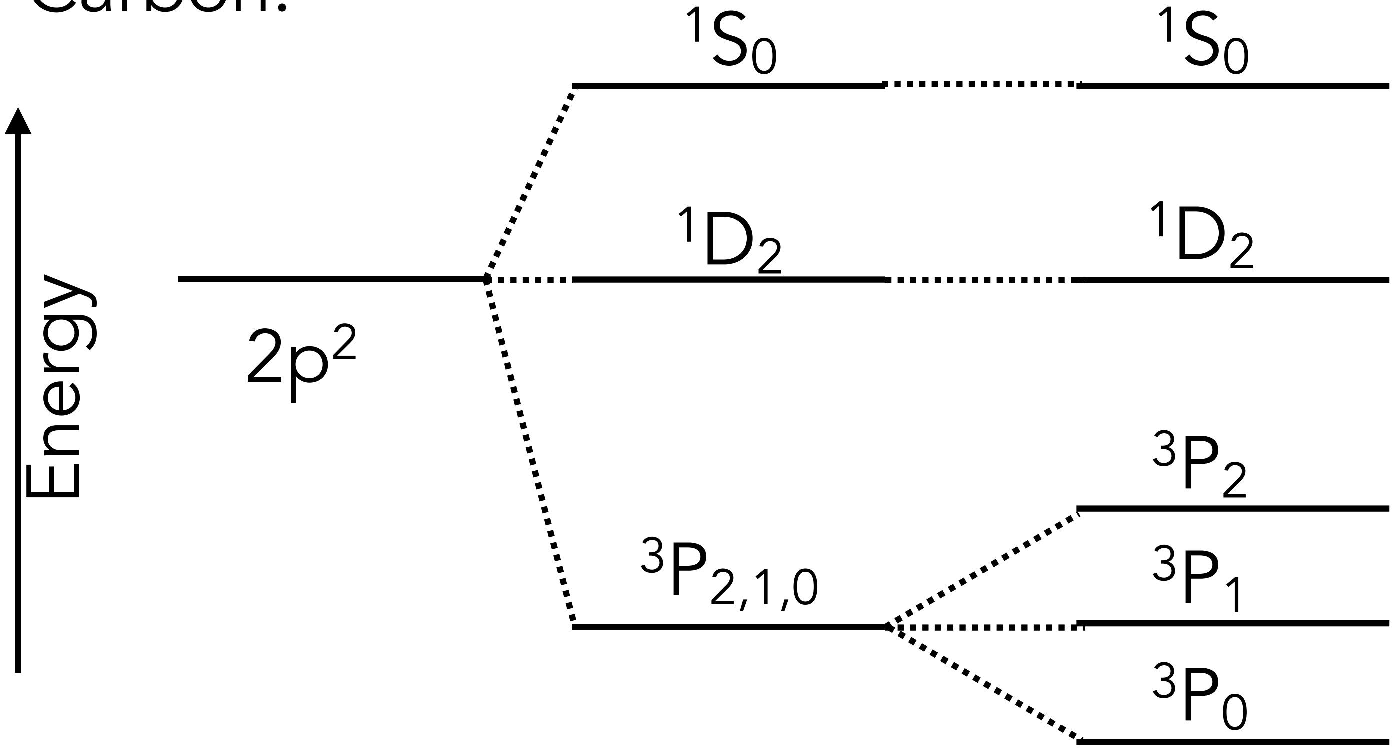
"Hund's Rules"

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

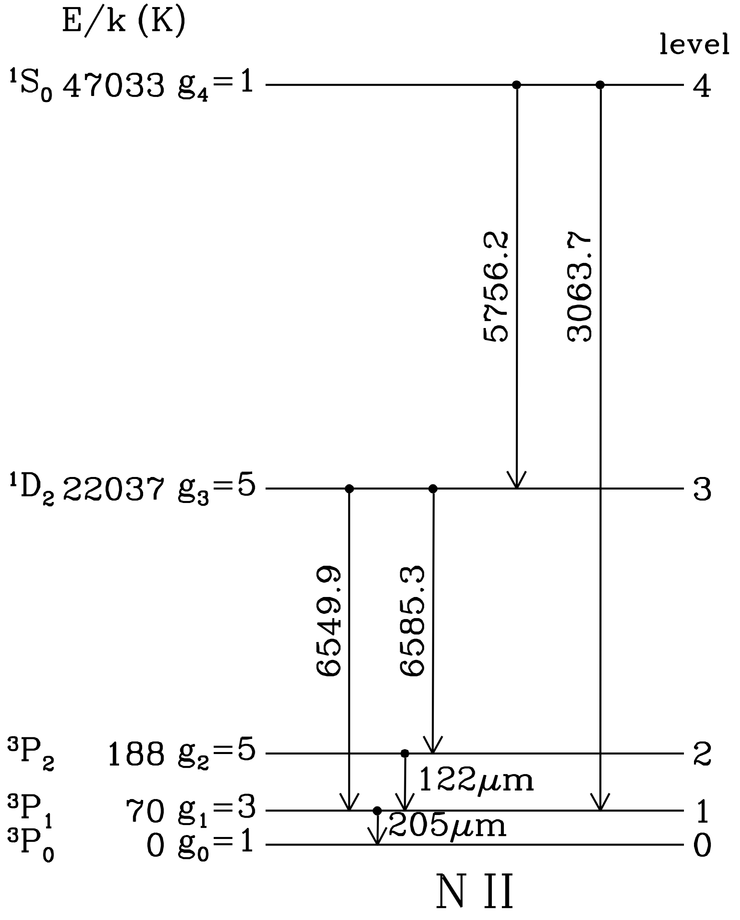
$${}^{2\mathbf{S}+1}\mathcal{L}^{p}_{\mathbf{J}}$$

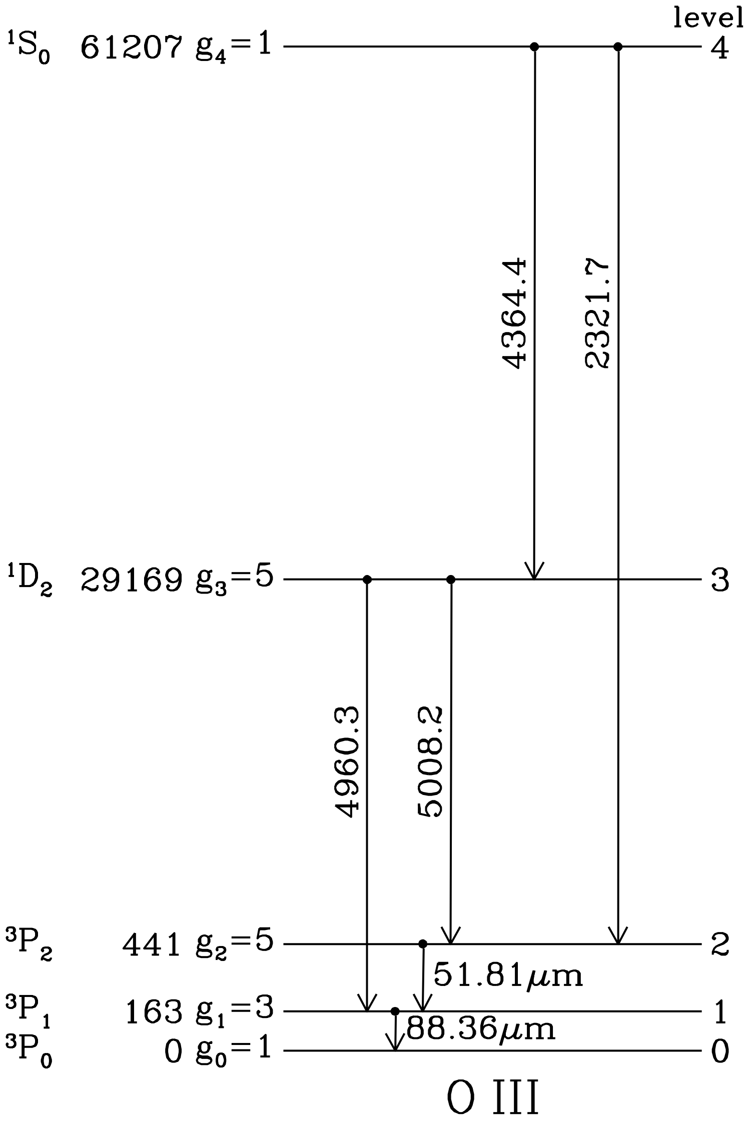
Carbon:



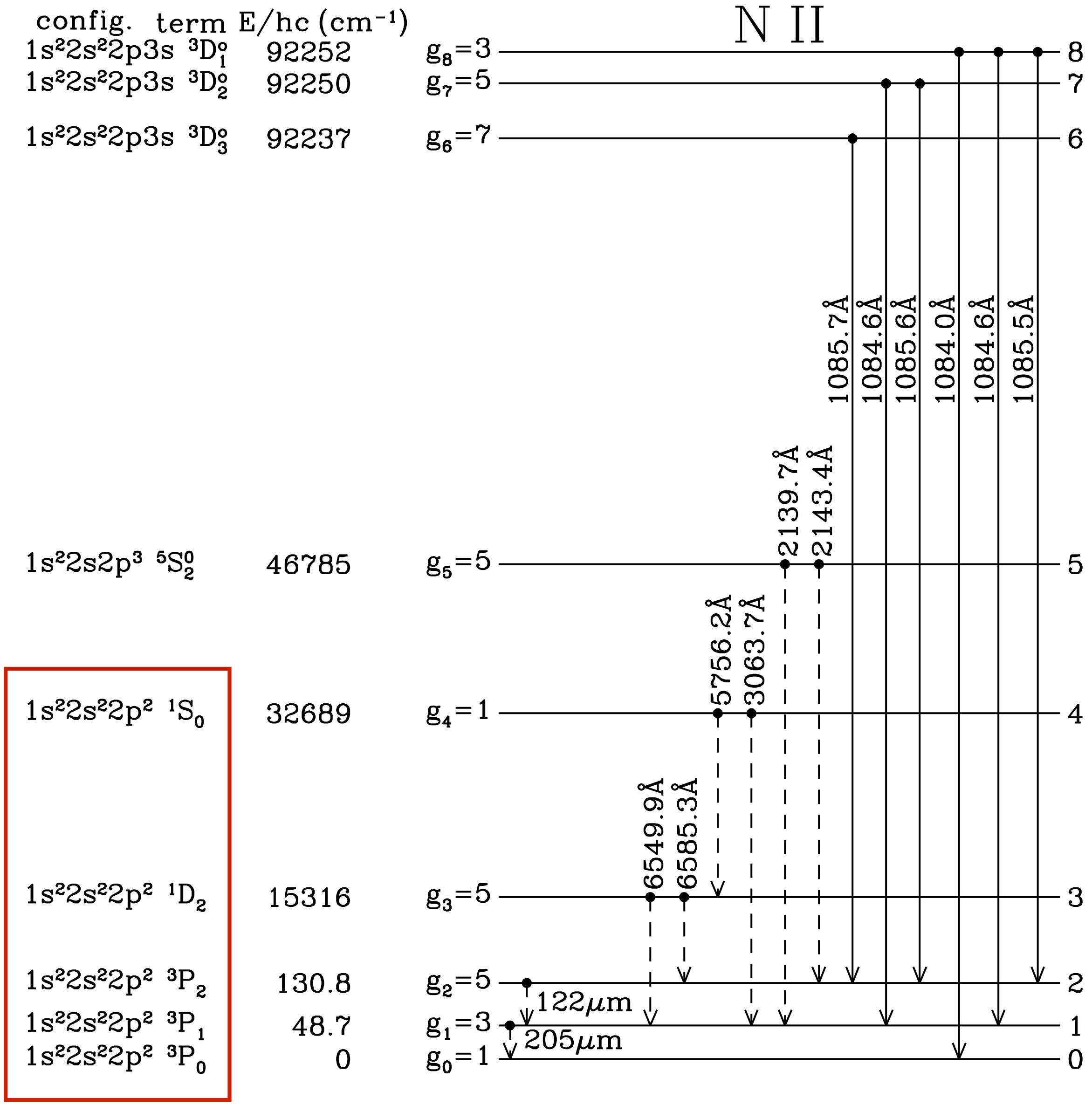
3) Higher J = higher energy if shell is less than half full (opposite otherwise).

Other examples of np^2 ground state configurations





First nine energy levels for 6 electron config, eg NII



ground

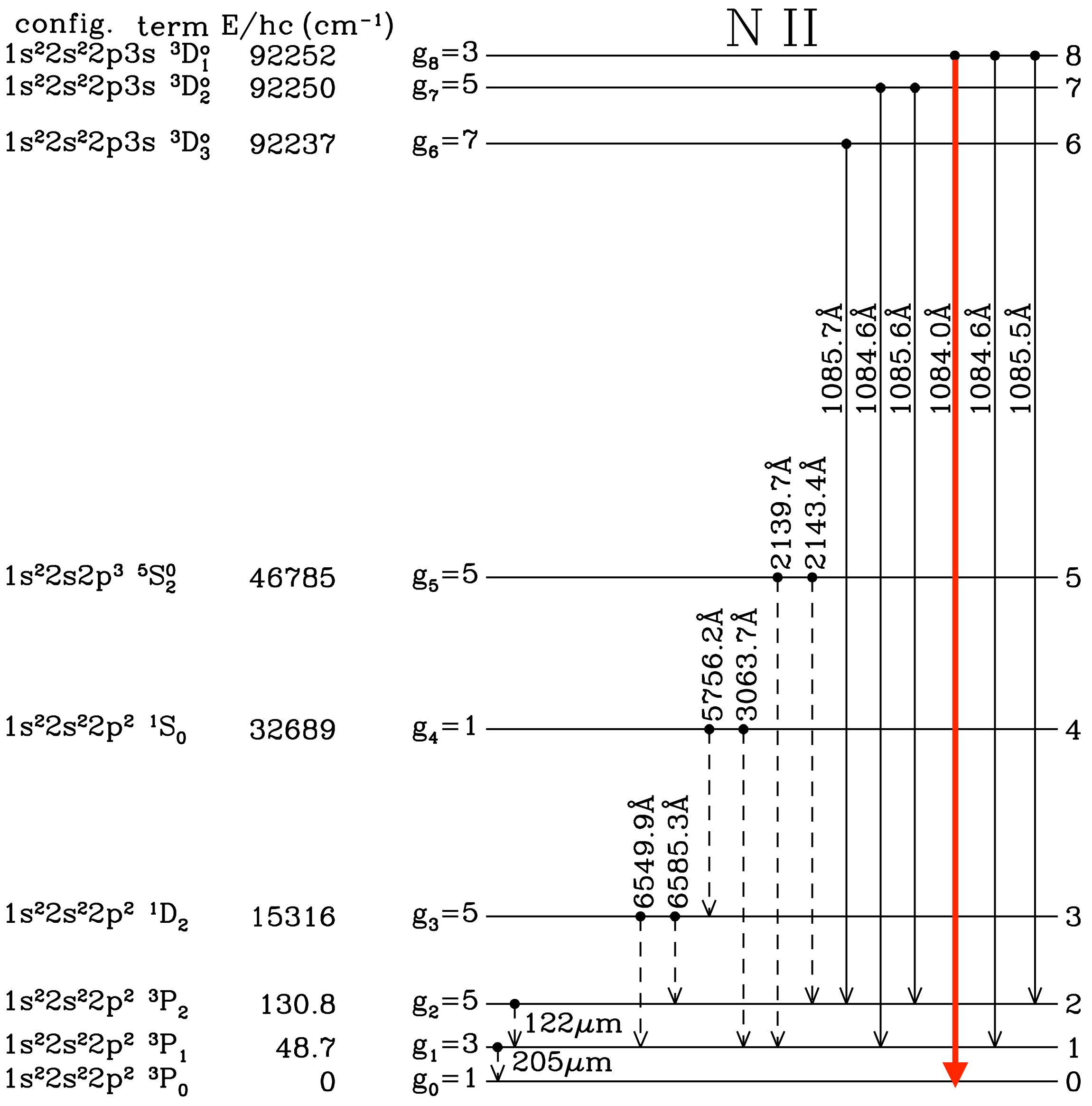
Selection Rules for Transitions

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 $\boldsymbol{nl}$ changes with $\Delta \boldsymbol{l} = \pm 1$ 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

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

NII 1084.0 Å $^3P_0$ - $^3D_1^o$



config.	term	E/hc (cm⁻¹)		
$1s^22s^22p3s$	$^3D_1^o$	92252	$g_8=3$	8
$1s^22s^22p3s$	$^3D_2^o$	92250	$g_7=5$	7
$1s^22s^22p3s$	$^3D_3^o$	92237	$g_6=7$	6
$1s^22s2p^3$	$^5S_2^o$	46785	$g_5=5$	5
$1s^22s^22p^2$	$^1S_0$	32689	$g_4=1$	4
$1s^22s^22p^2$	$^1D_2$	15316	$g_3=5$	3
$1s^22s^22p^2$	$^3P_2$	130.8	$g_2=5$	2
$1s^22s^22p^2$	$^3P_1$	48.7	$g_1=3$	1
$1s^22s^22p^2$	$^3P_0$	0	$g_0=1$	0

✓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 $\Delta \boldsymbol{l} = 0$

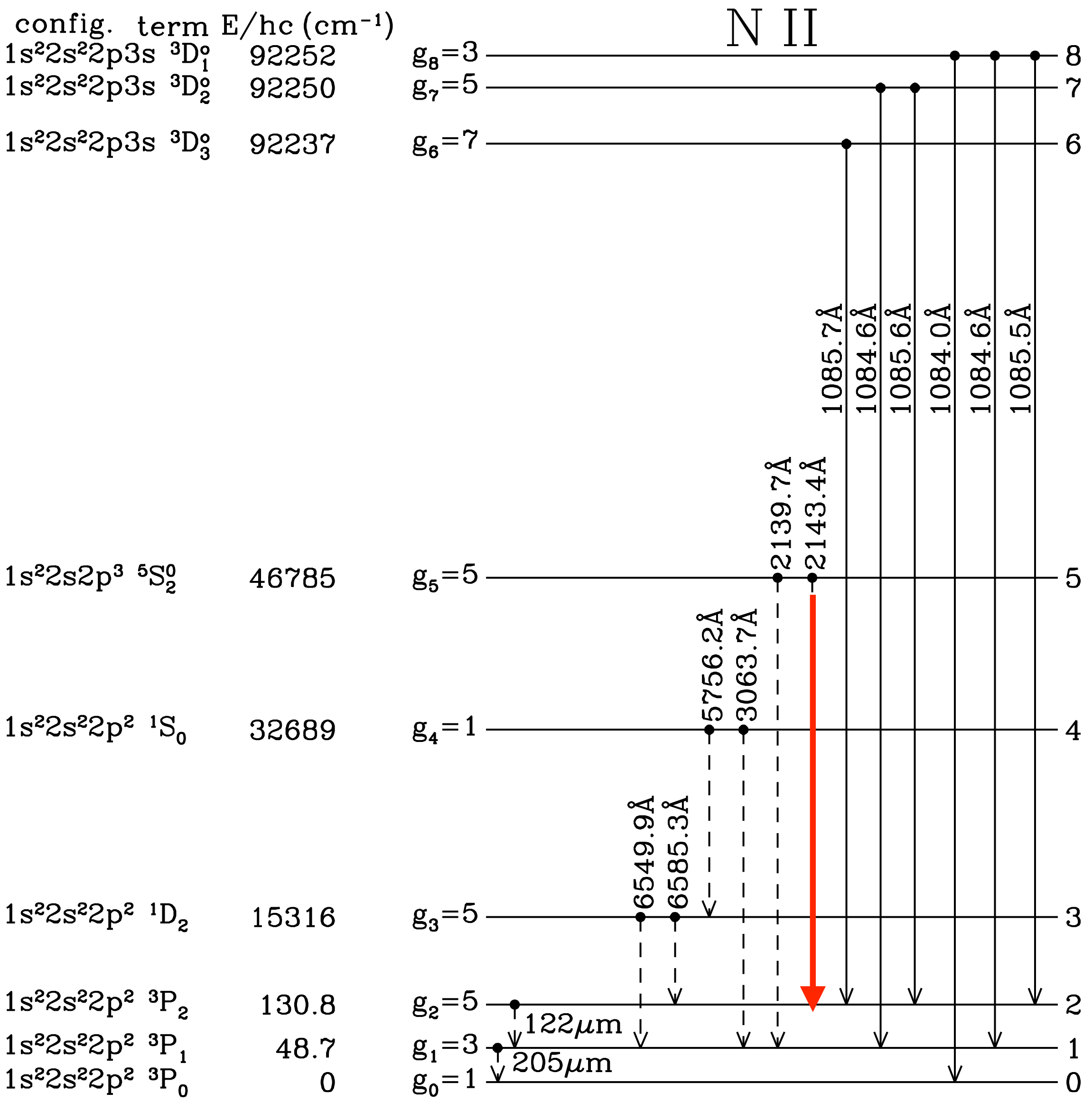
$$A_{ul} = 2.18 \times 10^8 \text{ s}^{-1}$$

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

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) $\Delta J = 0, \pm 1$, 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 $\Delta l = 0$

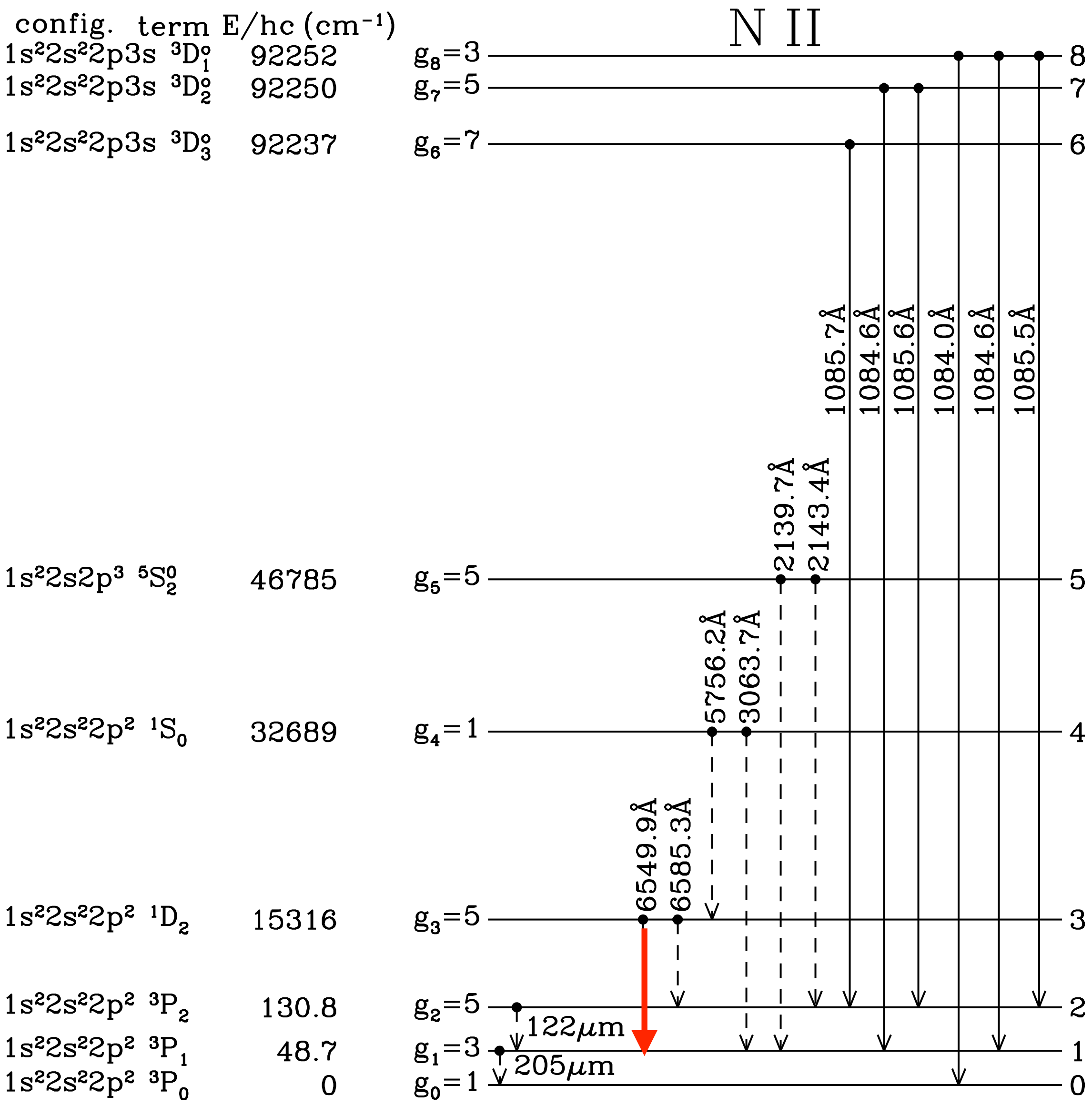
$$A_{ul} = 1.27 \times 10^2\ s^{-1}$$

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

[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 $\Delta \boldsymbol{l} = 0$

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

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

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 B_{lu}
so the line is generally optically thin

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