Attilio Rigamonti Pietro Carretta

Structure of Matter

An Introductory Course with Problems and Solutions

UNITEXT

Springer

Die Wahrheit ist das Kind der Zeit, nicht der Autoritaet.
Unsere Unwissenheit ist unendlich, tragen wir einen
Kubikmillimeter ab!
(from B. Brecht, in "Leben des Galilei")

There is no end to this wonderful world of experimental discovery
and mental constructions of reality as new facts become known.
That is why physicists have more fun than most people.
(Miklos Gyulassy)

To Luca Lorenzo Strozzi Rigamonti, with hope (A.R.)

To Gegia, Enri, Cate and Dario (P.C.)

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Preface

Intended Audience, Approach and Presentation

This text is intended for a course of about fifteen weeks for undergraduate students. It arises from the adaptation and the amendments to a text for a full-year course in Structure of Matter, written by one of the authors (A.R.) about thirty years ago. At that time only a few (if any) textbooks having the suited form for introduction to basic quantum properties of atoms, molecules and crystals in a comprehensive and interrelated way, were available. Along the last twenty years many excellent books pursuing the aforementioned aim have been published (some of them are listed at the end of this preface). Still there are reasons, in our opinion, to attempt a further text devoted to the quantum roots of condensed matter properties. A practical aspect in this regard involves the organization of the studies in Physics, after the huge scientific outburst of the various topics of fundamental and technological character in recent decades. In most Universities there is now a first period of three or four years, common to all the students and devoted to elementary aspects, followed by a more advanced program in rather specialized fields of Physics. The difficult task is to provide a common and formative introduction in the first period still suitable as a basis for building up more advanced courses and to bridge the large area between elementary physics and the topics pertaining to research activities. The present attempt towards a readable book, hopefully presenting those desired characteristics, essentially is based on a mixture of simplified institutional theory with solved problems. The hope, in this way, is to provide physical insights, basic culture and motivation, without deteriorating the possibility of more advanced subsequent learning.

Organization

Structure of Matter is such a wide field that a first task to undertake is how to confine an introductory text. The present status of that discipline represents a key construction of the scientific knowledge, possibly equated only by the unitary description of the electromagnetic phenomena. Even by limiting attention only to the conventional parts of the condensed matter, namely atoms, molecules and crystals, still we are left with an ample field. For instance, semiconductors or superconductors, the electric and magnetic properties of the matter and its interaction with the electromagnetic radiation, the microscopic mechanisms underlying solid-state devices as well as masers and lasers, are to be considered as belonging to the field of structure of matter (without mentioning the "artificial" matter involving systems such as nanostructures, photonic crystals or special materials obtained by subtle manipulations of atoms by means of special techniques). In this text the choice has been to limit the attention to key concepts and to the most typical aspects of atoms (Chapters 1-5), molecules (Chapters 7-10) and of crystalline solids (Chapters 11-14), looking at the basic "structural" aspects without dealing with the properties that originate from them. This choice is exemplified by referring to crystals: electronic states and quantum motions of the ions have been described without going into the details regarding the numerous and relevant properties related to these aspects. Only in a few particularly illustrative cases favoring better understanding or comprehensive view, derivation of some related properties has been given (examples are some thermodynamical properties due to nuclear motions in molecules and crystals or some of the electric or magnetic properties). Chapter 6 has the particular aim to lead the reader to an illustrative overview of quantum behaviors of angular momenta and magnetic moments, with an introduction to spin statistics, magnetic resonance and spin motions and a mention to spin thermodynamics, through the description of the adiabatic demagnetization used in order to approach the zero-temperature condition. All along the text emphasis is given to the role of spectroscopic experiments giving access to the quantum properties by means of electromagnetic radiation. In the spirit to limit the attention to key arguments, frequent referring is given to the electric dipole moment and to selection rules, rather than to other aspects of the many experiments of spectroscopic character used to explore the matter at microscopic level. Other unifying concepts present along the text are the ones embedded in statistical physics and thermal excitations, as it is necessary in view of the many-body character of condensed matter in equilibrium with a thermal reservoir.

Prerequisite, appendices and problems

Along the text the use of quantum mechanics, although continuous, only involves the basic background that the reader should have achieved in undergraduate courses. The knowledge in statistical physics is the one based on the Boltzmann, Fermi-Dirac and Bose-Einstein statistical distributions, with the relationships of thermodynamical quantities to the partition function (some of the problems work as proper recall, particularly for the statistical physics of paramagnets or for the black-body radiation). Finally the reader is assumed to have knowledge of classical electromagnetism and classical Hamiltonian mechanics. Appendices are intended to provide ad hoc recalls, in some cases applied to appropriate systems or to phenomena useful for illustration. The Gaussian cgs emu units are used. The problems should be considered entangled to the formal presentation of the arguments, being designed as an intrinsic part of the pathway the student should move by in order to grasp the key concepts. Some of the problems are simple applications of the equations and in these cases the solutions are only sketched. Other problems are basic building blocks and possibly expansions of the formal description. Then the various steps of the solution are presented in some detail. The aim of the mélange intuition-theory-exercises pursued in the text is to favor the acquisition of the basic knowledge in the wide and wonderful field of the condensed matter, emphasizing how phenomenological properties originate from the microscopic, quantum features of the nature.

It should be obvious that a book of this size can present only a minute fraction of the present knowledge in the field. If the reader could achieve even an elementary understanding of the atoms, the molecules and the crystals, how they are affected by electric and magnetic fields, how they interact with electromagnetic radiation and respond to thermal excitation, the book will have fulfilled its purpose.

The fundamental blocks of the physical world are thought to be the subnuclear elementary particles. However the beauty of the natural world rather originates from the architectural construction of the blocks occurring in the matter. Ortega Y Gasset wrote "If you wish to admire the beauty of a cathedral you have to respect for distance. If you go too close, you just see a brick". Furthermore, one could claim that the world of condensed matter more easily allows one to achieve a private discovery of phenomena. In this respect let us report what Edward Purcell wrote in his Nobel lecture: "To see the world for a moment as something rich and strange is the private reward of many a discovery".

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Dr. M. Medici is gratefully thanked for her careful revision of the typed text.

This book has been written while receiving inspiration from a number of text books dealing with particular items or from problems and exercises suggested or solved in them. The texts reported below are not recalled as a real "further-reading list", since it would be too ample and possibly useless. The list is more an acknowledgment of the suggestions received when seeking inspiration, information or advices.

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Contents

1

Atoms: general aspects

Topics

Central field approximation
Effective potential and one-electron eigenfunctions
Special atoms (hydrogenic, muonic, Rydberg)
Magnetic moments and spin-orbit interaction
Electromagnetic radiation, matter and transitions
Two-levels systems and related aspects

The aim of this and of the following three Chapters is the derivation of the main quantum properties of the atoms and the description of their behavior in magnetic and electric fields. We shall begin in the assumption of point-charge nucleus with mass much larger than the electron mass and by taking into account only the Coulomb energy. Other interaction terms, of magnetic origin as well as the relativistic effects, will be initially disregarded.

In the light of the **central field approximation** it is appropriate to recall the results pertaining to one-electron atoms, namely the **hydrogenic atoms** (§1.4). When dealing with the properties of typical multi-electron atoms, such as **alkali atoms** or **helium atom** (Chapter 2) one shall realize that relevant modifications to that simplified framework are actually required. These are, for instance, the inclusion of the **spin-orbit interaction** (recalled at §1.6) and the effects due to the **exchange degeneracy** (§1.3, discussed in detail at §2.2).

The properties of a useful reference model, the two-levels system, and some aspects of the electromagnetic radiation in interaction with matter, are recalled in Appendices and/or in *ad-hoc* problems at the end of the Chapter (Final Problems, F.I).

1.1 Central field approximation

The wave function $\psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N)$ describing the stationary state of the N electrons in the atom follows from the Schrödinger equation

$$\left[\frac{-\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_i \frac{Ze^2}{r_i} + \sum_{i\neq j}{}' \frac{e^2}{r_{ij}}\right]\psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N) = E\psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N)$$

$$\left[T_e + V_{ne} + V_{ee}\right]\psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N) = E\psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N) \quad (1.1)$$

where in the Hamiltonian one has the kinetic energy T_e, the potential energy V_{ne} describing the Coulomb interaction of the electrons with the nucleus of charge Ze and the electron-electron repulsive interaction V_{ee} (Fig. 1.1).

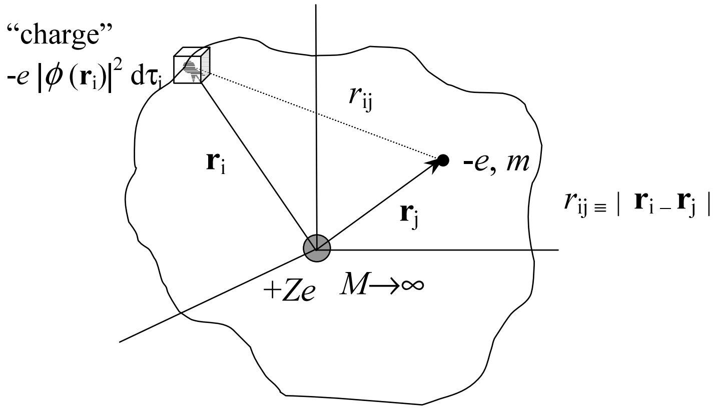

Fig. 1.1. Schematic view of multi-electrons atom. The nucleus is assumed as a point charge Ze, with mass M much larger than the mass m of the electron, of charge $-e$.

If the inter-electron interaction V_{ee} could be neglected, the total Hamiltonian would be $\mathcal{H} = \sum_i \mathcal{H}_i$, with $\mathcal{H}_i$ the one-electron Hamiltonian. Then $\psi(\mathbf{r}_1, \mathbf{r}_2, ...) = \prod_i \phi(\mathbf{r}_i)$, with $\phi(\mathbf{r}_i)$ the one-electron eigenfunction. V_{ee} does not allow one to separate the variables $\mathbf{r}_i$, in correspondence to the fact that the motion of a given electron does depend from the ones of the others. Furthermore V_{ee} is too large to be treated as a perturbation of $[T_e + V_{ne}]$. As we shall see (§2.2), even in the case of Helium atom, with only one pair of interacting electrons, the ground-state energy correction related to V_{ee} is about 30 percent of the energy of the unperturbed state correspondent to $V_{ee} = 0$.

The search for an approximate solution of Eq.1.1 can initiate by considering the form of the potential energy $V(\mathbf{r}_i)$, for a given electron, in the limiting