Solid surface as a physical problem

Bedřich Velický, František Máca

I.

NEVF 514 Surface Physics

Winter Term 2018 - 2019

Troja, 12-th October 2018

Introductory remarks

- This course concerns

  <u>theoretical aspects of surface physics</u>

- A few themes selected from a vast area
- All belong to the essentials
- The lectures address more physical aspects than technicalities $\Rightarrow$ suited for experimentalists

Surface as a physical problem

Real surfaces $\rightarrow$ surface $\equiv$ interface to vacuum

atomically clean — "the worst of all interfaces"

Four aspects

DISBALANCE OF BONDING FORCES	Surface tension; Structural changes: relaxation, reconstruction
ELECTRON DENSITY HIGH $\rightarrow$ LOW	Surface dipole, surface barrier Local $\rightarrow$ non-local electron exchange
SUBSTRATE vs. ADSORBATE	Substrate: semi-infinite … a reservoir Continuous energy bands, extended electron states $\times$ Adsorbate: discrete levels localized states Meeting in the sensitive surface area
COMPENSATIONS IN TOTAL ENERGY	Considerable variability of surface structures “vulnerability of surfaces”

• • • IMPLICATIONS FOR THE SURFACE THEORY

Implications for the surface theory

as a path to interpretation and prediction of experiments

- “empirical rules” & model intepretations often uncertain
- decision only possible by highly accurate *ab initio* calculations
- the problem of surfaces is a part of the general problem of condensed matter

Implications for the surface theory

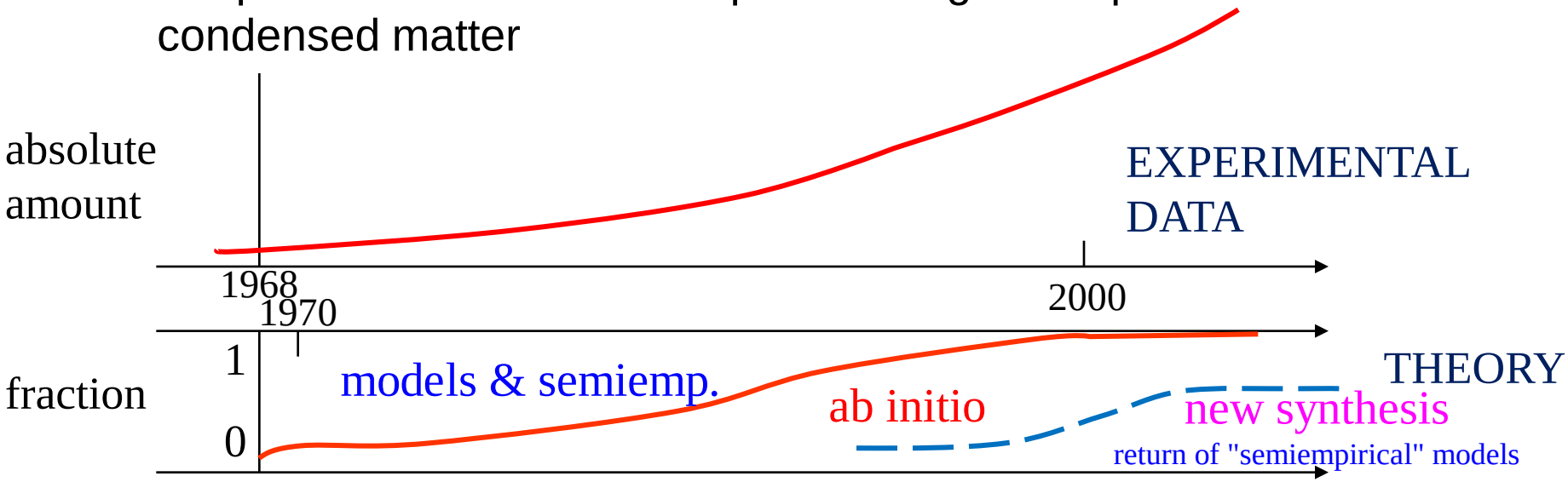
as a path to interpretation and prediction of experiments

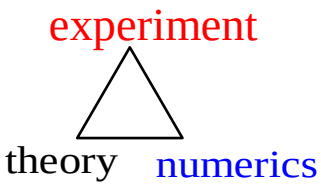
- "empirical rules" & model intepretations often uncertain
- decision only possible by highly accurate *ab initio* calculations
- the problem of surfaces is a very tricky part of the general problem of condensed matter

Implications for the surface theory

as a path to interpretation and prediction of experiments

- "empirical rules" & model intepretations often uncertain
- decision only possible by highly accurate *ab initio* calculations
- the problem of surfaces is a very tricky part of the general problem of condensed matter





WHY
- understanding the results
- generalization
- classification
- prediction

Digression: What happened 40+ years ago?

IN EXPERIMENTAL TECHNIQUES

- UHV
- MBE
- new surface probes
- dedicated SR sources
  Tantalus at SRC U. Madison-Wisconsin 1968

IN THEORETICAL TOOLS

- LDA Hohenberg&Kohn 1964, Kohn&Sham 1965
- GW Hedin 1965, Hedin&S.Lundquist 1967
- Hubbard Hamiltonian 1964 $\rightarrow$ LDA + U
- IIIrd generation computers: IBM 360 1964

The paradigm of condensed matter theory

- the problem of surfaces is a very tricky part of the general problem of condensed matter theory

THE PARADIGM [“theory of everything”] All Condensed Matter systems and processes can be fully described using ordinary non-relativistic quantum mechanics/statistics

The paradigm of condensed matter theory

- the problem of surfaces is a very tricky part of the general problem of condensed matter theory

THE PARADIGM [“theory of everything”] All Condensed Matter systems and processes can be fully described using ordinary ~~non~~ quasi-relativistic quantum mechanics/statistics

The paradigm of condensed matter theory

- the problem of surfaces is a very tricky part of the general problem of condensed matter theory

THE PARADIGM [“theory of everything”] All Condensed Matter systems and processes can be fully described using ordinary ~~non~~ quasi-relativistic quantum ~~mechanics~~ electrodynamics/statistics

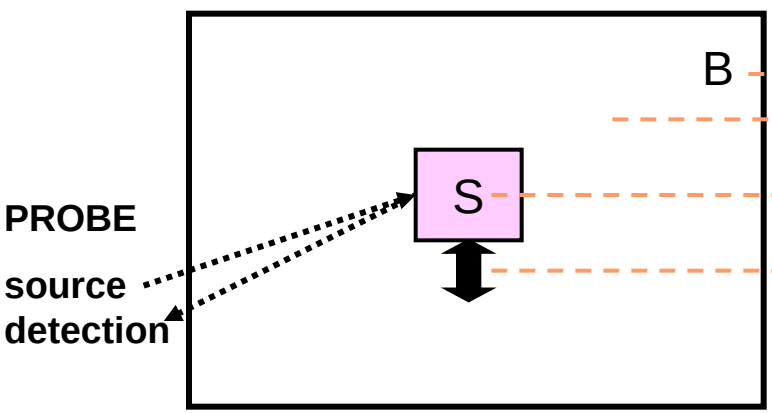
The paradigm of condensed matter theory

- the problem of surfaces is a very tricky part of the general problem of condensed matter theory

THE PARADIGM [“theory of everything”] All Condensed Matter systems and processes can be fully described using ordinary ~~non~~ quasi-relativistic quantum ~~mechanics~~ electrodynamics/statistics

IMPLEMENTATION -- as a parallel between the experiment and its theoretical image

EXPERIMENTAL SETUP



THEORETICAL COUNTERPART

B — vacuum chamber as a heat and particle bath infinite and keeping the temperature of the whole system

S — sample

B – S interaction in UHV reduced to fixed sample temperature

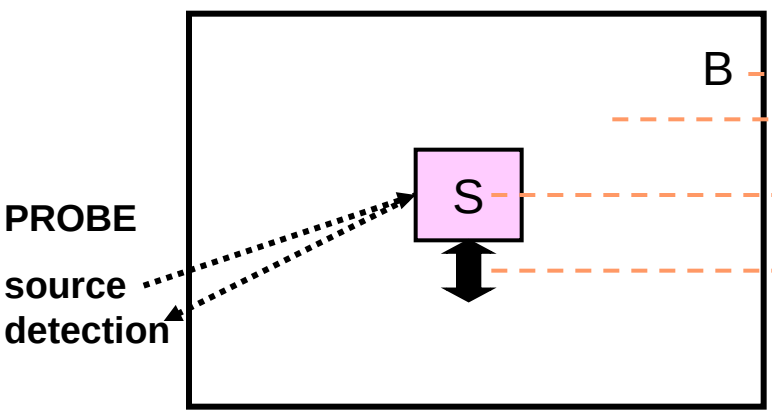
The paradigm of condensed matter theory

- the problem of surfaces is a very tricky part of the general problem of condensed matter theory

THE PARADIGM [“theory of everything”] All Condensed Matter systems and processes can be fully described using ordinary ~~non~~ quasi-relativistic quantum ~~mechanics~~ electrodynamics/statistics

IMPLEMENTATION -- as a parallel between the experiment and its theoretical image

EXPERIMENTAL SETUP



THEORETICAL COUNTERPART

B — vacuum chamber as a heat and particle bath infinite and keeping the temperature of the whole system

S — sample

B – S interaction in UHV reduced to fixed sample temperature

HAMILTONIAN

$$H_{\mathrm{TOT}} = H_{\mathrm{B}} + H_{\mathrm{S}} + H_{\mathrm{BS}}$$

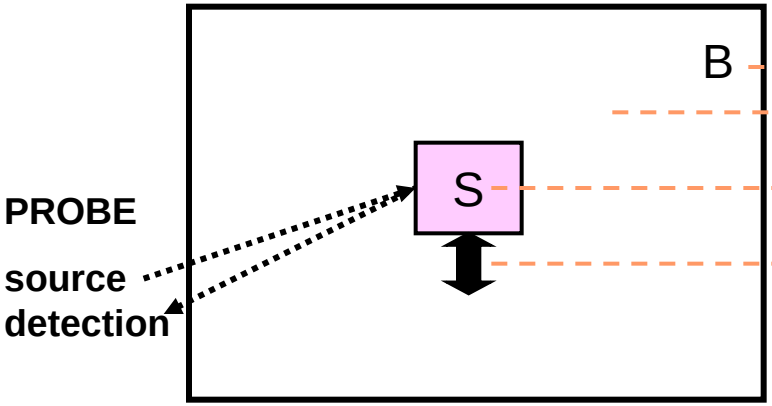
The paradigm of condensed matter theory

- the problem of surfaces is a very tricky part of the general problem of condensed matter theory

THE PARADIGM [“theory of everything”] All Condensed Matter systems and processes can be fully described using ordinary ~~non~~ quasi-relativistic quantum ~~mechanics~~ electrodynamics/statistics

IMPLEMENTATION -- as a parallel between the experiment and its theoretical image

EXPERIMENTAL SETUP



THEORETICAL COUNTERPART

vacuum chamber as a heat and particle bath infinite and keeping the temperature of the whole system

sample

B – S interaction in UHV reduced to fixed sample temperature

HAMILTONIAN

$$H_{\mathrm{TOT}} = H_{\mathrm{B}} + H + \cancel{U_{\mathrm{BS}}}$$

everything else $\rightarrow$ boundary conditions

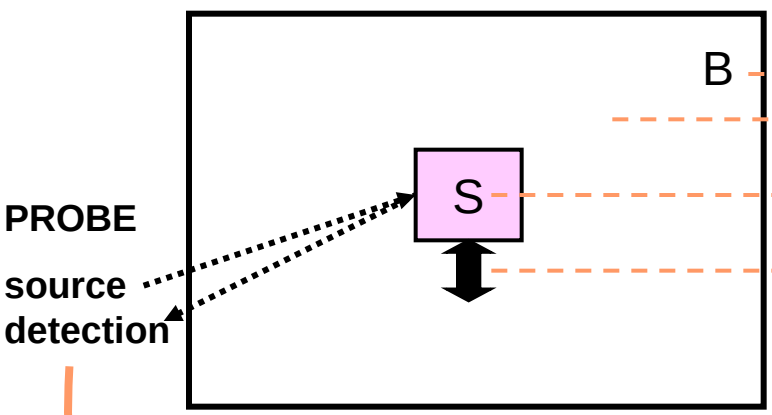
The paradigm of condensed matter theory

- the problem of surfaces is a very tricky part of the general problem of condensed matter theory

THE PARADIGM [“theory of everything”] All Condensed Matter systems and processes can be fully described using ordinary ~~non~~ quasi-relativistic quantum ~~mechanics~~ electrodynamics/statistics

IMPLEMENTATION -- as a parallel between the experiment and its theoretical image

EXPERIMENTAL SETUP



THEORETICAL COUNTERPART

B — vacuum chamber as a heat and particle bath infinite and keeping the temperature of the whole system

S — sample

B – S interaction in UHV reduced to fixed sample temperature

add $+U_{PS}$

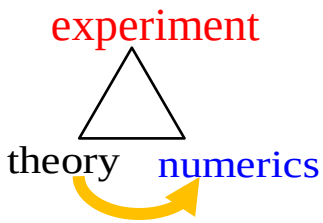
HAMILTONIAN

$$H_{TOT} = H_B + H + \cancel{U_{BS}}$$

everything else $\rightarrow$ boundary conditions

Standard procedure of the computational materials science

Recall:



(1) sample … atomic composition

atoms → nuclei + electrons

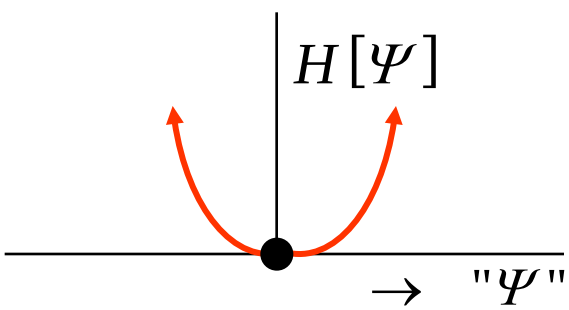
OR ions + valence electrons

(2) Schrödinger equation … at $T = 0$

$$\hat{H}\Psi(\boldsymbol{R},\boldsymbol{r}) = E\Psi(\boldsymbol{R},\boldsymbol{r}), \quad \boldsymbol{R} = \{\boldsymbol{R}_J\},\ J = 1,2,3\ldots \text{nuclei}$$

$$\boldsymbol{r} = \{\boldsymbol{r}_\ell\}, \quad \ell = 1,2,3\ldots \text{electrons}$$

(3) ground state (equilibrium at $T = 0$)



VARIATIONAL PRINCIPLE

$$\langle H \rangle = \min \qquad \delta\langle H \rangle = 0$$

$$\langle H \rangle = \langle \Psi | \hat{H} | \Psi \rangle = \text{internal energy}$$

Standard procedure of the computational materials science *cont'd*

(4) Adiabatic approximation

heavy sluggish nuclei — source of a classical external electrostatic field for the electrons

light nimble electrons
- follow immediately "adiabatically" the positions of the nuclei
- form a glue between the nuclei
- stabilize the electrostatic structure

… uncertainty relations

$$\hat{H}\Psi(\boldsymbol{R},\boldsymbol{r}) = E\Psi(\boldsymbol{R},\boldsymbol{r}),$$

$$\hat{H} = \hat{H}_n + \hat{H}_e + \hat{U}_{ne},\ \ \hat{H}_n = \hat{T}_n + \hat{U}_{nn},\ \ \hat{H}_e = \hat{T}_e + \hat{U}_{ee}$$

$\boxed{\text{Ansatz}}$ $$\Psi(\boldsymbol{R},\boldsymbol{r}) = \Phi_n(\boldsymbol{R})\cdot\Psi_e(\boldsymbol{R},\boldsymbol{r})$$

$$\left(\hat{H}_e + \hat{U}_{ne}\right)\Psi_e(\boldsymbol{R},\boldsymbol{r}) = \mathcal{E}_e(\boldsymbol{R})\cdot\Psi_e(\boldsymbol{R},\boldsymbol{r})$$ electrons

$$\left(\hat{H}_n + \mathcal{E}_e(\boldsymbol{R})\right)\Phi_n(\boldsymbol{R}) = E\cdot\Phi_n(\boldsymbol{R})$$ nuclei

Standard procedure of the computational materials science *cont'd*

(4) Adiabatic approximation *cont'd*

adiabatic total energy neglect completely kinetic energy of nuclei

$$E(\boldsymbol{R}) = \hat{U}_{nn}(\boldsymbol{R}) + \mathcal{E}_e(\boldsymbol{R})$$ total adiabatic energy

$$\nabla_R E\left(\boldsymbol{R}_0\right) = \boldsymbol{0}, \quad \frac{\partial}{\partial X_{J\alpha}} E(\boldsymbol{R}) = 0$$ equilibrium geometry

$$E\left(\boldsymbol{R}_0\right)$$ equilibrium energy

Standard procedure of the computational materials science *cont'd*

(4) Adiabatic approximation *cont'd*

adiabatic total energy neglect completely kinetic energy of nuclei

$$E(\boldsymbol{R}) = \hat{U}_{nn}(\boldsymbol{R}) + \mathcal{E}_e(\boldsymbol{R})$$ total adiabatic energy

$$\nabla_R E(\boldsymbol{R}_0) = \boldsymbol{0}, \quad \frac{\partial}{\partial X_{J\alpha}} E(\boldsymbol{R}) = 0$$ equilibrium geometry

$$E(\boldsymbol{R}_0)$$ equilibrium energy

When does the adiabatic approximation fail

- **electron – phonon interaction**
- **primary ion in SIMS, etc.**

Standard procedure of the computational materials science *cont'd*

(4) Adiabatic approximation *cont'd*

adiabatic total energy neglect completely kinetic energy of nuclei

$$E(\boldsymbol{R}) = \hat{U}_{nn}(\boldsymbol{R}) + \mathcal{E}_e(\boldsymbol{R})$$ total adiabatic energy

$$\nabla_R E(\boldsymbol{R}_0) = \boldsymbol{0}, \quad \frac{\partial}{\partial X_{J\alpha}} E(\boldsymbol{R}) = 0$$ equilibrium geometry

$$E(\boldsymbol{R}_0)$$ equilibrium energy

When does the adiabatic approximation fail

- **electron – phonon interaction**
- **primary ion in SIMS, etc.**

(5) Finally, we arrive at a truly difficult stage.

Approximate description of many electrons pair-wise interacting by the Coulomb force

In solids, this e – e interaction is neither weak nor short-range.

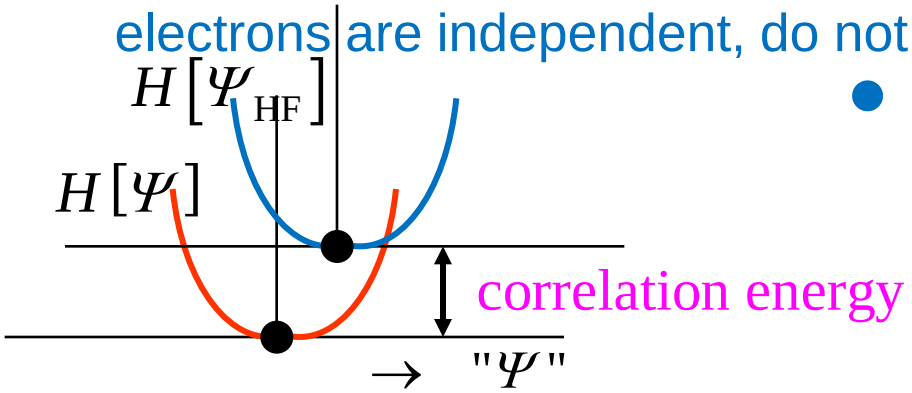
Simple approximations, weak coupling or the gas approximation both fail …

Interacting electrons in solids

- The Coulomb interaction between electrons is never really weak.
- Two traditional opposite limits

electrons	delocalized **itinerant**	localized **bound**
e – e interaction	pair interaction → **HF mean field approximation**	pair interaction at a distance **site to site exchange integrals**
quantum chemistry	Hund - Mulliken **LCAO**	Heitler – London **Valence Bond**
magnetism	Stoner - Slater **band magnetism**	(Dirac) – Heisenberg Hamiltonian

- The itinerant electron theories and their improvements fall under the category of ORBITAL THEORIES which dominate today.
- The orbital theories include the shell model of atoms, the molecular orbital theory in QCh, the band model of solid crystals.
- Problem Take Hartree - Fock, the archetype of orbital theories; HF electrons are independent, do not catch up the e - e correlations



- Possible improvements to HF

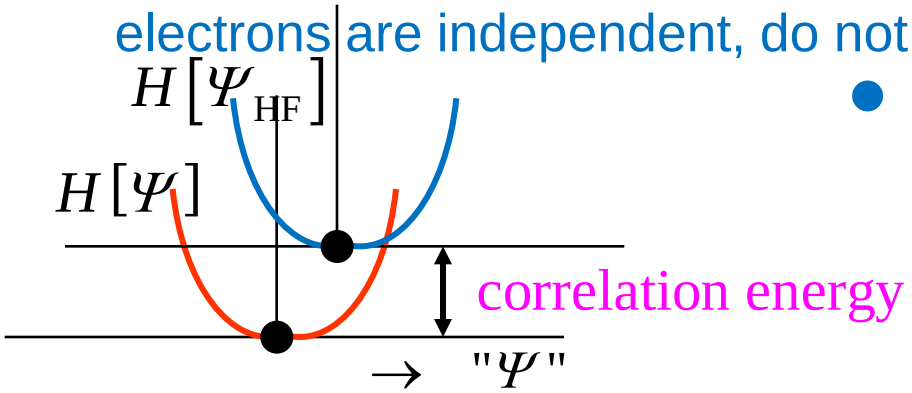
Configuration Interaction QCh Pople
Kohn - Sham orbitals CM Kohn
} NP 1998

Interacting electrons in solids

- The Coulomb interaction between electrons is never really weak.
- Two traditional opposite limits

electrons	delocalized **itinerant**	localized **bound**
e – e interaction	pair interaction → **HF mean field approximation**	pair interaction at a distance **site to site exchange integrals**
quantum chemistry	Hund - Mulliken **LCAO**	Heitler – London **Valence Bond**
magnetism	Stoner - Slater **band magnetism**	(Dirac) – Heisenberg Hamiltonian

- The itinerant electron theories and their improvements fall under the category of ORBITAL THEORIES which dominate today.
- The orbital theories include the shell model of atoms, the molecular orbital theory in QCh, the band model of solid crystals.
- Problem Take Hartree - Fock, the archetype of orbital theories; HF electrons are independent, do not catch up the e - e correlations



- Possible improvements to HF

~~Configuration Interaction~~ ~~QCh~~ ~~Pople~~
Kohn - Sham orbitals CM Kohn
} NP 1998

Sorting out the orbital theories

orbital theories

- model/semi-empirical
- LDA + U
- ab initio
  - 1-electron approx.
  - exact (beyond HF)

model/semi-empirical:

not suited for total energy

sensitive to parametrization

uses:

heuristics

parameters from ab initio

interpretation of ab initio

1-electron approx.: "ideal" case, no correlations

exact (beyond HF): correlations incorporated, additional approximations

self-consistent

These you may encounter

independent electrons
extended Hückel
Harrison param.

Hartree-Fock — best
Roothaan
Slater $X\alpha$
Hartree
Thomas-Fermi
CNDO et al. — worst

density functional LDA
quasiparticles GW
natural orbitals

Why everybody likes the orbital theories

…. a universal simple method: instead of SR for $N^{(e)}$=2, 92, …,10^{28} electrons …

(I.) one-electron Schrödinger equation

$$(-\frac{\hbar^2}{2m_e}\Delta + V(\boldsymbol{r}))\psi_\alpha(\boldsymbol{r}) = E_\alpha \psi_\alpha(\boldsymbol{r})$$

(II.) Many-electron state $\equiv$ sequence of occup. numbers $\{n_{\alpha\sigma}\}$

- add spin $\sigma = \uparrow, \downarrow$
- Pauli principle $0 \le n_{\alpha\sigma} \le 1$
- Aufbau principle fill from the bottom up

(III.) Charge balance $\sum n_{\alpha\sigma} = N_\uparrow^{(e)} + N_\downarrow^{(e)} = N^{(e)} = \sum Z_J$

defines Fermi energy

$$n_{\alpha\sigma} = f_{FD}(E_\alpha)\frac{1}{1+e^{\beta(E_\alpha - E_F)}}$$

… HOMO highest occupied

… LUMO lowest unoccupied

(IV.) Observables

local particle density $n(\boldsymbol{r}) = n_\uparrow(\boldsymbol{r}) + n_\downarrow(\boldsymbol{r})$

local spin density $m(\boldsymbol{r}) = n_\uparrow(\boldsymbol{r}) - n_\downarrow(\boldsymbol{r})$

$$n_\sigma(\boldsymbol{r}) = \langle \hat{n}_\sigma(\boldsymbol{r}) \rangle = \sum n_{\alpha\sigma} |\psi_{\alpha\sigma}(\boldsymbol{r})|^2$$ orbital interpretation

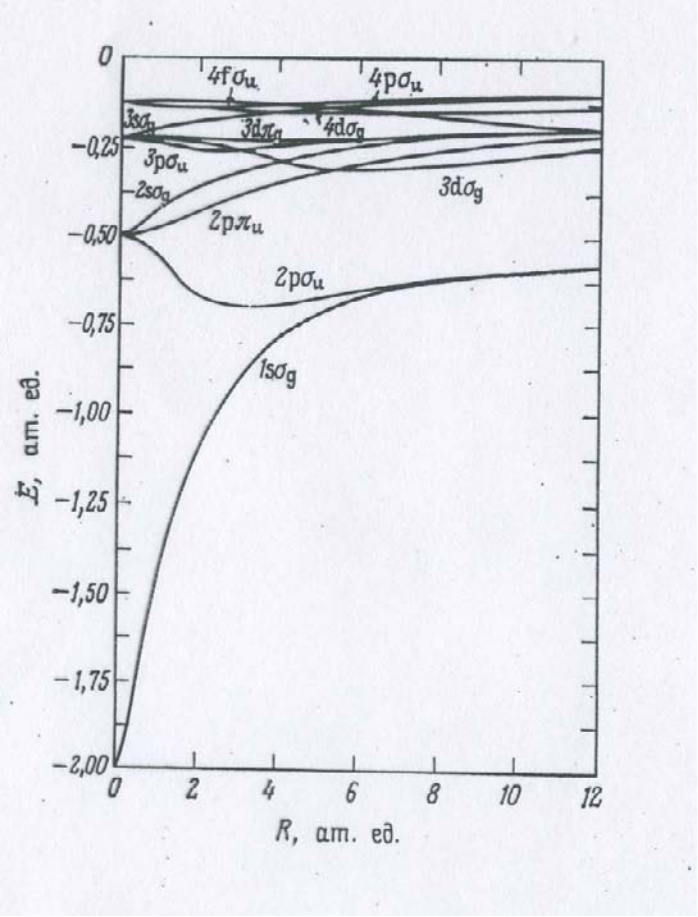
double average

Ion of hydrogen molecule H_2^+

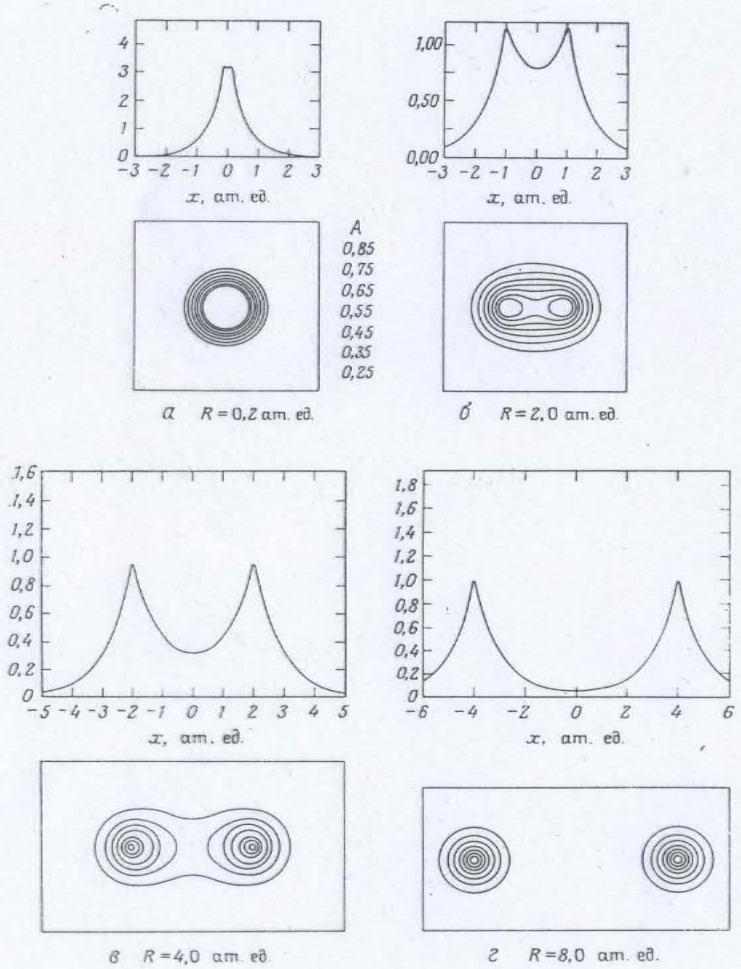
$$\varphi_A(\boldsymbol{r}) = \psi_{100}(\boldsymbol{r} - \boldsymbol{r}_A), \quad \varphi_B(\boldsymbol{r}) = \psi_{100}(\boldsymbol{r} - \boldsymbol{r}_B)$$

$$\psi_g = N_g(\varphi_A + \varphi_B) \quad \text{symmetry!!!}$$

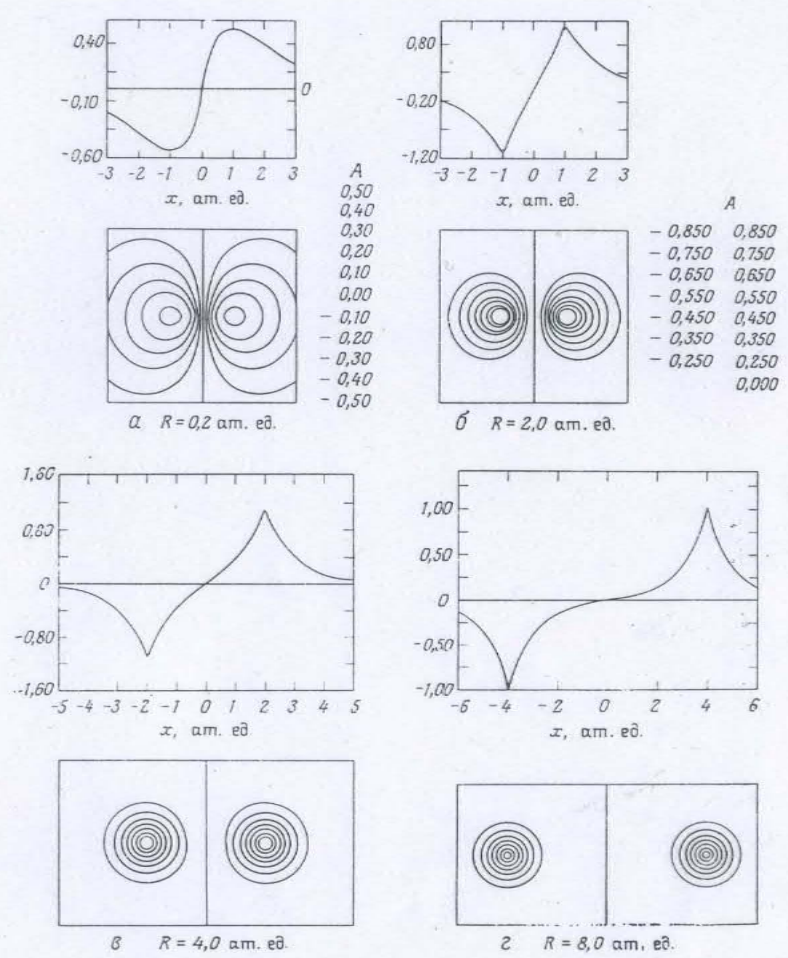
$$\psi_u = N_u(\varphi_A - \varphi_B) \quad \text{symmetry!!!}$$



Ion of hydrogen molecule H_2^+



$1s\sigma_g$



$2p\sigma_u$

Occupation of energy levels in an atom

The electron in a H_2^+ ion always occupies one orbital (solutions of the Schrödinger eq.) depending on its energy.

For many-electron atoms the Schrödinger eq. cannot be solved analytically!

1. The spatial arrangement of the atom is characterised by the same set of orbitals as for the one-electron hydrogen atom.
2. The orbitals are filled successively with the atom's electrons. In the ground state of the atom each electron prefers to fill the orbital which is lowest in energy. There are well-working rules (Madelung's rule, Hund's rules) of thumb for the ordering of the orbitals.
3. The number of electrons within a specific orbital is limited to a maximum of two by the Pauli exclusion principle: A quantum state specified by the four quantum numbers n, l, m and σ can be possessed by at most one particle at the same time. There are two quantum states associated with each orbital (spin).

Occupation of energy levels in an atom - empirical rules

The energy of a specific orbital is determined by the mean distance to the positively charged nucleus. But in many-electron atoms it is also dependent on the mutual repulsion of the electrons and the screening of the nuclear charges by inner electrons.

Madelung's rule

- The energy ordering is from lowest value of $n + l$ to the largest.
- When two orbitals have the same value of $n + l$ the one with smaller n is filled first.

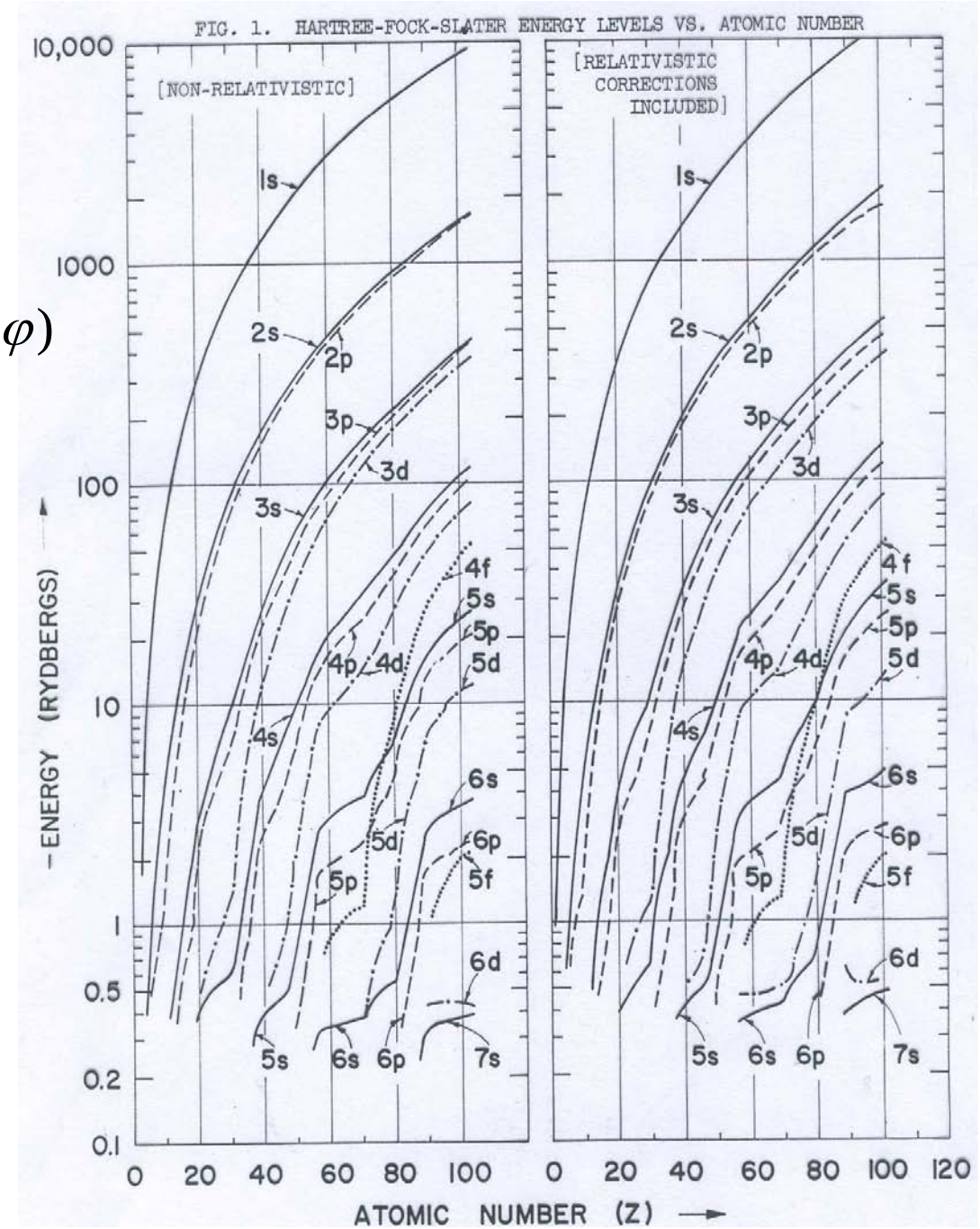
Hund's rule - regarding the m-degeneracy

- The number of unpaired electrons is maximized.
- Such unpaired electrons possess parallel spins, thus maximising the total spin of the outermost orbital.

HF energy levels in atoms

$$\hat{H}\psi_{n\ell m}(r,\vartheta,\varphi) = E_{n\ell}\psi_{n\ell m}(r,\vartheta,\varphi)$$

degeneracy $2\ell+1$

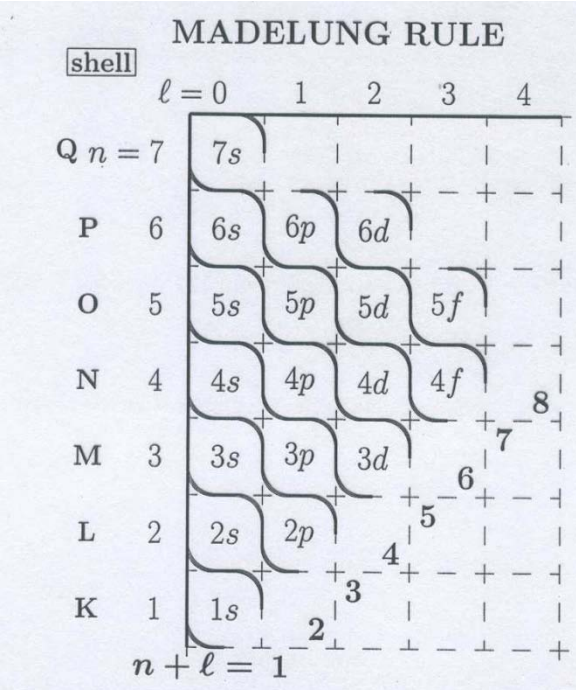


Occupation of energy levels in atoms

Z	Prvek	K	L		M			N				O			
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f
1	H	1													
2	He	2													
3	Li	2	1												
4	Be	2	2												
5	B	2	2	1											
6	C	2	2	2											
7	N	2	2	3											
8	O	2	2	4											
9	F	2	2	5											
10	Ne	2	2	6											
11	Na	2	2	6	1										
12	Mg	2	2	6	2										
13	Al	2	2	6	2	1									
14	Si	2	2	6	2	2									
15	P	2	2	6	2	3									
16	S	2	2	6	2	4									
17	Cl	2	2	6	2	5									
18	Ar	2	2	6	2	6									
19	K	2	2	6	2	6		1							
20	Ca	2	2	6	2	6		2							
21	Sc	2	2	6	2	6	1	2							
22	Ti	2	2	6	2	6	2	2							
23	V	2	2	6	2	6	3	2							
24	Cr	2	2	6	2	6	5	1							
25	Mn	2	2	6	2	6	5	2							
26	Fe	2	2	6	2	6	6	2							
27	Co	2	2	6	2	6	7	2							
28	Ni	2	2	6	2	6	8	2							
29	Cu	2	2	6	2	6	10	1							
30	Zn	2	2	6	2	6	10	2							
31	Ga	2	2	6	2	6	10	2	1						
32	Ge	2	2	6	2	6	10	2	2						
33	As	2	2	6	2	6	10	2	3						
34	Se	2	2	6	2	6	10	2	4						
35	Br	2	2	6	2	6	10	2	5						
36	Kr	2	2	6	2	6	10	2	6						
37	Rb	2	2	6	2	6	10	2	6			1			
38	Sr	2	2	6	2	6	10	2	6			2			
39	Y	2	2	6	2	6	10	2	6	1		2			
40	Zr	2	2	6	2	6	10	2	6	2		2			
41	Nb	2	2	6	2	6	10	2	6	4		1			
42	Mo	2	2	6	2	6	10	2	6	5		1			
43	Tc	2	2	6	2	6	10	2	6	6		1			
44	Ru	2	2	6	2	6	10	2	6	7		1			
45	Rh	2	2	6	2	6	10	2	6	8		1			
46	Pd	2	2	6	2	6	10	2	6	10					
47	Ag	2	2	6	2	6	10	2	6	10		1			
48	Cd	2	2	6	2	6	10	2	6	10		2			

Z	Prvek	K	L		M			N				O				P			Q
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
49	In	2	2	6	2	6	10	2	6	10		2	1						
50	Sn	2	2	6	2	6	10	2	6	10		2	2						
51	Sb	2	2	6	2	6	10	2	6	10		2	3						
52	Te	2	2	6	2	6	10	2	6	10		2	4						
53	J	2	2	6	2	6	10	2	6	10		2	5						
54	Xe	2	2	6	2	6	10	2	6	10		2	6						
55	Cs	2	2	6	2	6	10	2	6	10		2	6			1			
56	Ba	2	2	6	2	6	10	2	6	10		2	6			2			
57	La	2	2	6	2	6	10	2	6	10		2	6	1		2			
58	Ce	2	2	6	2	6	10	2	6	10	1	2	6	1		2			
59	Pr	2	2	6	2	6	10	2	6	10	2	2	6	1		2			
60	Nd	2	2	6	2	6	10	2	6	10	3	2	6	1		2			
61	Pm	2	2	6	2	6	10	2	6	10	4	2	6	1		2			
62	Sm	2	2	6	2	6	10	2	6	10	5	2	6	1		2			
63	Eu	2	2	6	2	6	10	2	6	10	6	2	6	1		2			
64	Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
65	Tb	2	2	6	2	6	10	2	6	10	8	2	6	1		2			
66	Dy	2	2	6	2	6	10	2	6	10	9	2	6	1		2			
67	Ho	2	2	6	2	6	10	2	6	10	10	2	6	1		2			
68	Er	2	2	6	2	6	10	2	6	10	11	2	6	1		2			
69	Tu	2	2	6	2	6	10	2	6	10	12	2	6	1		2			
70	Yb	2	2	6	2	6	10	2	6	10	13	2	6	1		2			
71	Lu	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
72	Hf	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
73	Ta	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
74	W	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
75	Re	2	2	6	2	6	10	2	6	10	14	2	6	5		2			
76	Os	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
77	Ir	2	2	6	2	6	10	2	6	10	14	3	6	7		2			
78	Pt	2	2	6	2	6	10	2	6	10	14	2	6	8		2			
79	Au	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
80	Hg	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
81	Tl	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
82	Pb	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
83	Bi	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
84	Po	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
85	At	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
86	Rn	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
87	Fr	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
88	Ra	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2
89	Ac	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
90	Th	2	2	6	2	6	10	2	6	10	14	2	6	10	1	2	6	1	2
91	Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
92	U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
93	Np	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
94	Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	5	2	6	1	2
95	Am	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6	1	2
96	Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2

Occupation of energy levels in atoms



Z	Prvek	K	L		M			N				O			
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f
1	H	1													
2	He	2													
3	Li	2	1												
4	Be	2	2												
5	B	2	2	1											
6	C	2	2	2											
7	N	2	2	3											
8	O	2	2	4											
9	F	2	2	5											
10	Ne	2	2	6											
11	Na	2	2	6	1										
12	Mg	2	2	6	2										
13	Al	2	2	6	2	1									
14	Si	2	2	6	2	2									
15	P	2	2	6	2	3									
16	S	2	2	6	2	4									
17	Cl	2	2	6	2	5									
18	Ar	2	2	6	2	6									
19	K	2	2	6	2	6		1							
20	Ca	2	2	6	2	6		2							
21	Sc	2	2	6	2	6	1	2							
22	Ti	2	2	6	2	6	2	2							
23	V	2	2	6	2	6	3	2							
24	Cr	2	2	6	2	6	5	1							
25	Mn	2	2	6	2	6	5	2							
26	Fe	2	2	6	2	6	6	2							
27	Co	2	2	6	2	6	7	2							
28	Ni	2	2	6	2	6	8	2							
29	Cu	2	2	6	2	6	10	1							
30	Zn	2	2	6	2	6	10	2							
31	Ga	2	2	6	2	6	10	2	1						
32	Ge	2	2	6	2	6	10	2	2						
33	As	2	2	6	2	6	10	2	3						
34	Se	2	2	6	2	6	10	2	4						
35	Br	2	2	6	2	6	10	2	5						
36	Kr	2	2	6	2	6	10	2	6						
37	Rb	2	2	6	2	6	10	2	6				1		
38	Sr	2	2	6	2	6	10	2	6				2		
39	Y	2	2	6	2	6	10	2	6	1			2		
40	Zr	2	2	6	2	6	10	2	6	2			2		
41	Nb	2	2	6	2	6	10	2	6	4			1		
42	Mo	2	2	6	2	6	10	2	6	5			1		
43	Tc	2	2	6	2	6	10	2	6	6			1		
44	Ru	2	2	6	2	6	10	2	6	7			1		
45	Rh	2	2	6	2	6	10	2	6	8			1		
46	Pd	2	2	6	2	6	10	2	6	10					
47	Ag	2	2	6	2	6	10	2	6	10			1		
48	Cd	2	2	6	2	6	10	2	6	10			2		

Z	Prvek	K	L		M			N				O				P			Q
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
49	In	2	2	6	2	6	10	2	6	10		2	1						
50	Sn	2	2	6	2	6	10	2	6	10		2	2						
51	Sb	2	2	6	2	6	10	2	6	10		2	3						
52	Te	2	2	6	2	6	10	2	6	10		2	4						
53	J	2	2	6	2	6	10	2	6	10		2	5						
54	Xe	2	2	6	2	6	10	2	6	10		2	6						
55	Cs	2	2	6	2	6	10	2	6	10		2	6			1			
56	Ba	2	2	6	2	6	10	2	6	10		2	6			2			
57	La	2	2	6	2	6	10	2	6	10		2	6	1		2			
58	Ce	2	2	6	2	6	10	2	6	10	1	2	6	1		2			
59	Pr	2	2	6	2	6	10	2	6	10	2	2	6	1		2			
60	Nd	2	2	6	2	6	10	2	6	10	3	2	6	1		2			
61	Pm	2	2	6	2	6	10	2	6	10	4	2	6	1		2			
62	Sm	2	2	6	2	6	10	2	6	10	5	2	6	1		2			
63	Eu	2	2	6	2	6	10	2	6	10	6	2	6	1		2			
64	Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
65	Tb	2	2	6	2	6	10	2	6	10	8	2	6	1		2			
66	Dy	2	2	6	2	6	10	2	6	10	9	2	6	1		2			
67	Ho	2	2	6	2	6	10	2	6	10	10	2	6	1		2			
68	Er	2	2	6	2	6	10	2	6	10	11	2	6	1		2			
69	Tu	2	2	6	2	6	10	2	6	10	12	2	6	1		2			
70	Yb	2	2	6	2	6	10	2	6	10	13	2	6	1		2			
71	Lu	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
72	Hf	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
73	Ta	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
74	W	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
75	Re	2	2	6	2	6	10	2	6	10	14	2	6	5		2			
76	Os	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
77	Ir	2	2	6	2	6	10	2	6	10	14	3	6	7		2			
78	Pt	2	2	6	2	6	10	2	6	10	14	2	6	8		2			
79	Au	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
80	Hg	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
81	Tl	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
82	Pb	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
83	Bi	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
84	Po	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
85	At	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
86	Rn	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
87	Fr	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
88	Ra	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2
89	Ac	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
90	Th	2	2	6	2	6	10	2	6	10	14	2	6	10	1	2	6	1	2
91	Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
92	U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
93	Np	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
94	Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	5	2	6	1	2
95	Am	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6	1	2
96	Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2

Digression: how to solve the Schrödinger eq.

one-electron Schrödinger equation

$$\left(-\frac{\hbar^2}{2m_e}\Delta + V(\boldsymbol{r})\right)\psi_\alpha(\boldsymbol{r}) = E_\alpha \psi_\alpha(\boldsymbol{r})$$

direct methods

on-shell at E_α
matching of the wave function
(boundary conditions)
textbook approach

!! KKR !!

variational methods

RITZ - GALERKIN
Schrödinger eq. $\rightarrow$ matrix problem

$$\psi = \sum_\lambda c_\lambda \varphi_\lambda$$

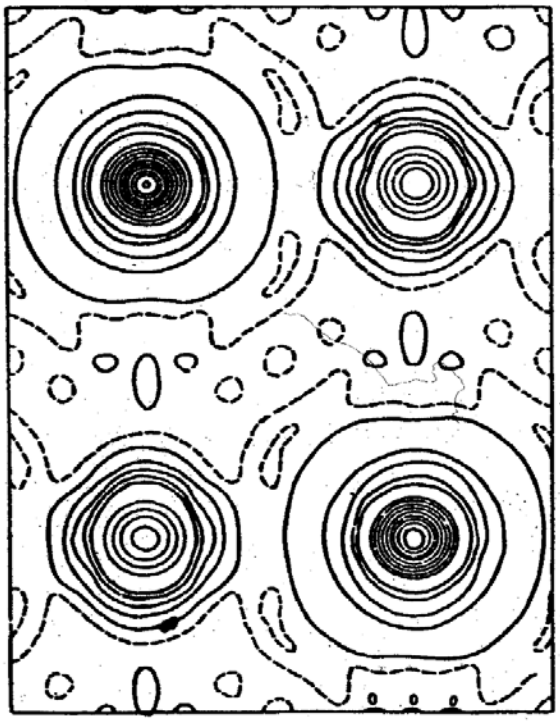
$$\sum_\mu \left(\underbrace{\langle\lambda|\hat{H}|\mu\rangle}_{H_{\lambda\mu}} - E\underbrace{\langle\lambda|\mu\rangle}_{S_{\lambda\mu}}\right)c_\mu = 0$$

!! OPW !!

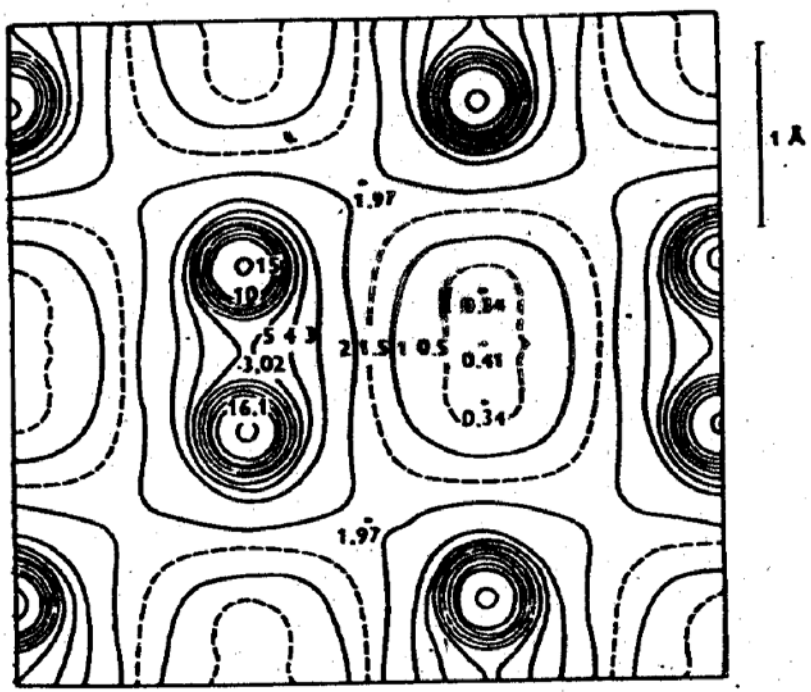
APW

LCAO

X - ray maps of electron density



rock salt



diamond

The end