Chem 241

Lecture 2

Homework Chapter 1

- Exercise: 2, 3, 5, 11, 12, 13, 15, 17, 20
- Problems: 10, 11, 12

Recap

- How the elements were formed

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m_e}{\hbar^2}(E - V)\psi = 0$$

- V = potential energy of electron in the field of the nucleus
- E is the total energy

Probability Density

$$\int \psi^2 \, d\tau = 1$$

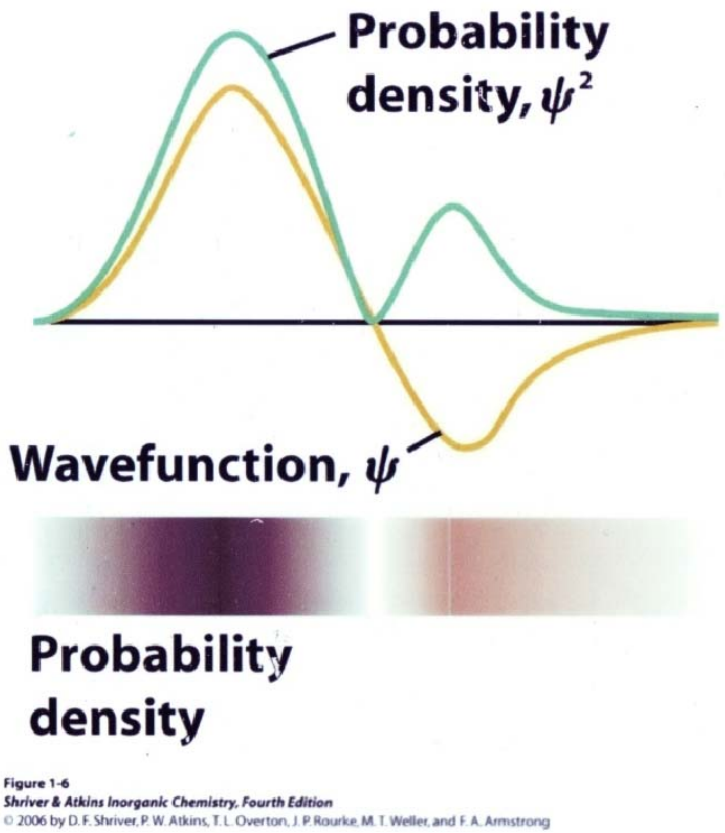

Figure 1-6
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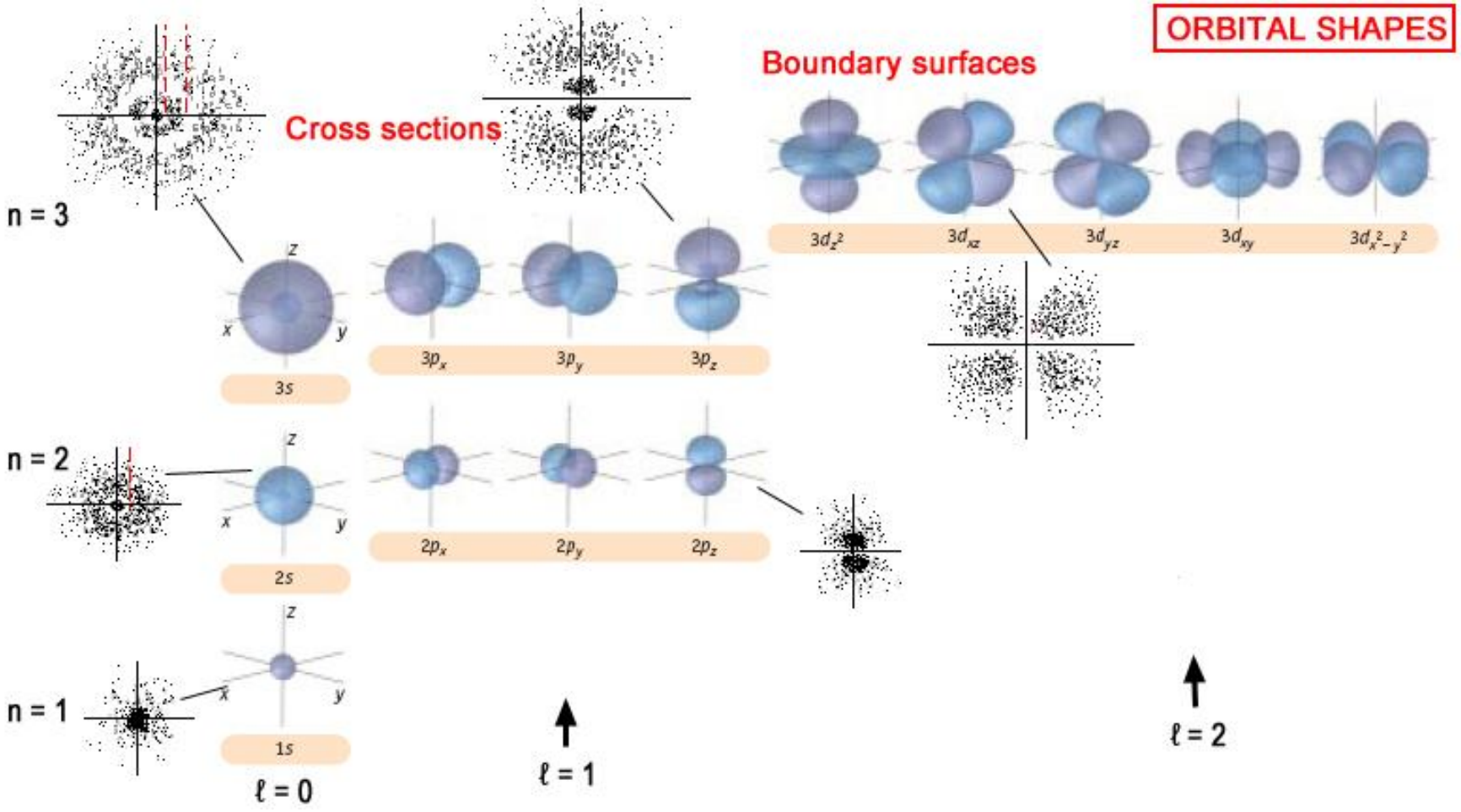
Orbitals

- Atomic orbitals defined by the wavefunction of an electron in a atom.
- Quantum Numbers – simplification of those waveforms
- n: principle q#
- l: angular orbital momentum q#
- m_l: magnetic q#

$$E = -\frac{hcRZ^2}{n^2} \quad \longleftrightarrow \quad \frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$R = \frac{m_e e^4}{8h^3 c\varepsilon_0^2}$$

Q#

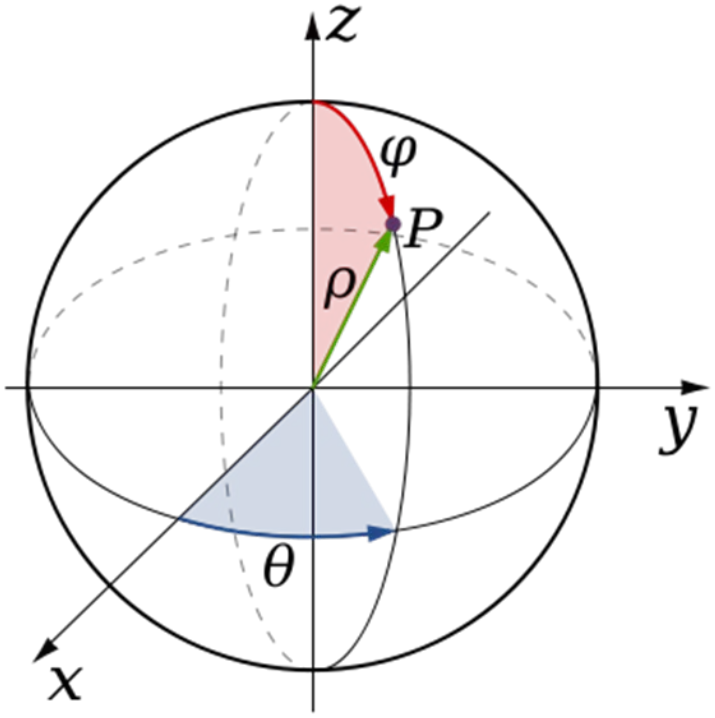

ORBITAL SHAPES
Boundary surfaces
Cross sections
n = 3
n = 2
n = 1
3s
3p_x
3p_y
3p_z
2s
2p_x
2p_y
2p_z
1s
3d_z²
3d_xz
3d_yz
3d_xy
3d_x²−y²
ℓ = 0
ℓ = 1
ℓ = 2

Spin

- s = intrinsic angular spin.
- For an electron s=1/2 always
- m_s = spin magnetic q#
- For and electron m_s = +1/2 or -1/2

The for q# n, l, m_l, m_s are used to characterize a electron in an atom

Polar Coordinates



Radial and Angular Functions

$$\psi_{nlm_i} = R_{nl}(r)Y(\theta,\phi)$$

Table 1.2 Hydrogenic orbitals

(a) Radial wavefunctions

$R_{nl}(r) = f(r)(Z/a_0)^{3/2}e^{-\rho/2}$

where a_0 is the Bohr radius (53 pm) and $\rho = 2Zr/na_0$

n	L	$f(r)$
1	0	2
2	0	$(1/2\sqrt{2})(2-\rho)$
2	1	$(1/2\sqrt{6})\rho$
3	0	$(1/9\sqrt{3})(6-6\rho+\rho^2)$
3	1	$(1/9\sqrt{6})(4-\rho)\rho$
3	2	$(1/9\sqrt{30})\rho^2$

Table 1-2 part 1
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Table 1.2 Hydrogenic orbitals

(b) Angular wavefunctions

$Y_{l,m_l}(\theta,\phi) = (1/4\pi)^{1/2}y(\theta,\phi)$

l	m_l	$y(\theta,\phi)$
0	0	1
1	0	$3^{1/2}\cos\theta$
1	±1	$3(3/2)^{1/2}\sin\theta e^{\pm i\phi}$
2	0	$(5/4)^{1/2}(3\cos^2\theta-1)$
2	±1	$3(15/4)^{1/2}\cos\theta\sin\theta e^{\pm i\phi}$
2	±2	$(15/8)^{1/2}\sin^2\theta e^{\pm 2i\phi}$

Table 1-2 part 2
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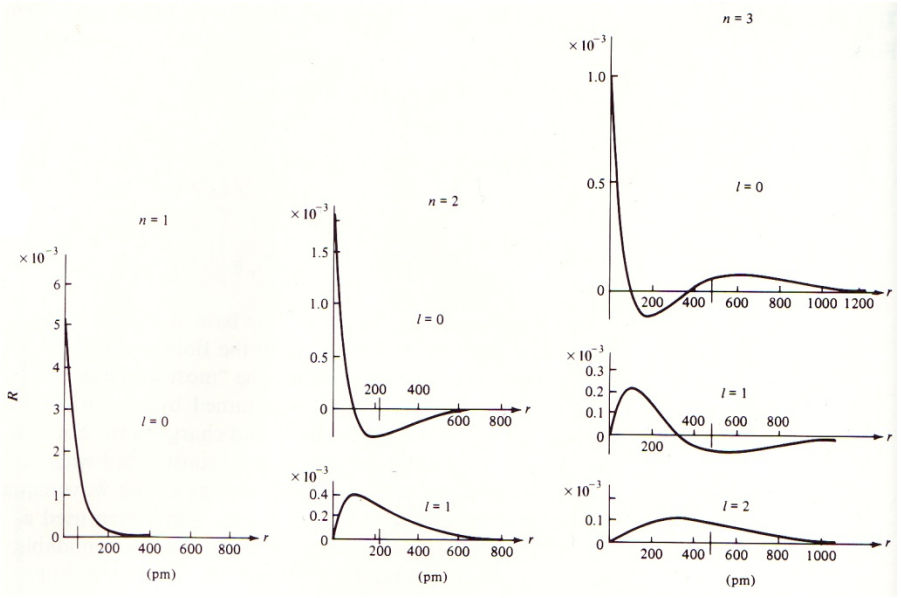
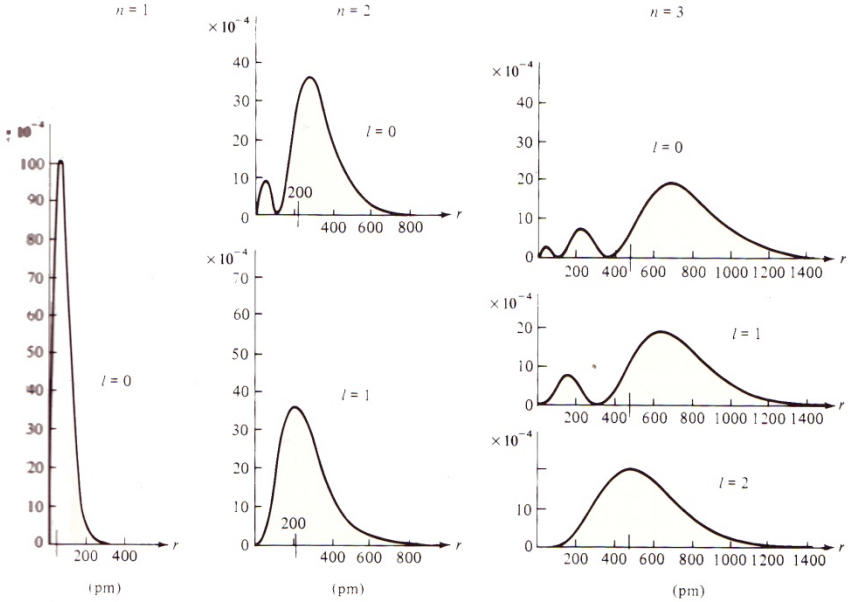
Radial Function graphed

- # of nodes = n-l-1



$$P(r) = r^2 R(r)$$



Angular function graphed

- # nodal planes = l

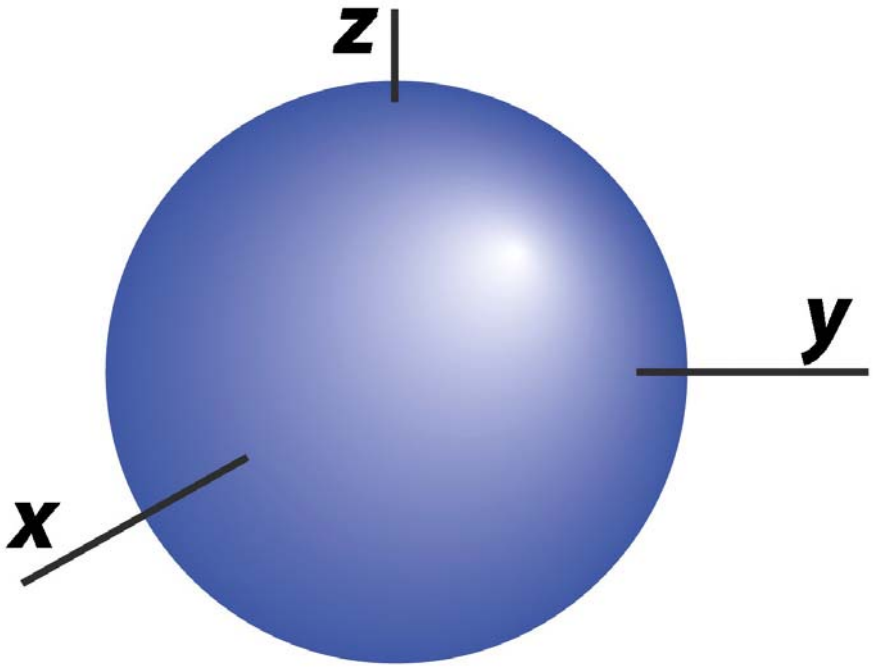


Figure 1-15
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p-orbitals

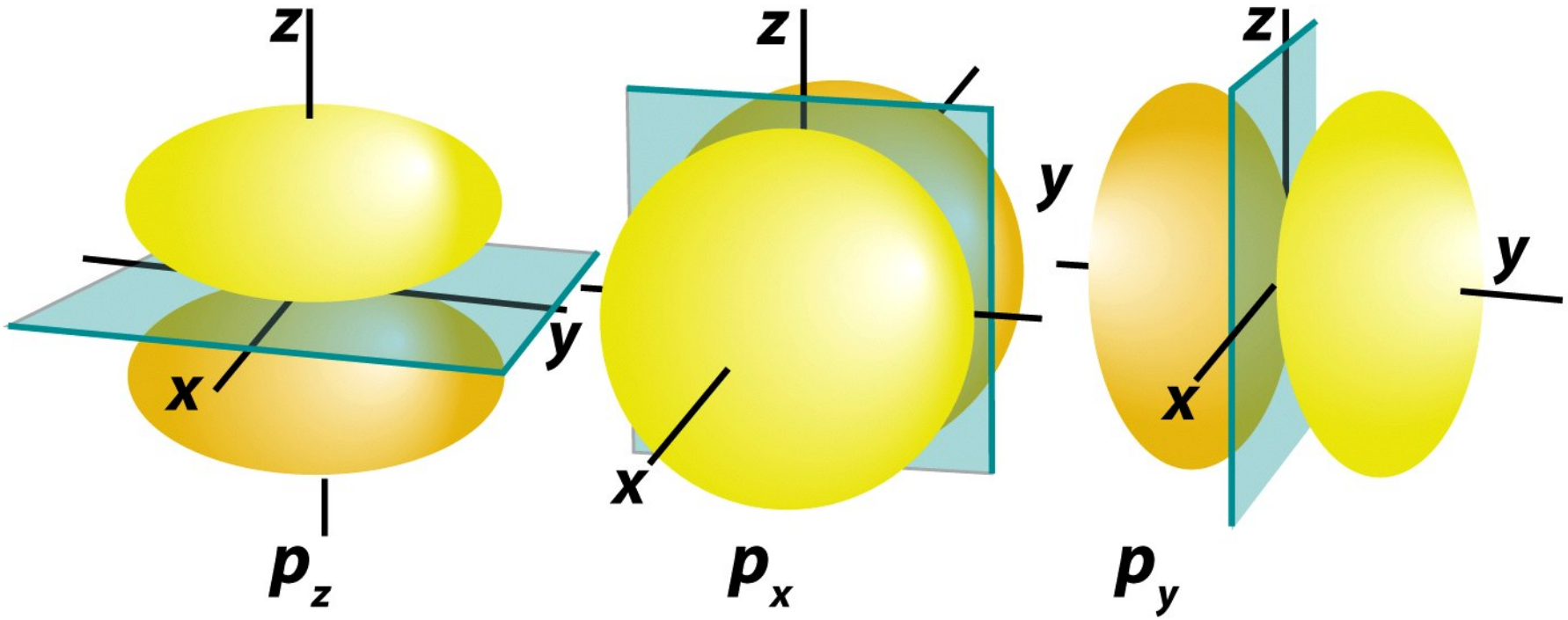

Figure 1-16
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d-orbitals

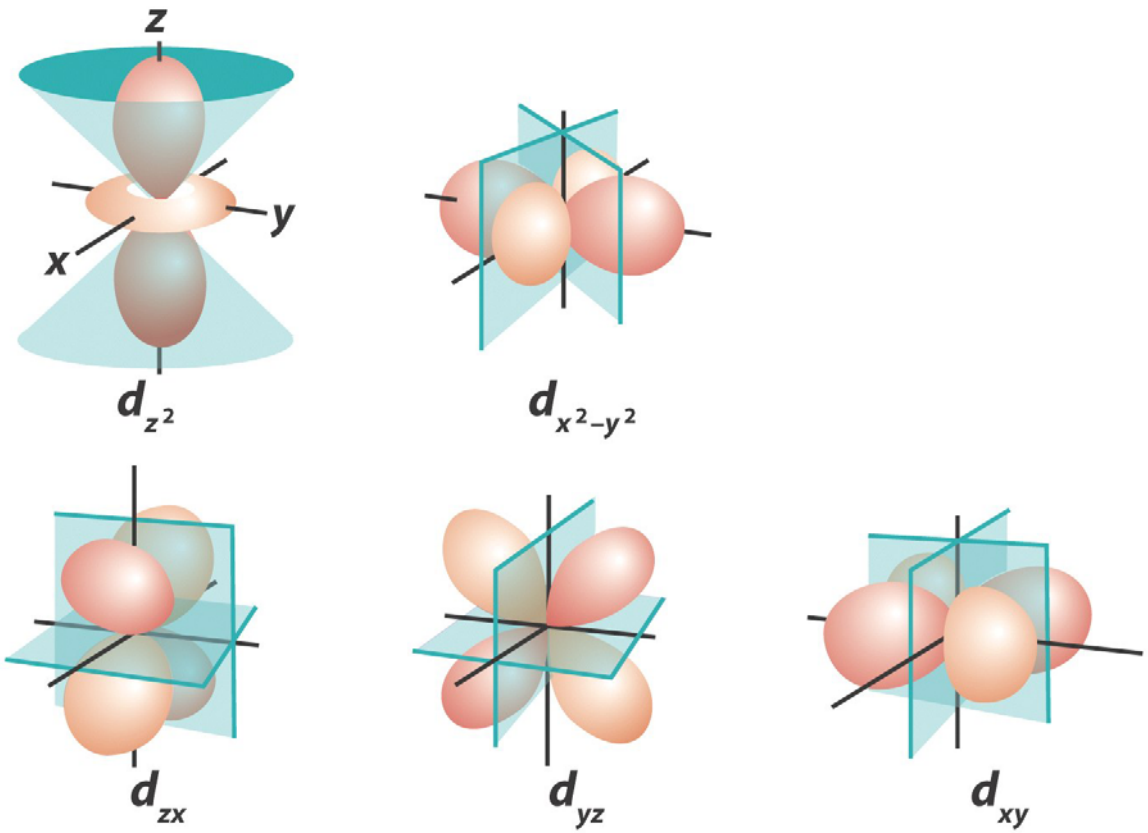

Figure 1-17
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f-orbitals

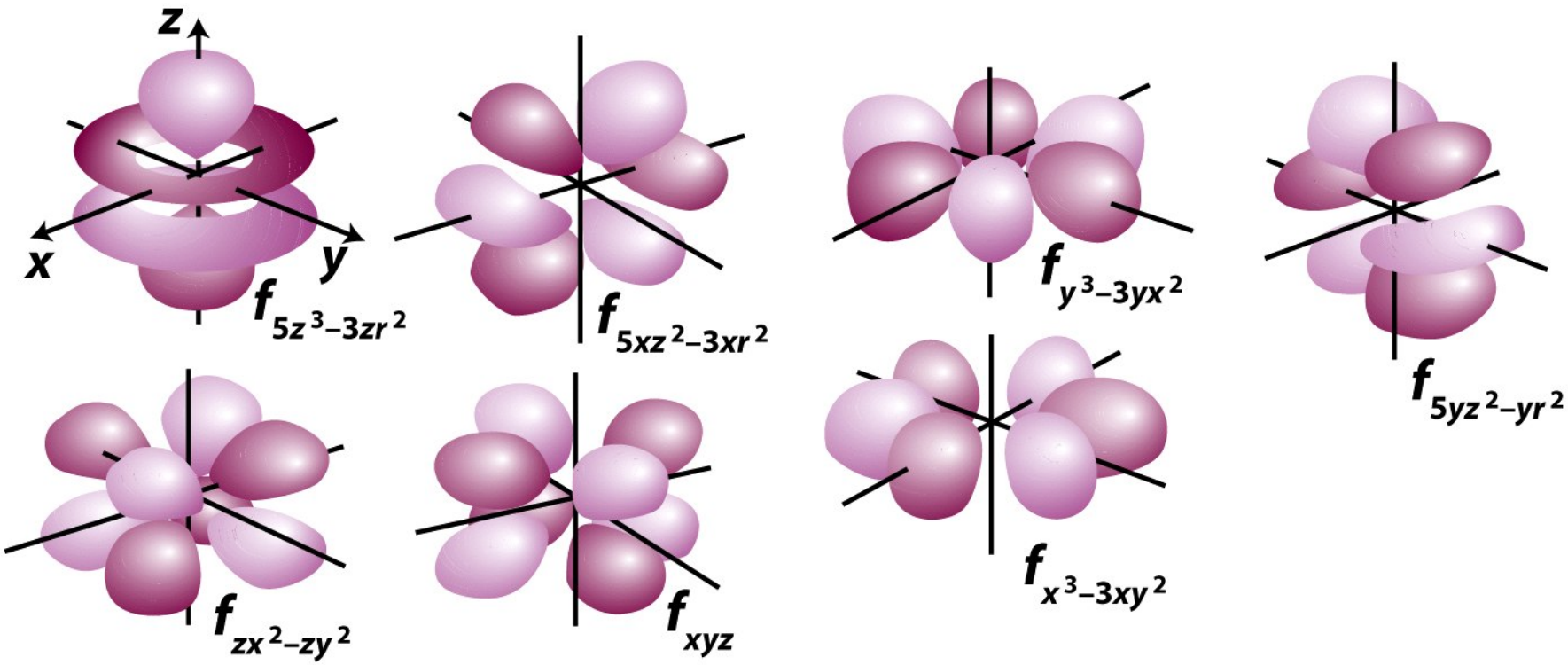

Figure 1-18
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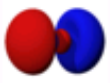
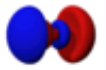
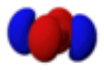
Whole wavefunction graphed

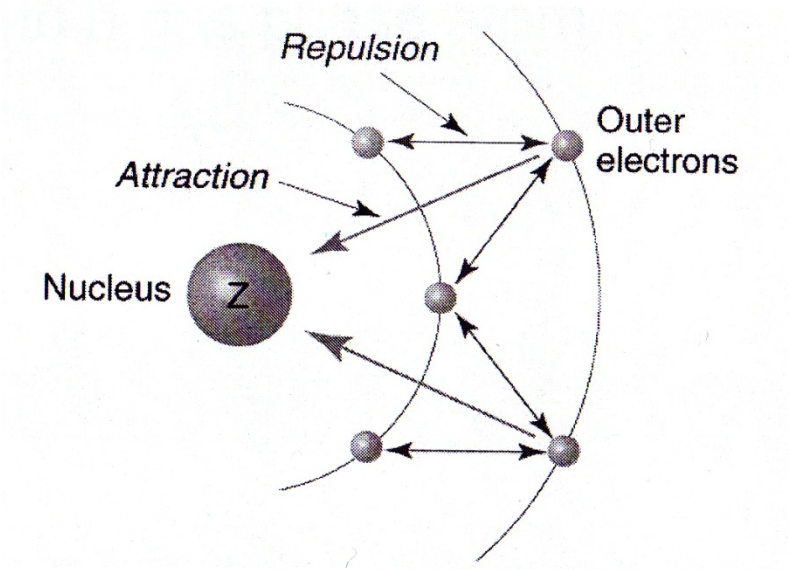
	s (l=0)	p (l=1)			d (l=2)					f (l=3)						
	m=0	m=0	m=±1		m=0	m=±1		m=±2		m=0	m=±1		m=±2		m=±3	
	s	p_z	p_x	p_y	d_{z^2}	d_{xz}	d_{yz}	d_{xy}	$d_{x^2-y^2}$	f_{z^3}	...	...	...	...	...	...
n=1																
n=2																
n=3																
n=4																
n=5										...	...	...	...	...	...	...
n=6					...	...	...	...	...	...	...	...	...	...	...	...
n=7		...	...	...	...	...	...	...	...	...	...	...	...	...	...	...

Multi electron atom

- Consider He – $1s^2$
- Pauli Exclusion Principle: No more than two electrons may occupy a single orbital. If two do, then their spins must be paired.
- Where does the next electron go since in hydrogenic atom 2s and 2p have the same energy?

Effective nuclear charge

- $Z_{eff} = Z - \sigma$
- σ : Is the shielding constant



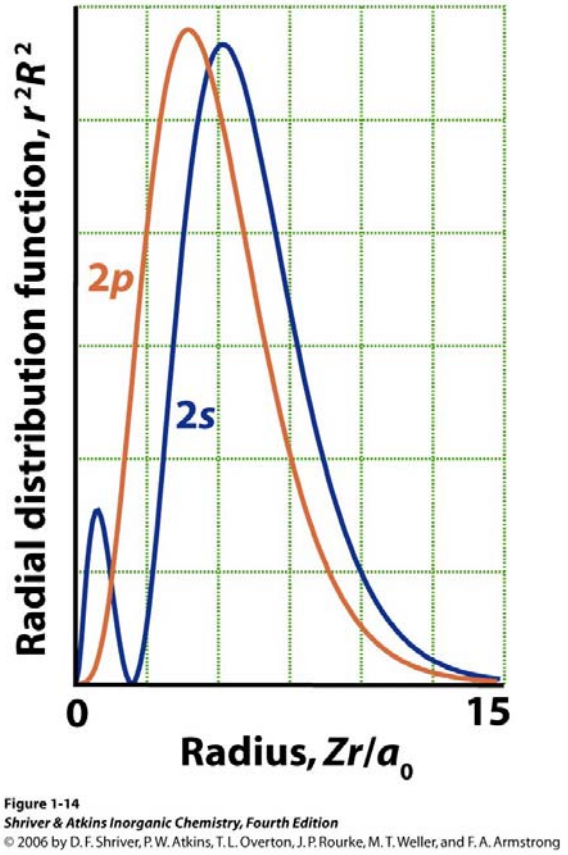


Figure 1-14
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Z_{eff}

ns<np<nd<nf

Table 1.3 Effective nuclear charges, Z_{eff}

	H							He
Z	1							2
1s	1.00							1.69
	Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
Z	3	4	5	6	7	8	9	10
1s	2.69	3.68	4.68	5.67	6.66	7.66	8.65	9.64
2s	1.28	1.91	2.58	3.22	3.85	4.49	5.13	5.76
2p			2.42	3.14	3.83	4.45	5.10	5.76
	Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
Z	11	12	13	14	15	16	17	18
1s	10.63	11.61	12.59	13.57	14.56	15.54	16.52	17.51
2s	6.57	7.39	8.21	9.02	9.82	10.63	11.43	12.23
2p	6.80	7.83	8.96	9.94	10.96	11.98	12.99	14.01
3s	2.51	3.31	4.12	4.90	5.64	6.37	7.07	7.76
3p			4.07	4.29	4.89	5.48	6.12	6.76

Table 1-3
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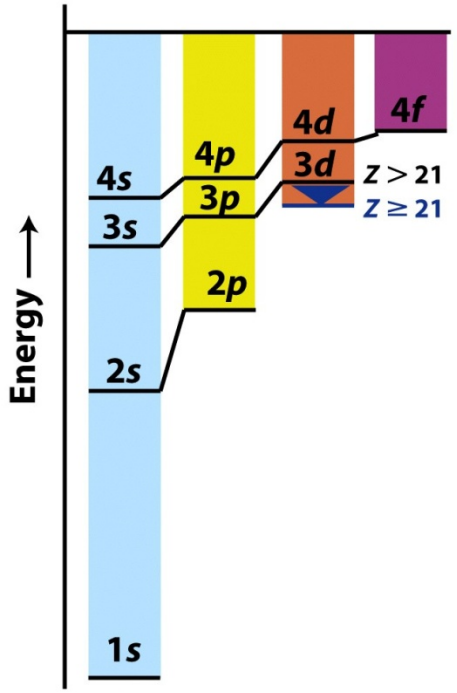

Figure 1-21
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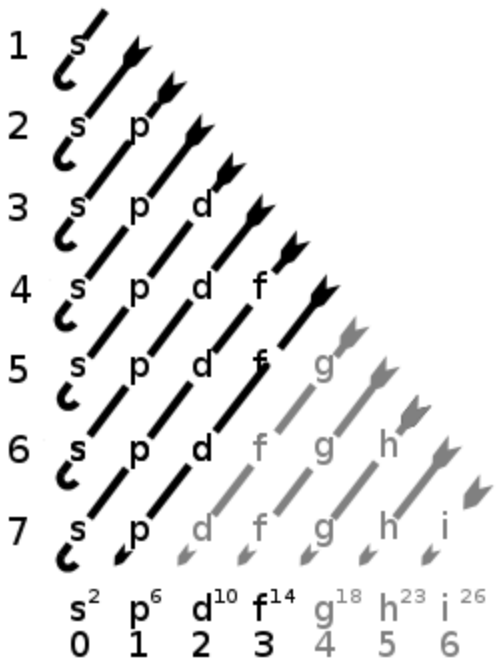
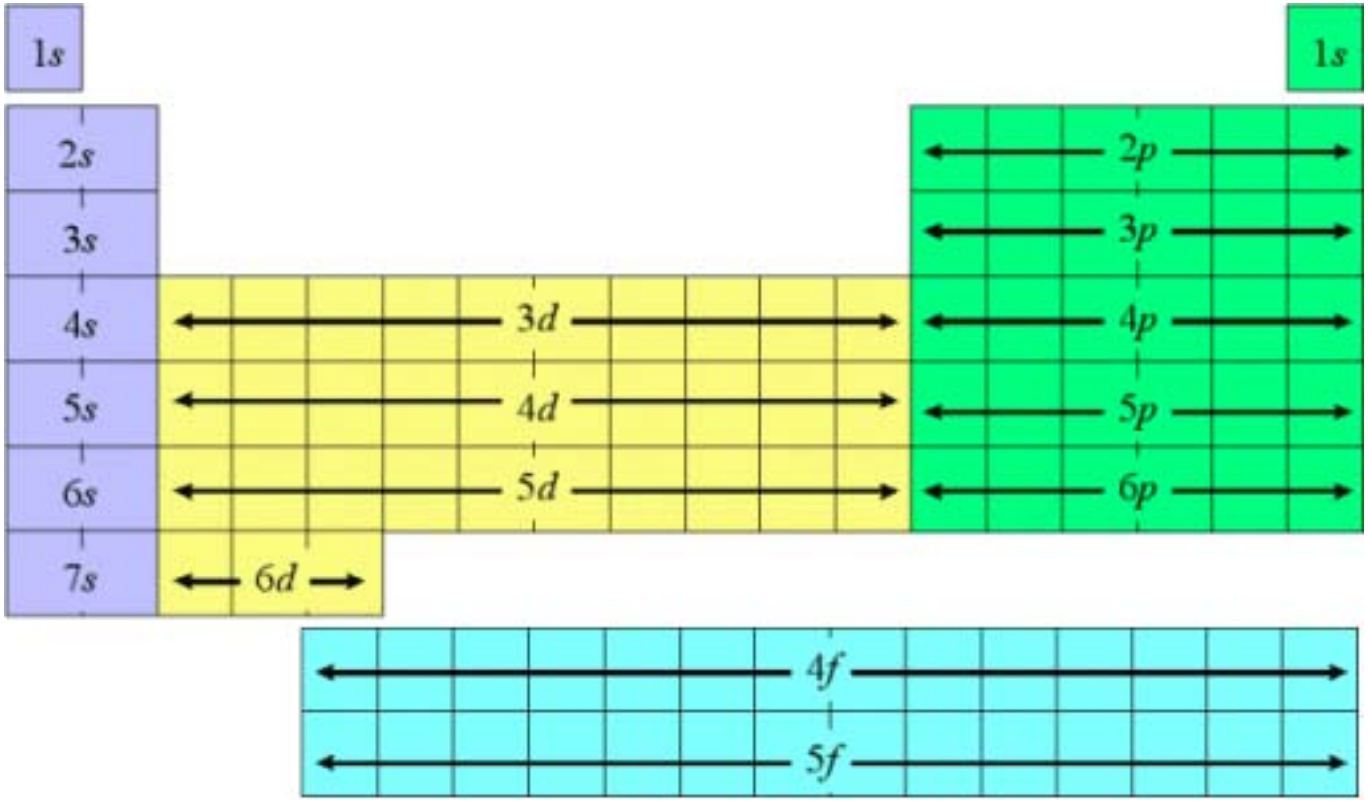
Building up

- Hund's Rule: every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin.

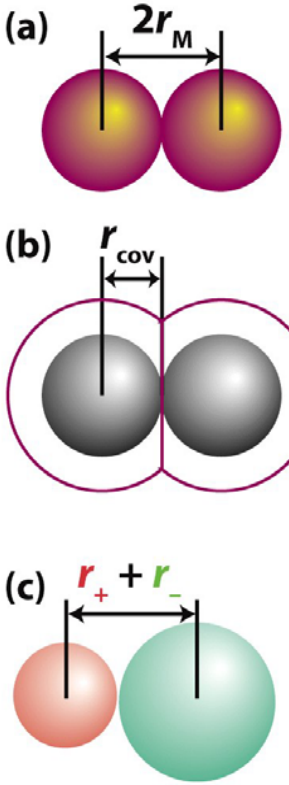


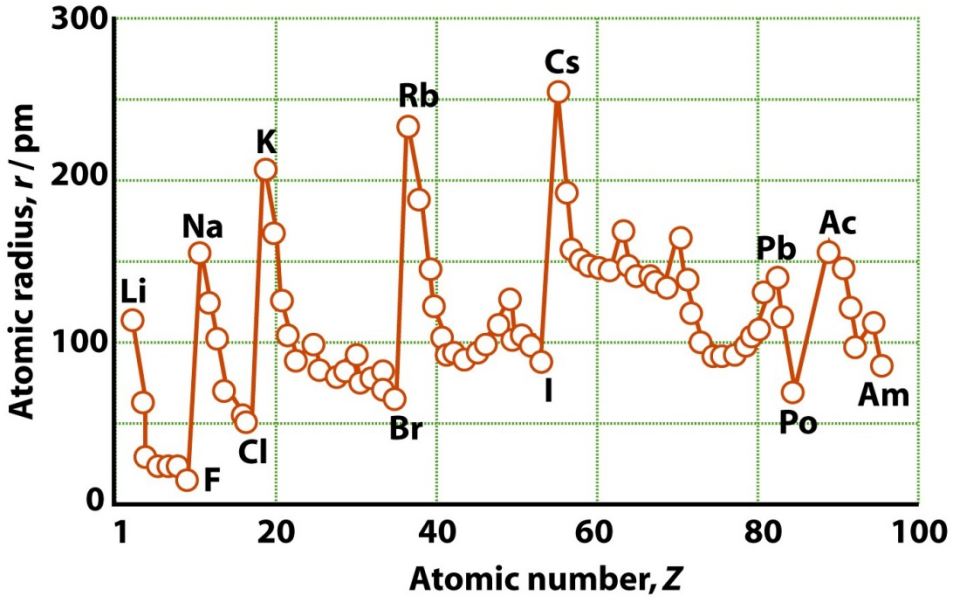
- He - $1s^2$
- C - $1s^2 2s^2 2p^2$ or $[He]2s^2 2p^2$
- V - $[Ar]4s^2 3d^3$
- Cr - $[Ar]\ 4s^1 3d^5$ not $4s^2 3d^4$

Periodic Table… again



Atomic Radii





Ionic Radius

Table 1.4 Atomic radii, *r*/pm*

Li	**Be**	**B**	**C**	**N**	**O**	**F**
157	112	88	77	74	66	64
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
191	160	143	118	110	104	99
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**
235	197	153	122	121	117	114
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**
250	215	167	158	141	137	133
Cs	**Ba**	**Tl**	**Pb**	**Bi**		
272	224	171	175	182		

Table 1.5 Ionic radii, *r*/pm*

Li^+	Be^{2+}	B^{3+}			N^{3-}	O^{2-}	F^-
59(4)	27(4)	11(4)			146	135(2)	128(2)
76(6)						138(4)	131(4)
						140(6)	133(6)
						142(8)	
Na^+	Mg^{2+}	Al^{3+}			P^{3-}	S^{2-}	Cl^-
99(4)	49(4)	39(4)			212	184(6)	181(6)
102(6)	72(6)	53(6)					
118(8)	89(8)						
K^+	Ca^{2+}	Ga^{3+}			As^{3-}	Se^{2-}	Br^-
138(6)	100(6)	62(6)			222	198(6)	196(6)
151(8)	112(8)						
159(10)	123(10)						
160(12)	134(12)						
Rb^+	Sr^{2+}	In^{3+}	Sn^{2+}	Sn^{4+}		Te^{2-}	I^-
152(6)	118(6)	79(6)	83(6)	69(6)		221(6)	220(6)
160(8)	125(8)	92(8)	93(8)				
173(12)	144(12)						
Cs^+	Ba^{2+}	Tl^{3+}					
167(6)	149(6)	88(6)					
174(8)	156(8)	Tl^+					
188(12)	175(12)	164(6)					

*Numbers in parentheses are the coordination number of the ion. For more values, see *Resource section* 1.

Table 1-5
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Ionization energy

- Ease in which an electron can be removed
- $A(g) \rightarrow A^{+}(g) + e^{-}(g)$
- $I = E(A^{+}) - E(A)$
- First Ionization Energy, I_1
- Second Ionization, I_2
- Energy is determined by the HOAO

Ionization Energy

Table 1.6 First and second (and some higher) ionization energies of the elements, $I/(\text{kJ mol}^{-1})$

H							**He**
1312							2373
							5259
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
513	899	801	1086	1402	1314	1681	2080
7297	1757	2426	2352	2855	3386	3375	3952
11809	14844	3660	4619	4577	5300	6050	6122
		25018					
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
495	737	577	786	1011	1000	1251	1520
4562	1476	1816	1577	1903	2251	2296	2665
6911	7732	2744	3231	2911	3361	3826	3928
		11574					
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
419	589	579	762	947	941	1139	1351
3051	1145	1979	1537	1798	2044	2103	3314
4410	4910	2963	3302	2734	2974	3500	3565
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
403	549	558	708	834	869	1008	1170
2632	1064	1821	1412	1794	1795	1846	2045
3900	4210	2704	2943	2443	2698	3197	3097
Cs	**Ba**	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**
375	502	590	716	704	812	926	1036
2420	965	1971	1450	1610	1800	1600	
3400	3619	2878	3080	2466	2700	2900	

Table 1-6
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$$I \propto \frac{Z_{eff}^2}{n^2}$$

Electron affinity

- Ease in which an electron can be added
- $A(g) + e^-(g) \rightarrow A^-(g)$
- $E_a = E(A) - E(A^-)$
- Energy is determined by the LUAO

Table 1.7 Electron affinities of the main-group elements, E_a/(kJ mol^{-1})*

H							**He**
72							−48
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
60	≤0	27	122	−8	141 −780	328	−116
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
53	≤0	43	134	72	200 −492	349	−96
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
48	2	29	116	78	195	325	−96
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
47	5	29	116	103	190	295	−77

Electronegativity

- The power of an atom to attract electrons when it is part of a compound
- Pauling - χ_p : based on bond formation
- Mulliken - $\chi_m = 1/2\ (I + E_a)$
- Allred-Rochow - $\chi_{AR} = 0.77 + \frac{35.90\ Z_{eff}}{(\frac{r}{pm})^2}$

EN

Table 1.8 Pauling χ_P, Mulliken, χ_M, and Allred–Rochow, χ_{AR}, electronegativities

H							**He**
2.20							5.5
3.06							
2.20							
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
0.98	1.57	2.04	2.55	3.04	3.44	3.98	
1.28	1.99	1.83	2.67	3.08	3.22	4.43	4.60
0.97	1.47	2.01	2.50	3.07	3.50	4.10	5.10
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
0.93	1.31	1.61	1.90	2.19	2.58	3.16	
1.21	1.63	1.37	2.03	2.39	2.65	3.54	3.36
1.01	1.23	1.47	1.74	2.06	2.44	2.83	3.30
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
0.82	1.00	1.81	2.01	2.18	2.55	2.96	3.0
1.03	1.30	1.34	1.95	2.26	2.51	3.24	2.98
0.91	1.04	1.82	2.02	2.20	2.48	2.74	3.10
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
0.82	0.95	1.78	1.96	2.05	2.10	2.66	2.6
0.99	1.21	1.30	1.83	2.06	2.34	2.88	2.59
0.89	0.99	1.49	1.72	1.82	2.01	2.21	2.40
Cs	**Ba**	**Tl**	**Pb**	**Bi**			
0.79	0.89	2.04	2.33	2.02			
0.70	0.90	1.80	1.90	1.90			
0.86	0.97	1.44	1.55	1.67			

Polarizabilty

- Ability to have its electron field distorted by another field

Fajan's Rules

→ Small, highly charged cations have polarizing ability.

→ Large, highly charged anions are easily polarized.

→ Cations that do not have noble-gas config. Are easily polarized.