

Contents

1	The Electronic Structure Determination	1
1.1	Variation Method (Molecular Orbital Linear Combination of Atomic Orbitals, MO-LCAO)	2
1.2	A Matrix Formulation of MO Calculations	3
1.3	The Hückel Approximation	4
1.3.1	The Case of the Allyl Anion (MO-LCAO by π Orbitals)	4
1.4	The Extended Hückel Procedure	6
1.5	Group Theory	10
1.5.1	Rules for the Elements Which Constitute a Group	12
1.5.2	Group Multiplication Tables	12
1.5.3	Representation of Symmetry Operations by Matrices	13
1.6	Irreducible Representations	16
1.6.1	Character Table of groups	17
1.6.2	Factoring the Total Representations into Irreducible Representation	18
1.6.3	Relation Between Molecular Wave Functions and Irreducible Representations	20
1.6.4	Obtaining Molecular Orbitals with a Given Symmetry	21
2	Symmetry Orbitals for Different Bis and Polyatomic Molecules	25
2.1	Homonuclear Diatomic Molecules A-A of the Periodic Table First Row	26
2.2	Water Molecule, as Example of Triatomic Molecule	29
2.3	Ammonia Molecule, as Example of Tetratomic Molecule	33
2.4	Methane Molecule, as Example of Pentatomic Molecule	36
2.5	Considerations About the Models of Chemical Bond in Use Before the Adoption of the Symmetry Molecular Orbital Model	36

3	Perturbation Theory	39
3.1	Interelectronic Repulsion Perturbation	40
3.2	Spin–Orbit Coupling Perturbation	43
3.3	Crystal Field Perturbation	45
3.3.1	Use of the Group Theory to Predict the Orbital Spitting in a Given Symmetry	47
3.4	Examples of Attribution of the Absorption Bands	55
3.5	Crystal Field Limits	58
3.6	Effect of Distortion from Cubic Symmetry	59
4	Magnetism	63
4.1	Interaction Between Electrons and Magnetic Field	65
4.2	Magnetic Susceptibility Expression for $S = 1/2$	69
4.3	Electron Spin Resonance	73
4.3.1	Hyperfine Nuclear Interaction	75
4.3.2	Hyperfine Interaction by Quantum Mechanical Approach	76
4.3.3	The Electronic Interaction with the Magnetic Field in Oriented Systems	77
4.3.4	The Electronic Interaction with the Magnetic Field in Oriented Systems	77
4.3.5	The Origin of the g Anisotropic Behavior	79
4.3.6	g Expressions for a d^1 Electronic Configuration in Tetragonal Symmetry Field	80
4.3.7	g Tensor Dependence on the Energy Level Trend of the Paramagnetic Centers	81
5	The Symmetry Properties Describe the Electronic Structure of Inorganic and Coordination Compounds	85
5.1	The Case of $[\text{Fe}_3 \text{Pt}_3 (\text{CO})_{15}]^{n-}$ $n = 2, 1$, and of $[\text{Fe}_3 \text{Pt}_3 (\text{CO})_{15}]^{2-n}$	85
5.2	Discussion of the Case	86
5.2.1	X-Ray Diffraction Studies	86
5.2.2	Diffuse Reflectance Spectra	87
5.2.3	Electron Spin Resonance (ESR) Spectra	87
5.3	Chemical Message	88
5.4	The Case of Adducts of NN'Ethylenebis (acetylacetoniminato) Cobalt (II)	89
5.5	Discussion of the Case	90
5.6	Chemical Message	92
5.7	The Case of Phthalocyaninato Co(II)	93
5.8	Discussion of the Case	94
5.8.1	Electron Spin Resonance (ESR) Spectra	94
5.8.2	Diffuse Reflectance Spectra	96

5.9	Chemical Message	96
5.10	The Case of Oxygen Reduction by CoPc Supported on Inorganic Oxide	96
5.11	Discussion of the Case	97
5.12	Chemical Message	97
5.13	The Case of Metal-Dispersed Inorganic Oxides	98
5.14	Discussion of the Case	98
5.14.1	Electron Spin Resonance of Decarbonylated Systems	98
5.14.2	Interaction with Oxygen	99
5.14.3	Interaction with Carbon Monoxide	100
5.14.4	Interaction with Carbon Monoxide and Oxygen	101
5.15	Chemical Message	101
5.16	The Case of Phosphate Glasses Containing Ruthenium and Titanium Ions	103
5.17	Discussion of the Case	103
5.18	Chemical Message	103
5.19	The Case of Superoxide Dismutase Enzyme, Interacting with Antitumor Drugs	105
5.20	Discussion of the Case	105
5.21	Chemical Message	106
5.22	The Case of Generation of Free Radicals in Intact Tissues	107
5.23	Discussion of the Case	108
5.24	Chemical Message	109
5.25	The Case of Functional Defects in Semiconductor Oxides: ZnO	109
5.26	Discussion of the Case	109
5.27	Chemical Message	111
5.28	The Case of Functional Defects in Semiconductor Oxides: SnO ₂	111
5.29	Discussion of the Case	111
5.29.1	Air Interaction with SnO ₂	111
5.29.2	Argon Interaction with SnO ₂	112
5.29.3	H ₂ and CO Interaction with SnO ₂ , in the Presence of Air	112
5.30	Chemical Message	114
5.31	The Case: Enhancing of the Oxide Sensing Properties by Transition Metal Ions	114
5.32	Discussion of the Case	115
5.33	Chemical Message	117
5.34	The Case of the Inhibitory Effect of Cu(II) Toward Protein Kinase C	117

5.35	Discussion of the Case	118
5.36	Chemical Message	119
5.37	The Case of the Catalytic Oxidation of Propenoidic Phenols	119
5.38	Discussion of the Case	120
5.39	The Case of Sn-Doped Solgel Silica Glasses	121
5.40	Discussion of the Case	121
5.41	Chemical Message	123
5.42	The Cases of Photocatalytic TiO ₂	123
5.43	Discussion of the Case	124
5.44	Chemical Message	126
5.45	The Case of Shape-Controlled TiO ₂ Nanoparticles	126
5.46	Discussion of the Case	126
5.47	Chemical Message	131
5.48	The Case of Charge Separation in TiO ₂ Embedded in Membrane	131
5.49	Discussion of the Case	132
5.50	Chemical Message	133
5.51	The Case of Shape-Controlled SnO ₂	134
5.52	Discussion of the Case	134
	5.52.1 Shape and Structure	134
	5.52.2 Identification of Defects	134
	5.52.3 Electrical Response	138
5.53	Chemical Message	139
5.54	The Case of Silica-Natural Rubber Composites	139
	5.54.1 Morphology of the Dispersed Filler	140
	5.54.2 Spin Probe Procedure	140
5.55	Chemical Message	142
5.56	The Case of Cis Diamino Dichloro Platinum (Cisplatin) Antitumor Drug [Pt(NH) ₃ Cl ₂]: Mechanism of Combinational Chemo-radiotherapy	144
5.57	Discussion of the Case	145
5.58	Chemical Message	148
5.59	The Case of Graphite Particles that Induce Reactive Oxygen Species in Cells	149
5.60	Discussion of the Case	150
5.61	Chemical Message	153
5.62	The Interaction of Graphite Defects with Oxygen Treated by Structural Studies	153
5.63	Discussion of the Case	155
	5.63.1 Electrochemistry	155
	5.63.2 Electron Spin Resonance Measurements	155

5.64	Chemical Message	156
5.65	The Case of Persistent Free Radicals in the Atmosphere	156
5.66	Discussion of the Case	157
5.67	Chemical Message	159
Appendix	163
References	183



Prof. Franca Morazzoni, Ph.D. in Chemistry at the University of Milano, became Associated Professor and then Full Professor of Inorganic Chemistry at the University of Milano-Bicocca. She founded the group of hybrid nanomaterials at the Department of Material Science in 2001. As an expert of physical methods in inorganic chemistry applied to hybrid materials, she published more than 250 papers in international journals. She was responsible of several national research projects in the field, participated to the development of inorganic nanofillers with controlled shapes, to be included in films or colloids, in collaboration with Pierluigi Turchetti. Several patents were signed on this topic. She was Vice Chair of the MINT COST action 2013-2015 on the organic-inorganic hybrid materials. Professor Morazzoni has supervised several Ph.D. students and until 2015 was director of the Ph.D. School of the University of Milano-Bicocca. She enjoys piano giving regularly performances.