SOLID-STATE SCIENCES

P. Fulde

ELECTRON CORRELATIONS IN MOLECULES AND SOLIDS

Third Enlarged Edition

分子和固体中的电子关联

第3版

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Peter Fulde

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in Molecules and Solids

Third, Enlarged Edition

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Preface

Since its first publication in 1991, sufficient time has elapsed for this book to undergo a number of improvements, extensions and updates made desirable by progress in the field. In particular, the projection and partitioning technique can now be formulated in a simple and appealing way that also enables us to easily derive the standard quantum-chemical approximations. Thus, extensive rewriting of Chaps. 4 and 5 was imperative. Chapter 6 now contains an extension of the cumulant formalism to excited states, while Chap. 7 formulates the projection method for finite temperature calculations.

The second part of the book, which presents various applications of the theory, also includes a number of extensions. Chapter 9, which deals with semiconductors, presents new and highly accurate results for the ground state based on the method of increments. In Chap. 11 the treatment of excitations in transition metals has been improved. Chapter 12 on strong correlations has been thoroughly rewritten to take account of new developments and insights. Chapters 13 and 14 have likewise been extended and modified; in particular, the section on high-T_c superconducting materials has been updated.

Without the immense support of Dr. H. Lotsch, the spiritus rector of the physical science program of Springer-Verlag, it would have taken far longer for this edition to appear. I am very grateful to him.

Dresden   P. Fulde
February 1995

Acknowledgements

Preface to the First Edition

Any participant in a quantum chemistry meeting will notice that the attendance of solid-state physicists is rather sparse, and the reverse holds true for solid-state physics conferences, where one will meet hardly any quantum chemists. This shows how little contact exists between these two very active and important fields of condensed matter research. This is regrettable because, as solid-state physics becomes more and more a materials science and as quantum chemists are able to treat larger and larger molecules, the topics of mutual interest in these two fields are rapidly increasing. In order to change this situation, monographs are required that emphasize the features common to quantum chemistry and solid-state physics. It is the aim of this book to make a contribution here. An attempt is made to present the problem of electron correlations in molecules and solids in a unified form. For that we need a framework within which we can treat not only molecules and solids but also weakly and strongly correlated electrons. Such a framework is provided here. Because the terminology is often quite different in quantum chemistry and solid-state physics we have tried to compromise by using vocabulary and notation which should be reasonably familiar to scientists in both fields.

The book is divided into two parts. The first seven chapters concentrate on the various methods and techniques which are used to treat electron correlations in molecules and solids, whereas Chaps. 8–14 deal mainly with applications. They range from atoms and molecules to semiconductors and metals, with special emphasis on transition metals. Particular attention is paid to strongly correlated electron systems, a topic to which the last three chapters are devoted. The Kondo effect and in particular heavy-fermion systems and the new high-temperature superconducting materials fall into that category.

Without the fine cooperation and the support of Dr. H. Lotsch of Springer-Verlag this book would have taken much longer to complete. Ms. D. Hollis, also of Springer-Verlag, made important improvements to the manuscript. I am thankful to both of them.

List of Abbreviations

AD	average density
AF	antiferromagnet
ARPES	angular resolved photoelectron spectroscopy
BCS	Bardeen, Cooper, Schrieffer
BIS	bremsstrahlung isochromat spectroscopy
BOA	bond orbital approximation
CEF	crystalline electric field
CEPA	coupled electron pair approximation
CGTO	contracted Gauss-type orbital
CI	configuration interaction
CI-SD	configuration interaction with single and double substitutions
CMO	canonical molecular orbital
CNDO	complete neglect of differential overlap
CPA	coherent potential approximation
DZ	double zeta
DZ + P	double zeta plus polarization function
EELS	electron energy loss spectroscopy
GTO	Gauss-type orbital
HF	Hartree-Fock
HOMO	highest occupied molecular orbital
INDO	intermediate neglect of differential overlap
LDA	local density approximation
LMO	localized molecular orbital
LSD	local spin density
MC-SCF	multiconfiguration self-consistent field
MNDO	modified neglect of differential overlap
MO	molecular orbital
MP-2(4)	Møller-Plesset perturbation expansion including second (fourth) order terms
MR-CI-SD	multireference configuration interactions using single and double excitations
NCA	noncrossing approximation
NO	natural orbital
OLRO	off-diagonal long range order
PCILO	perturbation configuration interaction using localized orbitals

PNO	pair natural orbital
RKKY	Ruderman, Kittel, Kasuya, Yoshida
RPA	random phase approximation
SCF	self-consistent field
SCR	self-consistent renormalization theory
SDW	spin density wave
SIC	self-interaction correction
STO	Slater-type orbital
TDA	Tamm-Dancoff approximation
TZ + P	triple-zeta plus polarization function
ZDO	zero differential overlap
1D (2D)	one (two) dimensional
2ph-TDA	two-particle hole Tamm-Dancoff approximation

Fourier Transforms

of operators: $a_{i\sigma} = \dfrac{1}{\sqrt{N_0}} \sum_{\mathbf{k}} a_{\mathbf{k}\sigma} e^{-i\mathbf{k}\cdot\mathbf{R}_i}$

$N_0 =$ number of sites

of functions: $F_i = \dfrac{1}{N_0} \sum_{\mathbf{k}} F_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}_i}$

Contents

1. Introduction

This book aims at bridging the gap between two active fields of research, i.e., quantum chemistry and solid-state theory. Soon after the development of quantum mechanics by *Heisenberg* [1.1], *Schrödinger* [1.2], *Born* and *Jordan* [1.3], *Dirac* [1.4], and others, the paper by *Heitler* and *London* [1.5] on the ground state of the H_2 molecule opened the way to a theoretical understanding of chemical bonding. Their work marks the beginning of quantum chemistry. The Heitler–London ansatz for the ground-state wavefunction of H_2 treats the two electrons as being strongly correlated, i.e., by excluding ionic configurations the two electrons stay completely out of each other's way. The ground state is a singlet and has the form

$$\psi_{HL}^S(\mathbf{r}_1,\mathbf{r}_2) = \tfrac{1}{2}[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2)](\alpha_1\beta_2 - \beta_1\alpha_2). \qquad (1.0.1)$$

The functions $\phi_{1,2}(\mathbf{r})$ are centered on atoms 1 and 2, and the spinors α and β refer to spin up and spin down, respectively.

A distinctly different approach to the problem of interacting electrons was taken shortly thereafter by *Hartree* [1.6], *Fock* [1.7], and *Slater* [1.8], who treated the electrons as being independent of each other and introduced the idea of the self-consistent field. The latter is the interaction field an electron experiences when we take a spatial average over the positions of all the other electrons. Within the independent-electron approximation, the ground-state wavefunction of H_2 is of the form

$$\psi_{HF}^S(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{2^{3/2}}[\phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2) + \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2)$$

$$+ \phi_2(\mathbf{r}_1)\phi_2(\mathbf{r}_2)](\alpha_1\beta_2 - \beta_1\alpha_2). \qquad (1.0.2)$$

One notices that the ionic configuration $\phi_1\phi_1$ and $\phi_2\phi_2$ in (1.0.2) enter with equal weight when compared with the nonionic configurations. Thus, when the two hydrogen atoms are pulled apart, the wavefunction does not reduce properly to the atomic limit. On the other hand, (1.0.1) does not reduce properly to the correct wavefunction in the limit of small atomic distances. As one might expect, the true ground state lies between the two extremes (1.0.1) and (1.0.2). Electron correlations reduce the ionic configuration relative to the nonionic ones, but they do not reduce them to zero as (1.0.1) suggests.

The forms (1.0.1) and (1.0.2) are prototypes of wavefunctions which apply not only to the H_2 molecule but, more generally, to both quantum chemistry

and to solid-state physics. They stand for localized versus delocalized electrons and have been the subject of countless discussions and controversies. Whether an improved calculation should start from a wavefunction of the Heitler–London (strong-correlation limit) or the Hartree–Fock form (limit of independent electrons) depends on how strong electron correlations become in a given molecule or solid. In principle, one would like to have a quantity which specifies the correlation strength in different bonds or atoms in a given chemical environment. This textbook intends to provide this information in a systematic fashion.

Two different roads have been pursued in quantum chemistry towards a qualitative and quantitative understanding of chemical bonding. *Pauling* [1.9] introduced and developed one of those approaches, basing it on the concept of resonance and resonance structures and essentially using the Heitler–London picture. The other one, the molecular orbital theory, was first developed by *Hund* [1.10] and *Mulliken* [1.11] and elaborated by *Slater* [1.8], *Hückel* [1.12], and others. It is based on the idea of independent electrons and hence corresponds to (1.0.2). When formulated broadly enough, both approaches described above are equivalent. In practice, however, often only the lowest-order corrections can be calculated for the two limiting cases. The molecular orbital theory has had great success, since most chemical bonds are relatively weakly correlated. It has failed, however, with certain metal-organic complexes or, as far as solids are concerned, with the copper-based high-temperature superconducting oxides, in which electron correlations are strong. The independent-electron approximation proves in those cases an inappropriate starting point.

This leads us to the theory of solids. *Sommerfeld* and *Bethe* [1.13] offered the first coherent presentation of a microscopic theory of solids. In particular, their theory of metals is based on *free* electrons. In view of the strong electron interactions, the fact that a theory of free electrons was so successful remained a puzzle for a long time. It was resolved only after the development of the concept of quasiparticles in Fermi liquids by *Landau* [1.14]. From his contribution we have gained the insight that the low-energy excitations of a metal can be described by quasiparticles which behave like electrons with renormalized mass, Fermi velocity, etc. This concept holds even for metals with strongly correlated electrons like the heavy-fermion systems. Whether it holds in all cases remains an open problem. As regards the high-T_c superconducting materials, for example, *Anderson* [1.15] has claimed that this is not the case.

The competition between the Heitler–London and independent-electron descriptions played an important role in the development of the theory of transition metals. Prominent representatives of the two approaches were *Van Vleck* [1.16] and *Slater* [1.17]. There is general consent today that in transition metals the d electrons are delocalized; it is also clear, however, that correlations among them are far from weak. Thus a number of atomic features – like Hund's rule coupling – persist despite delocalization. Correlations are particularly strong in some of the transition metal oxides; a well-known example is CoO. Were it not for the strong correlations, this substance would be

metallic, since it has one unpaired electron per formula unit. Instead, CoO is a Mott–Hubbard insulator because correlations prevent the charge fluctuations required for metallic conduction.

Methods based on the idea of a self-consistent field have been widely applied, in particular after the development of the local-density approximation to the density functional theory by *Hohenberg*, *Kohn*, and *Sham* [1.18, 19]. The concept of the self-consistent field was originally designed for the independent-electron approximation. Due to the development of the local-density approximation, the self-consistent field can be extended to include correlation contributions. Together with new methods for solving the Schrödinger equation, initiated by the development of the linearized versions of the muffin tin orbital and augmented plane wave methods [1.20, 21], local-density theory has penetrated all areas of solid-state theory. Despite its great success, however, it has not been able to provide more insight into the electron correlation problem. This is not surprising because the local-density approximation uses the correlation energy of a homogeneous electron gas as input. The important correlations due to the orbital structure of the electronic charge distributions (e.g., Hund's rule correlations) remain untouched by that approach.

Although many aspects of electron correlations are very similar in molecules and solids, the theoretical developments in the two fields have diverged to such an extent that today they often do not even share a common language. Regrettably, this divergence has prevented cross-fertilization between the two fields. One main obstacle has been the fact that the methods applied in quantum chemistry for the treatment of correlations in small molecules cannot be carried over to solids, in particular when electrons are well delocalized. From a physical point of view, however, this difficulty should be avoidable because the correlation hole around an electron is a fairly local object and does not differ much in a molecule and a corresponding solid (see e.g. [1.22]) – hence this book's emphasis on recently developed methods that overcome such difficulties (Chap. 5). Provided that the correlations are not too strong, self-consistent field calculations are a good starting point, and allow solids and molecules to be treated the same way and with the same accuracy. The development of quantum chemistry has proven that ab initio calculations based on controlled approximations capable of systematic improvement have made simpler computational schemes based on uncontrolled simplifications obsolete. Whether or not the same will eventually hold true for solid-state theory remains to be seen.

Systems with strong electron correlations require special attention. As long as the electron correlations are weak, the residual interactions, i.e., those interactions not described by the self-consistent field, are small and may be treated by expansion or variational methods. The unperturbed Hamiltonian H_0 is then of a single-particle form. When the correlations are strong, on the other hand, the unperturbed Hamiltonian H_0 must incorporate the dominant parts of the electron interactions, thus losing its single-particle form. The weak hybridizations then need to be treated approximately. The main difference