3.012 Fund of Mat Sci: Bonding – Lecture 8

THE PERIODIC TABLE

M. C. Escher, "Ascending and Descending," 1960. Image removed for copyright reasons.

PROF MAYES - 3-5 pm 13-5025

Homework for Fri Oct 7

- Study: 21.4, 23.1, 23.2, 23.3

- Exam – check all points mentioned in PS3.
- Study all paragraphs assigned from textbook.
- Old problem sets, quizzes, available on Stellar, together with solutions
- Office hours MONA 3.30 - 5pm

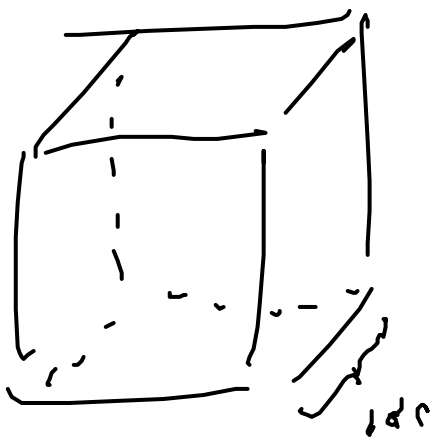
Last time:

1. Absorption/emission processes, XPS
2. Orbitals in a central potential
3. Accidental degeneracies removed by centripetal potential, and screening
4. Coupled ("Hartree") equations for a many electron atom
5. Spin

Many-electron case

$$\Psi(\vec{r}_1, \vec{r}_2) = \varphi_1(\vec{r}_1)\,\varphi_2(\vec{r}_2)$$

NO SELFISHNESS



$100 \times 100 \times 100 = 10^6$

10^{12}

10^{18}

Helium atom

$$\left[-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{2e^2}{4\pi\varepsilon_0 r_1} + \frac{e^2}{4\pi\varepsilon_0} \int \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2 \right] \varphi_1 =$$

$$= \varepsilon_1 \varphi_1$$

$$\left[-\frac{\hbar^2}{2m} \nabla_2^2 - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0} \int \frac{\rho(\vec{r}_1)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 \right] \varphi_2 =$$

$$= \varepsilon_2 \varphi_2$$

Hartree equations

Right experiment – wrong theory (Stern-Gerlach)

$$H \rightarrow \hat{H} + \frac{\mu_B}{\hbar}\hat{L}\vec{B} \rightarrow \hat{H} + \frac{\mu_B}{\hbar}\hat{L}_z B_z$$

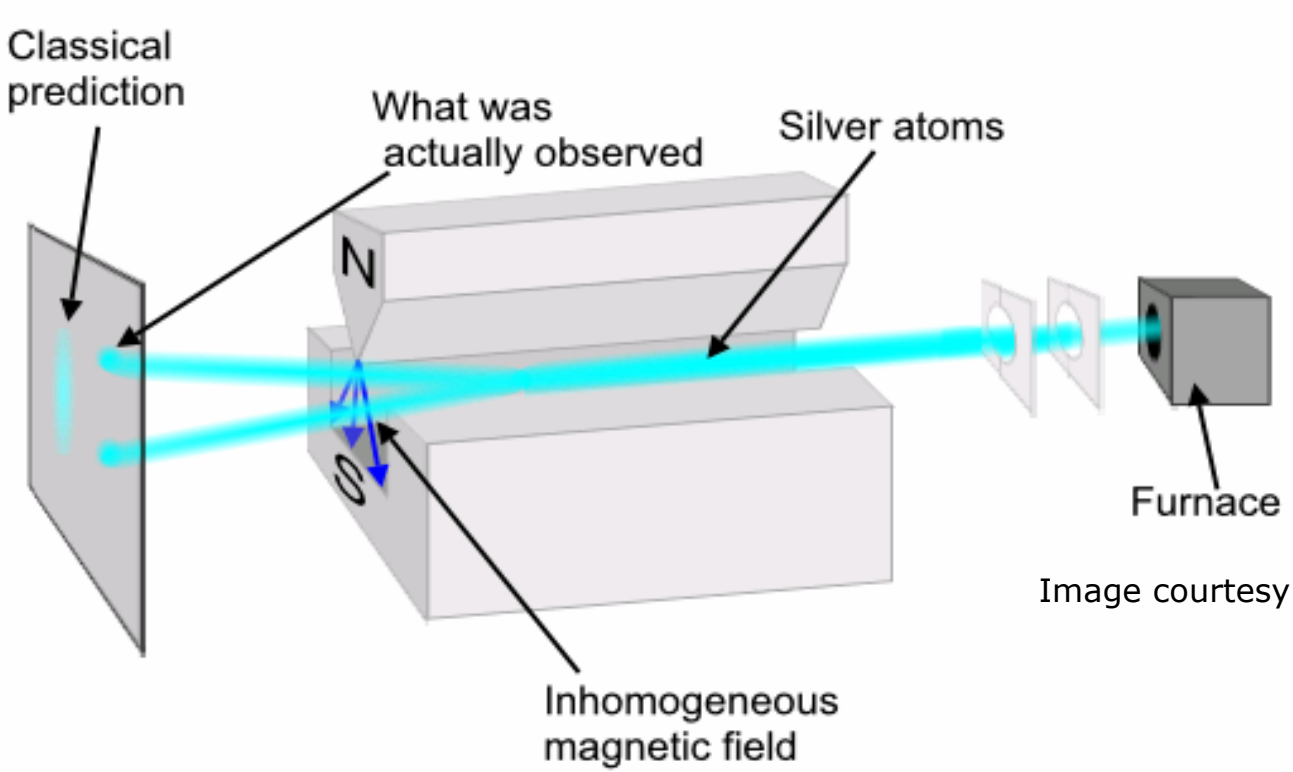


Image courtesy of Theresa Knott.

$$\hat{H} \rightarrow \hat{H} + \frac{\mu_B}{\hbar}(\hat{L} + 2\hat{S})\cdot\vec{B} = \hat{H} + \frac{\mu_B}{\hbar}(\hat{L}_z + 2\hat{S}_z)B_z$$

Goudsmit and Uhlenbeck

Spin Eigenvalues/Eigenfunctions

- Norm (s integer → bosons, half-integer → fermions)

$$\hat{S}^2 \Psi_{spin} = \hbar^2 s(s+1) \Psi_{spin}$$

- Z-axis projection (electron is a fermion with s=1/2)

$$\hat{S}_z \Psi_{spin} = \pm \frac{\hbar}{2} \Psi_{spin}$$

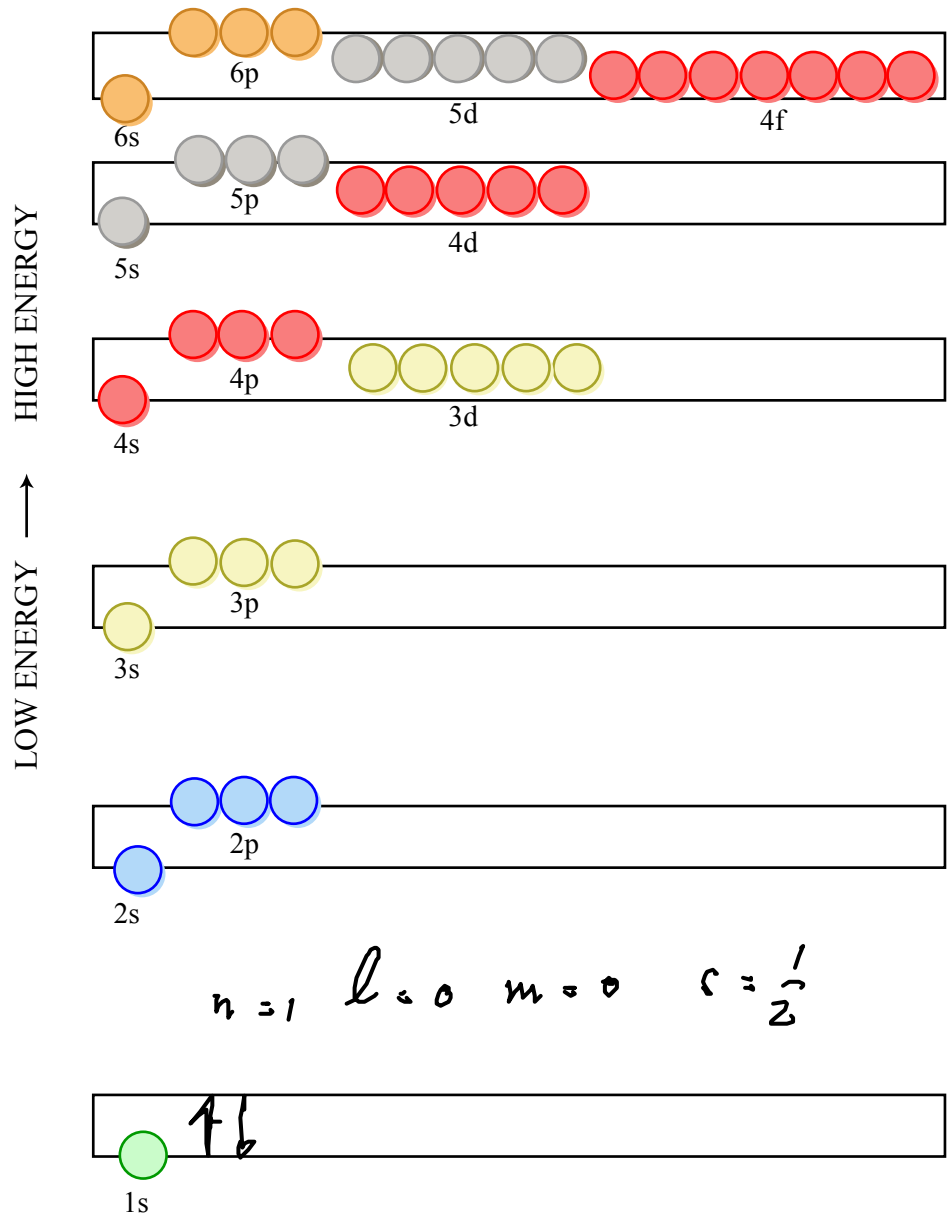
- Spin-orbital: product of the "space" wavefunction and the "spin" wavefunction

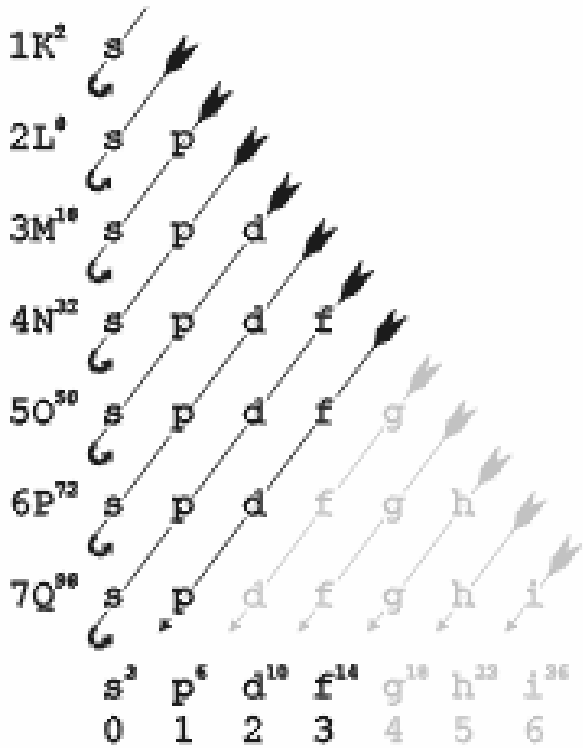
Pauli Exclusion Principle

We can't have two electrons in the same quantum state $\rightarrow$

Any two electrons in an atom cannot have the same 4 quantum numbers n,l,m,m_s

Auf-bau

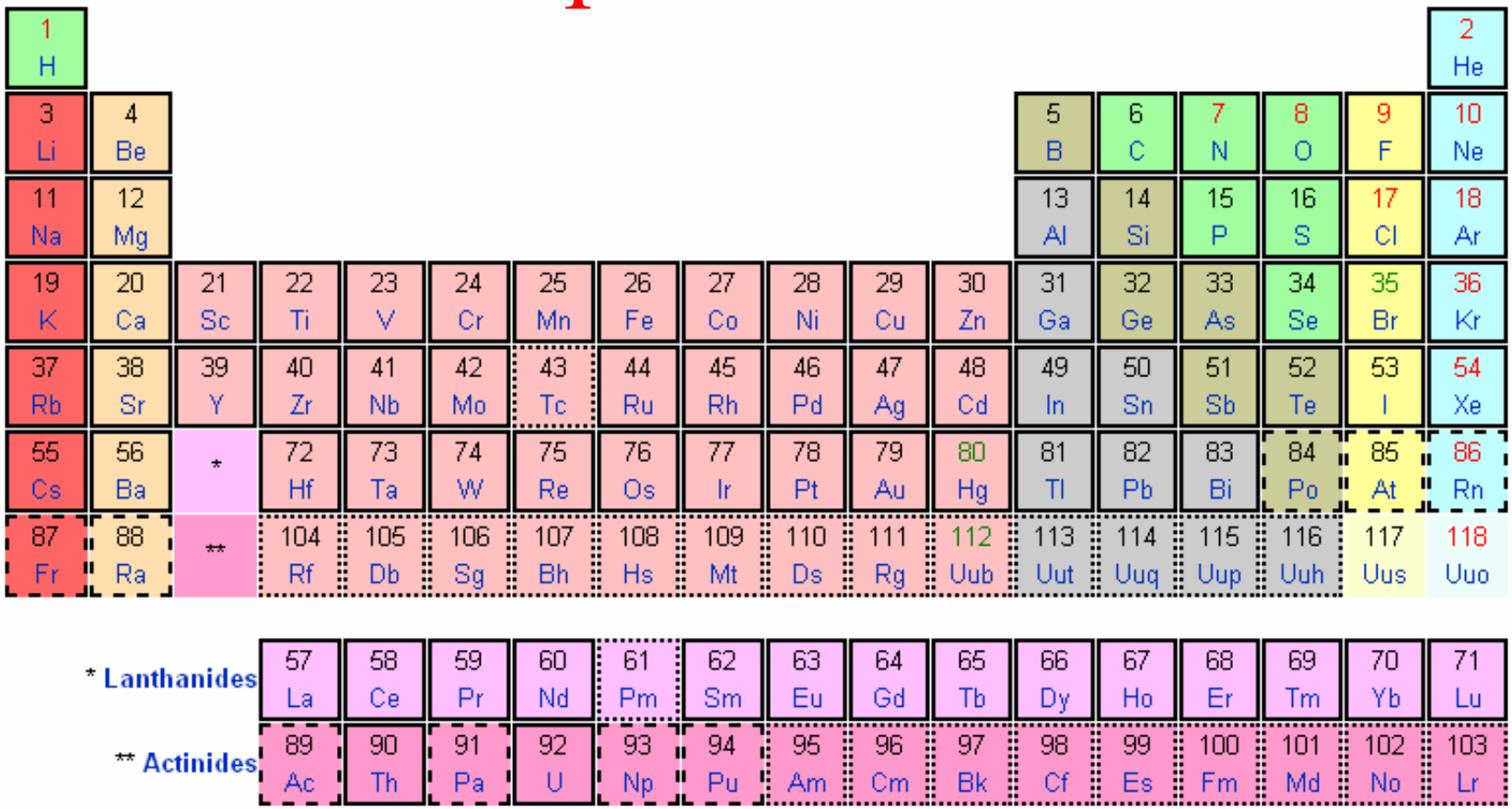




chemmix

Figure by MIT OCW.

The periodic table



Source: Wikipedia

Periodic Table – Electronic Configuration

Z	ELEMENT		ELECTRONIC* CONFIGURATION	TERM*	IONIZATION POTENTIAL (eV)
1	H	Hydrogen	1s	$^2S_{1/2}$	13.60
2	He	Helium	$1s^2$	$^1S_0$	24.59
3	Li	Lithium	[He]2s	$^2S_{1/2}$	5.39
4	Be	Beryllium	[He]$2s^2$	$^1S_0$	9.32
5	B	Boron	[He]$2s^2$2p	$^2P_{1/2}$	8.30
6	C	Carbon	[He]$2s^2$$2p^2$	$^3P_0$	11.26
7	N	Nitrogen	[He]$2s^2$$2p^3$	$^4S_{3/2}$	14.53
8	O	Oxygen	[He]$2s^2$$2p^4$	$^3P_2$	13.62
9	F	Fluorine	[He]$2s^2$$2p^5$	$^2P_{3/2}$	17.42
10	Ne	Neon	[He]$2s^2$$2p^6$	$^1S_0$	21.56
11	Na	Sodium	[Ne]3s	$^2S_{1/2}$	5.14
12	Mg	Magnesium	[Ne]$3s^2$	$^1S_0$	7.65
13	Al	Aluminium	[Ne]$3s^2$3p	$^2P_{1/2}$	5.99
14	Si	Silicon	[Ne]$3s^2$$3p^2$	$^3P_0$	8.15
15	P	Phosphorus	[Ne]$3s^2$$3p^3$	$^4S_{3/2}$	10.49
16	S	Sulphur	[Ne]$3s^2$$3p^4$	$^3P_2$	10.36
17	Cl	Chlorine	[Ne]$3s^2$$3p^5$	$^2P_{3/2}$	12.97
18	Ar	Argon	[Ne]$3s^2$$3p^6$	$^1S_0$	15.76
19	K	Potassium	[Ar]4s	$^2S_{1/2}$	4.34
20	Ca	Calcium	[Ar]$4s^2$	$^1S_0$	6.11
21	Sc	Scandium	[Ar]$4s^2$3d	$^2D_{3/2}$	6.54
22	Ti	Titanium	[Ar]$4s^2$$3d^2$	$^3F_2$	6.82
23	V	Vanadium	[Ar]$4s^2$$3d^3$	$^4F_{3/2}$	6.74
24	Cr	Chromium	[Ar]$4s^2$$3d^5$	$^7S_3$	6.77
25	Mn	Manganese	[Ar]$4s^2$$3d^5$	$^6S_{5/2}$	7.44
26	Fe	Iron	[Ar]$4s^2$$3d^6$	$^5D_4$	7.87
27	Co	Cobalt	[Ar]$4s^2$$3d^7$	$^4F_{9/2}$	7.86
28	Ni	Nickel	[Ar]$4s^2$$3d^8$	$^3F_4$	7.64
29	Cu	Copper	[Ar]$4s3d^{10}$	$^2S_{1/2}$	7.73
30	Zn	Zinc	[Ar]$4s^2$$3d^{10}$	$^1S_0$	9.39
31	Ga	Gallium	[Ar]$4s^2$$3d^{10}$4p	$^2P_{1/2}$	6.00
32	Ge	Germanium	[Ar]$4s^2$$3d^{10}$$4p^2$	$^3P_0$	7.90
33	As	Arsenic	[Ar]$4s^2$$3d^{10}$$4p^3$	$^4S_{3/2}$	9.81
34	Se	Selenium	[Ar]$4s^2$$3d^{10}$$4p^4$	$^3P_2$	9.75
35	Br	Bromine	[Ar]$4s^2$$3d^{10}$$4p^5$	$^2P_{3/2}$	11.81
36	Kr	Krypton	[Ar]$4s^2$$3d^{10}$$4p^6$	$^1S_0$	14.00
37	Rb	Rubidium	[Kr]5s	$^2S_{1/2}$	4.18
38	Sr	Strontium	[Kr]$5s^2$	$^1S_0$	5.70
39	Y	Yttrium	[Kr]$5s^2$4d	$^2D_{3/2}$	6.38
40	Zr	Zirconium	[Kr]$5s^2$$4d^2$	$^3F_2$	6.84
41	Nb	Niobium	[Kr]5s$4d^4$	$^6D_{1/2}$	6.88
42	Mo	Molybdenum	[Kr]5s$4d^5$	$^7S_3$	7.10
43	Tc	Technetium	[Kr]$5s^2$$4d^5$	$^6S_{5/2}$	7.28
44	Ru	Ruthenium	[Kr]$5s^2$$4d^7$	$^5F_5$	7.37
45	Rh	Rhodium	[Kr]$5s^2$$4d^8$	$^4F_{9/2}$	7.46
46	Pd	Palladium	[Kr]$4d^{10}$	$^1S_0$	8.34
47	Ag	Silver	[Kr]5s$4d^{10}$	$^2S_{1/2}$	7.58
48	Cd	Cadmium	[Kr]$5s^2$$4d^{10}$	$^1S_0$	8.99
49	In	Indium	[Kr]$5s^2$$4d^{10}$5p	$^2P_{1/2}$	5.79
50	Sn	Tin	[Kr]$5s^2$$4d^{10}$$5p^2$	$^3P_0$	7.34
51	Sb	Antimony	[Kr]$5s^2$$4d^{10}$$5p^3$	$^4S_{3/2}$	8.64
52	Te	Tellurium	[Kr]$5s^2$$4d^{10}$$5p^4$	$^3P_2$	9.01
53	I	Iodine	[Kr]$5s^2$$4d^{10}$$5p^5$	$^2P_{3/2}$	10.45
54	Xe	Xenon	[Kr]$5s^2$$4d^{10}$$5p^6$	$^1S_0$	12.13
55	Cs	Cesium	[Xe]6s	$^2S_{1/2}$	3.89
56	Ba	Barium	[Xe]$6s^2$	$^1S_0$	5.21
57	La	Lanthanum	[Xe]$6s^2$5d	$^2D_{3/2}$	5.58
58	Ce	Cerium	[Xe]($6s^2$4f5d)	($^1G_4$)	5.47
59	Pr	Praseodymium	[Xe]($6s^2$$4f^2$)	($^4I_{9/2}$)	5.42
60	Nd	Neodymium	[Xe]$6s^2$$4f^4$	$^5I_4$	5.49
61	Pm	Promethium	[Xe]($6s^2$$4f^5$)	($^6H_{5/2}$)	5.55
62	Sm	Samarium	[Xe]$6s^2$$4f^6$	$^7F_0$	5.63
63	Eu	Europium	[Xe]$6s^2$$4f^7$	$^8S_{7/2}$	5.67
64	Gd	Gadolinium	[Xe]$6s^2$$4f^7$5d	$^9D_2$	6.14
65	Tb	Terbium	[Xe]($6s^2$$4f^9$)	$^6H_{15/2}$	5.85
66	Dy	Dysprosium	[Xe]($6s^2$$4f^{10}$)	($^5I_8$)	5.93
67	Ho	Holmium	[Xe]($6s^2$$4f^{11}$)	($^4I_{15/2}$)	6.02
68	Er	Erbium	[Xe]($6s^2$$4f^{12}$)	($^3H_6$)	6.10
69	Tm	Thulium	[Xe]$6s^2$$4f^{13}$	$^2F_{7/2}$	6.18
70	Yb	Ytterbium	[Xe]$6s^2$$4f^{14}$	$^1S_0$	6.25
71	Lu	Lutetium	[Xe]$6s^2$$4f^{14}$5d	$^2D_{3/2}$	5.43
72	Hf	Hafnium	[Xe]$6s^2$$4f^{14}$$5d^2$	$^3F_2$	7.0
73	Ta	Tantalum	[Xe]$6s^2$$4f^{14}$$5d^3$	$^4F_{3/2}$	7.89
74	W	Tungsten	[Xe]$6s^2$$4f^{14}$$5d^4$	$^5D_0$	7.98
75	Re	Rhenium	[Xe]$6s^2$$4f^{14}$$5d^5$	$^6S_{5/2}$	7.88
76	Os	Osmium	[Xe]$6s^2$$4f^{14}$$5d^6$	$^5D_4$	8.7
77	Ir	Iridium	[Xe]$6s^2$$4f^{14}$$5d^7$	($^4F_{9/2}$)	9.1
78	Pt	Platinum	[Xe]6s$4f^{14}$$5d^9$	$^3D_3$	9.0
79	Au	Gold	[Xe]6s$4f^{14}$$5d^{10}$	$^2S_{1/2}$	9.23
80	Hg	Mercury	[Xe]$6s^2$$4f^{14}$$5d^{10}$	$^1S_0$	10.44
81	Tl	Thallium	[Xe]$6s^2$$4f^{14}$$5d^{10}$6p	$^2P_{1/2}$	6.11
82	Pb	Lead	[Xe]$6s^2$$4f^{14}$$5d^{10}$$6p^2$	$^3P_0$	7.42
83	Bi	Bismuth	[Xe]$6s^2$$4f^{14}$$5d^{10}$$6p^3$	$^4S_{3/2}$	7.29
84	Po	Polonium	[Xe]$6s^2$$4f^{14}$$5d^{10}$$6p^4$	$^3P_2$	8.42
85	Ar	Astatine	[Xe]($6s^2$$4f^{14}$$5d^{10}$$6p^5$)	$^2P_{3/2}$	9.5
86	Rn	Radon	[Xe]$6s^2$$4f^{14}$$5d^{10}$$6p^6$	$^1S_0$	10.75
87	Fr	Francium	[Rn]7s	$^2S_{1/2}$	4.0
88	Ra	Radium	[Rn]$7s^2$	$^1S_0$	5.28
89	Ac	Actinium	[Rn]$7s^2$6d	$^2D_{3/2}$	6.9
90	Th	Thorium	[Rn]$7s^2$$6d^2$	$^3F_2$	
91	Pa	Protactinium	[Rn]($7s^2$$5f^2$6d)	($^4K_{11/2}$)	
92	U	Uranium	[Rn]$7s^2$$5f^3$6d	$^5L_6$	4.0
93	Np	Neptunium	[Rn]$7s^2$$5f^4$6d	$^5L_{11/2}$	
94	Pu	Plutonium	[Rn]$7s^2$$5f^6$	$^7F_0$	5.8
95	Am	Americium	[Rn]$7s^2$$5f^7$	$^8S_{7/2}$	6.0
96	Cm	Curium	[Rn]$7s^2$$5f^7$6d	$^9D_2$	
97	Bk	Berkelium	[Rn]$7s^2$$5f^9$6d	$^8H_{17/2}$	
98	Cf	Californium	[Rn]$7s^2$$5f^{10}$	$^5I_8$	
99	Es	Einsteinium	[Rn]$7s^2$$5f^{11}$	$^4I_{15/2}$	
100	Fm	Fermium	[Rn]($7s^2$$5f^{12}$)	($^3H_6$)	
101	Md	Mendelevium	[Rn]($7s^2$$5f^{13}$)	($^2F_{7/2}$)	
102	No	Nobelium	[Rn]($7s^2$$5f^{14}$)	($^1S_0$)	
103	Lw	Lawrencium	[Rn]$7s^2$$5f^{14}$6d	($^2D_{3/2}$)	

**Configurations and terms in parentheses are estimated.*

Electronic configuration, term value, and ionization potential of the atoms in their ground state.

Figure by MIT OCW.

Atomic radii

Graph of atomic radius plotted against atomic number removed for copyright reasons.
See http://www.webelements.com/webelements/properties/text/image-line/atomic-radius-emp.html.

Graphs of ionization enthalpy plotted against atomic number removed for copyright reasons.

Graphs of electron affinity plotted against atomic number removed for copyright reasons.
See http://www.webelements.com/webelements/properties/text/image-line/electron-affinity.html
and http://www.webelements.com/webelements/properties/text/image-cityscape/electron-affinity.html.

Good Quantum Numbers

$$\frac{d\langle A\rangle}{dt} = \frac{d\langle \Psi|\hat{A}|\Psi\rangle}{dt} = \frac{1}{ih}\langle[\hat{A},\hat{H}]\rangle$$

If A commutes with the Hamiltonian, its expectation value does not change with time (it's a constant of motion – if we are in an eigenstate, that quantum number will remain constant)

Variational Principle

$$E[\Phi] = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

$$E[\Phi] \geq E_0$$

If $E[\Phi] = E_0$, then Φ is the ground state wavefunction, and viceversa…