

# 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

### 3 The moving electron: electrical properties 205

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