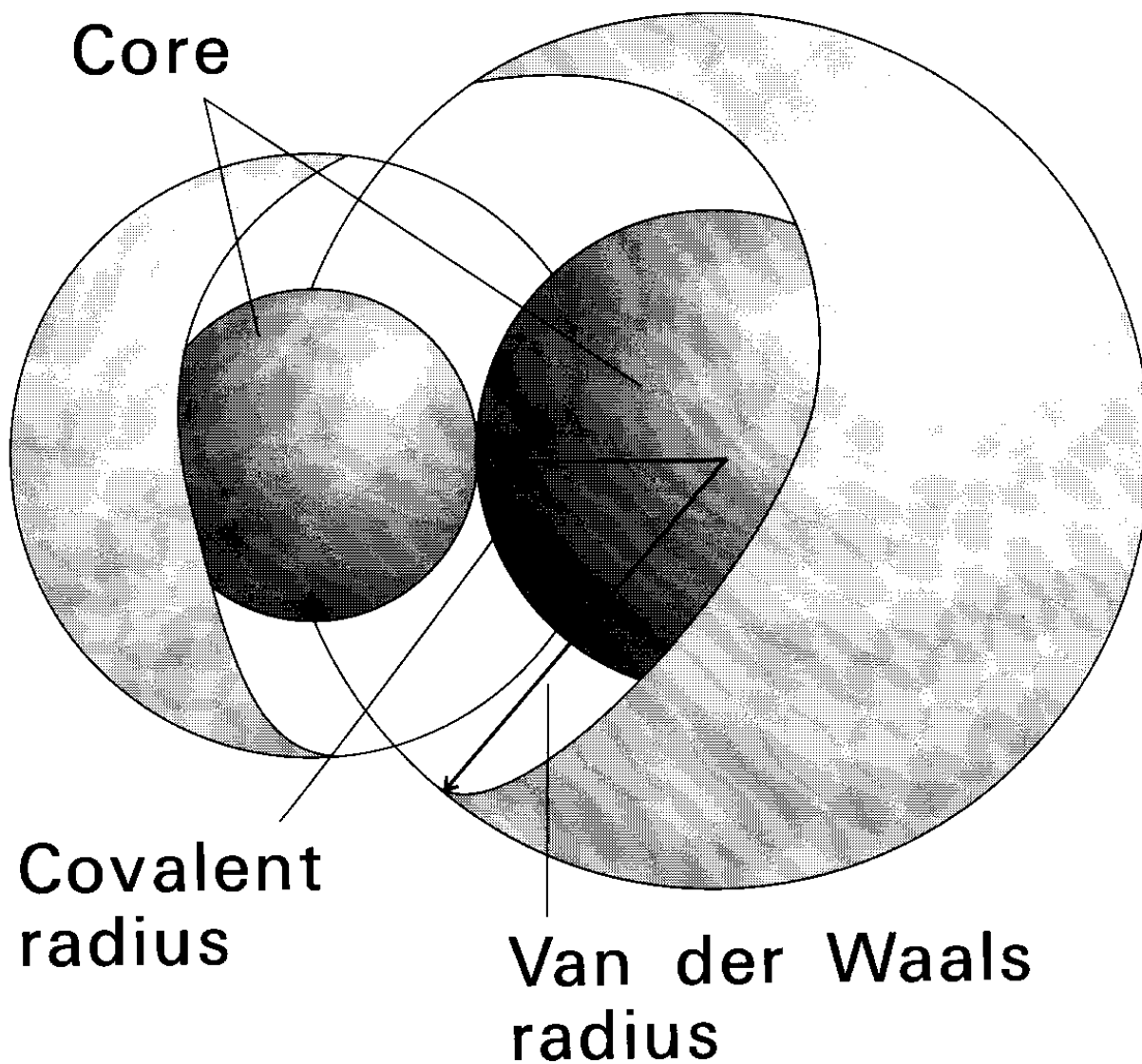


Calculated Orbital Energies as a
Function of Effective Nuclear Charge



Covalent vs. Van der Waals Radius

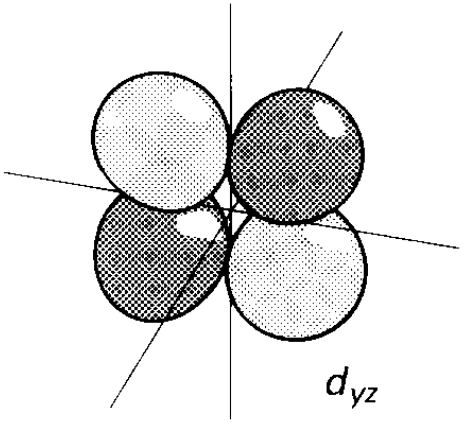
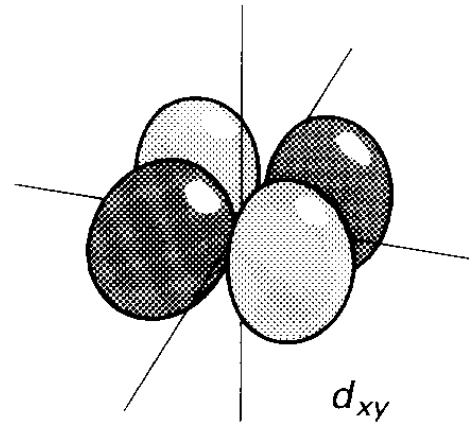
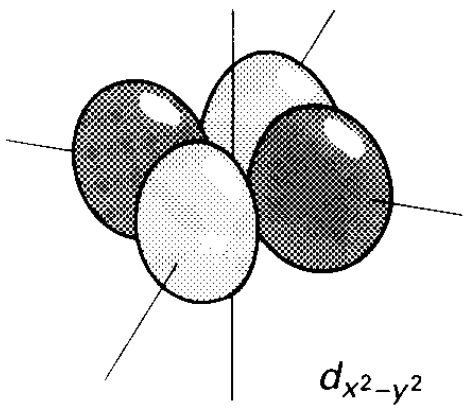
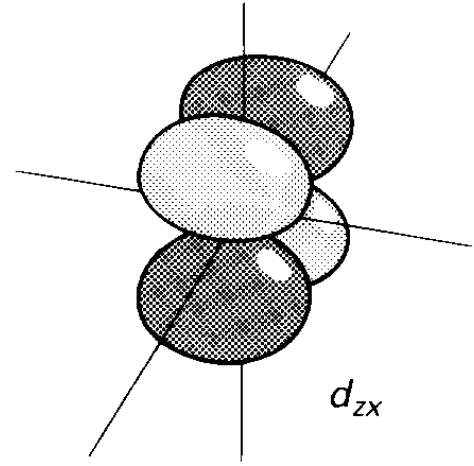
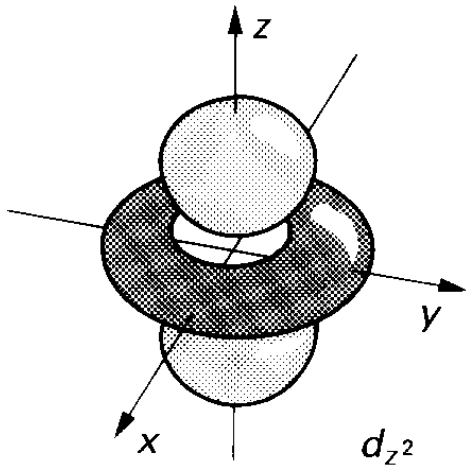
Table 1.8 Electron affinities of the main-group elements (in electronvolts*)

H							He
0.754							-0.5
Li	Be	B	C	N	O	F	Ne
0.618	-0.5	0.277	1.263	-0.07	1.461	3.399	1.2
					-8.75		
Na	Mg	Al	Si	P	S	Cl	Ar
0.548	-0.4	0.441	1.385	0.747	2.077	3.617	-1.0
					-5.51		
K	Ca	Ga	Ge	As	Se	Br	Kr
0.502	-0.3	0.30	1.2	0.81	2.021	3.365	-1.0
Rb	Sr	In	Sn	Sb	Te	I	Xe
0.486	-0.3	0.3	1.2	1.07	1.971	3.059	-0.8

*To convert to kJ mol^{-1} , multiply by 96.485.

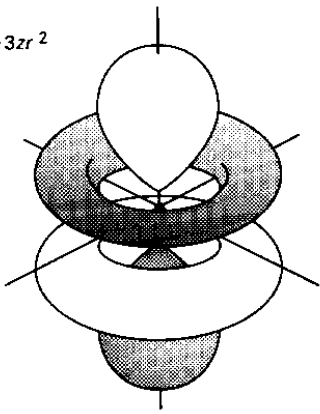
The first values refer to the formation of the ion X^- from the neutral atom X , the second value to the formation of X^{2-} from X^- .

Source: H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data*, **14**, 731 (1985)

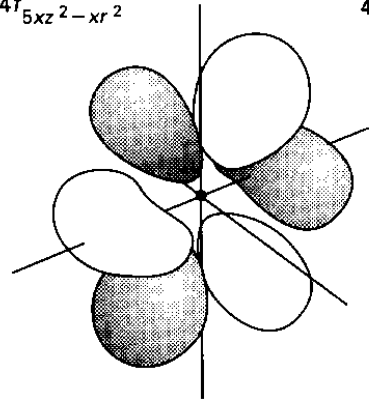


Hydrogen d Type Orbitals

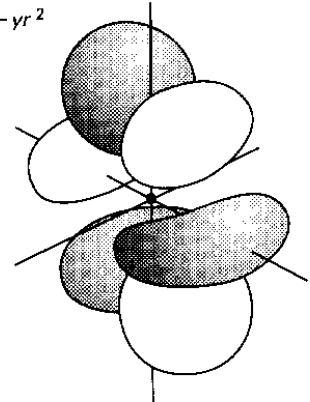
$$4f_{5z^3-3zr^2}$$



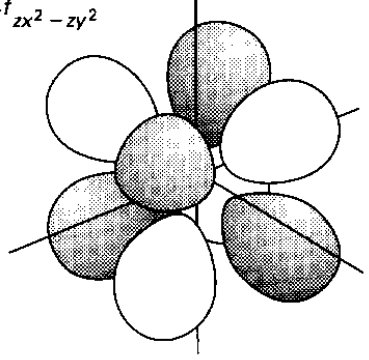
$$4f_{5xz^2-xr^2}$$



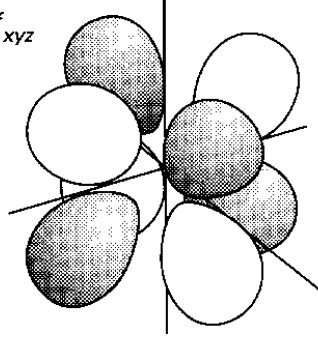
$$4f_{5yz^2-yr^2}$$



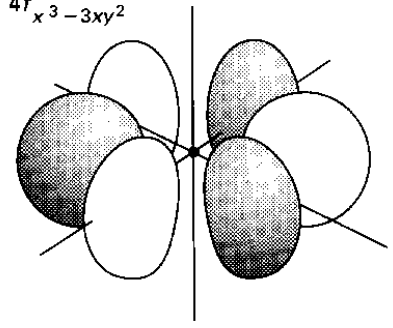
$$4f_{zx^2-zy^2}$$



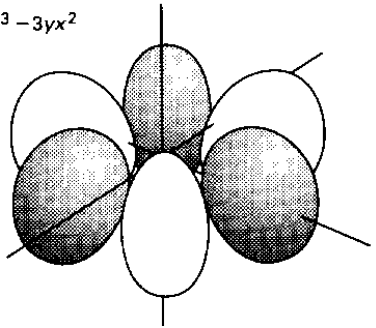
$$4f_{xyz}$$



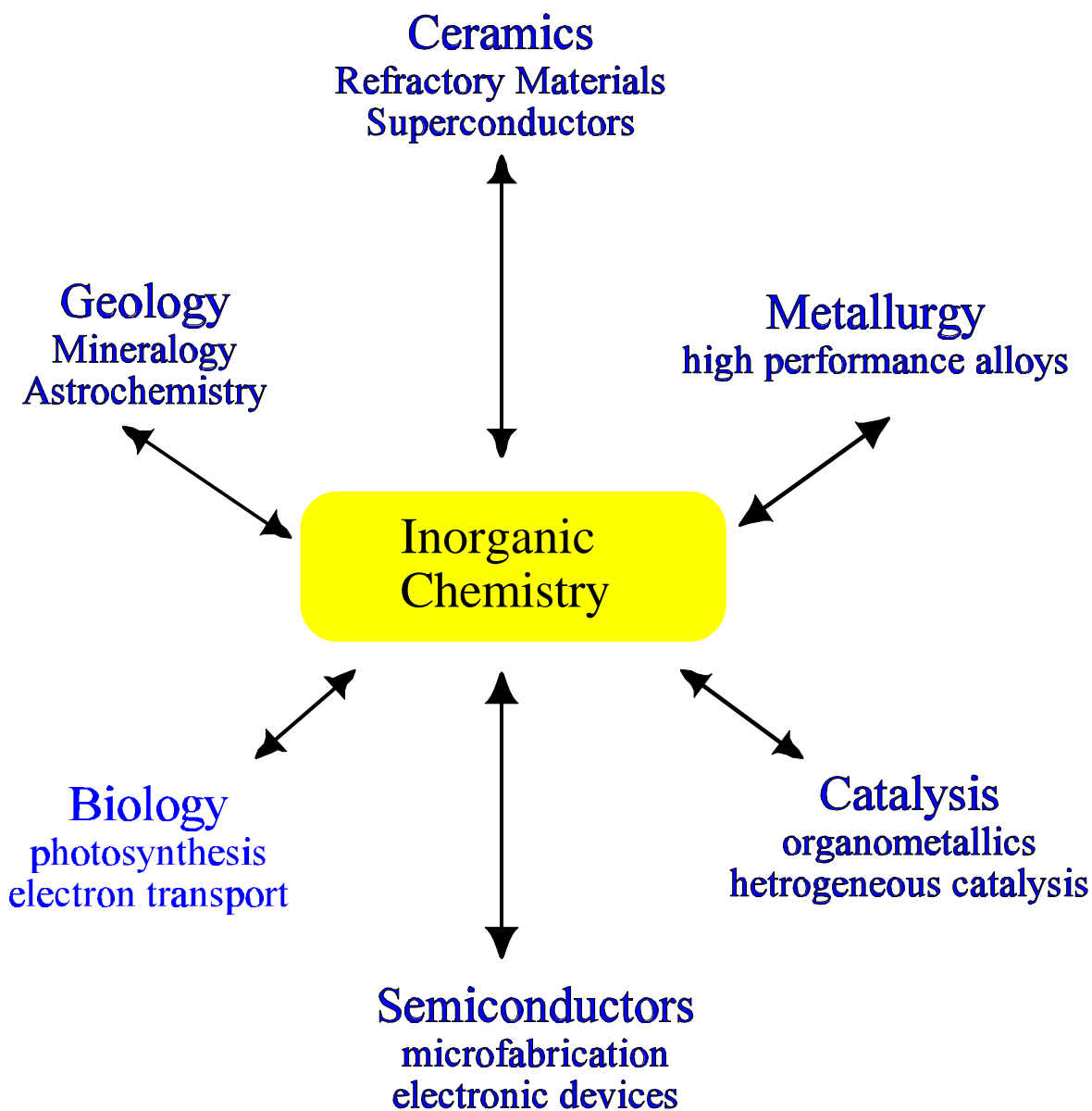
$$4f_{x^3-3xy^2}$$



$$4f_{y^3-3yx^2}$$



Hydrogen *f* type orbitals



Ionization Energies

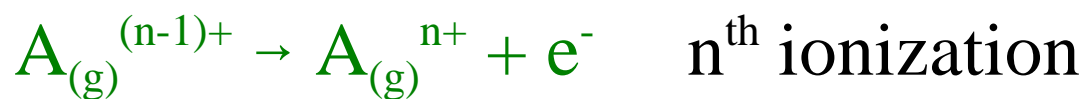


TABLE 10.8 IONIZATION ENERGIES OF GASEOUS ATOMS (kJ mol⁻¹)*

Atomic Number	Symbol	I_1	I_2	I_3	I_4
1	H	1312.0			
2	He	2372.3	5250.3		
3	Li	520.2	7298.1	11815.0	
4	Be	899.5	1757.1	14848.6	21006.5
5	B	800.7	2427.0	3659.7	25025.8
6	C	1086.4	2352.6	4620.4	6222.7
7	N	1402.3	2856.1	4578.1	7475.0
8	O	1313.9	3388.3	5300.5	7469.2
9	F	1681.1	3374.1	6050.5	8407.7
10	Ne	2080.6	3952.3	6122.4	9372
11	Na	495.8	4561.5	6910.1	9543.7
12	Mg	737.7	1450.7	7732.6	10542.4
13	Al	577.5	1816.7	2744.8	11577.4
14	Si	786.5	1577.1	3231.6	4355.5
15	P	1011.7	1903.2	2911.6	4956.4
16	S	999.5	2251.4	3360.2	4564.3
17	Cl	1251.2	2297.7	3822.1	5158.5
18	Ar	1520.6	2665.8	3931.0	5770.6
19	K	418.8	3051.7	4419.5	5877.3
20	Ca	589.8	1145.5	4912.4	6491.0
21	Sc	633.1	1235.0	2388.7	7090.4
22	Ti	658.1	1309.9	2652.5	4174.5
23	V	650.3	1414.0	2828.1	4506.5
24	Cr	652.8	1591.8	2987.1	4738
25	Mn	717.5	1509.0	3248.4	4940
26	Fe	759.4	1561.9	2957.6	5290
27	Co	758.8	1648.4	3232.3	4950
28	Ni	736.9	1753.0	3408.2	5300
29	Cu	745.5	1957.9	3553.9	5330
30	Zn	906.4	1733.3	3832.6	5730
31	Ga	578.8	1979.2	2963.2	6200
32	Ge	762.2	1537.5	3302.1	4410.4
33	As	946.7	1797.9	2735.5	4838.0
34	Se	940.9	2044.3	2973.6	4143.4
35	Br	1139.9	2103.6	3463.0	4565.0
36	Kr	1350.7	2350.4	3565.3	5070
37	Rb	403.0	2632.6	3827	5080
38	Sr	549.5	1064.2	4200	5500
54	Xe	1170.3	2046.4	3099.5	
55	Cs	375.7	2233		
56	Ba	502.9	965.3	3453.6	

* Values mainly calculated from D. D. Wagman et al., The NBS tables of chemical thermodynamic properties, *Journal of Physical and Chemical Reference Data*, **11**, Supplement 2, 1982.

Madelung's Rule

- I. Energy increases with increasing $n + l$
- II. For identical values of $n + l$, energy increases with increasing n

$$\begin{array}{cccccccccc} 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < \dots \\ 1 & 2 & 3 & 3 & 4 & 4 & 5 & 5 & : & (n + l) \end{array}$$

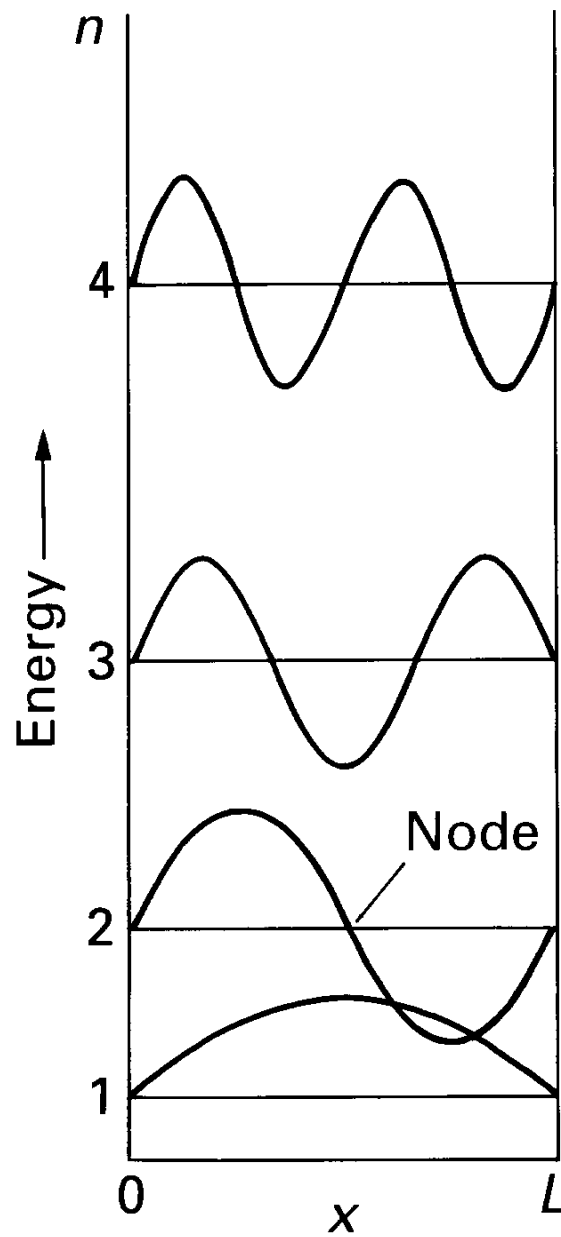
Reason:

Shielding of the nuclear charge by the innermost electrons:

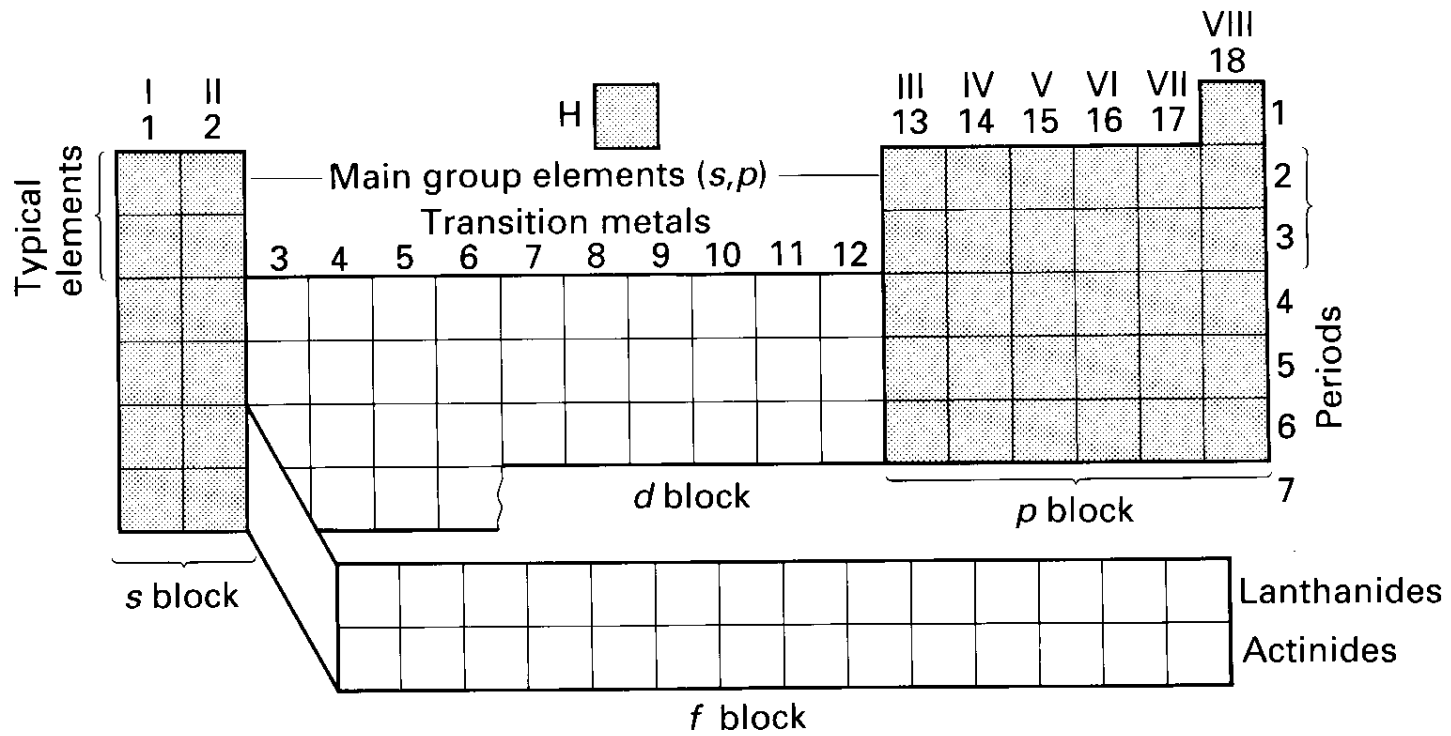
$$Z_{\text{eff}} = Z - S \quad (S - \text{contribution due to screening of nuclear charge by innermost electrons})$$

Orbital penetration:

$$s > p > d > f$$



Nodal Properties of Standing Waves



Periodic Classification of the Elements

Photoelectron Spectrum of Gaseous Argon (Mg K α x-radiation)

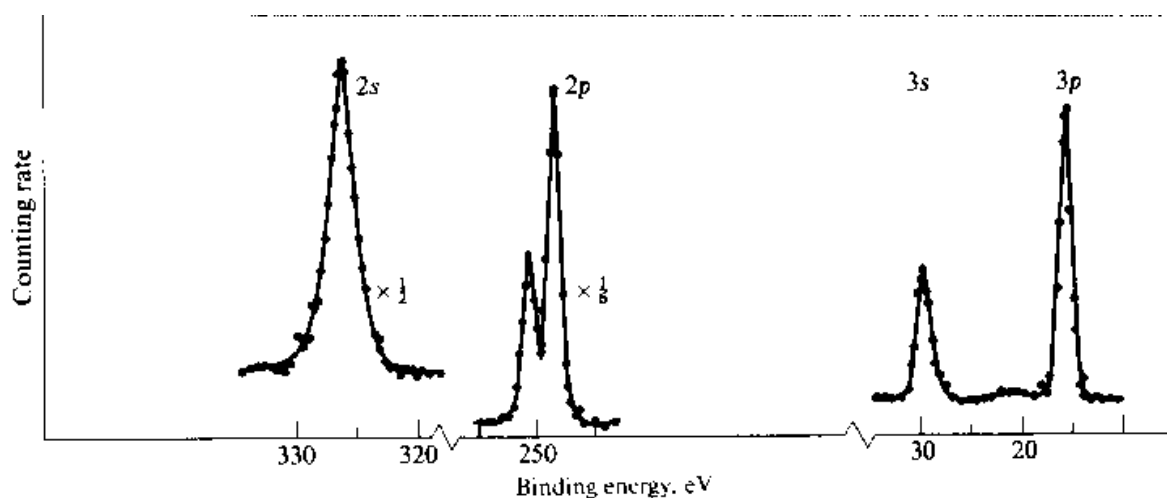
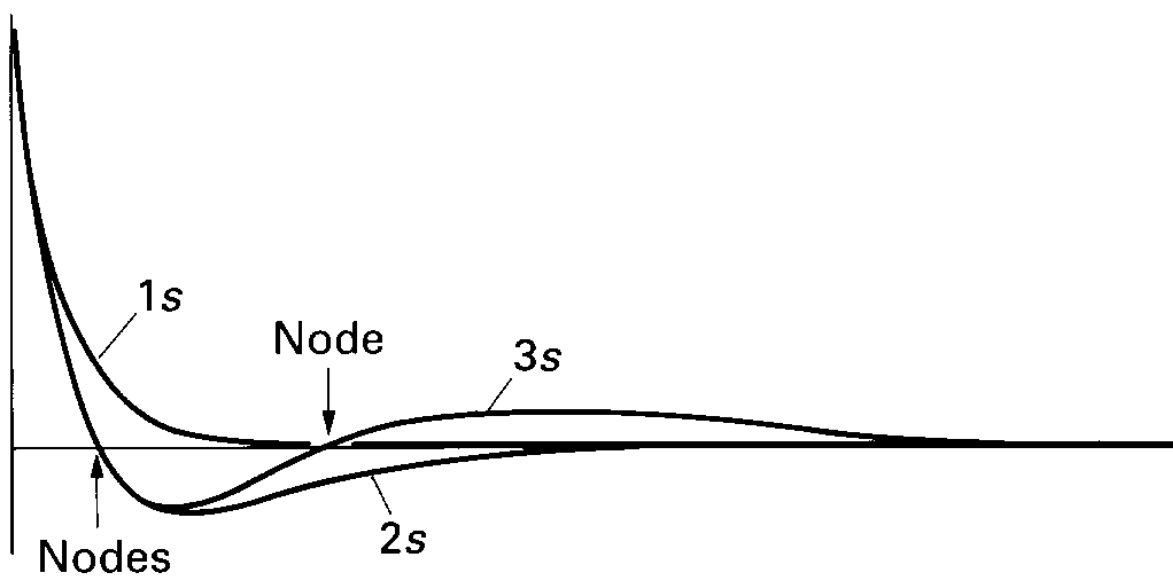


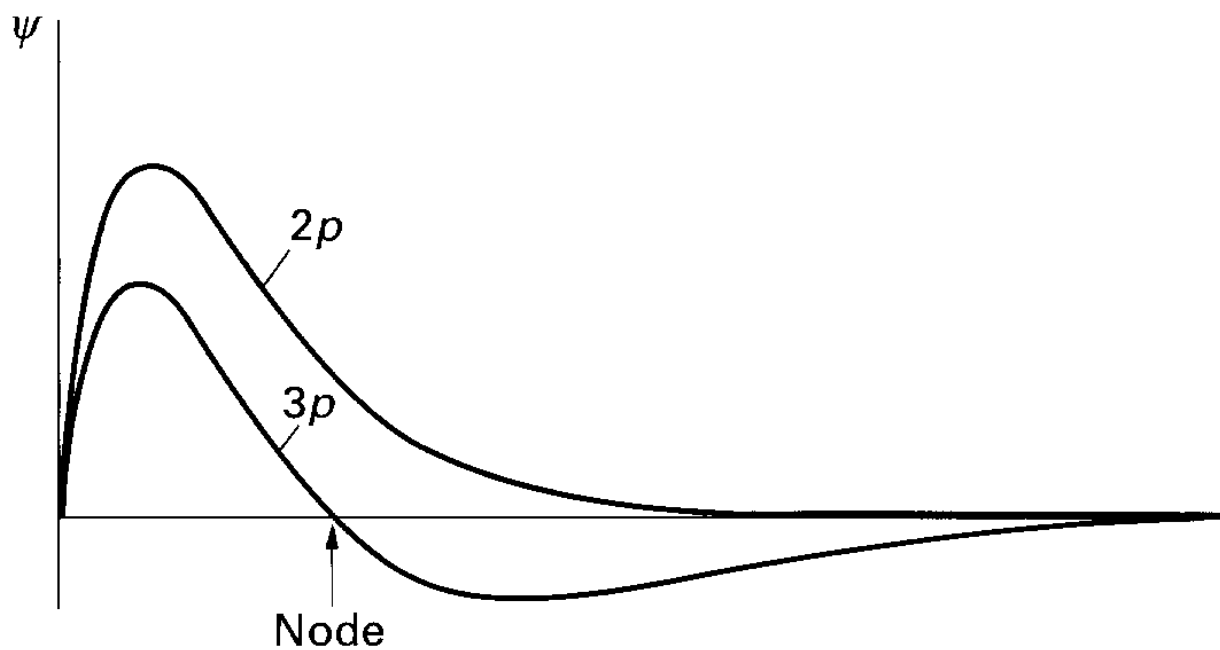
TABLE 1.6
Ionization energies of argon†

Level	I , eV
$3p_{3/2}$	15.759
$3p_{1/2}$	15.937
$3s$	29.24
$2p_{3/2}$	248.52
$2p_{1/2}$	250.55
$2s$	326.3
$1s$	3205.9

† K. Siegbahn et al., "ESCA Applied to Free Molecules," North-Holland, Amsterdam, 1969.

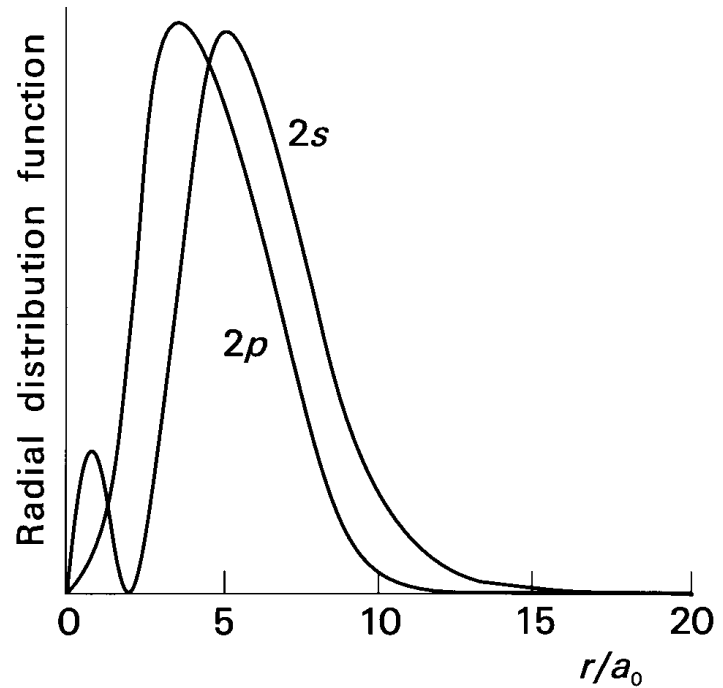
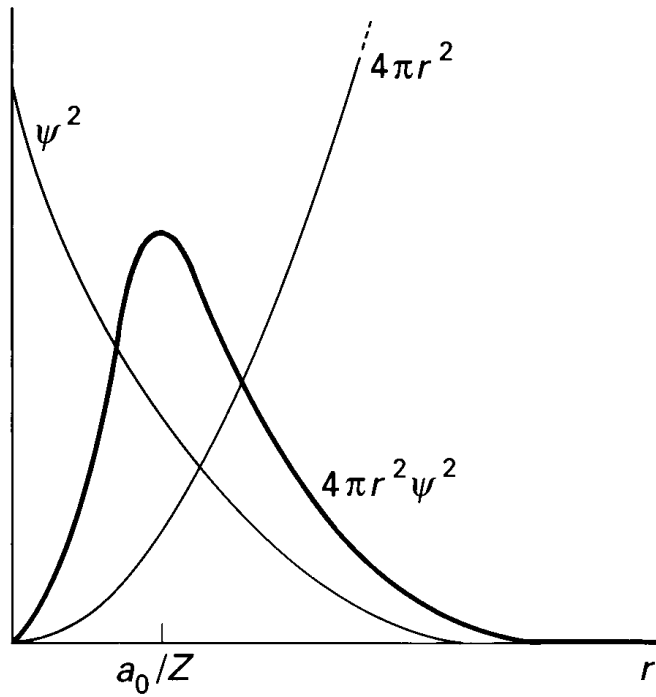


1.14

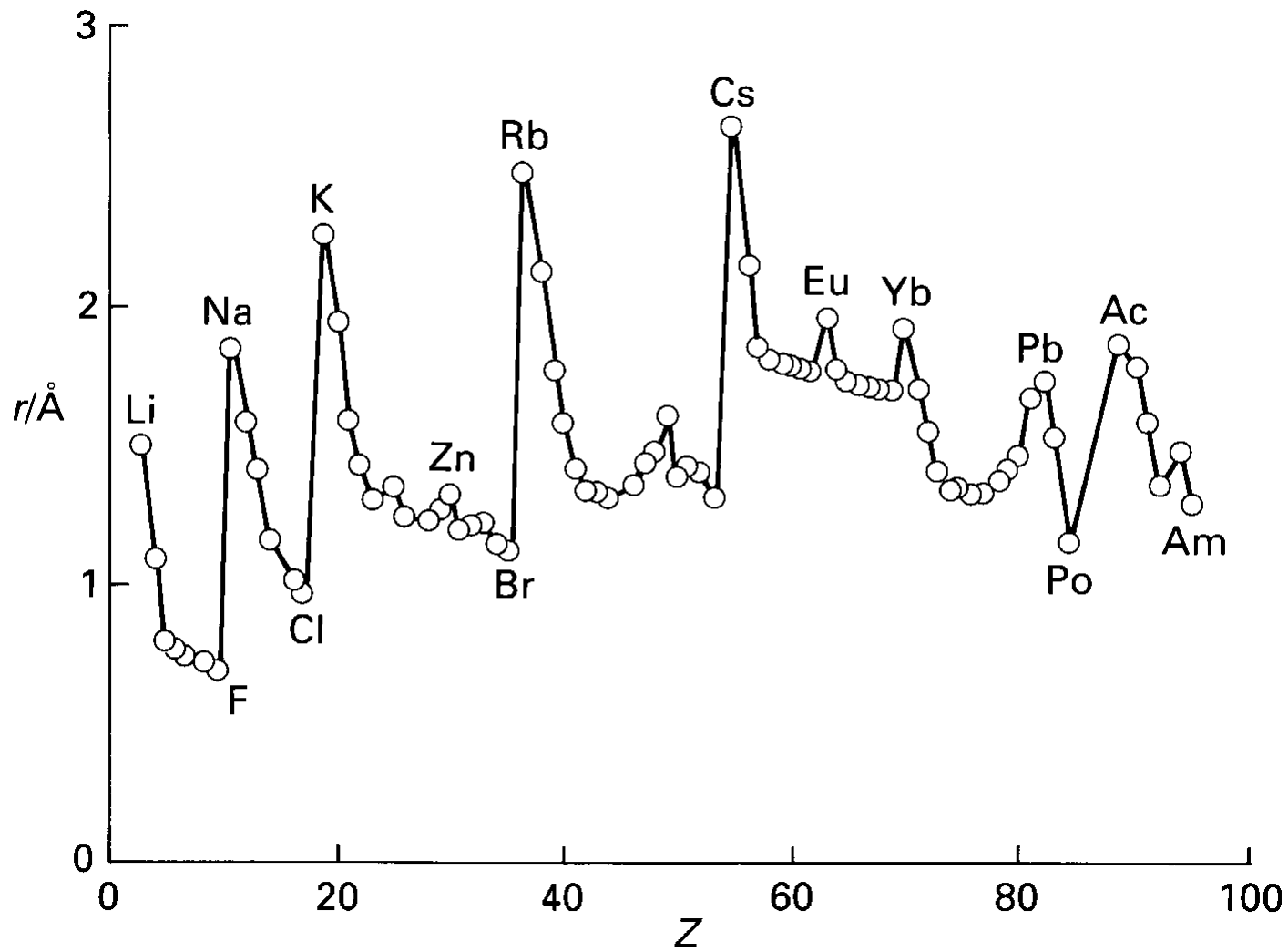


1.15

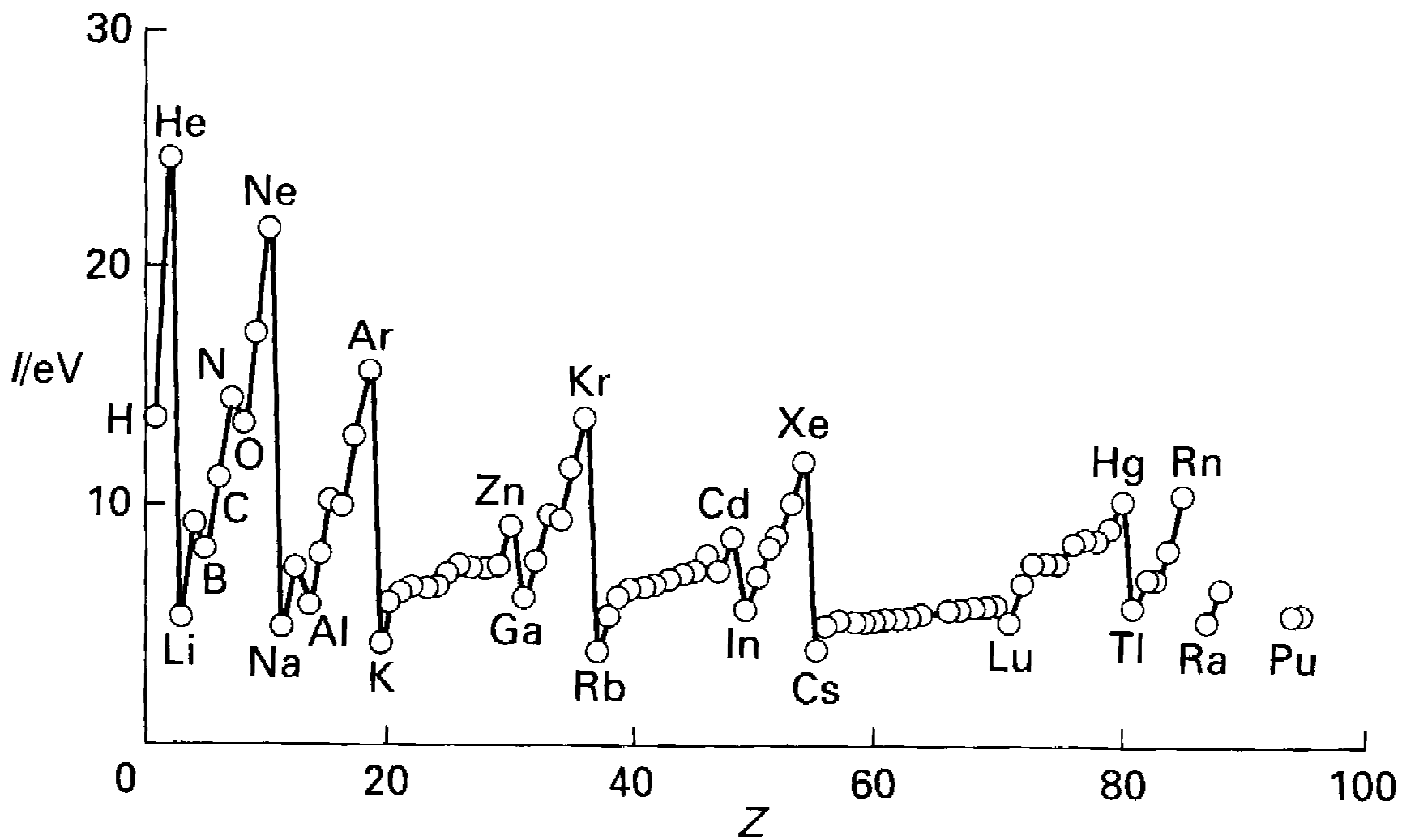
Radial Nodes for Hydrogen s and p Atomic Orbitals



Radial Distribution Function - Comparison of 2s and 2p Atomic Orbitals



Trends in Atomic Radius



Trends in Ionization Energies

Aufbau Principle and Electron Configurations

- I. Each element is “built up” systematically from the previous by the addition of both one proton (to the nucleus) and one electron
- II. The electron is placed in the lowest energy orbital available (maximum 2 electrons/orbital)

Examples:

H:	$1s^1$	
He:	$1s^2$	
Li:	$1s^2 2s^1$	[He] $2s^1$
Be:	$1s^2 2s^2$	[He] $2s^2$
B:	$1s^2 2s^2 2p^1$	[He] $2s^2 2p^1$
C:	$1s^2 2s^2 2p^2$	[He] $2s^2 2p^2$
N:	$1s^2 2s^2 2p^3$	[He] $2s^2 2p^3$
O:	$1s^2 2s^2 2p^4$	[He] $2s^2 2p^4$
F:	$1s^2 2s^2 2p^5$	[He] $2s^2 2p^5$
Ne:	$1s^2 2s^2 2p^6$	[He] $2s^2 2p^6$
Na:	$1s^2 2s^2 2p^1 3s^1$	[Ne] $3s^1$
Ca:	$1s^2 2s^2 2p^1 3s^2$	[Ne] $3s^2$
Al:	$1s^2 2s^2 2p^1 3s^1 3p^1$	[Ne] $3s^2 2p^1$