

Contents

Introduction (2)	xxi
Chapter 1: Electronic Orbital Interactions in Periodic Systems	1
1.1 Primitive lattice.....	5
1.2 Wave vector	8
1.3 Inverse lattice.....	11
1.4 First Brillouin zone (FBZ).....	14
1.5 Properties of the FBZ	15
1.6 A few words on Bloch functions	15
1.6.1 Waves in 1D.....	15
1.6.2 Waves in 2D.....	18
1.7 Infinite crystal as a limit of a cyclic system.....	21
1.7.1 Origin of the band structure	21
1.7.2 Born–von Kármán condition in 1D	23
1.7.3 k dependence of orbital energy.....	25
1.8 A triple role of the wave vector.....	26
1.9 Band structure	26
1.9.1 Born–von Kármán boundary condition in 3D	26
1.9.2 Crystal orbitals from Bloch functions (LCAO CO method)	28
1.9.3 SCF LCAO CO equations	31
1.9.4 Band width	32
1.9.5 Fermi level and energy gap: insulators, metals, and semiconductors ..	33
1.10 Solid state quantum chemistry.....	39
1.10.1 Why do some bands go up?	40
1.10.2 Why do some bands go down?	41
1.10.3 Why do some bands stay constant?	41
1.10.4 More complex behavior explainable – examples	41
1.11 The Hartree–Fock method for crystals	50
1.11.1 Secular equation	50
1.11.2 Integration in the FBZ	52
1.11.3 Fock matrix elements	53
1.11.4 Iterative procedure (SCF LCAO CO)	55
1.11.5 Total energy	55

1.12	Long-range interaction problem	56
1.12.1	Fock matrix corrections	57
1.12.2	Total energy corrections	59
1.12.3	Multipole expansion applied to the Fock matrix	61
1.12.4	Multipole expansion applied to the total energy	65
1.13	Back to the exchange term	68
1.14	Choice of unit cell	70
1.14.1	Field compensation method	73
1.14.2	The symmetry of subsystem choice	75
Chapter 2: Correlation and Anticorrelation of Electronic Motions		81
VARIATIONAL METHODS USING EXPLICITLY CORRELATED WAVE FUNCTIONS		
2.1	Correlation cusp condition	89
2.2	The Hylleraas CI method	93
2.3	Two-electron systems	94
2.3.1	Harmonium – the harmonic helium atom	94
2.3.2	High accuracy: the James–Coolidge and Kołos–Wolniewicz functions	96
2.3.3	High accuracy: neutrino mass	99
2.4	Exponentially correlated Gaussian functions	101
2.5	Electron holes	102
2.5.1	Coulomb hole (“correlation hole”)	102
2.5.2	Exchange hole (“Fermi hole”)	105
VARIATIONAL METHODS WITH SLATER DETERMINANTS		
2.6	Static electron correlation	112
2.7	Dynamic electron correlation	112
2.8	Anticorrelation, or do electrons stick together in some states?	118
2.9	Valence bond (VB) method	126
2.9.1	Resonance theory – hydrogen molecule	126
2.9.2	Resonance theory – polyatomic case	129
2.10	Configuration interaction (CI) method	134
2.10.1	Brillouin theorem	136
2.10.2	Convergence of the CI expansion	137
2.10.3	Example of H ₂ O	137
2.10.4	Which excitations are most important?	140
2.10.5	Natural orbitals (NOs) – a way to shorter expansions	140
2.10.6	Size inconsistency of the CI expansion	142
2.11	Direct CI method	142
2.12	Multireference CI method	143
2.13	Multiconfigurational self-consistent field (MC SCF) method	144

2.13.1	Classical MC SCF approach	145
2.13.2	Unitary MC SCF method	146
2.13.3	Complete active space (CAS SCF) method is size-consistent	148
NONVARIATIONAL METHODS WITH SLATER DETERMINANTS		
2.14	Coupled cluster (CC) method	149
2.14.1	Wave and cluster operators	151
2.14.2	Relationship between CI and CC methods	152
2.14.3	Solution of the CC equations	153
2.14.4	Example: CC with double excitations	156
2.14.5	Size consistency of the CC method	158
2.15	Equation of motion method (EOM-CC)	159
2.15.1	Similarity transformation	159
2.15.2	Derivation of the EOM-CC equations	159
2.16	Many-body perturbation theory (MBPT)	162
2.16.1	Unperturbed Hamiltonian	162
2.16.2	Perturbation theory – slightly different presentation	163
2.16.3	MBPT machinery – part one: energy equation	164
2.16.4	Reduced resolvent or the “almost” inverse of $(E_0^{(0)} - \hat{H}^{(0)})$	165
2.16.5	MBPT machinery – part two: wave function equation	166
2.16.6	Brillouin–Wigner perturbation theory	168
2.16.7	Rayleigh–Schrödinger perturbation theory	168
2.17	Møller–Plesset version of Rayleigh–Schrödinger perturbation theory	169
2.17.1	Expression for MP2 energy	170
2.17.2	Is the MP2 method size-consistent?	171
2.17.3	Convergence of the Møller–Plesset perturbation series	173
2.17.4	Special status of double excitations	174
NONVARIATIONAL METHODS USING EXPLICITLY CORRELATED WAVE FUNCTIONS		
2.18	Møller–Plesset R12 method (MP2-R12)	176
2.18.1	Resolution of identity (RI) method or density fitting (DF)	177
2.18.2	Other RI methods	178
Chapter 3: Chasing the Correlation Dragon: Density Functional Theory (DFT) ...		191
3.1	Electronic density – the superstar	194
3.2	Electron density distributions – Bader analysis	196
3.2.1	Overall shape of ρ	196
3.2.2	Critical points	197
3.2.3	Laplacian of the electronic density as a “magnifying glass”	202
3.3	Two important Hohenberg–Kohn theorems	204

3.3.1	Correlation dragon resides in electron density: equivalence of Ψ_0 and ρ_0	204
3.3.2	A secret of the correlation dragon: the existence of energy functional minimized by ρ_0	207
3.4	The Kohn–Sham equations	211
3.4.1	A Kohn–Sham system of noninteracting electrons	211
3.4.2	Chasing the correlation dragon into an unknown part of the total energy	212
3.4.3	Derivation of the Kohn–Sham equations	213
3.5	Trying to guess the appearance of the correlation dragon	218
3.5.1	Local density approximation (LDA)	218
3.5.2	Nonlocal density approximation (NLDA)	219
3.5.3	The approximate character of the DFT versus apparent rigor of <i>ab initio</i> computations	220
3.6	On the physical justification for the exchange–correlation energy	221
3.6.1	The electron pair distribution function	221
3.6.2	Adiabatic connection: from what is known towards the target	222
3.6.3	Exchange–correlation energy and the electron pair distribution function	226
3.6.4	The correlation dragon hides in the exchange–correlation hole	227
3.6.5	Electron holes in spin resolution	227
3.6.6	The dragon’s ultimate hide-out: the correlation hole!	229
3.6.7	Physical grounds for the DFT functionals	232
3.7	Visualization of electron pairs: electron localization function (ELF)	233
3.8	The DFT excited states	238
3.9	The hunted correlation dragon before our eyes	239
Chapter 4: The Molecule Subject to Electric or Magnetic Fields		253
4.1	Hellmann–Feynman theorem	256
ELECTRIC PHENOMENA		
4.2	The molecule immobilized in an electric field	260
4.2.1	The electric field as a perturbation	261
4.2.2	The homogeneous electric field	266
4.2.3	The nonhomogeneous electric field: multipole polarizabilities and hyperpolarizabilities	275
4.3	How to calculate the dipole moment	277
4.3.1	Coordinate system dependence	278
4.3.2	Hartree–Fock approximation	278
4.3.3	Atomic and bond dipoles	279
4.3.4	Within the zero-differential overlap approximation	280
4.4	How to calculate the dipole polarizability	280
4.4.1	Sum over states (SOS) method	281

4.4.2	Finite field method	284
4.4.3	What is going on at higher electric fields	289
4.5	A molecule in an oscillating electric field	290

MAGNETIC PHENOMENA

4.6	Magnetic dipole moments of elementary particles	294
4.6.1	Electron	294
4.6.2	Nucleus	295
4.6.3	Dipole moment in the field	296
4.7	NMR spectra – transitions between the nuclear quantum states	299
4.8	Hamiltonian of the system in the electromagnetic field	301
4.8.1	Choice of the vector and scalar potentials	301
4.8.2	Refinement of the Hamiltonian	302
4.9	Effective NMR Hamiltonian	306
4.9.1	Signal averaging	307
4.9.2	Empirical Hamiltonian	307
4.9.3	Nuclear spin energy levels.....	312
4.10	The Ramsey theory of the NMR chemical shift	319
4.10.1	Shielding constants	320
4.10.2	Diamagnetic and paramagnetic contributions	321
4.11	The Ramsey theory of NMR spin–spin coupling constants	322
4.11.1	Diamagnetic contribution.....	322
4.11.2	Paramagnetic contribution.....	323
4.11.3	Coupling constants.....	324
4.11.4	The Fermi contact coupling mechanism	325
4.12	Gauge-invariant atomic orbitals (GIAOs).....	326
4.12.1	London orbitals	327
4.12.2	Integrals are invariant.....	328

Chapter 5: Intermolecular Interactions..... 337

THEORY OF INTERMOLECULAR INTERACTIONS

5.1	Idea of the rigid interaction energy	341
5.2	Idea of the internal relaxation	342
5.3	Interacting subsystems	343
5.3.1	Natural division	343
5.3.2	What is most natural?.....	344
5.4	Binding energy	346
5.5	Dissociation energy	346
5.6	Dissociation barrier	347
5.7	Supermolecular approach.....	347
5.7.1	Accuracy should be the same	347

5.7.2	Basis set superposition error (BSSE)	349
5.7.3	Good and bad news about the supermolecular method	350
5.8	Perturbational approach	351
5.8.1	Intermolecular distance – what does it mean?	351
5.8.2	Polarization approximation (two molecules)	352
5.8.3	Intermolecular interactions: physical interpretation	357
5.8.4	Electrostatic energy in the multipole representation plus the penetration energy	361
5.8.5	Induction energy in the multipole representation	368
5.8.6	Dispersion energy in the multipole representation	369
5.8.7	Resonance interaction – excimers	376
5.9	Symmetry-adapted perturbation theory (SAPT)	377
5.9.1	Polarization approximation is illegal	377
5.9.2	Constructing a symmetry-adapted function	378
5.9.3	The perturbation is always large in polarization approximation	379
5.9.4	Iterative scheme of SAPT	381
5.9.5	Symmetry forcing	385
5.9.6	A link to the variational method – the Heitler–London interaction energy	388
5.9.7	Summary: the main contributions to the interaction energy	389
5.10	Convergence problems	392
5.10.1	Padé approximants may improve convergence	393
5.11	Nonadditivity of intermolecular interactions	398
5.11.1	Interaction energy represents the nonadditivity of the total energy	398
5.11.2	Many-body expansion of the rigid interaction energy	398
5.11.3	What is additive, what is not?	401
5.11.4	Additivity of the electrostatic interaction	401
5.11.5	Exchange nonadditivity	402
5.11.6	Induction nonadditivity	406
5.11.7	Additivity of the second-order dispersion energy	409
5.11.8	Nonadditivity of the third-order dispersion interaction	410
ENGINEERING OF INTERMOLECULAR INTERACTIONS		
5.12	Idea of molecular surface	411
5.12.1	van der Waals atomic radii	411
5.12.2	A concept of molecular surface	411
5.12.3	Confining molecular space – the nanovessels	412
5.12.4	Molecular surface under high pressure	413
5.13	Decisive forces	414
5.13.1	Distinguished role of the valence repulsion and electrostatic interaction	414
5.13.2	Hydrogen bond	415
5.13.3	Coordination interaction	417

5.13.4	Electrostatic character of molecular surface – the maps of the molecular potential	418
5.13.5	Hydrophobic effect	420
5.14	Construction principles	424
5.14.1	Molecular recognition – synthons.....	424
5.14.2	“Key-lock,” template-like, and “hand-glove” synthon interactions	424
5.14.3	Convex and concave – the basics of strategy in the nanoscale.....	427
Chapter 6:	Chemical Reactions	437
6.1	Hypersurface of the potential energy for nuclear motion	442
6.1.1	Potential energy minima and saddle points	443
6.1.2	Distinguished reaction coordinate (DRC)	446
6.1.3	Steepest descent path (SDP).....	446
6.1.4	Higher-order saddles.....	447
6.1.5	Our goal	447
6.2	Chemical reaction dynamics (a pioneers’ approach)	448
	<i>AB INITIO APPROACH</i>	
6.3	Accurate solutions (three atoms)	453
6.3.1	Coordinate system and Hamiltonian	453
6.3.2	Solution to the Schrödinger equation	456
6.3.3	Berry phase.....	458
	<i>APPROXIMATE METHODS</i>	
6.4	Intrinsic reaction coordinate (IRC)	460
6.5	Reaction path Hamiltonian method	463
6.5.1	Energy close to IRC	463
6.5.2	Vibrational adiabatic approximation	465
6.5.3	Vibrational nonadiabatic model	471
6.5.4	Application of the reaction path Hamiltonian method to the reaction $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$	473
6.6	Acceptor–donor (AD) theory of chemical reactions.....	479
6.6.1	A simple model of nucleophilic substitution – MO, AD, and VB formalisms	479
6.6.2	MO picture \rightarrow AD picture	480
6.6.3	Reaction stages.....	484
6.6.4	Contributions of the structures as the reaction proceeds	489
6.6.5	Nucleophilic attack – the model is more general: $\text{H}^- + \text{ethylene} \rightarrow \text{ethylene} + \text{H}^-$	492
6.6.6	The model looks even more general: the electrophilic attack $\text{H}^+ + \text{H}_2 \rightarrow \text{H}_2 + \text{H}^+$	495
6.6.7	The model works also for the nucleophilic attack on the polarized bond	496

6.7	Symmetry-allowed and symmetry-forbidden reactions	501
6.7.1	Woodward–Hoffmann symmetry rules	501
6.7.2	AD formalism	501
6.7.3	Electrocyclic reactions	502
6.7.4	Cycloaddition reaction	504
6.7.5	Barrier means a cost of opening the closed shells	508
6.8	Barrier for the electron transfer reaction	509
6.8.1	Diabatic and adiabatic potential	509
6.8.2	Marcus theory	511
6.8.3	Solvent-controlled electron transfer	516
Chapter 7: Information Processing – The Mission of Chemistry		533
7.1	Multilevel supramolecular structures (statics)	537
7.1.1	Complex systems	537
7.1.2	Self-organizing complex systems	537
7.1.3	Cooperative interactions	540
7.1.4	Combinatorial chemistry – molecular libraries	541
7.2	Chemical feedback – a steering element (dynamics)	543
7.2.1	A link to mathematics – attractors	543
7.2.2	Bifurcations and chaos	545
7.2.3	Brusselator without diffusion	547
7.2.4	Brusselator with diffusion – dissipative structures	553
7.2.5	Hypercycles	555
7.2.6	From self-organization and complexity to information	555
7.3	Information and informed matter	556
7.3.1	Abstract theory of information	557
7.3.2	Teaching molecules	559
7.3.3	Dynamic information processing of chemical waves	561
7.3.4	Molecules as computer processors	568
7.3.5	The mission of chemistry	573
Appendix A: Dirac Notation for Integrals		581
Appendix B: Hartree–Fock (or Molecular Orbitals) Method		583
Appendix C: Second Quantization		587
Appendix D: Population Analysis		595
Appendix E: Pauli Deformation		601
Appendix F: Hydrogen Atom in Electric Field – Variational Approach		609

<i>Appendix G: Multipole Expansion</i>	613
<i>Appendix H: NMR Shielding and Coupling Constants – Derivation</i>	627
<i>Appendix I: Acceptor–Donor Structure Contributions in the MO Configuration</i> ...	635
<i>Acronyms and Their Explanation</i>	639
<i>Author Index</i>	647
<i>Subject Index</i>	653
<i>Sources of Photographs and Figures</i>	657
<i>Tables</i>	659