H. Periodic Table

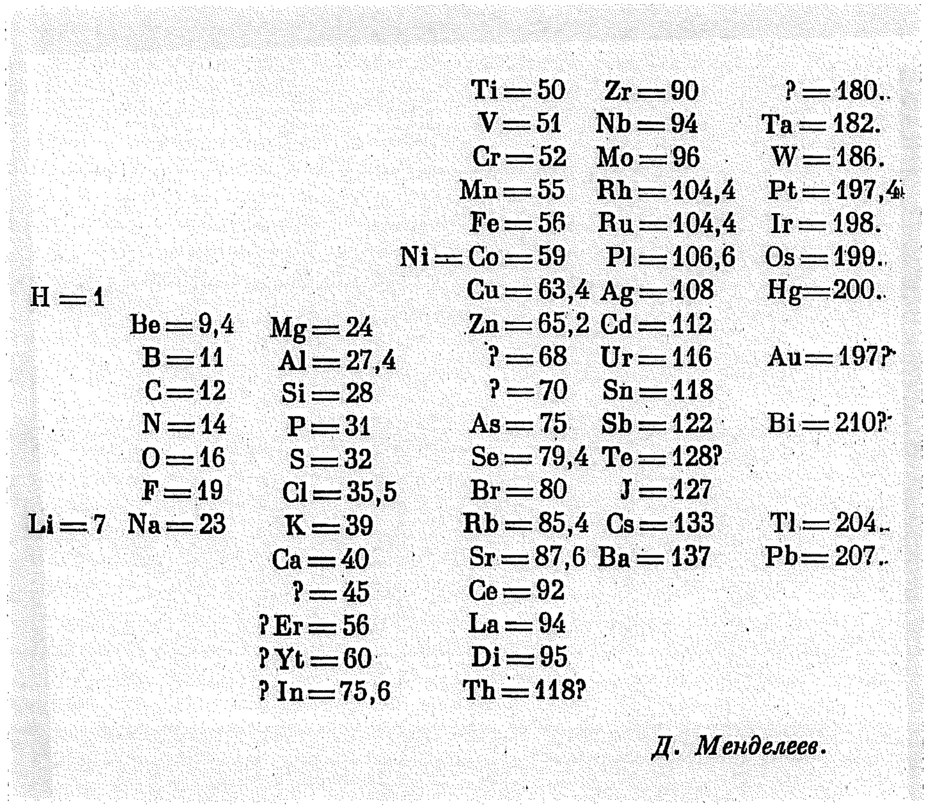
- Schrödinger Equation + $\underbrace{\text{Independent Particle Approximation}}_{\text{atomic orbitals}}$

  + Pauli Exclusion Principle

  Explain much physics of atoms and the periodic table

- Ground state:

  fill electrons into atomic orbitals according to Pauli Exclusion Principle



			Ti = 50	Zr = 90	? = 180.
			V = 51	Nb = 94	Ta = 182.
			Cr = 52	Mo = 96	W = 186.
			Mn = 55	Rh = 104,4	Pt = 197,4
			Fe = 56	Ru = 104,4	Ir = 198.
			Ni = Co = 59	Pl = 106,6	Os = 199.
H = 1			Cu = 63,4	Ag = 108	Hg = 200.
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112	
	B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?
	O = 16	S = 32	Se = 79,4	Te = 128?	
	F = 19	Cl = 35,5	Br = 80	J = 127	
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204.
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207.
		? = 45	Ce = 92		
		? Er = 56	La = 94		
		? Yt = 60	Di = 95		
		? In = 75,6	Th = 118?		

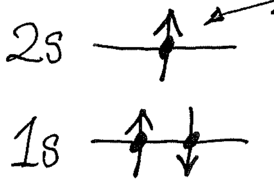
Д. Менделеев.

Mendeleev's original February 1869 publication of his short-form periodic system, entitled "An Attempt at a System of Elements, Based on Their Atomic Weight and Chemical Affinity."

Mendeleev 1869 version

2019 is the International Year of the Periodic Table
(as declared by the United Nations)

Lithium ($Z=3$)



can be up or down

[filled $\underbrace{\text{"1s shell"}}_{\text{"spins cancelled" in closed shell}}$ (or closed shell)]

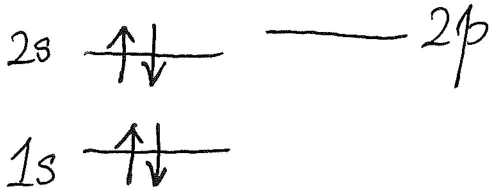
- $\underbrace{\text{1s electrons}}_{\text{not involved in chemistry}}$ are $\underbrace{\text{tightly bound}}_{\text{see } Z=3 \ (+3e \text{ nucleus})}$
- 2s electron is much less tightly bound (screening effect of 1s electrons)

  ⇒ $\underbrace{\text{easier}}$ to set the 2s electron free

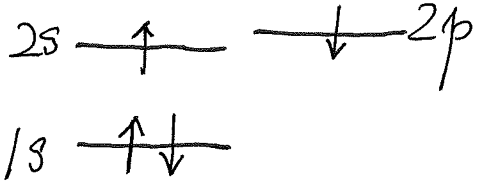
  ↳ smaller $\underbrace{\text{ionization energy}}_{\text{energy to turn lithium atom into } Li^+ \text{ ion.}}$ (~5.4 eV) than H and He atoms

- $1s^2\,2s^1$ Term Symbol: ${}^2S_{1/2}$ (for ${}^{2S+1}L_J$)

Beryllium (Z = 4)



Ground state



(schematic)

First excited state

- Term Symbol

$$^1S_0$$

All spins paired up

- $S = 0 \Rightarrow 2S+1 = 1$ (superscript)
- S-states involved ($L = 0$, thus S)
- $J = 0$ (subscript)

- don't need much energy to excite (2.7 eV) to first excited state
- The lonely 2p and 2s electrons can form chemical bonds with other atom

∴ Chemically active

Boron to Neon ($Z=5$ to $Z=10$) [filling 2p states]

- Boron ($Z=5$): $1s^2\ 2s^2\ 2p^1$ Term Symbol: $^2P_{1/2}$

$$\overset{1s^2 2s^2 2p^1}{B},\ C,\ N,\ O,\ F,\ \overset{1s^2 2s^2 2p^6}{Ne}$$

- Florine ($Z=9$): F^- ion has $2p^6$ closed shell structure

  F^- ion has lower energy than F atom!

  $\Rightarrow$ $\underbrace{\text{give out energy}}_{\text{electron affinity}}$ when F catches an electron to form F^-

  electron affinity [3.4 eV for Florine]

- Quantum Mechanically, need to do two calculations (one for $\hat{F}$, one for $\hat{F}^-$) to get electron affinity

  different Hamiltonians

Aside: What to learn in more advanced Atomic Physics Courses?

Carbon: $1s^2\ 2s^2\ 2p^2$

$2p$ — — — — — — $m_\ell = 1, 0, -1$

$m_s = +\frac{1}{2}, -\frac{1}{2}$

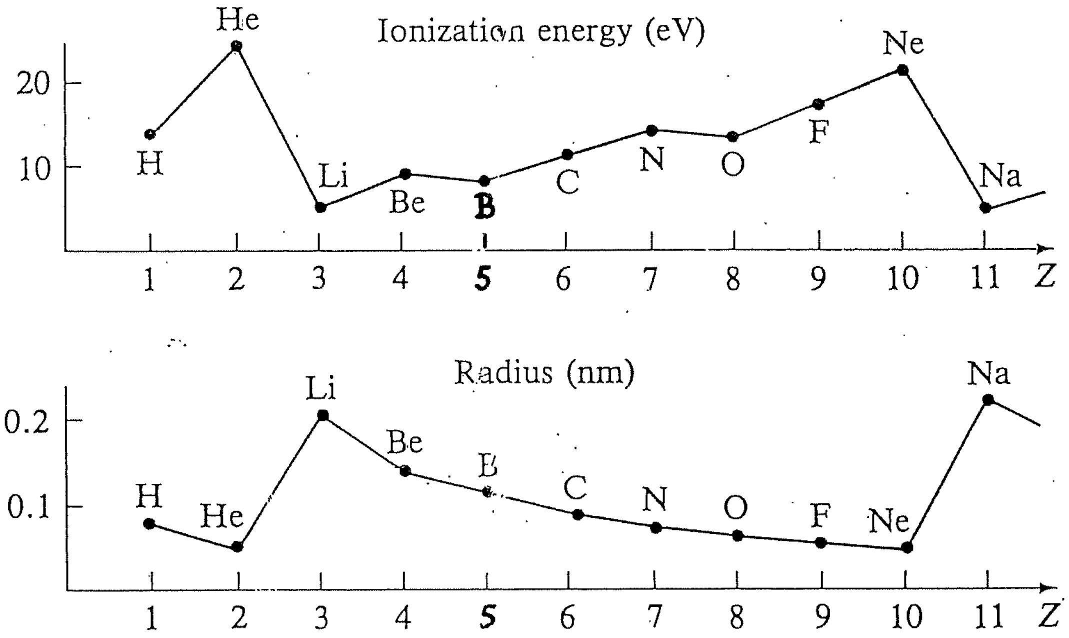
How to put two electrons to achieve lowest energy?

[there are $15 = \frac{6!}{2!4!}$ ways, which has lowest energy?]

Idea: $\underbrace{\hat{H}_{atom} \neq \text{IPA}}$

difference becomes perturbation

results summarized as Hund's rules



The ionization energies and atomic radii of the first 11 elements.

Both quantities can also be calculated by QM (Hartree-Fock)

- Ionization energy of atoms shows periodic behaviour

e.g. Na has low ionization energy

Chemistry of sodium

(3s electron sees screened Z_{eff}) (3s farthest away)

- Helium behaves like Ne [both are closed-shell atoms]
- Li behaves like Na $\underbrace{\text{[closed shell + 1 electron]}}_{\text{alkali metals}}$,

The Other Elements

Electron configurations of the ground states of the first 18 elements.

First shell	Second shell	Third shell
$_1$H : $1s^1$	$_3$Li : $1s^22s^1$	$_{11}$Na : $1s^22s^22p^63s^1$
$_2$He : $1s^2$	$_4$Be : $1s^22s^2$	$_{12}$Mg : $1s^22s^22p^63s^2$
	$_5$B : $1s^22s^22p^1$	$_{13}$Al : $1s^22s^22p^63s^23p^1$
	$_6$C : $1s^22s^22p^2$	$_{14}$Si : $1s^22s^22p^63s^23p^2$
	$_7$N : $1s^22s^22p^3$	$_{15}$P : $1s^22s^22p^63s^23p^3$
	$_8$O : $1s^22s^22p^4$	$_{16}$S : $1s^22s^22p^63s^23p^4$
	$_9$F : $1s^22s^22p^5$	$_{17}$Cl : $1s^22s^22p^63s^23p^5$
	$_{10}$Ne : $1s^22s^22p^6$	$_{18}$Ar : $1s^22s^22p^63s^23p^6$

Potassium (Z = 19)

19th electron → $\underbrace{\text{3d or 4s ?}}_{\text{have to do a QM calculation}}$

turns out 4s level is slightly lower in energy

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

[The outer electrons are usually referred to as the valence electrons. (價電子)

They govern the valence, e.g. K^+, and hence the chemistry.]

Calcium (Z = 20)

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

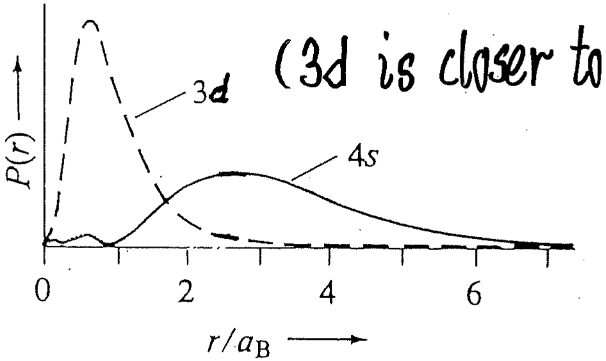
Transition Metals (Filling in 3d states (10 of them))

Sc Ti V Cr Mn Fe Co Ni Cu Zn

They have similarities.

Why?

- Chemistry is usually determined by the outer (4s) electrons



(3d is closer to nucleus)

Typical radial probability distributions for a $3d$ and $4s$ electron in the transition elements ${}_{21}$Sc through ${}_{30}$Zn. Note how the $4s$ distribution peaks more than four times farther out than the $3d$. For this reason it is the $4s$ electrons that determine the chemical properties of the transition metals.

- Transition Metals differ only in number of 3d electrons
  ⇒ they have similar chemical properties

3d elements are important magnetic materials

- How to fill in 5 electrons in d-orbitals?

$$\begin{array}{lccccc} \text{e.g. } 3d^5 & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ (\ell=2)\,[\text{d states}]\ m_\ell: & -2 & -1 & 0 & +1 & +2 \end{array}$$

Maximize the total spin S quantum number as allowed by Pauli Principle

[as many parallel spins are possible]

This is $\underbrace{\text{Hund's rule}}_{\text{"rules" summarizing results of many QM calculations}}$ (Hund's rule #1)

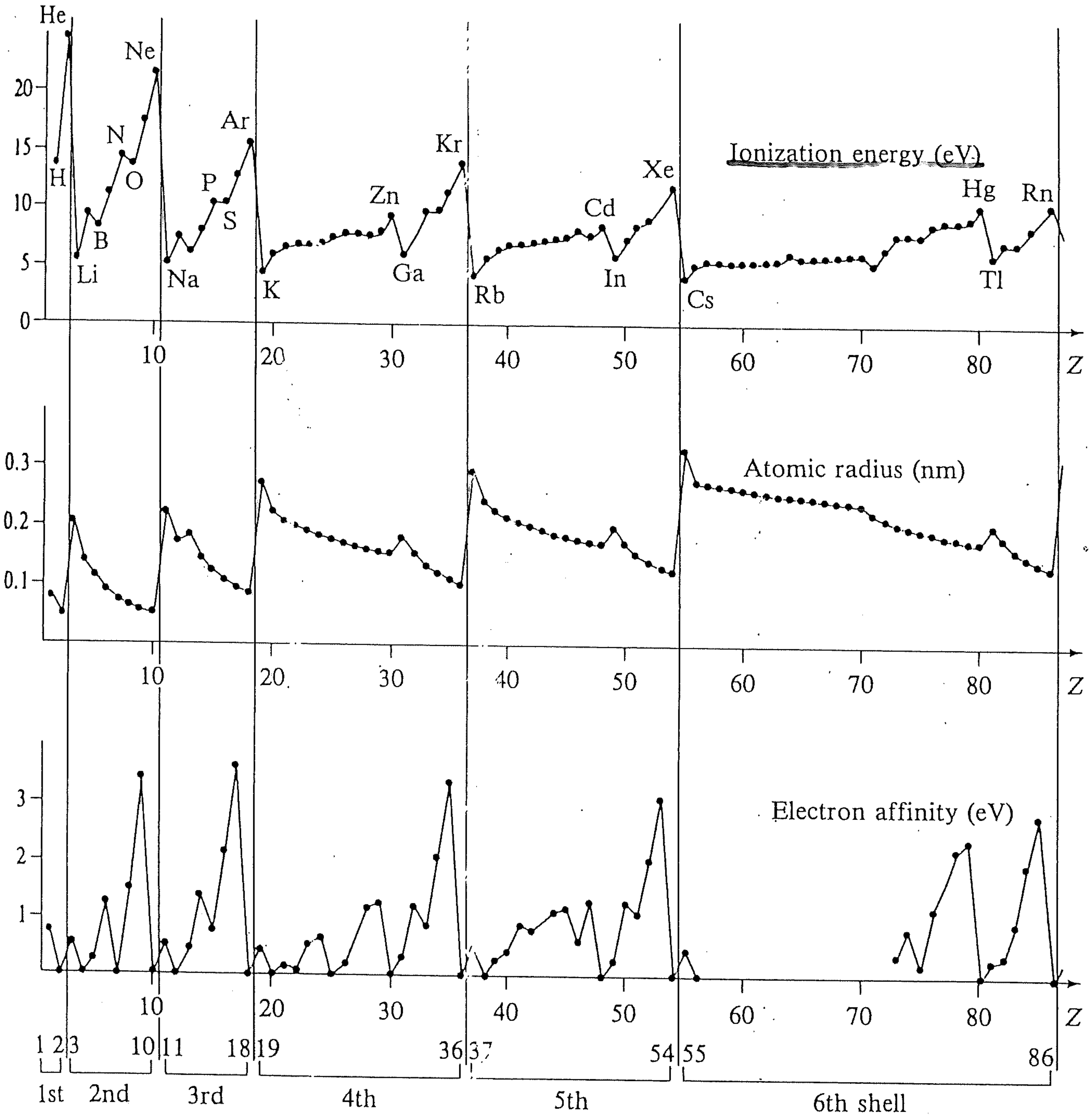
- This is how some atoms acquire a NET magnetic dipole moment
- When magnetic moments of different atoms tend to align (at low temperature), we have ferromagnetism (note: originated from spin (entirely quantum))

After the transition metals,

$$\underbrace{\text{Ga} \quad \text{Ge} \quad \text{As} \quad \text{Se}}_{\text{important elements in semiconductor physics/industry}} \quad \text{Br} \quad \text{Kr} \ (Z=36) \ \text{fill up 4p states}$$

- Si, Ge (elemental semiconductors)
- GaAs, InP (compound III-V semiconductors)
- HgTe, CdTe, CdSe (compound II-VI semiconductors)

Periodicity in physical properties of elements



Ionization energy, atomic radius, and electron affinity as functions of atomic number Z. The vertical lines separate complete shells. The electron affinities for elements 57 through 72 have not been measured.

IUPAC Periodic Table of the Elements

Key:

atomic number
Symbol
name
conventional atomic weight
standard atomic weight

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** hydrogen 1.008 [1.0078, 1.0082]																	2 **He** helium 4.0026
3 **Li** lithium 6.94 [6.938, 6.997]	4 **Be** beryllium 9.0122											5 **B** boron 10.81 [10.806, 10.821]	6 **C** carbon 12.011 [12.009, 12.012]	7 **N** nitrogen 14.007 [14.006, 14.008]	8 **O** oxygen 15.999 [15.999, 16.000]	9 **F** fluorine 18.998	10 **Ne** neon 20.180
11 **Na** sodium 22.990	12 **Mg** magnesium 24.305 [24.304, 24.307]											13 **Al** aluminium 26.982	14 **Si** silicon 28.085 [28.084, 28.086]	15 **P** phosphorus 30.974	16 **S** sulfur 32.06 [32.059, 32.076]	17 **Cl** chlorine 35.45 [35.446, 35.457]	18 **Ar** argon 39.95 [39.792, 39.963]
19 **K** potassium 39.098	20 **Ca** calcium 40.078(4)	21 **Sc** scandium 44.956	22 **Ti** titanium 47.867	23 **V** vanadium 50.942	24 **Cr** chromium 51.996	25 **Mn** manganese 54.938	26 **Fe** iron 55.845(2)	27 **Co** cobalt 58.933	28 **Ni** nickel 58.693	29 **Cu** copper 63.546(3)	30 **Zn** zinc 65.38(2)	31 **Ga** gallium 69.723	32 **Ge** germanium 72.630(8)	33 **As** arsenic 74.922	34 **Se** selenium 78.971(8)	35 **Br** bromine 79.904 [79.901, 79.907]	36 **Kr** krypton 83.798(2)
37 **Rb** rubidium 85.468	38 **Sr** strontium 87.62	39 **Y** yttrium 88.906	40 **Zr** zirconium 91.224(2)	41 **Nb** niobium 92.906	42 **Mo** molybdenum 95.95	43 **Tc** technetium	44 **Ru** ruthenium 101.07(2)	45 **Rh** rhodium 102.91	46 **Pd** palladium 106.42	47 **Ag** silver 107.87	48 **Cd** cadmium 112.41	49 **In** indium 114.82	50 **Sn** tin 118.71	51 **Sb** antimony 121.76	52 **Te** tellurium 127.60(3)	53 **I** iodine 126.90	54 **Xe** xenon 131.29
55 **Cs** caesium 132.91	56 **Ba** barium 137.33	57-71 lanthanoids	72 **Hf** hafnium 178.49(2)	73 **Ta** tantalum 180.95	74 **W** tungsten 183.84	75 **Re** rhenium 186.21	76 **Os** osmium 190.23(3)	77 **Ir** iridium 192.22	78 **Pt** platinum 195.08	79 **Au** gold 196.97	80 **Hg** mercury 200.59	81 **Tl** thallium 204.38 [204.38, 204.39]	82 **Pb** lead 207.2	83 **Bi** bismuth 208.98	84 **Po** polonium	85 **At** astatine	86 **Rn** radon
87 **Fr** francium	88 **Ra** radium	89-103 actinoids	104 **Rf** rutherfordium	105 **Db** dubnium	106 **Sg** seaborgium	107 **Bh** bohrium	108 **Hs** hassium	109 **Mt** meitnerium	110 **Ds** darmstadtium	111 **Rg** roentgenium	112 **Cn** copernicium	113 **Nh** nihonium	114 **Fl** flerovium	115 **Mc** moscovium	116 **Lv** livermorium	117 **Ts** tennessine	118 **Og** oganesson

57 **La** lanthanum 138.91	58 **Ce** cerium 140.12	59 **Pr** praseodymium 140.91	60 **Nd** neodymium 144.24	61 **Pm** promethium	62 **Sm** samarium 150.36(2)	63 **Eu** europium 151.96	64 **Gd** gadolinium 157.25(3)	65 **Tb** terbium 158.93	66 **Dy** dysprosium 162.50	67 **Ho** holmium 164.93	68 **Er** erbium 167.26	69 **Tm** thulium 168.93	70 **Yb** ytterbium 173.05	71 **Lu** lutetium 174.97
89 **Ac** actinium	90 **Th** thorium 232.04	91 **Pa** protactinium 231.04	92 **U** uranium 238.03	93 **Np** neptunium	94 **Pu** plutonium	95 **Am** americium	96 **Cm** curium	97 **Bk** berkelium	98 **Cf** californium	99 **Es** einsteinium	100 **Fm** fermium	101 **Md** mendelevium	102 **No** nobelium	103 **Lr** lawrencium

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For notes and updates to this table, see www.iupac.org. This version is dated 1 December 2018.

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United Nations
Educational, Scientific and
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2019 IYPT

International Year
of the Periodic Table
of Chemical Elements

IUPAC

1 December 2018 version

Electronic Configurations of the Elements

Z	Symbol	Ground Configuration	Ionization Energy (eV)
1	H	$1s^1$	13.595
2	He	$1s^2$	24.581
3	Li	[He] $2s^1$	5.390
4	Be	$2s^2$	9.320
5	B	$2s^2 2p^1$	8.296
6	C	$2s^2 2p^2$	11.256
7	N	$2s^2 2p^3$	14.545
8	O	$2s^2 2p^4$	13.614
9	F	$2s^2 2p^5$	17.418
10	Ne	$2s^2 2p^6$	21.559
11	Na	[Ne] $3s^1$	5.138
12	Mg	$3s^2$	7.644
13	Al	$3s^2 3p^1$	5.984
14	Si	$3s^2 3p^2$	8.149
15	P	$3s^2 3p^3$	10.484
16	S	$3s^2 3p^4$	10.357
17	Cl	$3s^2 3p^5$	13.01
18	Ar	$3s^2 3p^6$	15.755
19	K	[Ar] $4s^1$	4.339
20	Ca	$4s^2$	6.111
21	Sc	$3d 4s^2$	6.54
22	Ti	$3d^2 4s^2$	6.83
23	V	$3d^3 4s^2$	6.74
24	Cr	$3d^5 4s$	6.76
25	Mn	$3d^5 4s^2$	7.432
26	Fe	$3d^6 4s^2$	7.87
27	Co	$3d^7 4s^2$	7.86
28	Ni	$3d^8 4s^2$	7.633
29	Cu	$3d^{10} 4s^1$	7.724
30	Zn	$3d^{10} 4s^2$	9.391
31	Ga	$3d^{10} 4s^2 4p^1$	6.00
32	Ge	$3d^{10} 4s^2 4p^2$	7.88
33	As	$3d^{10} 4s^2 4p^3$	9.81
34	Se	$3d^{10} 4s^2 4p^4$	9.75
35	Br	$3d^{10} 4s^2 4p^5$	11.84
36	Kr	$3d^{10} 4s^2 4p^6$	13.996
37	Rb	[Kr] $5s^1$	4.176
38	Sr	$5s^2$	5.692
39	Y	$4d 5s^2$	6.377
40	Zr	$4d^2 5s^2$	6.835
41	Nb	$4d^4 5s^1$	6.881
42	Mo	$4d^5 5s^1$	7.10
43	Tc	$4d^5 5s^2$	7.228
44	Ru	$4d^7 5s^1$	7.365
45	Rh	$4d^8 5s^1$	7.461
46	Pd	$4d^{10}$	8.33
47	Ag	$4d^{10} 5s^1$	7.574
48	Cd	$4d^{10} 5s^2$	8.991
49	In	$4d^{10} 5s^2 5p^1$	5.785
50	Sn	$4d^{10} 5s^2 5p^2$	7.342
51	Sb	$4d^{10} 5s^2 5p^3$	8.639
52	Te	$4d^{10} 5s^2 5p^4$	9.01

[From Serway et al., "Modern Physics"]

AP-IX-⑭

Cont'd

Z	Symbol	Ground Configuration	Ionization Energy (eV)
53	I	$4d^{10}5s^25p^5$	10.454
54	Xe	$4d^{10}5s^25p^6$	12.127
55	Cs	[Xe] $6s^1$	3.893
56	Ba	$6s^2$	5.210
57	La	$5d6s^2$	5.61
58	Ce	$4f5d6s^2$	6.54
59	Pr	$4f^36s^2$	5.48
60	Nd	$4f^46s^2$	5.51
61	Pm	$4f^56s^2$	
62	Fm	$4f^66s^2$	5.6
63	Eu	$4f^76s^2$	5.67
64	Gd	$4f^75d6s^2$	6.16
65	Tb	$4f^96s^2$	6.74
66	Dy	$4f^{10}6s^2$	6.82
67	Ho	$4f^{11}6s^2$	
68	Er	$4f^{12}6s^2$	
69	Tm	$4f^{13}6s^2$	
70	Yb	$4f^{14}6s^2$	6.22
71	Lu	$4f^{14}5d6s^2$	6.15
72	Hf	$4f^{14}5d^26s^2$	7.0
73	Ta	$4f^{14}5d^36s^2$	7.88
74	W	$4f^{14}5d^46s^2$	7.98
75	Re	$4f^{14}5d^56s^2$	7.87
76	Os	$4f^{14}5d^66s^2$	8.7
77	Ir	$4f^{14}5d^76s^2$	9.2
78	Pt	$4f^{14}5d^86s^2$	8.88
79	Au	[Xe, $4f^{14}5d^{10}$] $6s^1$	9.22
80	Hg	$6s^2$	10.434
81	Tl	$6s^26p^1$	6.106
82	Pb	$6s^26p^2$	7.415
83	Bi	$6s^26p^3$	7.287
84	Po	$6s^26p^4$	8.43
85	At	$6s^26p^5$	
86	Rn	$6s^26p^6$	10.745
87	Fr	[Rn] $7s^1$	
88	Ra	$7s^2$	5.277
89	Ac	$6d7s^2$	6.9
90	Th	$6d^27s^2$	
91	Pa	$5f^26d7s^2$	
92	U	$5f^36d7s^2$	4.0
93	Np	$5f^46d7s^2$	
94	Pu	$5f^67s^2$	
95	Am	$5f^77s^2$	
96	Cm	$5f^76d7s^2$	
97	Bk	$5f^86d7s^2$	
98	Cf	$5f^{10}7s^2$	
99	Es	$5f^{11}7s^2$	
100	Fm	$5f^{12}7s^1$	
101	Mv	$5f^{13}7s^2$	
102	No	$5f^{14}7s^2$	
103	Lw	$5f^{14}6d7s^2$	
104	Ku	$5f^{14}6d^27s^2$	

Note: The bracket notation is used as a shorthand method to avoid repetition in indicating inner shell electrons. Thus, [He] represents $1s^2$, [Ne] represents $1s^22s^22p^6$, [Ar] represents $1s^22s^22p^63s^23p^6$, and so on.

Summary

- Quantum Mechanics is key to understand atoms
- Atomic orbitals resulted from reducing (approximating) many-electron problem to single-electron problem
- Pauli Exclusion Principle is a consequence of anti-symmetric requirement of many-electron wavefunctions
- Atomic Orbitals + Pauli Exclusion Principle (both are QM results) explain much physics of atoms and the periodic table

  [physics unaccounted for by IPA gives further details]

Two Asides (Optional)

(1) Many electrons ⇒ many orbital AM's and many spin AM's

How to add them up? Spin-Orbit Interaction?

(2) What are the Hund's rules?

Aside 1: How about Spin-Orbit Interaction in other atoms?

- It is important! Many electrons ⇒ many $\vec{L}_i$ and many $\vec{S}_i$ (i labels electrons)

LS coupling	JJ coupling
1/. Form Total $\vec{L}$ first $\vec{L} = \sum_i \vec{L}_i$	1/. Form $\vec{J}_i$ (total angular momentum of particle i) $\vec{J}_i = \vec{L}_i + \vec{S}_i$
2/. Form Total $\vec{S}$ first $\vec{S} = \sum_i \vec{S}_i$	2/. $\vec{J}_i$ interacts with $\vec{J}_j$
3/. Then $\vec{L}$ and $\vec{S}$ interact	

- Which mechanism is more important?
  - Depends on which element
- Exp't: features in spectrum

Aside 2: Hund's Rules

- E.g. $1s^2\ 2s^2\ 2p^2$ →
  - There are 6 2p-states
  - How to fill two electrons for ground state?
- Each atom is a separate QM problem [each filling is a QM calculation]
- Frederick Hund gave three empirical rules

  [student of Born]

Friedrich Hund (b. 1896) received his Ph.D. in physics from the University of Göttingen in 1922. In 1926 he and Robert Mulliken worked together at Göttingen on the theory of molecular orbitals. Although Hund was not mentioned by the Nobel Prize committee, Mulliken has stated that he would have been glad to share the Nobel Prize with Hund. Hund was professor of theoretical physics at Rostock, Leipzig, Jena, Frankfurt, and Göttingen.

- Values of L, S, J for the states of lowest energy are determined by Hund's rules (HRs). These rules are applied one by one in the order of HR1, HR2, HR3.

HR1 S takes the maximum value allowed by the Pauli Exclusion principle [meaning: as many as possible of electrons have parallel spins]

Practically, each electron, up to half the number of states in the shell, gives +½ to S. Beyond half-fill, each electron gives -½ to S.

[HR1 goes first and determines S]

HR2 $\quad L$ takes the maximum value that is consistent with S

[meaning: electrons have their orbital angular momenta as well aligned as possible, after fixing S]

[HR2 goes second to fix L]

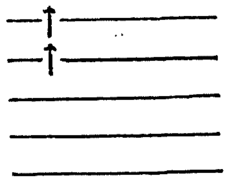
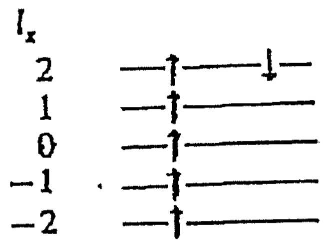
- HR1 and HR2 are robust [always hold] (∵ due to Coulomb interaction)
- Work for isolated atoms and ions

HR3 $\quad J = |L-S|$ for a shell less than half-fill

$J = L+S$ for a shell more than half-fill

- HR3 is less robust (∵ associated with spin-orbit interaction)
- may fail due to influence of neighboring ions (in solids) and/or applied B_{ext}

Examples

		V^{3+} ion	Fe^{2+} ion
	Number of 3d electrons	2	6
	Occupancy of states as given by Hund's rules		
HR1	Hund's rule 1: determination of S. Make as many spins parallel as possible	$S = \frac{1}{2} + \frac{1}{2}$ $= 1$	$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} - \frac{1}{2}$ $= 2$
HR2	Hund's rule 2: determination of L. Make $\sum l_z$ as large as possible	$L = \sum l_z$ $= 2 + 1 = 3$	$L = 2 + 1 + 0 - 1 - 2 + 2$ $= 2$
HR3	Hund's rule 3: determination of J.	Shell less than half-full $J = \lvert L - S \rvert = 2$	Shell more than half-full $J = L + S = 4$
	Spectroscopic notation, $^{2S+1}L_J$	$^3F_2$	$^5D_4$ $^{2S+1}L_J$

Use of Hund's rules to calculate the quantum numbers S, L and J of the ground states of the V^{3+} and Fe^{2+} ions. The 3d shell has $l = 2$ so there are $2l + 1$ sublevels corresponding to $l_z = -2, -1, 0, 1, 2$ as indicated. In the spectroscopic notation, values of L of 0, 1, 2, 3, 4, 5, 6,… are indicated by letters S, P, D, F, G, H, I,..