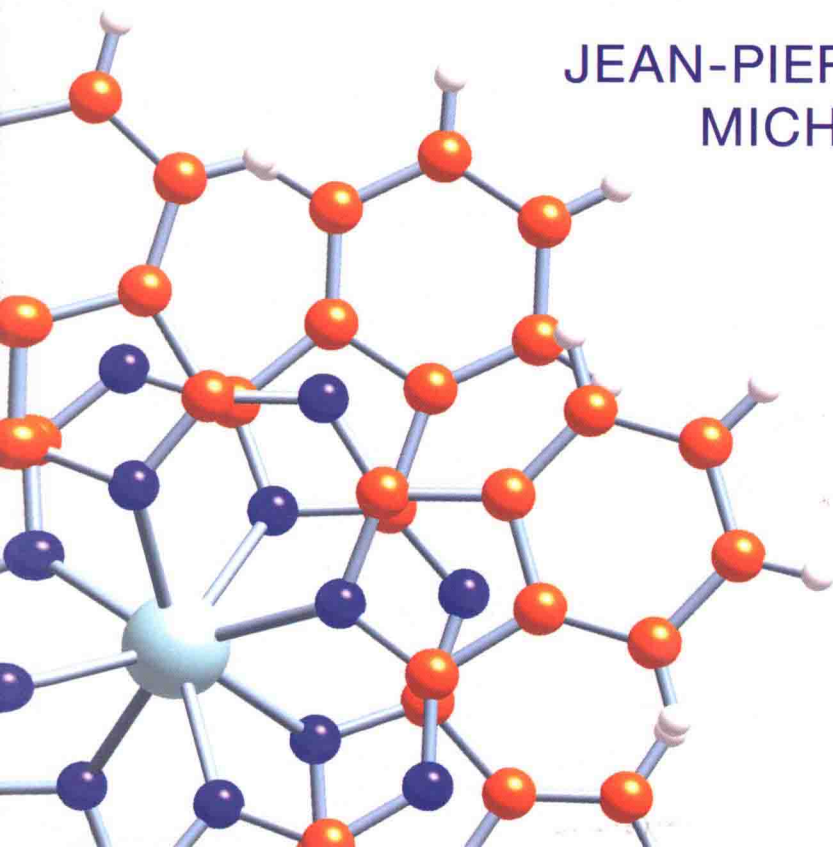




# Electrons in Molecules

From Basic Principles to Molecular Electronics

JEAN-PIERRE LAUNAY AND  
MICHEL VERDAGUER



OXFORD

# Electrons in Molecules

From Basic Principles  
to Molecular Electronics

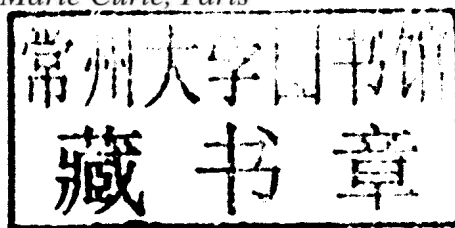
---

JEAN-PIERRE LAUNAY

*Université Paul Sabatier, Toulouse*

MICHEL VERDAGUER

*Université Pierre et Marie Curie, Paris*



OXFORD  
UNIVERSITY PRESS

**OXFORD**  
UNIVERSITY PRESS

Great Clarendon Street, Oxford, OX2 6DP,  
United Kingdom

Oxford University Press is a department of the University of Oxford.  
It furthers the University's objective of excellence in research, scholarship,  
and education by publishing worldwide. Oxford is a registered trade mark of  
Oxford University Press in the UK and in certain other countries

© Jean-Pierre Launay and Michel Verdaguer 2014

The moral rights of the authors have been asserted

First Edition published in 2014

Impression: 1

All rights reserved. No part of this publication may be reproduced, stored in  
a retrieval system, or transmitted, in any form or by any means, without the  
prior permission in writing of Oxford University Press, or as expressly permitted  
by law, by licence or under terms agreed with the appropriate reprographics  
rights organization. Enquiries concerning reproduction outside the scope of the  
above should be sent to the Rights Department, Oxford University Press, at the  
address above

You must not circulate this work in any other form  
and you must impose this same condition on any acquirer

Published in the United States of America by Oxford University Press  
198 Madison Avenue, New York, NY 10016, United States of America

British Library Cataloguing in Publication Data  
Data available

Library of Congress Control Number: 2013938572

ISBN 978-0-19-929778-8

Printed and bound by  
CPI Group (UK) Ltd, Croydon, CR0 4YY

Links to third party websites are provided by Oxford in good faith and  
for information only. Oxford disclaims any responsibility for the materials  
contained in any third party website referenced in this work.

# Preface

Electrons in molecules . . . Both objects—electron and molecule—have a long, rich, and complex history. Both words began to be used as elusive concepts in the nineteenth century before gaining well-established scientific status at the turn of the twentieth century. Several tens of years of common endeavour, failures, and achievements by chemists and physicists, based on experimental and theoretical work, were necessary to reach consensus. The word ‘electron’ (from the Greek *élektron*, amber) was proposed by Stoney in 1894, to name the elementary negative charge of the particle, whereas ‘molecule’ comes from the diminutive of the Latin *moles* (mass), introduced in modern Latin by Gassendi as *molecula*. The emergence of the scientific concept of ‘molecule’, and its clear distinction from atoms and equivalents, was the result of big controversies (pros and cons in Karlsruhe Congress, 1860), but laid the foundations of the basic understanding of chemistry, molecular chemistry, and associated industrial synthetic processes. It opened the door to the understanding of complex, highly organized, and biological matter. Elucidation of the nature of the electron as a corpuscle and as a wave, and its role in atoms and molecules, gave rise to quantum mechanics. Today, everyone knows that molecules are quantum objects built from atoms sharing some of their electrons to establish chemical bonds.

*Electrons in molecules* . . . The title can also be read as ‘understanding the electronic structure and electronic properties of molecules’. Electrons are dividing their roles in a molecular entity: some ensure the chemical bonds and allow the stability of the molecules, while others are less bound to the atomic core and provide the molecules with their fancy properties—magnetic, electrical, photo-physical, colour, luminescence—allowing their use in molecular electronics, nanosciences, and so on . . . This book is based on the simple idea that such apparently different properties present a profound unity, relying on basic concepts of quantum mechanics and symmetry. This conclusion emerged from informal discussions which we had many years ago with numerous colleagues, and was fed by our teaching experiences at undergraduate and graduate levels.

The backbone of the book was designed accordingly. Chapter 1 briefly presents the basic quantum concepts as a common introduction to the broad domain encompassed by the properties. The molecular orbital approach is the red thread throughout the book, and its advantages and its limitations are carefully discussed. We then treat consecutively the magnetic properties (Chapter 2, ‘The localized electron’), electron transfer and electrical properties (Chapter 3, ‘The moving electron’), the photo-physical properties (Chapter 4, ‘The excited electron’), and finally, molecular electronics (Chapter 5, ‘The mastered electron’). So doing, we introduce the specific aspects of each of the

subjects, and try to enlighten them by returning systematically to the basic concepts. The goal is to better understand each topic and to show the transversal connections between many of them.

The book's content is shaped by a few specific features. First, it could be important to specify *what this book is not*: it is *not* a compilation of recent research results. There are many reviews in the specialized literature, which periodically updates the huge amount of data and results associated with the particular topics evoked here. We did not even consider the idea of being exhaustive in a given field. Each of the chapters could have been, and in some cases have already been, the subject of *several* books.

Second, we concentrate on *concepts* and use as little mathematics as possible. We try to give as much physical and chemical meaning as possible to the equations. We try to explain the logic and goal of calculations—the price being to skip some intermediate developments, which are left to the reader.

Third, we stress the importance of interdisciplinarity: to tackle ambitious challenges, we think deeply that in this domain one has to mix together chemistry, physics, and materials science. The book performs constant trips between these areas and between theory and experiment. Such a step appears compulsory to achieve the breakthroughs, allowing the progress of knowledge and the realization of practically useful materials and devices. Furthermore, in the recently popularized field of nanosciences, the division between physics and chemistry tends to vanish. But the round-trip ideas between chemist and physicist, between theoretician and experimentalist, are essential for adapting the molecule(s) to the instrument, or *vice versa*, and to be able finally to explore and demonstrate new phenomena.

Fourth, the book is fed by our lifelong experience of molecular chemists, synthesizing molecules and molecular assemblies specially designed to present given physical properties. A few quantum concepts constitute the background. Chemical synthesis provides the planned molecules (most often conceived after discussion to fit the needs of the physicist, the machine, or the demonstration). Beautiful physics experiments follow, with innovative setups and incredible enhanced sensitivities. Our book describes such experiments and their results, but stresses the contribution of molecular chemistry, which has sometimes been overlooked. It is indeed important to realize that this discipline has reached such a state of maturity that it can be considered as the science of elaborating three-dimensional objects of sub-nanometre size by rational design, with the possibility of predicting and fine-tuning their properties. A long time has passed since discoveries were made because a molecule was available on the shelf. Now, more and more, they are extensively designed before, and for, the experiment. The book is rich in many such examples. And when it happens that unexpected molecules arise, the curious scientist is always ready to foresee how they can be exploited to initiate new lines of research.

A fifth point is the importance of technology and instrumentation: huge progress has been made possible only because new equipment has been devised, such as the STM and its multiple variants, or the squid and its miniaturized evolutions. The race towards single-molecule properties, as opposed to the study of statistical ensembles, is now a strong motivation of research in all the fields covered in the book, as shown in the last chapter.

Such integrated content was conceived for an audience of students in chemistry, physics, and materials sciences, having a preliminary basic knowledge of the theory of symmetry and quantum mechanics. We taught most of the content of the book at undergraduate and graduate levels in chemistry and materials science courses in various places, French or foreign (European, Asian, and American) universities or French ‘grandes écoles’. Our goal is to provide fundamental knowledge and, above all, a solid *understanding* not only to beginners to boost their *curiosity* and *creativity* to design and obtain new materials with exciting new electronic properties, but also to already specialized researchers or engineers, to enlarge their vision to complementary fields and favour cross-fertilizing of other disciplines. We would always appreciate remarks and suggestions from our readers.\*

\* Every effort has been made to contact the holders of copyright in materials reproduced in this book. Any omissions will be rectified in future printings if notice is given to the publisher.

The content of our lectures varied systematically from one year to another to follow scientific trends and to integrate remarks and suggestions from our students and from our colleagues in neighbouring specialities. We are grateful to them. We also benefited from passionate discussions with coworkers and colleagues in our respective laboratories: Centre d’Elaboration de Matériaux et d’Etudes Structurales, CEMES (J.-P.L.) at Université Paul Sabatier in Toulouse, and Chimie Inorganique et Matériaux Moléculaires, CIM2 (M.V.) at Université Pierre et Marie Curie in Paris—both units of the Centre National de la Recherche Scientifique, the French institution supporting scientific research. Our colleagues will recognize their work, and fingerprints, here and there. Many thanks!

Thus, starting from our initial project, such exchanges and experiences transformed the book and its integrated content from principles to applications, resulting in a volume which, it appears, is unique in the literature at this level.

Our final word is directed to our families: our wives, Marie-Hélène and Jacqueline, and our daughters, sons, and grand-children, who endured, and sometimes accepted with incredulous smiles, the too long gestation of this volume.

Jean-Pierre Launay  
Michel Verdaguer

*Cordon, Escalquens, Palaiseau, Paris, Toulouse*  
*September 2013*

# Abbreviations and symbols

1D	one-dimension
2D	two-dimension
3D	three-dimension
A	absorbance
A	acceptor
$\alpha$	Coulomb integral
$\alpha$	spin up
AC	alternating current
AFM	atomic force microscope
AM1	Austin model 1
AND	AND gate
AO	atomic orbital
$\beta$	decay coefficient
$\beta$	resonance integral
$\beta$	spin down
B3LYP	Becke 3-parameter Lee Yang Parr
BCS	Bardeen Cooper Schrieffer
BO	Bloch orbital
bpm	2,6-bis[bis(2-pyridylmethyl)aminomethyl]4-methylphenol
bpy	2,2'-bipyridine
btz	bi-dihydrothiazine
BS	Broken Symmetry
C	carbon
C	constant
C <sub>2v</sub> C <sub>s</sub>	symmetry point group
C <sub>60</sub>	C <sub>60</sub> molecule
c, c <sub>i</sub> , c <sub>ij</sub>	coefficient
$\chi$ , $\chi'$ , $\chi''$	magnetic susceptibility
CAS-SCF	complete active space self consistent field
cat	catecholate
CDW	charge density wave
cgs	cgs unit system
CN <sup>-</sup>	cyanide
CNDO	complete neglect of differential overlap
CNT	carbon nanotube
CO	carbon monoxide

## Abbreviations and symbols

CO	charge order
CO	crystal orbital
CT	charge-transfer
D	Zero field splitting parameter
D	spectroscopic term
D, d	distance
D	donor
$\tilde{D}$	anisotropy tensor
$\Delta$	ligand field parameter
$D_{\infty}, D_{2h}$	symmetry point group
$\Delta_{oct}$	octahedral ligand field parameter
$\delta_{rs}$	Kronecker symbol
$\Delta_t$	tetrahedral ligand field parameter
DFT	density functional theory
DNA	deoxyribonucleic acid
DOS	density of states
dpp	dipyridophenazine
Dq	ligand field parameter
e, e <sup>-</sup>	electron
E	energy
E	identity operation
E	Zero field splitting parameter
e, e <sub>g</sub> , E <sub>g</sub>	symmetry labels
E <sub>g</sub>	band gap
$\varepsilon$	monoelectronic energy
$\varepsilon$	permittivity
E°	standard potential (electrochemistry)
emu	electromagnetic unit system
EPR	electron paramagnetic resonance
ES	excited state
ESQC	elastic scattering quantum chemistry
EXAFS	extended X-ray absorption fine structures
Fe <sub>8</sub>	Fe <sub>8</sub> iron complex
$\phi$	atomic orbital
$\phi$	polar angle
$\Phi$	total wave function
FET	field-effect transistor
fsa or H <sub>4</sub> (fsa)en	N,N'-(2-hydroxy-3-carboxybenzilidene)-ethanediamine)
$\gamma$	decay coefficient
g	g-factor
G	free enthalpy
g	gerade
GS	ground state
GVB	generalized valence bond
H	enthalpy
<b>h, H</b>	hamiltonian
h	Planck constant



HDVV	Heisenberg Dirac van Vleck
$h_{\text{eff}}$ , $H_{\text{eff}}$	effective Hamiltonian
HL	Heitler London
HM	Hund Mulliken
HOCO	highest occupied crystal orbital
HOMO	highest occupied molecular orbital
$i$	complex number $i$ ( $i^2 = -1$ )
$i$	inversion centre
INDO	intermediate neglect of differential overlap method
INHIBIT	INHIBIT gate
INS	inelastic neutron scattering
IP	Ionization potential
IR	infrared
IR	irreducible representation
ITRS	international technology roadmap for semiconductors
$j$ , $J_{ij}$	coupling constant
$j$ , $j_0$ , $j_{ij}$ $J$ , $J_{ij}$	two-centre two-electron integrals
$j$ , $J$	orbital quantum number
$j$ - $j$	$j$ - $j$ coupling
$k$ , $K$ , $k_{ij}$ , $K_{ij}$	two-electron exchange integral
$K$	equilibrium constant
$K$	Kelvin
$K$	kinetic energy
$k$ , $k_B$	Boltzmann constant
KCP	potassium tetracyanoplatinate
KS-DFT	Kohn-Sham orbitals in DFT
$\mathbf{l}$ , $\mathbf{L}$	angular momentum operator
$l$ , $L$	quantum number
$\lambda$	mean free path
$\lambda$	$\lambda$ parameter
$\lambda$	wavelength
LCAO	linear combination of atomic orbitals
LD-LISC	ligand driven-light induced spin cross-over
LDOS	local density of states
LIESST	light induced excited spin state trapping
LMCT	Ligand metal charge transfer
LS	Russell Saunders coupling
LUMO	lowest unoccupied molecular orbital
LVCO	lowest vacant crystal orbital
LYP	Lee Yang Parr
$M$	magnetization
$m$	mass
$M$	molar, mole
$M$	molar mass
$m$	quantum number
$M$	transition dipole moment
$\mu_B$	Bohr magneton
$\mu$	magnetic moment

## Abbreviations and symbols

$\mu_e$	electron magnetic moment
$\mu_{\text{eff}}$	effective magnetic moment
$\text{Mn}_{12}$	$\text{Mn}_{12}$ manganese complex
MBPT	many-body perturbation theory
MCD	magnetic circular dichroism
MC-SCF	multiconfigurational SCF
MINDO	modified intermediate neglect of differential overlap
$m_j, M_J$	quantum number
$m_l, M_L$	quantum number
MLCT	metal ligand charge transfer
MMCT	metal metal charge transfer
MNDO	modified neglect of diatomic overlap
MO	molecular orbital
$m_s, M_S$	spin quantum number
$M_S$	magnetization at saturation
MWNT	multiwall nanotube
$N_A$	Avogadro constant
NDDO	neglect of differential diatomic overlap
NDR	negative differential resistance
NMR	nuclear magnetic resonance
$O_h$	octahedral symmetry point group
OLED	organic light-emitting diode
OR	OR gate
ox	oxalate
P	projection operator
P	probability
PB	Prussian blue
PBA	Prussian blue analogue
pba	1,3-propanebis(oxamate)
PIPT	photo-induced phase transition
phen	1,10-phenantroline
ptz	1-propyl tetrazole
PTZ	phenothiazine
py	pyridine
pz	pyrazine
PPP	Pariser Parr Pople
$\Psi, \psi$	wavefunction
q, Q	electric charge
Q	nuclear coordinate
R	gas constant
R	radial function
r	distance operator
r	radius
S	entropy
S	overlap integral
$s, S$	spin quantum number
$s, S$	spin angular momentum operator
$S^2$	spin operator

SALC	symmetry-adapted linear combination
SAM	self-assembled monolayer
SCF	self consistent field
SCM	single chain magnet
SI	Système International
SIM	single ion magnet
SMM	single molecule magnet
SO	symmetry orbital
SOMO	singly occupied molecular orbital
SDW	spin density wave
SH	spin-Hamiltonian
$\Sigma$	spin function
sq	semiquinone
SQUID	superconducting quantum interference device
STM	scanning tunnelling microscope
SWNT	single-walled nanotube
T	absolute temperature
$\Theta$	Bloch orbital
$\theta$	polar angle
t	time
t, T, $t_{2g}$ , $T_{2g}$	symmetry labels
t	transfer integral
$T_{1/2}$	half-conversion temperature
$T_c$	critical temperature
$T_C$	Curie temperature
TCNQ	tetracyanoquinodimethane
$T_d$	tetrahedral symmetry point group
TD-DFT	time-dependent DFT
T(E)	transmission coefficient
tmen	tetramethyl 1,2-ethanediamine
TMMC	tetramethyl ammonium manganese chloride
TTF	tetrathiafulvalene
u	ungerade
U	two-electron repulsion integral (one-centre)
U	potential energy
UHV	ultra-high vacuum
UV	ultra-violet
V	electric potential
V	two-electron repulsion integral (two-centre)
V	Volt
v	speed
VSEPR	valence shell electron pair repulsion
VSIP	valence state ionization potential
VSM	Vibrating Sample Magnetometer
W	energy
W	energy bandwidth
W	watt
$W_P$	polaron energy

## Abbreviations and symbols

$\chi$	crystal orbital
XANES	X-ray absorption near edge structures
XMCD	X-ray magnetic circular dichroism
XOR	XOR gate
Y	angular function spherical harmonics
Z	partition function
Z	atomic number
$Z_{\text{eff}}$	effective atomic number
ZFS	Zero-field splitting

# Contents

Abbreviations and symbols	xiii
---------------------------	------

<b>1 Basic concepts</b>	<b>1</b>
1.1 Electron: an old, complex, and exciting story	2
1.2 Electrons in atoms	4
1.2.1 The electron in the simplest atom: hydrogen	4
1.2.2 The hydrogenoid ion	7
1.2.3 Helium and other atoms	7
1.3 Electrons in molecules	10
1.3.1 Dihydrogen molecule, H <sub>2</sub>	11
1.3.2 AB molecules	16
1.3.3 Dioxygen molecule, O <sub>2</sub>	17
1.3.4 Water molecule, H <sub>2</sub> O	21
1.3.5 Organic molecular systems	23
1.3.6 Coordination complexes	27
1.3.7 Influence of the electronic structure on the geometric structure: the Jahn–Teller effect	35
1.4 Electrons in molecular solids	39
1.4.1 From molecular rings to infinite linear chains	39
1.4.2 Brillouin zone, energy dispersion curve, Fermi level, and density of states	43
1.4.3 Peierls distortion	45
1.4.4 Crystal orbitals: more than one orbital per cell	46
1.4.5 Towards 3D systems	48
1.5 Effects of interelectronic repulsion	49
1.5.1 Position of the problem	49
1.5.2 The quantitative molecular orbital (MO) method	54
1.5.3 The valence bond (VB) model: comparison with the MO model	67
1.5.4 Density-functional theory (DFT) methods	73
1.6 A fundamental quantum effect: tunnelling	74
References	77
 <b>2 The localized electron: magnetic properties</b>	 <b>78</b>
2.1 Introduction	78
2.2 A new look at the electron	81
2.2.1 Orbital and spin angular momenta of the electron	81
2.2.2 Magnetic properties of one electron in an atom	84
2.2.3 The total angular momentum	86

2.3	Physical quantities, definitions, units, and measurements	86
2.3.1	Physical quantities and definitions	86
2.3.2	Units in magnetism	87
2.3.3	Magnetic measurements	89
2.3.4	Understanding the susceptibilities: from Langevin to Van Vleck's formula	94
2.4	Many-electron atoms, mononuclear complexes, and spin cross-over	99
2.4.1	Many-electron atoms	99
2.4.2	Mononuclear complexes, electronic structure	104
2.4.3	Spin cross-over: phenomenon and models	109
2.5	Spin Hamiltonian (SH) approach	127
2.5.1	One-centre spin Hamiltonian	128
2.5.2	Two-centre spin Hamiltonians with spin operators $S_1$ and $S_2$	132
2.5.3	More than two centres	135
2.6	Orbital interactions and exchange	138
2.6.1	Basic theoretical background	140
2.6.2	From hydrogen to transition metal complexes	145
2.6.3	Other models: from the pioneers to modern computations	154
2.6.4	Ferromagnetic and antiferromagnetic coupling in dinuclear complexes with one spin per centre	157
2.6.5	Complexes with several spins per centre	163
2.7	Extended molecular magnetic systems	172
2.7.1	The one-dimensional world: a Hamiltonian and synthesis factory	172
2.7.2	Bimetallic ferrimagnetic chains: an improbable route to 3D magnets	176
2.7.3	Three-dimensional frameworks, Prussian blue analogues	185
2.8	Magnetic anisotropy and slow relaxation of the magnetization	191
2.8.1	Single-molecule magnets (SMM)	191
2.8.2	Single-chain magnets (SCM)	199
2.8.3	Single-ion magnets (SIM)	201
	References	202
<b>3</b>	<b>The moving electron: electrical properties</b>	<b>205</b>
3.1	Basic parameters controlling electron transfer	205
3.1.1	The electronic interaction between neighbouring sites: the $V_{ab}$ parameter	206
3.1.2	The structural change of the surrounding: the $\lambda$ parameter	209
3.1.3	The interelectronic repulsion: the $U$ parameter	217
3.1.4	The interplay of parameters	217
3.2	Electron transfer in discrete molecular systems	218
3.2.1	Intermolecular transfer	218
3.2.2	Intramolecular transfer: mixed valence compounds	231
3.3	Conductivity in extended molecular solids	266
3.3.1	Conductivity: definitions, models, and significant parameters	266
3.3.2	Extended metallic molecular systems and band theory	269

3.3.3	Peierls instability in 1D: electron–phonon interactions	286
3.3.4	Beyond the one-electron description: narrow-band systems or no band at all	304
	References	323
<b>4</b>	<b>The excited electron: photophysical properties</b>	<b>326</b>
4.1	Introduction	326
4.2	Fundamentals in photophysics: absorption, emission, and excited states	327
4.2.1	Energy levels	328
4.2.2	Transition probabilities	330
4.2.3	Nuclear relaxation after excitation	332
4.3	Electron transfer in the excited state	333
4.3.1	Properties of the excited state: the example of $[\text{Ru}(\text{bpy})_3]^{2+*}$	333
4.3.2	Molecular photodiodes	335
4.3.3	Light-emitting diodes (LED)	338
4.3.4	Photovoltaic devices	342
4.3.5	Harnessing photochemical energy: towards water photolysis	345
4.3.6	Ultrafast electron transfer	348
4.4	Energy transfer	351
4.4.1	Theoretical treatment of energy transfer	352
4.4.2	Some examples	358
4.5	Photomagnetism	364
4.5.1	Introduction	364
4.5.2	Photomagnetism in spin cross-over systems	366
4.5.3	Photomagnetism originating from metal–metal charge transfer	373
	References	385
<b>5</b>	<b>The mastered electron: molecular electronics</b>	<b>387</b>
5.1	Introduction and historical account	387
5.2	Hybrid molecular electronics	392
5.2.1	Realization of metal–molecule–metal connections	392
5.2.2	Principles of electrical conduction in nanosystems	396
5.2.3	Molecular wires	422
5.2.4	Molecular diode (rectifier)	426
5.2.5	Memory effect and negative differential resistance in two-terminal devices	431
5.2.6	Two-terminal devices under constraint (pressure, light)	436
5.2.7	Three-terminal devices: field-effect transistor (FET)	441
5.2.8	Nanotubes, graphene, and devices	443
5.2.9	Molecular spintronics	449
5.3	Behaviour of ensemble of molecules	456
5.3.1	Systems studied in solution	456
5.3.2	Systems studied in the solid state	460

5.4	Towards quantum computing	462
5.4.1	Standard quantum computing	462
5.4.2	Quantum Hamiltonian computing	465
5.5	Conclusion and perspectives	466
	References	468

	<i>Index</i>	473
--	--------------	-----



# Basic concepts

# 1

In this chapter we establish, in a progressive way, how to describe the quantum properties of the constituents of matter—atoms, molecules, and extended molecular solids—with an emphasis on the behaviour of electrons, starting from first principles. Since the achievements of quantum mechanics, this step is in principle feasible. In this manner, Paul A. M. Dirac wrote: ‘The fundamental physical laws necessary to the mathematical theory of most parts of the physics and the whole of chemistry are completely known, and the difficulty is only that the exact applications of these laws lead to equations too complex to be solved exactly.’

It is true that the equation named after Schrödinger, under its stationary (1.1) or time-dependent (1.2) forms

$$\mathbf{H}\Psi_n = E_n\Psi_n \quad (1.1)$$

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi \quad (1.2)$$

allows theoretical determination of the eigenwavefunctions  $\Psi_n$  and the eigenenergies  $E_n$  which define the system and its change with time. In these formulae,  $\mathbf{H}$  is an operator which operates on the wavefunction  $\Psi$ ,  $i$  is the complex number  $i^2 = -1$ ,  $\hbar$  is the Planck constant, and the  $\frac{\partial}{\partial t}$  operator is the partial derivative as a function of time  $t$ .

The ‘only’ difficulty, following Dirac, is that the operator must take into account *all* the interactions—in particular, the interactions between electrons—but *we are unable to write them analytically in an exact way*, two thirds of a century after Dirac. To solve the problem, *it is necessary to use some approximations*. It will be the purpose of the first part of this book to introduce some models useful to the description of the structure and the electronic structure of molecules and solids. These models will then be used to forecast the properties.

It is then possible to understand that the approximations realized, and the predictions made from them, should be compared in a systematic way to the experiments, source, and criterion of any model: the agreement model-forecasting experiment leads us to ascertain the validity of the model and presents the possibility of its safe use in a chosen experimental domain.