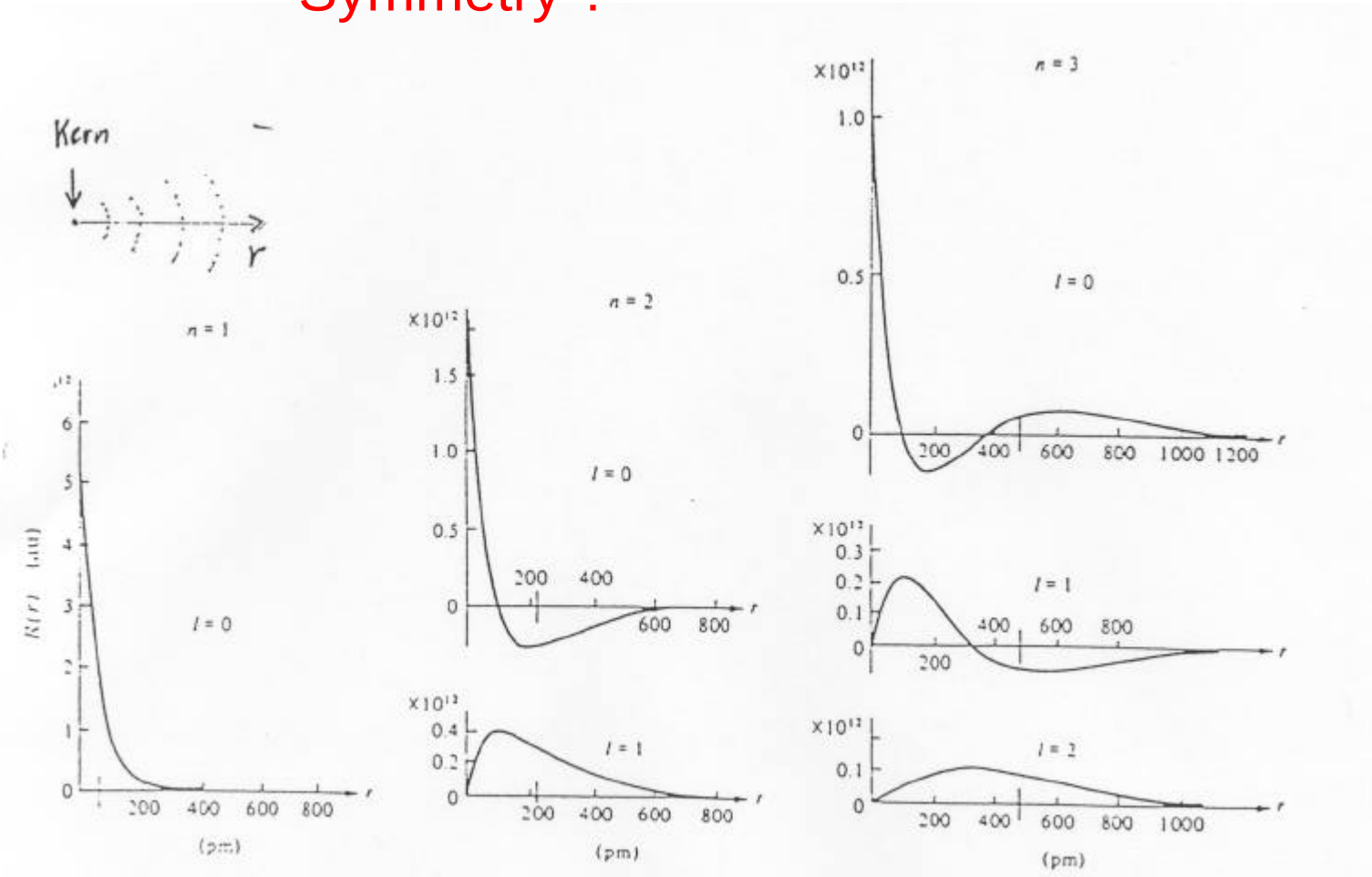
Skript zur Vorlesung Anorganische Chemie I

Atomic orbitals

Radial part

Symmetry ?

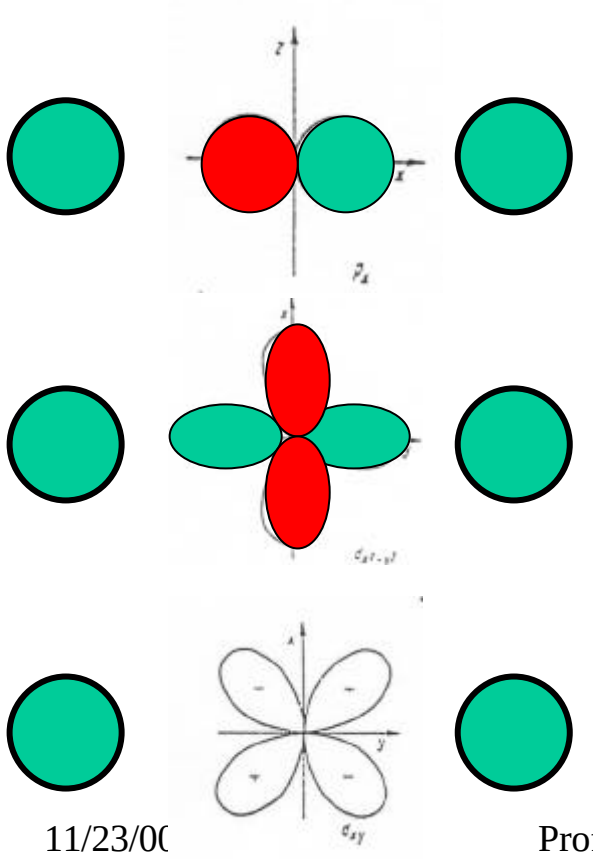


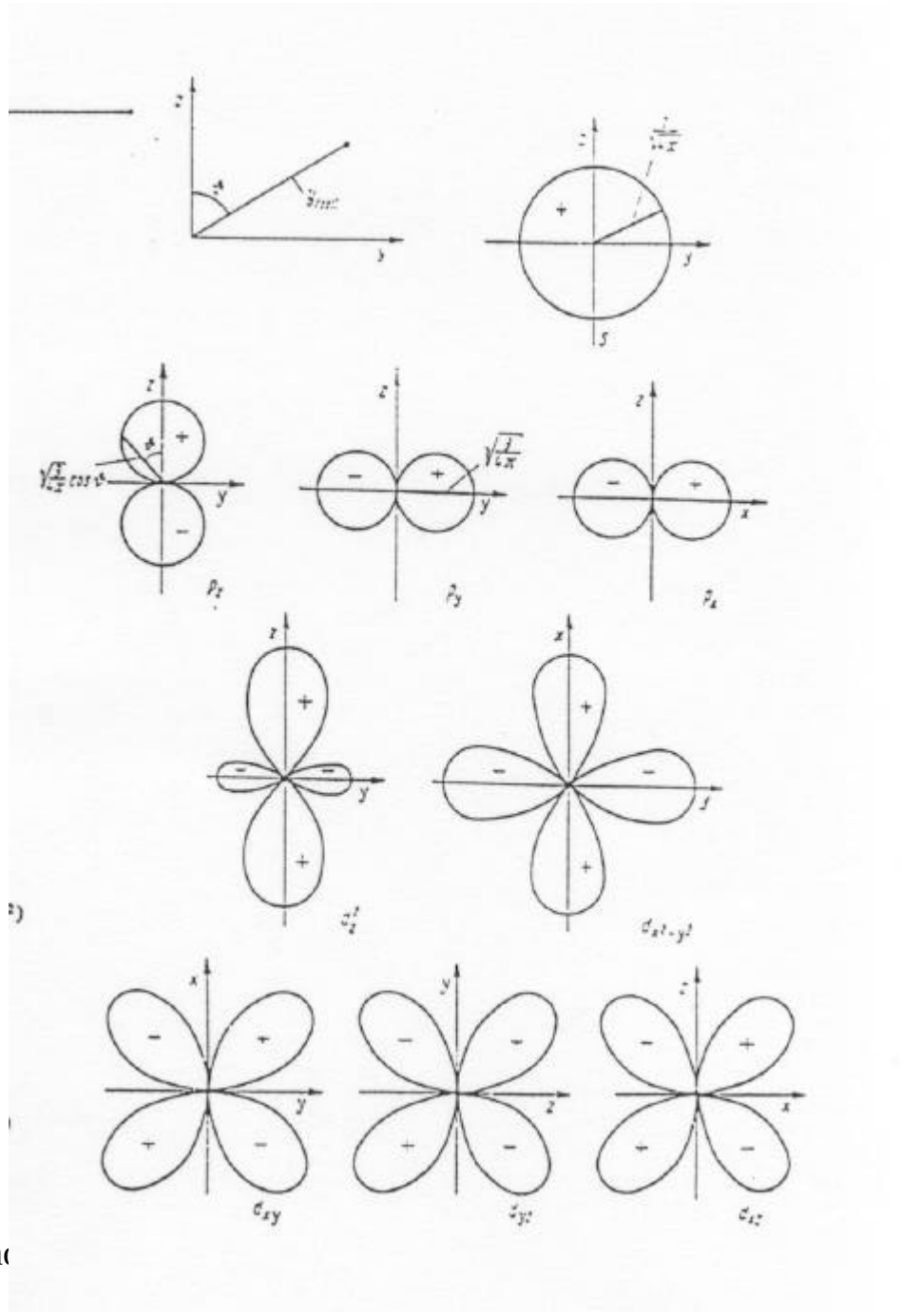
Radialer Anteil der Eigenfunktionen des Wasserstoff-Atoms für $n = 1, 2, 3$. [Aus G. Herzberg, „Atomic Spectra and Atomic Structure", Dover Publications, Inc., New York, 1944.]

Atomic orbitals

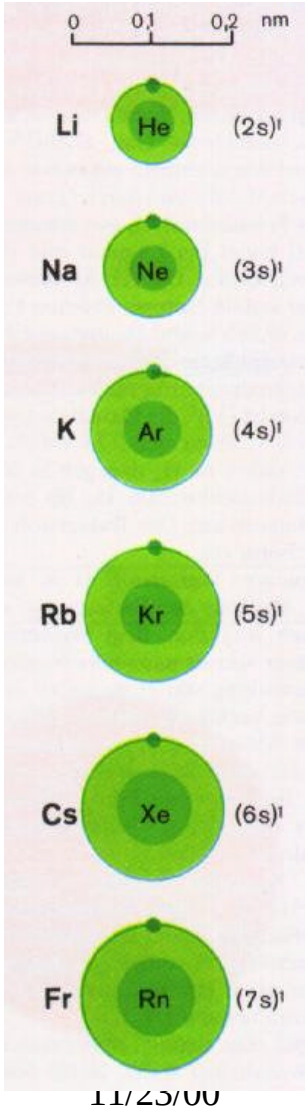
Angular part

Symmetry ?





Orbital energies and shielding



Contraction

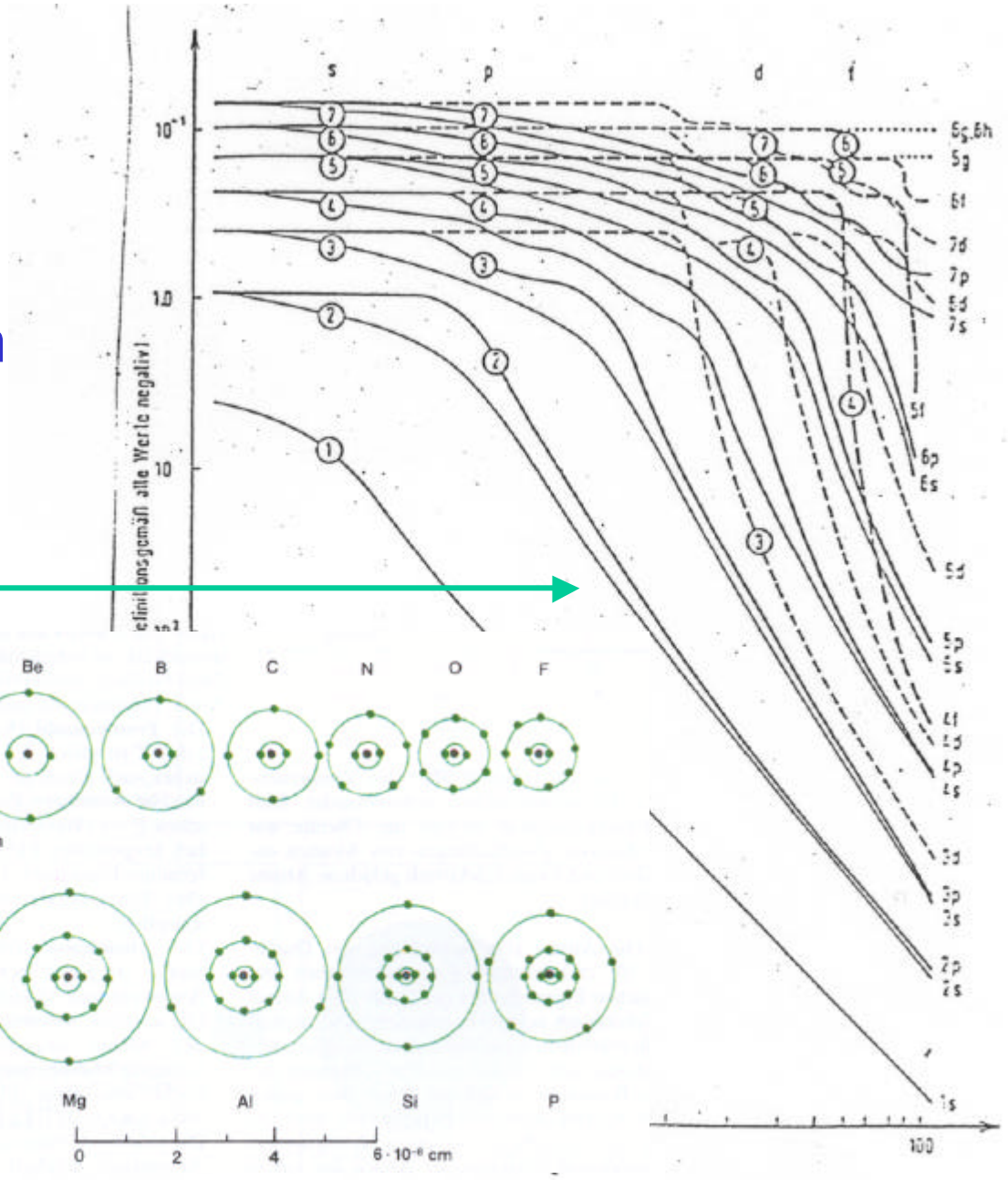
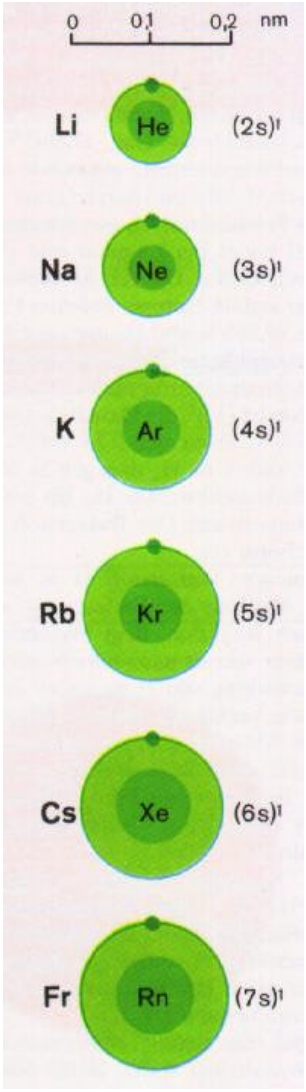
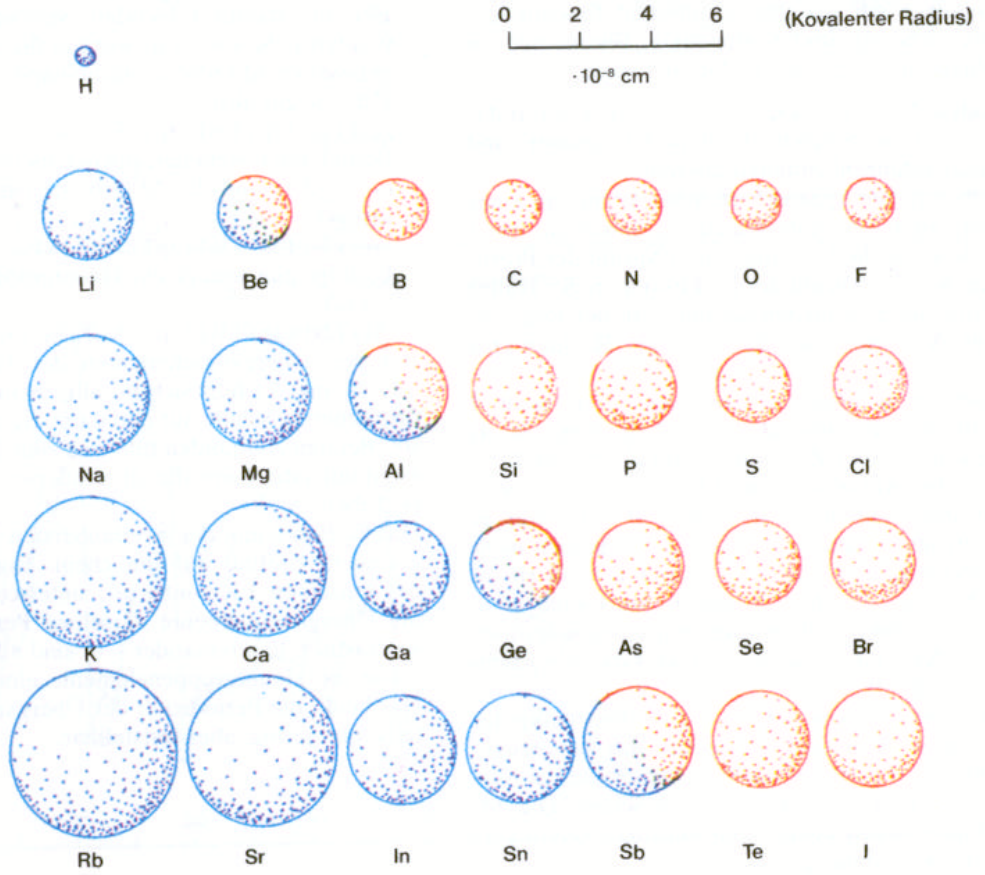
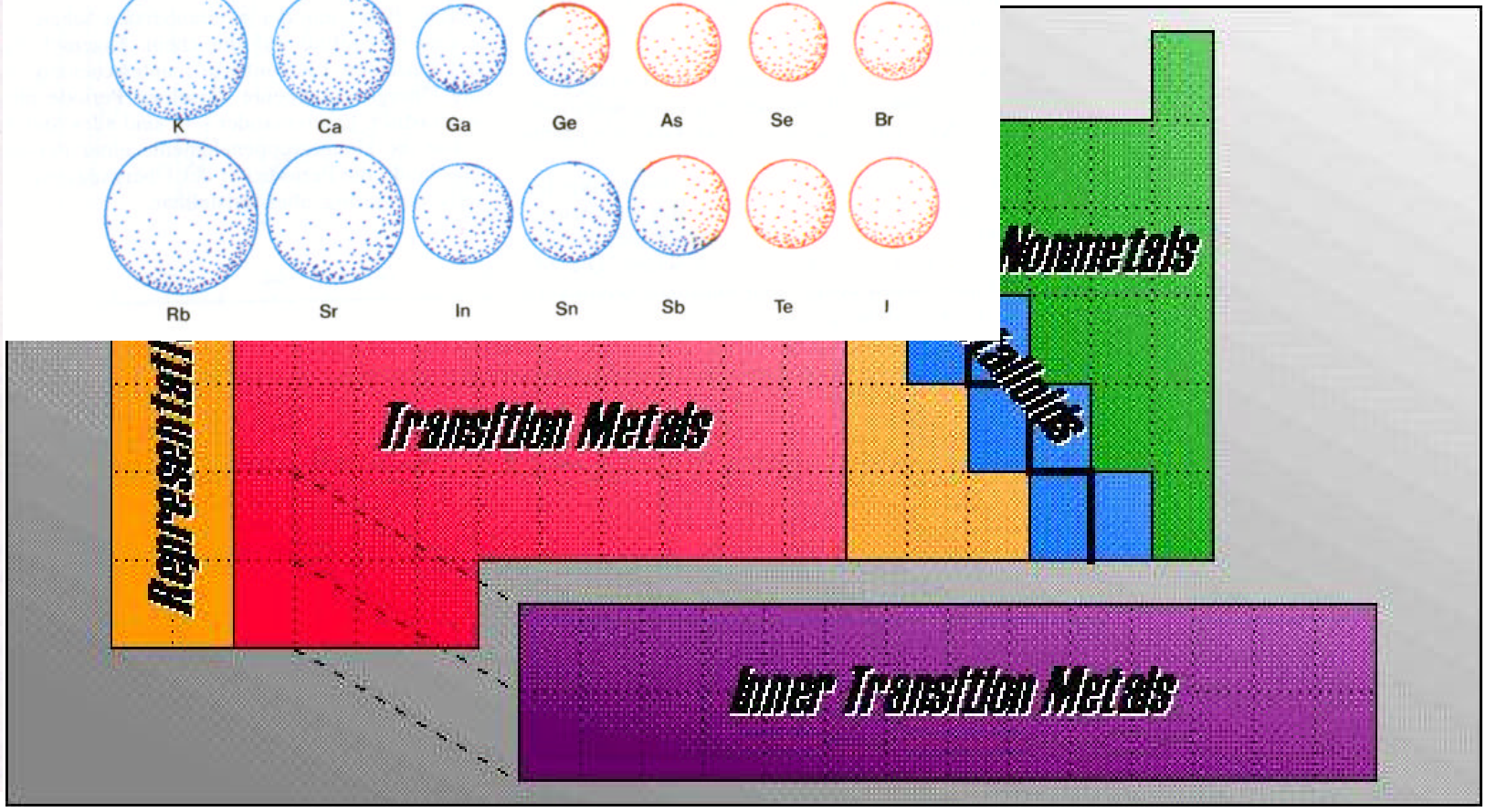


Abb. 3–17. Relativenergien, E, der Atomorbitale als Funktion der Kernladung, Z (Ordnungszahl). Es handelt sich um geglättete Kurven unter Vernachlässigung kleiner beobachteter Fluktuationen. Beide Variablen sind in einem logarithmischen Maßstab dargestellt. [Der größte Teil der Daten stammt von R. Latter, Phys. Rev. 99, 510 (1955).]

Orbital energies and contraction

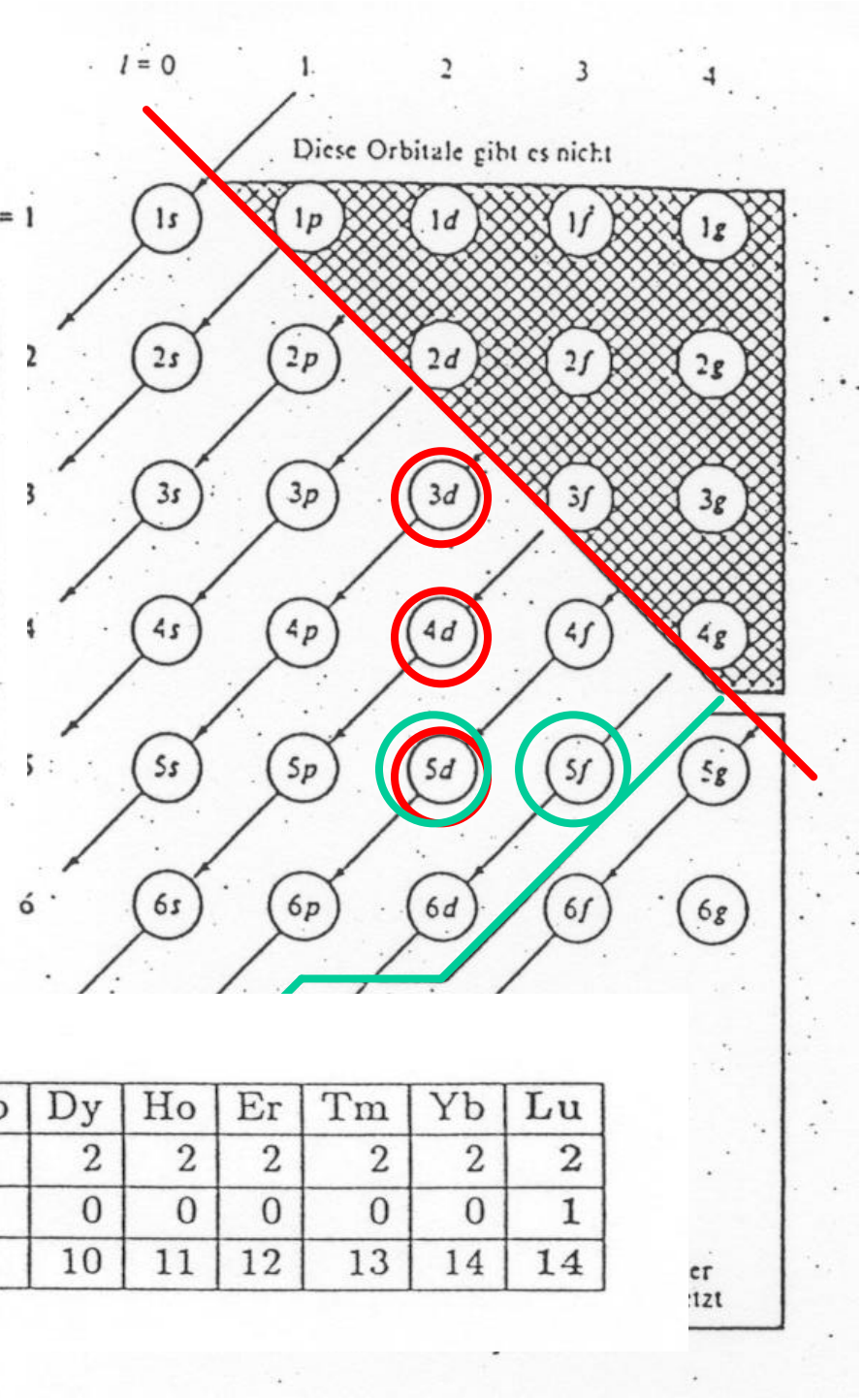






Orbital energies and orbital filling

Orbital/Atom	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10
4p	0	0	0	0	0	0	0	0	0	0
Orbital/Atom	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5s	2	2	2	1	2	2	2	2	1	2
4d	1	2	3	5	5	6	7	8	10	10
5p	0	0	0	0	0	0	0	0	0	0
Orbital/Atom	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10
6p	0	0	0	0	0	0	0	0	0	0



5d allows for bonding
5f not

O/A	La	Ce	Pr	Nd	Pm	Sm	En	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
6s	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
5d	1	0	0	0	0	0	0	1	0	0	0	0	0	0	1
4f	0	2	3	4	5	6	7	7	9	10	11	12	13	14	14

Electron spin and magnetism

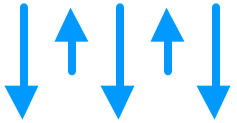
electron : charge + spin

interaction: coulomb magnetic

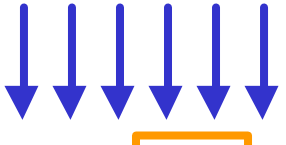
e-e : repulsive > attractive

$$\mu_s = \frac{eh}{4\pi m} 2\sqrt{s(s+1)} = \mu_B 2\sqrt{s(s+1)}$$

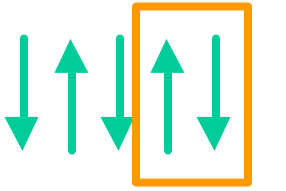
Orbital/Atom	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10
4p	0	0	0	0	0	0	0	0	0	0
Orbital/Atom	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5s	2	2	2	1	2	2	2	2	1	2
4d	1	2	3	5	5	6	7	8	10	10
5p	0	0	0	0	0	0	0	0	0	0
Orbital/Atom	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10
6p	0	0	0	0	0	0	0	0	0	0



paramagnetic / ferromagnetic



diamagnetic / antiferromagnetic



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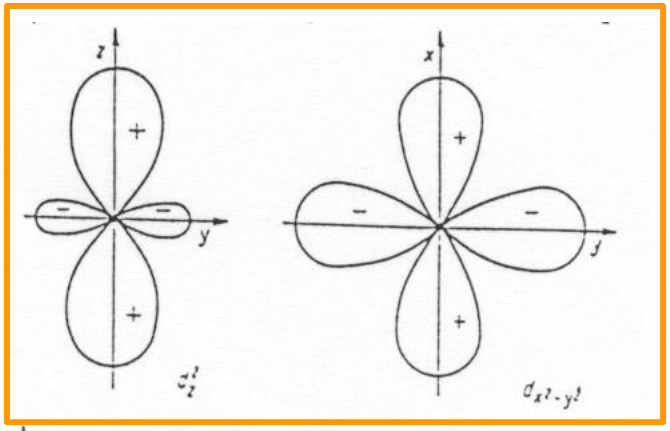

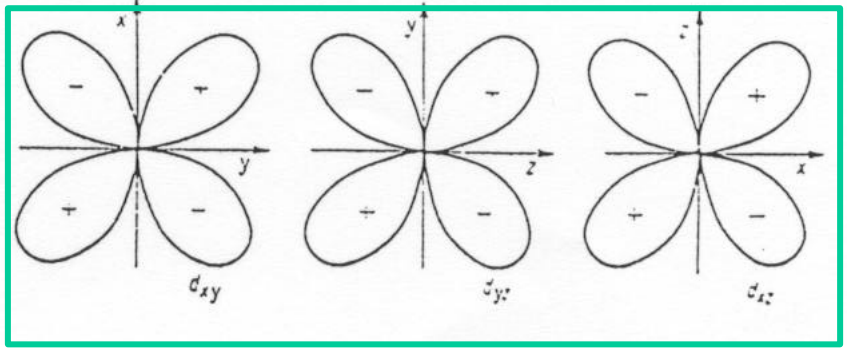

Orbital/Atom	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10
4p	0	0	0	0	0	0	0	0	0	0
Orbital/Atom	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5s	2	2	2	1	2	2	2	2	1	2
4d	1	2	3	5	5	6	7	8	10	10
5p	0	0	0	0	0	0	0	0	0	0
Orbital/Atom	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10
6p	0	0	0	0	0	0	0	0	0	0

octahedral environment

free atom

high spin

low spin

d^5

d^5

Electron Loss - Cations

Orbital/Atom	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10
4p	0	0	0	0	0	0	0	0	0	0
Orbital/Atom	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5s	2	2	2	1	2	2	2	2	1	2
4d	1	2	3	5	5	6	7	8	10	10
5p	0	0	0	0	0	0	0	0	0	0
Orbital/Atom	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10
6p	0	0	0	0	0	0	0	0	0	0

Electron acquisition - anions

Electron affinity

$$F^- \longrightarrow F + e \qquad IE(F^-) = EA(F) = +328[kJmol^{-1}] \qquad (14)$$

EA(P)	=	71	kJ mol^{-1}	EA(F)	<	EA(Cl)
EA(S)	=	200	kJ mol^{-1}	EA(O)	<	EA(S)
EA(Si)	=	132	kJ mol^{-1}	EA(N)	<	EA(P)