

# Contents

<b>Introduction</b> .....	<b>xix</b>
<b>Chapter 1: The Magic of Quantum Mechanics</b> .....	<b>1</b>
1.1 History of a revolution .....	5
1.2 Postulates of quantum mechanics .....	18
1.3 The Heisenberg uncertainty principle .....	41
1.4 The Copenhagen interpretation of the world.....	46
1.5 How to disprove the Heisenberg principle? The Einstein–Podolsky–Rosen’s recipe .....	47
1.6 The life and death of Schrödinger’s cat .....	49
1.7 Bilocation.....	50
1.8 The magic of erasing the past .....	53
1.9 A test for common sense: the Bell inequality.....	54
1.10 Photons violate the Bell inequality .....	57
1.11 Teleportation .....	59
1.12 Quantum computing .....	62
<b>Chapter 2: The Schrödinger Equation</b> .....	<b>69</b>
2.1 Symmetry of the nonrelativistic Hamiltonian and the conservation laws ...	72
2.1.1 Invariance with respect to translation .....	77
2.1.2 Invariance with respect to rotation .....	79
2.1.3 Invariance with respect to permutation of identical particles (fermions and bosons) .....	80
2.1.4 Invariance of the total charge.....	80
2.1.5 Fundamental and less fundamental invariances .....	81
2.1.6 Invariance with respect to inversion – parity .....	81
2.1.7 Invariance with respect to charge conjugation.....	85
2.1.8 Invariance with respect to the symmetry of the nuclear framework ....	86
2.1.9 Conservation of total spin .....	86
2.1.10 Indices of spectroscopic states .....	87
2.2 Schrödinger equation for stationary states .....	87
2.2.1 Wave functions of class Q .....	90
2.2.2 Boundary conditions.....	93

2.3	The time-dependent Schrödinger equation .....	96
2.3.1	Evolution in time.....	96
2.3.2	Time dependence of mechanical quantities.....	97
2.3.3	Mean energy is conserved .....	99
2.3.4	Symmetry is conserved .....	99
2.3.5	Energy-time uncertainty principle .....	100
2.3.6	Meditations at water spring.....	103
2.3.7	Linearity.....	104
2.4	Evolution after switching a perturbation .....	104
2.4.1	Time-independent perturbation – the two-state model .....	106
2.4.2	Oscillating perturbation – the two-state model .....	108
2.4.3	Short-time perturbation – the first-order approach .....	110
2.4.4	Time-independent perturbation and the Fermi Golden Rule.....	112
2.4.5	Oscillating perturbation and the Fermi Golden Rule.....	114
<b>Chapter 3: Beyond the Schrödinger Equation .....</b>		<b>123</b>
3.1	A glimpse of classical relativity theory .....	127
3.1.1	The vanishing of apparent forces .....	127
3.1.2	The Galilean transformation .....	130
3.1.3	The Michelson–Morley experiment.....	131
3.1.4	The Galilean transformation crashes.....	133
3.1.5	The Lorentz transformation .....	134
3.1.6	New law of adding velocities.....	137
3.1.7	The Minkowski space–time continuum.....	138
3.1.8	How do we get $E = mc^2$ ? .....	142
3.2	Towards relativistic quantum mechanics .....	144
3.3	The Dirac equation .....	147
3.3.1	The electronic sea and the day of glory.....	147
3.3.2	The Dirac equations for electron and positron .....	151
3.3.3	Spinors and bispinors .....	151
3.3.4	What next? .....	153
3.3.5	Large and small components of the bispinor .....	153
3.3.6	How to avoid drowning in the Dirac sea.....	154
3.3.7	From Dirac to Schrödinger – how to derive the nonrelativistic Hamiltonian?.....	156
3.3.8	How does the spin appear? .....	157
3.3.9	Simple questions .....	159
3.4	The hydrogen-like atom in Dirac theory .....	159
3.4.1	Step by step: calculation of the hydrogen-like atom ground state within Dirac theory .....	160
3.5	Larger systems .....	166

3.6	Beyond the Dirac equation...	170
3.6.1	The Breit equation .....	171
3.6.2	A few words about quantum electrodynamics.....	173
<b>Chapter 4: Exact Solutions – Our Beacons .....</b>		<b>185</b>
4.1	Free particle .....	188
4.2	Box with ends (and the music) .....	189
4.3	Cyclic box .....	193
4.3.1	Comparison of two boxes: hexatriene and benzene .....	196
4.4	Carbon nanotube .....	200
4.5	Single barrier .....	203
4.5.1	Tunneling effect below the barrier height.....	203
4.5.2	Surprises for energies larger than the barrier .....	207
4.6	The magic of two barriers .....	210
4.6.1	Magic energetic gates (resonance states) .....	211
4.6.2	Strange flight over two barriers .....	215
4.7	Harmonic oscillator .....	217
4.8	Morse oscillator .....	224
4.9	Rigid rotator .....	229
4.10	Hydrogen-like atom .....	232
4.10.1	Positronium and its short life in molecules .....	242
4.11	What do all these solutions have in common? .....	242
4.12	Hooke helium atom (harmonium) .....	243
4.13	Hooke molecules .....	244
4.14	Charming SUSY and new solutions.....	249
4.14.1	SUSY partners .....	250
4.14.2	Relation between the SUSY partners .....	251
4.15	Beacons and pearls of physics .....	255
<b>Chapter 5: Three Fundamental Approximate Methods .....</b>		<b>263</b>
5.1	Variational method .....	265
5.1.1	Variational principle .....	265
5.1.2	Variational parameters lead to the variational method .....	269
5.1.3	Linear variational parameters or the Ritz method .....	271
5.2	Method of moments .....	273
5.3	Perturbational method .....	274
5.3.1	Rayleigh–Schrödinger approach .....	274
5.3.2	Hylleraas variational principle .....	280
5.3.3	Hylleraas equation .....	281
5.3.4	Degeneracy .....	282
5.3.5	Convergence of the perturbational series .....	284

5.4	Virial theorem as a probe of wave function quality .....	287
5.4.1	Classical mechanics – the virial .....	287
5.4.2	Looking at stars – the discovery of dark matter .....	288
5.4.3	Quantum mechanics .....	288
5.4.4	A review of examples .....	290
5.4.5	What about the mean values calculated with an approximate solution? .....	292
5.4.6	Quantum chemistry: how useful is the virial theorem? .....	297
<b>Chapter 6: A Key Concept of Molecular 3D Structure – Separation of Electronic and Nuclear Motions .....</b>		<b>305</b>
6.1	Separation of the center-of-mass motion .....	311
6.2	Exact (nonadiabatic) theory .....	315
6.3	Adiabatic approximation .....	318
6.4	Born–Oppenheimer approximation .....	320
6.5	Vibrations of a rotating molecule .....	321
6.5.1	One more analogy .....	323
6.5.2	What vibrates, what rotates? .....	324
6.5.3	The key message: the potential energy surface (PES) and molecular shape .....	326
6.6	Basic principles of electronic, vibrational and rotational spectroscopy .....	332
6.6.1	Electronic and vibrational structure .....	332
6.6.2	Rotational structure .....	332
6.7	Approximate separation of rotations and vibrations .....	335
6.8	Understanding the IR spectrum of a diatomic: HCl .....	336
6.8.1	Selection rules are consequences of conservation laws .....	337
6.8.2	Microwave spectrum gives the internuclear distance .....	339
6.8.3	IR spectrum and isotopic effect .....	339
6.8.4	Internuclear distance .....	341
6.8.5	Why we have a spectrum “envelope” .....	341
6.8.6	Intensity of isotopomers’ peaks .....	342
6.9	A quasiharmonic approximation .....	342
6.10	Polyatomic molecules .....	344
6.10.1	Kinetic energy expression .....	344
6.10.2	Quasirigid model – simplifying by Eckart conditions .....	346
6.10.3	Approximation: decoupling of rotations and vibrations .....	348
6.10.4	Spherical, symmetric, and asymmetric tops .....	348
6.10.5	Separation of translational, rotational, and vibrational motions .....	350
6.11	Types of states .....	351
6.11.1	Repulsive potential .....	351
6.11.2	“Hook-like” curves .....	351
6.11.3	Continuum .....	353

6.11.4	Wave function “measurement” .....	355
6.12	Adiabatic, diabatic, and nonadiabatic approaches .....	358
6.13	Crossing of potential energy curves for diatomics .....	361
6.13.1	The noncrossing rule .....	361
6.13.2	Simulating the harpooning effect in the NaCl molecule .....	363
6.14	Polyatomic molecules and the conical intersection .....	367
6.14.1	Branching space and seam space .....	369
6.14.2	Conical intersection .....	369
6.14.3	Berry phase .....	371
6.14.4	The role of the conical intersection – nonradiative transitions and photochemical reactions .....	373
6.14.5	What is the number of conical intersections? .....	375
6.15	A travel beyond the adiabatic approximation .....	377
6.15.1	Vibronic coupling .....	377
6.15.2	Consequences for the quest of superconductors .....	381
6.15.3	Photostability of proteins and DNA .....	383
6.15.4	Muon-catalyzed nuclear fusion .....	386
6.15.5	“Russian dolls” – or a molecule within molecule .....	388
<b>Chapter 7: Motion of Nuclei .....</b>		<b>397</b>
7.1	Rovibrational spectra – an example of accurate calculations: atom–diatomic molecule .....	401
7.1.1	Coordinate system and Hamiltonian .....	401
7.1.2	Anisotropy of the potential $V$ .....	403
7.1.3	Adding the angular momenta in quantum physics .....	404
7.1.4	Application of the Ritz method .....	405
7.2	Force fields (FFs) .....	406
7.3	Local molecular mechanics .....	411
7.3.1	Bonds that cannot break .....	411
7.3.2	Bonds that can break .....	413
7.4	Global molecular mechanics .....	413
7.4.1	Multiple minima catastrophe .....	413
7.4.2	Is it the global minimum which counts? .....	414
7.5	Small amplitude harmonic motion – normal modes .....	416
7.5.1	Theory of normal modes .....	417
7.5.2	Zero-vibration energy .....	426
7.6	Molecular dynamics .....	427
7.6.1	What does molecular dynamics offer us? .....	429
7.6.2	What to worry about? .....	431
7.6.3	Molecular dynamics of nonequilibrium processes .....	431
7.6.4	Quantum classical molecular dynamics .....	433

7.7	Simulated annealing .....	434
7.8	Langevin dynamics .....	435
7.9	Monte Carlo dynamics .....	435
7.10	Car–Parrinello dynamics .....	443
7.11	Cellular automata .....	446
<b>Chapter 8: Orbital Model of Electronic Motion in Atoms and Molecules .....</b>		<b>457</b>
8.1	Hartree–Fock method – a bird’s eye view .....	463
8.1.1	Spin orbitals as the one-electron building blocks .....	464
8.1.2	Variables .....	465
8.1.3	Slater determinant .....	465
8.1.4	What is the Hartree–Fock method all about? .....	468
8.2	Towards the optimal spin orbitals and the Fock equation .....	469
8.2.1	Dirac notation for integrals .....	469
8.2.2	Energy functional to be minimized .....	470
8.2.3	Energy minimization with constraints .....	471
8.2.4	Slater determinant subject to a unitary transformation .....	475
8.2.5	The $\hat{J}$ and $\hat{K}$ operators are invariant .....	476
8.2.6	Diagonalization of the Lagrange multipliers .....	477
8.2.7	Optimal spin orbitals are solutions of the Fock equation (general Hartree–Fock [GHF] method) .....	478
8.2.8	“Unrestricted” Hartree–Fock (UHF) method .....	479
8.2.9	The closed shell systems and the restricted Hartree–Fock (RHF) method .....	479
8.2.10	Iterative solution: the Self-Consistent Field (SCF) method .....	488
8.3	Total energy in the Hartree–Fock method .....	490
8.4	Computational technique: atomic orbitals as building blocks of the molecular wave function .....	492
8.4.1	Centering of the atomic orbital .....	494
8.4.2	Slater-type orbitals (STOs) .....	494
8.4.3	Gaussian-type orbitals (GTOs) .....	495
8.4.4	Linear combination of atomic orbitals (LCAO) method .....	499
8.4.5	Basis sets of atomic orbitals .....	504
8.4.6	The Hartree–Fock–Roothaan method (SCF LCAO MO) .....	504
8.4.7	Some practical problems .....	507
8.5	Back to foundations .....	510
8.5.1	When does the RHF method fail? .....	510
8.5.2	Fukutome classes .....	514

## RESULTS OF THE HARTREE-FOCK METHOD

8.6	Mendeleev periodic table .....	521
8.6.1	All atoms are similar to the hydrogen atom – the orbital model of an atom .....	521
8.6.2	Shells and subshells .....	522
8.6.3	Educated guess of atomic orbitals – the Slater rules .....	528
8.6.4	Atomic radii .....	529
8.7	The nature of the chemical bond – quantum makes a difference .....	531
8.7.1	The simplest chemical bond: $H_2^+$ in the MO picture .....	531
8.7.2	Can we see a chemical bond? .....	536
8.8	Excitation energy, ionization potential, and electron affinity (RHF approach) .....	537
8.8.1	Approximate energies of electronic states .....	537
8.8.2	Singlet or triplet excitation? .....	539
8.8.3	Hund's rules .....	540
8.8.4	Hund's rules for the atomic terms .....	541
8.8.5	Ionization potential and electron affinity (Koopmans' theorem) .....	544
8.9	Towards a chemical picture – localization of molecular orbitals .....	547
8.9.1	Can a chemical bond be defined in a polyatomic molecule? .....	548
8.9.2	The external localization methods .....	549
8.9.3	The internal localization methods .....	550
8.9.4	Examples of localization .....	552
8.9.5	Localization in practice – computational technique .....	554
8.9.6	The chemical bonds of $\sigma$ , $\pi$ , $\delta$ symmetry .....	555
8.9.7	Electron pair dimensions and the foundations of chemistry .....	558
8.9.8	Hybridization or mixing one-center AOs .....	561
8.10	A minimal model of a molecule .....	571
8.11	The isolobal analogy .....	578
<b>Appendix A: Reminding Matrices and Determinants .....</b>		<b>589</b>
<b>Appendix B: A Few Words on Spaces, Vectors, and Functions .....</b>		<b>595</b>
<b>Appendix C: Group Theory in Spectroscopy .....</b>		<b>605</b>
<b>Appendix D: A Two-State Model .....</b>		<b>655</b>
<b>Appendix E: Dirac Delta Function .....</b>		<b>659</b>
<b>Appendix F: Translation Versus Momentum and Rotation Versus Angular Momentum .....</b>		<b>665</b>

<i>Appendix G: Vector and Scalar Potentials</i> .....	673
<i>Appendix H: Optimal Wave Function for the Hydrogen-Like Atom</i> .....	683
<i>Appendix I: The Virial Theorem</i> .....	685
<i>Appendix J: Space- and Body-Fixed Coordinate Systems</i> .....	691
<i>Appendix K: Orthogonalization</i> .....	697
<i>Appendix L: Diagonalization of a Matrix</i> .....	703
<i>Appendix M: Secular Equation <math>(H - \epsilon S) c = 0</math></i> .....	705
<i>Appendix N: Slater–Condon Rules</i> .....	707
<i>Appendix O: Lagrange Multipliers Method</i> .....	719
<i>Appendix P: Penalty Function Method</i> .....	725
<i>Appendix Q: Molecular Integrals with Gaussian-Type Orbitals 1s</i> .....	729
<i>Appendix R: Singlet and Triplet States for Two Electrons</i> .....	731
<i>Appendix S: The Hydrogen Molecular Ion in the Simplest Atomic Basis Set</i> .....	735
<i>Appendix T: Dipole Moment of a Lone Pair</i> .....	741
<i>Acronyms and Their Explanation</i> .....	745
<i>Author Index</i> .....	753
<i>Subject Index</i> .....	759
<i>Tables</i> .....	763