0 Foreword

0.1 Introductory Remarks

A solid or, more generally, condensed matter is a complex quantum-mechanical many-body-system consisting of $\sim 10^{23}$ electrons and nuclei per cm^3. The most important foundations of its theoretical description are electronic-structure theory and statistical mechanics. Due to the complexity of the quantum-mechanical many-body problem there is a large variety of phenomena and properties. Their description and understanding is the purpose of this lecture course on "condensed-matter theory". Keywords are, e.g., crystal structure, hardness, magnetism, electrical conductivity, thermal conductivity, superconductivity, etc.. The name of this lecture (*Theoretical Materials Science*) indicates that we intend to go a step further, i.e., "condensed matter" is replaced by "materials". This is a small, but nevertheless important generalization. When we talk about materials, then, in addition to phenomena and properties, we also think of potential applications, i.e., the possible function of materials, like in electronic, magnetic, and optical devices (solar cells or light emitters), sensor technology, catalysts, lubrication, and surface coatings (e.g. with respect to protection against corrosion, heat, and mechanical scratch-resistance). It is obvious that these functions, which are determined to a large extent by properties on a nanometer length scale, play an important role in many technologies, on which our lifestyle and the wealth of our society are based. In fact, every new commercial product is based on improved or even novel materials. Thus, the identification of new materials and their property profiles can open new opportunities in fields such as energy, transport, safety, information, and health.

About 200,000 different inorganic materials are known to exist, but the properties, e.g., hardness, elastic constants, thermal or electrical conductivity, are know for very few of them. Considering that there are about 100 different atoms in the periodic table and that unit cells of crystals can have sizes anywhere between one and hundred atoms (or even more), considering surfaces, nanostructures, heterostructures, organic materials and organic/inorganic hybrids, the amount of different, possible materials is practical infinite. Thus, it is likely that there are hitherto unknown or unexplored materials with unknown but immensely useful property profiles. Finding structure in this huge data space of different materials and reaching better understanding of the materials properties is a fascinating scientific goal of fundamental research. And, there is no doubt that identifying new materials can have truly significant socio-economical impact.

This role of materials science has been realized by at least two influential "science and engineering initiatives" of US presidents: the "national nanotechnology initiative" by B. Clin-

ton (2000) and the "materials genome initiative" by B. Obama (2011). Such initiatives come with no money. They just identify and describe a promising new route. In the mentioned two examples, these initiatives were worked out convincingly, and various funding agencies (from basic research to engineering to military) got together and created significant programs. This has changed the research landscape not just in the US but in the world. – In both cases our research group had been on these routes already and fully profited from the developments without changing.

The field of electronic-structure theory, applied to materials-science problems, is in an important, active phase with rapid developments in

- the underlying theory,

- new methods,

- new algorithms, and

- new computer codes.

For several years now a theory is evolving that, taking advantage of high and highest performance computers, allows an atomistic modeling of complex systems with predictive power, starting from the fundamental equations of many-body quantum mechanics. The two central ingredients of such *ab initio* theories are the reliable description of the underlying elementary processes (e.g. breaking and forming of chemical bonds) and a correct treatment of their dynamics and statistical mechanics.

Because of the importance of quantum-mechanical many-body effects in the description of the interactions in polyatomic systems up to now a systematic treatment was rarely possible. The complexity of the quantum mechanical many-body problem required the introduction of approximations, which often were not obvious. The development of the underlying theory (density-functional theory, DFT) started in 1964[1]. But "only" since 1978 (or 1982)[2] reliable calculations for solids have been carried out. Only these allow to check the validity of possibly reasonable (and often necessary) approximations and to give the reasons for their success; or demonstrate which approximations have to be abandoned. Today this development has reached a feasible level for many types of problems, but it is not completed yet.

With these DFT-based (and related) computational methods, the approximations, which in many existing text books are introduced *ad hoc*, can be inspected. Further it is possible to make quantitative predictions, e.g., for the properties of new materials. But still *theoretical condensed-matter physics* or *theoretical materials science* is in an active state of development. Phenomena that are still only badly understood (or not at all) include phase transitions, disorder, catalysis, defects (meta-, bi-stabilities), properties of quantum

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[1]To some extend earlier concepts by Thomas, Fermi, Hartree, and Slater may be considered as preparation for this route.

[2]V.L. Moruzzi, J.F. Janak, and A.R. Williams, *Calculated Electronic Properties of Metals*, Pergamon Press (1978) ISBN 0-08-022705-8; and M.T. Yin and M.L. Cohen, *Theory of static structural properties, crystal stability, and phase transformations: Application to Si and Ge*, Phys. Rev. B **26**, 5668 (1982).

dots, crystal growth, crystal structure prediction, systems containing f-electrons, high-temperature-superconductivity, electronic excitation, and electrical and thermal transport.

Modern *theoretical materials science* is facing two main challenges:

1. Explain experimentally found properties and phenomena and place them in a bigger context. This is done by developing models, i.e., by a reduction to the key physical processes. This enables a qualitative or semi-quantitative understanding. As mentioned before, there are examples for which these tasks are not accomplished, yet.

2. Predict properties of systems that have not been investigated experimentally so far – or situations that cannot be investigated by experiments directly. The latter include conditions of very high pressures or conditions that are chemically or radioactively harsh. A recent development is concerned with building a "library of hitherto unknown materials". We will get back to this project at the end of this lecture.

The latter point shall be illustrated by the following examples:

1) Until recently it was not possible to study the viscosity and the melting temperature of iron at pressures that exist at the earth core, but this has been calculated since about 1999[3]).

2) The element carbon exists in three solid phases: i) as amorphous solid and in crystalline form ii) as graphite and iii) as diamond[4,5]. Graphite is the most stable phase, i.e., the one with the lowest internal energy. At normal conditions, diamond is only a metastable state, but with a rather long lifetime. Usually when carbon atoms are brought together graphite or an amorphous phase is formed. Only under certain conditions (pressure, temperature) present in the earth mantle diamonds can be formed. Therefore, in a certain sense, diamonds are known only accidentally. It cannot be excluded that also other elements (Si, Ge, Ag, Au, etc.) can exist in other yet unknown modifications (polymorphs). Examples for new, artificially created materials are semiconductor quantum dots, quantum wire systems, or epitaxial magnetic layers[6]. Once the interactions between atoms are understood,

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[3]D. Alfe, M.J. Gillan, and G.D. Price, Nature **401**, 462 (1999).

[4]Diamond is the hardest known material, i.e., it has the highest bulk modulus. Diamonds without defects are most transparent to light. At room temperature their thermal conductivity is better than that of any other material.

[5]This statement is slightly oversimplified: Since 1985 fullerenes (e.g. C_{60}) and since 1991 carbon nanotubes are known. From the latter, "soft matter" can be formed and they can also be used directly as nanomaterials (for example as nanotube transistors). These systems will be discussed in more detail later.

[6]In 1988, Albert Fert and Peter Grünberg independently discovered that an increased magnetoresistive effect (hence dubbed "giant magnetoresistance" or GMR) can be obtained in magnetic multilayers. These systems essentially consist of an alternate stack of ferromagnetic (e.g., Fe, Co, Ni, and their alloys) and non-ferromagnetic (e.g., Cr, Cu, Ru, etc.) metallic layers. It is unusual that a basic effect like GMR leads to commercial applications in less than a decade after its discovery: Magnetic field sensors based on GMR were already introduced into the market as early as 1996 and by now, e.g., all read heads for hard discs are built that way. In 2007 Albert Fert and Peter Grünberg were awarded the Nobel Prize in physics.

materials with completely new physical properties could be predicted theoretically. As an example, the theoretical investigation of semiconductor and/or metal heterostructures is currently used to attempt the prediction of new materials for light-emitting diodes (LEDs) and of new magnetic memory devices. Likewise, researchers hope to find new catalysts by the theoretical investigation of alloys and surface alloys with new compositions (for which no bulk-analogue exists). Albeit this sounds like being very close to practical application, it should be noted that applications of such theoretical predictions cannot be expected in the too near future, because in industry many practical details (concerning the technical processes, cost optimization, etc.) are crucial to decide whether a physical effect will be used in real devices or not.

It is also interesting to note that 38 Nobel prizes have been awarded for work in the field of or related to materials science since 1980. They are listed in the following. More details, also review papers describing the work behind the prize can be found here: http://www.nobelprize.org/:

1981 Physics: Nicolaas Bloembergen and Arthur L. Schawlow "for their contribution to the development of laser spectroscopy"
Kai M. Siegbahn "for his contribution to the development of high-resolution electron spectroscopy"

1981 Chemistry: Kenichi Fukui and Roald Hoffmann "for their theories, developed independently, concerning the course of chemical reactions"

1982 Physics: Kenneth G. Wilson "for his theory for critical phenomena in connection with phase transitions"

1982 Chemistry: Aaron Klug "for his development of crystallographic electron microscopy and his structural elucidation of biologically important nuclei acid-protein complexes"

1983 Chemistry: Henry Taube "for his work on the mechanisms of electron transfer reactions, especially in metal complexes"

1984 Chemistry: Robert Bruce Merrifield "for his development of methodology for chemical synthesis on a solid matrix"

1985 Physics: Klaus von Klitzing "for the discovery of the quantized Hall effect"

1985 Chemistry: Herbert A. Hauptman and Jerome Karle "for their outstanding achievements in the development of direct methods for the determination of crystal structures"

1986 Physics: Ernst Ruska "for his fundamental work in electron optics and for the design of the first electron microscope"
Gerd Binnig and Heinrich Rohrer "for their design of the scanning tunneling microscope"

1986 Chemistry: Dudley R. Herschbach, Yuan T. Lee, and John C. Polanyi "for their contributions concerning the dynamics of chemical elementary processes"

1987 Physics: J. Georg Bednorz and K. Alexander Müller "for their important break-through in the discovery of superconductivity in ceramic materials"

1987 Chemistry: Donald J. Cram, Jean-Marie Lejn, and Charles J. Pedersen "for their development and use of molecules with structure-specific interactions of high selectivity"

1988 Chemistry: Johann Deisenhofer, Robert Huber, and Hartmut Michel, "for the determination of the three-dimensional structure of a photosynthetic reaction centre"

1991 Physics: Pierre-Gilles de Gennes "for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers"

1991 Chemistry: Richard R. Ernst "for his contributions to the development of the methodology of high resolution nuclear magnetic resonance (NMR) spectroscopy"

1992 Chemistry: Rudolph A. Marcus "for his contributions to the theory of electron transfer reactions in chemical systems"

1994 Physics: Bertram N. Brockhouse "for the development of neutron spectroscopy", and Clifford G. Shull "for the development of the neutron diffraction technique".

1996 Physics: David M. Lee, Douglas D. Osheroff, and Robert C. Richardson "for their discovery of superfluidity in Helium-3"

1996 Chemistry: Robert F. Curl Jr., Sir Harold W. Kroto, Richard E. Smalley "for their discovery of fullerenes"

1997 Physics: Steven Chu, Claude Cohen-Tannoudji, and William D. Phillips "for development of methods to cool and trap atoms with laser light"

1998 Physics: Robert B. Laughlin, Horst L. Störmer, and Daniel C. Tsui "for their discovery of a new form of quantum fluid with fractionally charged excitations"

1998 Chemistry: Walter Kohn "for his development of the density-functional theory"
John A. Pople "for his development of computational methods in quantum chemistry"

1999 Chemistry: Ahmed H. Zewail "for his studies of the transition states of chemical reactions using femtosecond spectroscopy"

2000 Physics: Zhores I. Alferov and Herbert Kroemer "for developing semiconductor heterostructures used in high-speed- and opto-electronics", and Jack S. Kilby "for his part in the invention of the integrated circuit"

2000 Chemistry: Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa, "for the discovery and development of conductive polymers"

2001 Physics: Eric A. Cornell, Wolfgang Ketterle, and Carl E. Wieman "for the achievement of Bose-Einstein condensation in dilute gases of alkali atoms, and for early fundamental studies of the properties of the condensates"

2003 Physics: Alexei A. Abrikosov, Vitaly L. Ginzburg, and Anthony J. Leggett "for pioneering contributions to the theory of superconductors and superfluids"

2005 Physics: Roy J. Glauber "for his contribution to the quantum theory of optical coherence" and John L Hall and Theodor Hänsch for their contributions to the development of laser-based precision spectroscopy, including the optical comb technique"

2007 Physics: Albert Fert and Peter Grünberg "for their discovery of Giant Magnetoresistance"

2007 Chemistry: Gerhard Ertl "for his studies of chemical processes on solid surfaces"

2009 Physics: Charles K. Kao "for groundbreaking achievements concerning the transmission of light in fibers for optical communication"
Willard S. Boyle and George E. Smith "for the invention of an imaging semiconductor circuit - the CCD sensor"

2010 Physics: Andre Geim and Konstantin Novoselov "for groundbreaking experiments regarding the two-dimensional material graphene"

2011 Chemistry: Dan Shechtman "for the discovery of quasicrystals".

2013 Chemistry: Martin Karplus, Michael Levitt, and Arieh Warshel "for the development of multiscale models for complex chemical systems".

2014 Physics: Isamu Akasaki, Hiroshi Amano and Shuji Nakamura "for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources".

2014 Chemistry: Eric Betzig, Stefan W. Hell and William E. Moerner "for the development of super-resolved fluorescence microscopy".

2016 Physics: David J. Thouless, F. Duncan M. Haldane and J. Michael Kosterlitz "for theoretical discoveries of topological phase transitions and topological phases of matter".

2016 Chemistry: Jean-Pierre Sauvage, Sir J. Fraser Stoddart and Bernard L. Feringa "for the design and synthesis of molecular machines".

In the above list I ignored Nobel prizes in the field of biophysics, though some developments in this area are now becoming part of condensed-matter physics. The length of this list reflects the fact that materials science is an enormously active field of research and an important one for our society as well.

Some remarks on the above list: The quantum-Hall-effect (Nobel prize 1985) is understood these days, but for its "variant" the "fractional quantum-Hall-effect" (Nobel prize 1998) this is true only in a limited way. The latter is based on the strong correlation of the electrons and even these days unexpected results are found.

The theory of high-T_c superconductivity (Nobel prize 1987) is still unclear. High-T_c superconductors seem to feature Cooper pairs with a momentum signature of different symmetry than conventional BCS-superconductors. Typically, high-T_c superconductors have a complex atomic structure and consist of at least four elements (e.g., La, Ba, Cu, O). However, in recent years also simpler systems have been found with rather high T_c, e.g., MgB_2 (T_c= 39 K) and in 2015 hydrogen sulfide (H_2S) was found to undergo a superconducting transition at high pressure (around 150 GP) near 203 K, the highest temperature superconductor known to date. The latter two examples are materials that had been know since many decades, but their properties had only been investigated recently and the noted results were not expected.

In this lecture:

1. Equations will not fall down from heaven, but we will derive them from first principles;

2. we will not only give the mathematical derivation, but also, and in particular, we will develop a physical feeling, i.e., we will spend a noticeable amount of time in interpreting equations;

3. we will give the reasons for approximations and clarify their physical meaning and the range of validity (as much as this is possible).

In contrast to most text books we will start with the "adiabatic principle" and subsequently discuss the quantum mechanical nature of the electron-electron interaction. In most text books both are introduced only in the middle or at the end.

In the first part of the lecture we will restrict ourselves – unless stated otherwise – to $T \approx 0$ K. Sometimes an extrapolation to $T \neq 0$ K is unproblematic. Still, one should keep in mind that for $T \neq 0$ K important changes and new effects can occur (e.g. due to entropy).

0.2   Literature for This Lecture

Author: Ashcroft, Neil W. and Mermin, N. David
Title: Solid state physics
Place: Philadelphia, PA
Year: 1981
Publisher: Saunders College Publishing
ISBN: 0-03-083993-9 = 0-03-049346-3

Author: Kittel, Charles
Title: Quantum theory of solids
Place: Hoboken, NJ
Year: 1963
Publisher: John Wiley & Sons, Inc.

Author: Ziman, John M.
Title: Principles of the theory of solids
Place: Cambridge
Year: 1964
Publisher: Cambridge University Press

Author: Madelung, Otfried
Title: Festkörpertheorie, 3 Bände
Place: Berlin
Year: 1972
Publisher: Springer

Author: Dreizler, Reiner M. and Gross, Eberhard K. U.
Title: Density functional theory: an approach to the quantum many-body problem
Place: Berlin
Year: 1990
Publisher: Springer
ISBN: 3-540-51993-9 = 0-387-51993-9

Author: Parr, Robert G. and Yang, Weitao
Title: Density-functional theory of atoms and molecules
Place: Oxford
Year: 1994
Publisher: Oxford University Press
ISBN: 0-19-509276-7

Author: Marder, Michael P.
Title: Condensed matter physics
Place: New York
Year: 2000
Publisher: John Wiley & Sons, Inc.
ISBN: 0-471-17779-2

Author: Martin, Richard M.
Title: Electronic Structure
Place: Cambridge
Year: 2004
Publisher: Cambridge University Press

Author: Marvin L. Cohen and Steven G. Louie
Title: Fundamentals of Condensed Matter Physics
Place: Cambridge
Year: 2016

0.3 Symbols and Terms Used in This Lecture

$-e$ charge of the electron

$+e$ charge of the proton

m mass of the electron

$\mathbf{r}_k$ position of electron k

σ_k spin of electron k

Z_K nuclear number of atom K

Z_{v_K} valence of atom K

M_K mass of nucleus K

$\mathbf{R}_K$ position of nucleus K

ϕ electric field

Ψ many-body wave function of the electrons and nuclei

Λ nuclear wave function

Φ many-body wave function of the electrons

φ single-particle wave function of the electrons

χ spin wave function

$\{\mathbf{R}_I\} \equiv \{\mathbf{R}_1,...,\mathbf{R}_M\}$ atomic positions

$\{\mathbf{r}_i\sigma_i\} \equiv \{\mathbf{r}_1\sigma_1,...,\mathbf{r}_N\sigma_N\}$ electron coordinates (position and spin)

ε_0 dielectric constant of the vacuum

ϵ_i single-particle energy of electron i

V_g volume of the base region

Ω volume of a primitive cell

$v_I(\mathbf{r_k})$ potential created by nucleus I at position of the k-th electron, $\mathbf{r_k}$

V^{BO} potential-energy surface (PES) or Born-Oppenheimer energy surface

0.4 Atomic Units

All over this lecture I will use SI-units (**S**ystème **I**nternational d'Unités).

Often, however, so-called atomic units (a.u.) are introduced in order to simplify the notation in quantum mechanics. For historic reasons two slightly different conventions exist. For both we have:

$$\text{length}: \quad \frac{4\pi\varepsilon_0\hbar^2}{me^2} = 1 \text{ bohr} = 0.529177 \text{ Å} = 0.0529177\,\text{nm} \quad , \tag{0.1}$$

but then two different options have been established: Rydberg atomic units and Hartree atomic units.

	$\dfrac{e^2}{4\pi\varepsilon_0}$	$\hbar$	m	energy $= \dfrac{\hbar^2}{2ma_B^2}$	$\dfrac{\hbar^2}{2m}$	Hamilton operator for the hydrogen atom
Rydberg a.u.	2	1	0.5	1 Ry = 13.606 (eV)	1	$-\nabla^2 + \dfrac{2}{r}$
Hartree a.u.	1	1	1	1 Ha = 27.212 (eV)	0.5	$-\dfrac{1}{2}\nabla^2 + \dfrac{1}{r}$