ATOMS AND HUND'S RULES

Let us generalize what we saw with the He atom to the case of an atom with Z (identical) electrons. The idea is that we need a wavefunction which is globally (spatial · spin) anti-symmetric for exchange of any pair of electrons. Slater's discriminant comes to help us, although the problem of explicitly writing the wavefunction of Z identical fermions quickly gets out of hands.

Let us define some notation:

one-electron state with angular momentum ℓ : use letter s, p, d, f for $\ell = 0, 1, 2, 3$ respectively

one-electron state in energy level n : add n in front of letter

$2p$ = electron in state $|2\ 1\ m\rangle$ ($m = \pm 1, 0$ are all possible)

$(2p)^3$ = three electrons in state with $n=2$ and $\ell = 1$: values of m and spin of each electron will need to satisfy Pauli's exclusion principle: for each electron m can be ± 1 or 0, and $m_s = \pm 1/2$, but not all $(3 \cdot 2)^3$ states are allowed by Pauli's exclusion principle

Hund's rules tell us how electrons occupy the available orbitals and spin states, while satisfying Pauli's exclusion principle and including the effects of Coulomb repulsion.

#1: the lowest energy configuration maximizes the total spin:

$$\text{"}S\text{"} = \sum m_s \quad \text{(sum over } Z \text{ electrons)}$$

#2: the lowest energy state maximizes the total ORBITAL angular momentum:

$$\text{"}L\text{"} = \sum m_\ell$$

#3 : in a more than half-filled (n, ℓ) shell, the lowest energy state minimizes the total angular momentum "J"
in a more than half filled shell, $J = L + S$ has the lowest energy

Heuristic explanation :

#1 : I can get max spin only in a symmetric spin state $\Rightarrow$ this goes with an anti-symmetric spatial state, which minimizes electrostatic energy due to Coulomb repulsion

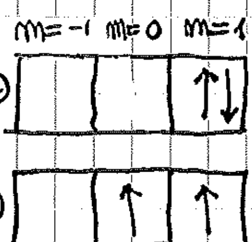
#2 : very questionable classical argument : max orbital angular momentum achieved when electrons orbiting in the same direction ; this way, they cross their paths less often, thus minimizing Coulomb interaction

#3 : minimizing J means that L and S are in opposite directions : then $\vec{L} \cdot \vec{S} < 0$ and spin-orbit energy is negative

Examples :

Carbon $Z = 6$ $(1s)^2 (2s)^2 (2p)^2$

p orbital : possible ways to fill up



(a) "S" = 0 "L" = 2 , L = 2 J = 2

(b) "S" = 1 L = 1 or 2 J = 2 or 1 or 0 if L=1 ; 3 or 2 or 1 if L=2
"L" = 1
(L = 2) reject by symmetry requirement : makes total wavefunction symmetric, but I need it to be anti-symmetric (see note 2)

#1 : need to take (b), maximizes "S"

#2 : does not apply, only one possible value for "L"

#3 : need to take state with minimum value for J : J = 0

Notation : $^{2S+1}L_J$. Carbon ground state is $^3P_0$ (capital letters for TOTAL S, L, J)

Titanium $Z = 22$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 \underline{3d^2}$

d orbital: -2	-1	m=0	1	2	"S"	"L"	L	J
				↑↓	0	4	4	4
		↑	↑		1	1	4,3,2,1	5,4,3,2,1,0 depending on L
			↑	↑	1	3	4,3	4, 3, 2 $L=3$ 5, 4, 3 $L=4$

reject by symmetry requirement (see NOTE 2) → 4

at least: "L" = 3 → 3

#1 : "S" = 1

#2 : "L" = 3 $\Longrightarrow$ ground state of Ti is $^3F_2$

#3 : $J = 2$

NOTE: the sketch with election placement helps identifying the values of "S" and "L", but it does not univocally identify the possible values of $\vec{L}$ and $\vec{J}$, which instead needs to be inferred from the values of "S" and "L".
A good guen is : $J = |\text{"L"} - \text{"S"}|$, but do make sure that it makes sense.

NOTE 2: make sure that state is compatible with being anti-symmetric. In the Titanium case, I cannot have a spin triplet with $L=4$ because both the spin and spatial wavefunctions would be symmetric for particle exchange.

Fast recipe : $^{2S+1}L_J$ when $L = \text{"L"}$, $S = \text{"S"}$ and $J = |\text{"L"} - \text{"S"}|$ ($\leq$ half-full shell) or $J = \text{"L"} + \text{"S"}$ ($>$ half-full shell). But make sure it makes sense (i.e., is anti-symmetric).

Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1.01																	2 He Helium 4.00
3 Li Lithium 6.94	4 Be Beryllium 9.01											5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18
11 Na Sodium 22.99	12 Mg Magnesium 24.31											13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.95
19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.88	23 V Vanadium 50.94	24 Cr Chromium 51.99	25 Mn Manganese 54.94	26 Fe Iron 55.93	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.39	31 Ga Gallium 69.73	32 Ge Germanium 72.61	33 As Arsenic 74.92	34 Se Selenium 78.09	35 Br Bromine 79.90	36 Kr Krypton 84.80
37 Rb Rubidium 84.49	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.94	43 Tc Technetium 98.91	44 Ru Ruthenium 101.07	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 127.6	53 I Iodine 126.90	54 Xe Xenon 131.29
55 Cs Cesium 132.91	56 Ba Barium 137.33	57-71 Lanthanides	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.85	75 Re Rhenium 186.21	76 Os Osmium 190.23	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	82 Pb Lead 207.20	83 Bi Bismuth 208.98	84 Po Polonium [208.98]	85 At Astatine 209.98	86 Rn Radon 222.02
87 Fr Francium 223.02	88 Ra Radium 226.03	89-103 Actinides	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

57 La Lanthanum 138.91	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium 144.91	62 Sm Samarium 150.36	63 Eu Europium 151.97	64 Gd Gadolinium 157.25	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 173.04	71 Lu Lutetium 174.97
89 Ac Actinium 227.03	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium 237.05	94 Pu Plutonium 244.06	95 Am Americium 243.06	96 Cm Curium 247.07	97 Bk Berkelium 247.07	98 Cf Californium 251.08	99 Es Einsteinium [254]	100 Fm Fermium 257.10	101 Md Mendelevium 258.10	102 No Nobelium 259.10	103 Lr Lawrencium [262]

Alkali Metal | Alkaline Earth | Transition Metal | Basic Metal | Semimetal | Nonmetal | Halogen | Noble Gas | Lanthanide | Actinide