## CONTENTS

	Preface	vvi
	Treface	~~!
	How to use the workbooks, exercises, and problems	xxvii
	Degenerate elgenvalues mitsubortal	
Chapter 1	Why quantum mechanics?	1
	Molecular vibrations	1
	Radiation by a hot body	2
	The stability of atoms	3
e M	and the standard of the signalian characterian and the	
Chapter 2	Dynamic variables and operators	5
	Operators: the definition	5
	Examples of operators	6
	Operations with operators	7
	Operator addition	7
	Operator multiplication	8
	Powers of operators	9
	The commutator of two operators	9
	Linear operators	11
	distribution of the second sec	

Some properties of eigenVallaks whith the properties of

Position and palential energy operators ex-

STE

v

	Dynamical variables as operators	11
	Position and potential energy operators	12
	Potential energy operator	13
	The momentum operator	14
	The kinetic energy operator	14
	The total energy (the Hamiltonian)	16
	Angular momentum	17
	Supplement 2.1 Review of complex numbers	21
	Complex functions of real variables	24
Chapter 3	The eigenvalue problem	25
	The eigenvalue problem: definition and examples	25
	The eigenvalue problem for $\hat{p}_r$	26
	$\hat{p}_x$ has an infinite number of eigenvalues	26
	The eigenvalue problem for angular momentum	27
	If two operators commute, they have the same	
	eigenfunctions	29
	Degenerate eigenvalues	30
	Which eigenfunctions have a meaning in physics?	32
	Not all eigenfunctions are physically meaningful	32
	Normalization	32
	A relaxed condition	33
	An example: the eigenfunctions of kinetic energy	34
	One-dimensional motion in the force-free,	
	unbounded space	34
	The eigenfunctions of the kinetic energy operator	35
	Which of these eigenfunctions can be normalized?	37
	Boundary conditions: the particle in a box	38
	Forcing the eigenfunctions to satisfy the boundary	
	conditions	38
	Quantization	40
	The particle cannot have zero kinetic energy	40
	Imposing the boundary conditions removes the trouble	?
	with normalization	42
	Some properties of eigenvalues and eigenfunctions	42

Chapter 4	What do we measure when we study quantum systems?	45
	Introduction	45
	The preparation of the initial state	46
	Not all quantum systems have "well-defined" energy	46
	Three examples of energy eigenstates	48
	A particle in a one-dimensional box	49
	The vibrational energy of a diatomic molecule	50
	The energy eigenstates of the hydrogen atom	51
	Energy measurements by electron scattering	52
	Electron scattering from a gas of diatomic molecules	53
	Energy measurements by photon emission	57
	Photon emission	57
	Applications	58
Chapter 5	Some results are certain, most are just probable	61
	Introduction	61
	What is the outcome of an electron-scattering experiment?	62
	Classical interpretation of the experiment	63
	The quantum description of the experiment	64
	Probabilities	65
	A discussion of photon absorption measurements	68
	Why the outcome of most absorption experiments is	
	certain	69
	A discussion of photon emission measurements	69
	A one-photon, one-molecule experiment	70
	The probabilities of different events	72
Chapter 6	The physical interpretation of the wave	145
	function	73
	Application to a vibrating diatomic molecule	75
	Data for HCl	76
	Interpretation	79

vii

	Average values	79
	The effect of position uncertainty on a diffraction	
	experiment	80
	The effect of position uncertainty in an ESDAID	
	experiment	81
	The total ann and the literal particular and	
Chapter 7	Tunneling	85
	Classically forbidden region	85
	How large is the accessible region?	85
	The classically allowed region for an oscillator	86
	Tunneling depends on mass and energy	89
	Tunneling junctions	90
	Scanning tunneling microscopy	91
Chapter 8	Particle in a box	95
	Define the system	95
	The classical Hamiltonian	96
	Ouantizing the sustem	97
	The boundary conditions	98
	Solving the eigenvalue problem (the Schrödinger equation)	
	for the particle in a box	100
	Separation of variables	100
	Boundary conditions	101
	The behavior of a particle in a box	104
	The ground state energy is not zero	105
	Degeneracy	107
	Degeneracy is related to the symmetry of the system	109
	The eigenfunctions are normalized	111
	Orthogonality	112
	The position of a particle in a given state	113
Chapter 0	Light omission and absorption:	
chapter 9	the phenomena	117
	Introduction	117

viii

Cł

Cł

C

	Average values	79
	The effect of position uncertainty on a diffraction	
	experiment	80
	The effect of position uncertainty in an ESDAID	
	experiment	81
	The total marga the Bardlonbalta water	
napter 7	Tunneling	85
	Classically forbidden region	85
	How large is the accessible region?	85
	The classically allowed region for an oscillator	86
	Tunneling depends on mass and energy	89
	Tunneling junctions	90
	Scanning tunneling microscopy	91
napter 8	Particle in a box	95
	Define the system	05
	The classical Hamiltonian	90
	Oughtizing the sustem	90
	The boundary conditions	08
	Solving the aigenvalue problem (the Schrödinger equation)	90
	for the particle in a box	100
	Separation of variables	100
	Poundary conditions	100
	The behavior of a particle in a box	101
	The ground state energy is not zero	104
	Degeneracy	105
	Degeneracy is related to the summetry of the system	107
	The eigenfunctions are normalized	111
	Orthogonality	119
	The position of a particle in a given state	112
	The position of a particle in a given state	110
napter 9	Light emission and absorption:	
	the phenomena	117
	Introduction	117

viii

	Average values	79
	The effect of position uncertainty on a diffraction	
	experiment	80
	The effect of position uncertainty in an ESDAID	
	experiment	81
Chapter 7	Tunneling	85
	Classically forbidden region	85
	How large is the accessible region?	85
	The classically allowed region for an oscillator	86
	Tunneling depends on mass and energy	89
	Tunneling junctions	90
	Scanning tunneling microscopy	91
Chapter 8	Particle in a box	95
chapter o	ter 5	
	Define the system	95
	The classical Hamiltonian	96
	Quantizing the system	97
	The boundary conditions	98
	Solving the eigenvalue problem (the Schrödinger equation	)
	for the particle in a box	100
	Separation of variables	100
	Boundary conditions	101
	The behavior of a particle in a box	104
	The ground state energy is not zero	105
	Degeneracy	107
	Degeneracy is related to the symmetry of the system	109
	The eigenfunctions are normalized	111
	Orthogonality	112
	The position of a particle in a given state	113
Chapter 9	Light emission and absorption:	
76	the phenomena	117
	Introduction	117

145

146

146

147

149

	Light absorption and emission: the phenomena	118
	An absorption experiment	118
	Characterization of an absorption spectrum	119
	Why the transmitted intensity is low at certain	
	frequencies	120
	Emission spectroscopy	122
	Units	126
	How to convert from one unit to another	128
	Why we need to know the laws of light absorption	
	and emission	130
10	Light emission and absorption: Einstein's	
	phenomenological theory	135
	Introduction	135
	Photon absorption and emission: the model	136
	Photon energy and energy conservation	136
	How to reconcile this energy conservation with	
	the existence of a line-width	137
	The model	137
	Photon absorption and emission: the rate equations	138
	The rate of photon absorption	138
	The rate of spontaneous photon emission	139
N.M.	The rate of stimulated emission	140
	The total rate of change of $N_0$ (or $N_1$ )	140
	Photon absorption and emission: the detailed balance	141
	Molecules in thermal equilibrium with radiation	141
	The detailed balance	143
	The solution of the rate equations	144
	Using the detailed balance results to simplify the	

rate equation

Analysis of the result: saturation

The ground state population when the molecules are continuously exposed to light

Why Einstein introduced stimulated emission

The initial conditions

Chapter

The rate of population relaxation151Chapter 11Light absorption: the quantum theory153Introduction153Quantum theory of light emission and absorption154The absorption probability154Electrodynamic quantities: light pulses154Electromagnetic quantities: the polarization of light156Electromagnetic properties: the direction of157Electromagnetic quantities: the energy and the intensity of the pulse157The properties of the molecule: the transition dipole moment (\style{\beta} \beta \b
Chapter 11Light absorption: the quantum theory153Introduction153Quantum theory of light emission and absorption154The absorption probability154Electrodynamic quantities: light pulses154Electromagnetic quantities: light pulses154Electromagnetic quantities: the polarization of light156Electromagnetic quantities: the direction of157Electromagnetic quantities: the energy and the intensity of the pulse157The properties of the molecule: the transition dipole moment ( $\psi_{f}   \hat{\mathbf{m}}   \psi_{i}$ )158The properties of the molecule: the line shape159How the transition probability formula is used162The probability of stimulated emission163Validity conditions163Single molecule spectroscopy and the spectroscopy of an ensemble of molecules165Chapter 12Light emission and absorption by a particle in a box and a harmonic oscillator169
Introduction153Quantum theory of light emission and absorption154The absorption probability154Electrodynamic quantities: light pulses154Electromagnetic quantities: the polarization of light156Electromagnetic properties: the direction of157Electromagnetic quantities: the energy and the157intensity of the pulse157The properties of the molecule: the transition dipole158moment $\langle \Psi_{\rm f}   \hat{\bf m}   \Psi_{\rm i} \rangle$ 158The properties of the molecule: the line shape159How the transition probability formula is used162The probability of stimulated emission163Validity conditions163The connection to Einstein's B coefficient163Single molecule spectroscopy and the spectroscopy of an ensemble of molecules165Chapter 12Light emission and absorption by a particle in a box and a harmonic oscillator169
Quantum theory of light emission and absorption154The absorption probability154Electrodynamic quantities: light pulses154Electromagnetic quantities: light pulses156Electromagnetic properties: the polarization of light156Electromagnetic properties: the direction of157Electromagnetic quantities: the energy and the intensity of the pulse157The properties of the molecule: the transition dipole moment $\langle \psi_{\rm f}   \hat{\bf m}   \psi_{\rm i} \rangle$ 158The properties of the molecule: the line shape159How the transition probability formula is used162The probability of stimulated emission163Validity conditions163The connection to Einstein's B coefficient163Single molecule spectroscopy and the spectroscopy of an ensemble of molecules165Chapter 12Light emission and absorption by a particle in a box and a harmonic oscillator169
The absorption probability154Electrodynamic quantities: light pulses154Electromagnetic quantities: the polarization of light156Electromagnetic properties: the direction of157propagation157Electromagnetic quantities: the energy and the intensity of the pulse157The properties of the molecule: the transition dipole moment $\langle \Psi_{\rm f}   \hat{\bf m}   \Psi_{\rm i} \rangle$ 158The properties of the molecule: the line shape159How the transition probability formula is used162The probability of stimulated emission163Validity conditions163The connection to Einstein's B coefficient163Single molecule spectroscopy and the spectroscopy of an ensemble of molecules165Chapter 12Light emission and absorption by a particle in a box and a harmonic oscillator169
Electrodynamic quantities: light pulses154Electromagnetic quantities: the polarization of light156Electromagnetic properties: the direction of157propagation157Electromagnetic quantities: the energy and the157intensity of the pulse157The properties of the molecule: the transition dipole158moment {\nu_f  \mathbf{m} \nu_i}158The properties of the molecule: the line shape159How the transition probability formula is used162The probability of stimulated emission163Validity conditions163Single molecule spectroscopy and the spectroscopy of an ensemble of molecules165Chapter 12Light emission and absorption by a particle in a box and a harmonic oscillator169
Electromagnetic quantities: the polarization of light Electromagnetic properties: the direction of propagation156157Propagation157Electromagnetic quantities: the energy and the intensity of the pulse157The properties of the molecule: the transition dipole moment $\langle \Psi_{\rm f}   \hat{\mathbf{m}}   \Psi_{\rm i} \rangle$ 158The properties of the molecule: the line shape159How the transition probability formula is used162The probability of stimulated emission163Validity conditions163The connection to Einstein's B coefficient163Single molecule spectroscopy and the spectroscopy of an ensemble of molecules165Chapter 12Light emission and absorption by a particle in a box and a harmonic oscillator169
Electromagnetic properties: the direction of propagation157Electromagnetic quantities: the energy and the intensity of the pulse157Electromagnetic quantities: the energy and the intensity of the pulse157The properties of the molecule: the transition dipole moment $\langle \Psi_{\rm f}   \hat{\mathbf{m}}   \Psi_{\rm i} \rangle$ 158The properties of the molecule: the transition dipole Mow the transition probability formula is used162The properties of the molecule: the line shape159How the transition probability formula is used163Validity conditions163The connection to Einstein's B coefficient163Single molecule spectroscopy and the spectroscopy of an ensemble of molecules165Chapter 12Light emission and absorption by a particle in a box and a harmonic oscillator169
propagation157Electromagnetic quantities: the energy and the intensity of the pulse157The properties of the molecule: the transition dipole moment {\\$\\$\\$\\$\\$\\$\\$\\$\\$\\$\\$\\$moment158The properties of the molecule: the line shape159How the transition probability formula is used162The probability of stimulated emission163Validity conditions163The connection to Einstein's B coefficient163Single molecule spectroscopy and the spectroscopy of an ensemble of molecules165Chapter 12Light emission and absorption by a particle in a box and a harmonic oscillator169
Electromagnetic quantities: the energy and the intensity of the pulse157The properties of the molecule: the transition dipole moment $\langle \psi_{\rm f}   \hat{\mathbf{m}}   \psi_{\rm i} \rangle$ 158The properties of the molecule: the line shape159How the transition probability formula is used162The probability of stimulated emission163Validity conditions163The connection to Einstein's B coefficient163Single molecule spectroscopy and the spectroscopy of an ensemble of molecules165Chapter 12Light emission and absorption by a particle in a box and a harmonic oscillator169
intensity of the pulse157The properties of the molecule: the transition dipolemoment $\langle \psi_{\rm f}   \hat{\mathbf{m}}   \psi_{\rm i} \rangle$ 158The properties of the molecule: the line shape159How the transition probability formula is used162The probability of stimulated emission163Validity conditions163The connection to Einstein's B coefficient163Single molecule spectroscopy and the spectroscopy of an ensemble of molecules165Chapter 12Light emission and absorption by a particle in a box and a harmonic oscillator169
The properties of the molecule: the transition dipole moment $\langle \psi_{\rm f}   \hat{\mathbf{m}}   \psi_{\rm i} \rangle$ 158The properties of the molecule: the line shape159How the transition probability formula is used162The probability of stimulated emission163Validity conditions163The connection to Einstein's B coefficient163Single molecule spectroscopy and the spectroscopy of an ensemble of molecules165Chapter 12Light emission and absorption by a particle in a box and a harmonic oscillator169
moment ⟨ψ <sub>f</sub>  m̂ ψ <sub>i</sub> ⟩       158         The properties of the molecule: the line shape       159         How the transition probability formula is used       162         The probability of stimulated emission       163         Validity conditions       163         The connection to Einstein's B coefficient       163         Single molecule spectroscopy and the spectroscopy of an ensemble of molecules       165         Chapter 12       Light emission and absorption by a particle in a box and a harmonic oscillator       169
The properties of the molecule: the line shape159How the transition probability formula is used162The probability of stimulated emission163Validity conditions163The connection to Einstein's B coefficient163Single molecule spectroscopy and the spectroscopy of an ensemble of molecules165Chapter 12Light emission and absorption by a particle in a box and a harmonic oscillator169
How the transition probability formula is used162The probability of stimulated emission163Validity conditions163The connection to Einstein's B coefficient163Single molecule spectroscopy and the spectroscopy of an ensemble of molecules165Chapter 12Light emission and absorption by a particle in a box and a harmonic oscillator169
The probability of stimulated emission163Validity conditions163Validity conditions163The connection to Einstein's B coefficient163Single molecule spectroscopy and the spectroscopy of an ensemble of molecules165Chapter 12Light emission and absorption by a particle in a box and a harmonic oscillator169
Validity conditions163The connection to Einstein's B coefficient163Single molecule spectroscopy and the spectroscopy of an ensemble of molecules165Chapter 12Light emission and absorption by a particle in a box and a harmonic oscillator169
The connection to Einstein's B coefficient163Single molecule spectroscopy and the spectroscopy of an ensemble of molecules165Chapter 12Light emission and absorption by a particle in a box and a harmonic oscillator169
Single molecule spectroscopy and the spectroscopy of an ensemble of molecules165Chapter 12Light emission and absorption by a particle in a box and a harmonic oscillator169
an ensemble of molecules 165 Chapter 12 Light emission and absorption by a particle in a box and a harmonic oscillator 169
Chapter 12 Light emission and absorption by a particle in a box and a harmonic oscillator 169
Chapter 12 Light emission and absorption by a particle in a box and a harmonic oscillator 169
in a box and a harmonic oscillator 169
Introduction 169
Light absorption by a particle in a box 170
Ouantum dots 170
Photon absorption probability 172
The amount of light and its frequency 173
The energies and absorption frequencies 173
The transition dipole 174
The energy eigenfunctions for a particle in a box 174
The dipole operator $\hat{m}$ 175
The role of light polarization 176

х

a particle in a box The first selection rule Physical interpretation The second selection rule A calculation of the spectrum in arbitrary units Light absorption by a harmonic oscillator The eigenstates and eigenvalues of a harmonic oscillator The transition dipole The molecular orientation and polarization Chapter 13 Two-particle systems Introduction The Schrödinger equation for the internal motion The laboratory coordinate system The energy Because there is no external force, the system moves with constant velocity A coordinate system with the origin in the center of mass The total energy in terms of momentum The Hamiltonian operator The total energy in terms of momentum The Hamiltonian of the quasi-particle The Go of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The poperties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum in the motion of the two-particle system The motion of the angular momentum		The evaluation of the transition moment for	
The first selection rule Physical interpretation The second selection rule A calculation of the spectrum in arbitrary units Light absorption by a harmonic oscillator The eigenstates and eigenvalues of a harmonic oscillator The transition dipole The molecular orientation and polarization <b>Chapter 13 Two-particle systems</b> Introduction The Schrödinger equation for the internal motion The laboratory coordinate system The energy Because there is no external force, the system moves with constant velocity A coordinate system with the origin in the center of mass The total energy in terms of momentum The Hamiltonian operator The concept of quasi-particle The Hamiltonian of the quasi-particle The Hamiltonian of the quasi-particle in spherical coordinates The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum in the motion of the two-particle system The wordinger equation of the quasi-particle and the square of the angular momentum in the motion of the two-particle system		a particle in a box	176
Physical interpretation The second selection rule A calculation of the spectrum in arbitrary units Light absorption by a harmonic oscillator The eigenstates and eigenvalues of a harmonic oscillator The transition dipole The molecular orientation and polarization Chapter 13 Two-particle systems Introduction The Schrödinger equation for the internal motion The Schrödinger equation for the internal motion The laboratory coordinate system The energy Because there is no external force, the system moves with constant velocity A coordinate system with the origin in the center of mass The total energy in terms of momentum The Hamiltonian operator The concept of quasi-particle The Hamiltonian of the quasi-particle The Hamiltonian of the quasi-particle The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum in the motion of the two-particle system The wordinger equation of the quasi-particle and the square of the angular momentum in the motion of the two-particle system The wordinger equation of the quasi-particle and the square of the angular momentum		The first selection rule	178
The second selection rule A calculation of the spectrum in arbitrary units Light absorption by a harmonic oscillator The eigenstates and eigenvalues of a harmonic oscillator The transition dipole The molecular orientation and polarization <b>Chapter 13 Two-particle systems</b> Introduction The Schrödinger equation for the internal motion The Schrödinger equation for the internal motion The laboratory coordinate system The energy Because there is no external force, the system moves with constant velocity A coordinate system with the origin in the center of mass The total energy in terms of momentum The Hamiltonian operator The concept of quasi-particle The Hamiltonian of the quasi-particle The Hamiltonian of the quasi-particle in spherical coordinates The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum in the motion of the two-particle system		Physical interpretation	178
A calculation of the spectrum in arbitrary units Light absorption by a harmonic oscillator The eigenstates and eigenvalues of a harmonic oscillator The transition dipole The molecular orientation and polarization <b>Chapter 13 Two-particle systems</b> Introduction The Schrödinger equation for the internal motion The Schrödinger equation for the internal motion The laboratory coordinate system The energy Because there is no external force, the system moves with constant velocity A coordinate system with the origin in the center of mass The total energy in terms of momentum The Hamiltonian operator The concept of quasi-particle The Hamiltonian of the quasi-particle in spherical coordinates The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum in the motion of the two-particle system The colution of the two-particle system The schrödinger equation of the quasi-particle and the square of the angular momentum in the motion of the two-particle system The evolution of the two-particle system The word of the angular momentum		The second selection rule	178
Light absorption by a harmonic oscillator The eigenstates and eigenvalues of a harmonic oscillator The transition dipole The molecular orientation and polarization <b>Chapter 13 Two-particle systems</b> Introduction The Schrödinger equation for the internal motion The Schrödinger equation for the internal motion The laboratory coordinate system The energy Because there is no external force, the system moves with constant velocity A coordinate system with the origin in the center of mass The total energy in terms of momentum The Hamiltonian operator The concept of quasi-particle The Hamiltonian of the quasi-particle The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum in the motion of the two-particle system The evolution of the two-particle system The evolution of the two-particle system The schrödinger equation of the quasi-particle and the square of the angular momentum in the motion of the two-particle system The evolution of the two-particle system The evolution of the two-particle system The evolution of the angular momentum		A calculation of the spectrum in arbitrary units	180
The eigenstates and eigenvalues of a harmonic oscillator The transition dipole The molecular orientation and polarization Chapter 13 Two-particle systems Introduction The Schrödinger equation for the internal motion The laboratory coordinate system The energy Because there is no external force, the system moves with constant velocity A coordinate system with the origin in the center of mass The total energy in terms of momentum The Hamiltonian operator The concept of quasi-particle The Hamiltonian of the quasi-particle in spherical coordinates The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum in the motion of the two-particle system The evolution of the two-particle system		Light absorption by a harmonic oscillator	181
oscillator The transition dipole The molecular orientation and polarization Chapter 13 Two-particle systems Introduction The Schrödinger equation for the internal motion The Schrödinger equation for the internal motion The laboratory coordinate system The energy Because there is no external force, the system moves with constant velocity A coordinate system with the origin in the center of mass The total energy in terms of momentum The Hamiltonian operator The concept of quasi-particle The Hamiltonian of the quasi-particle in spherical coordinates The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum in the motion of the two-particle system The evolution of the two-particle system The evolution of the two-particle system		The eigenstates and eigenvalues of a harmonic	
The transition dipole The molecular orientation and polarization (Chapter 13 Two-particle systems Introduction The Schrödinger equation for the internal motion The laboratory coordinate system The energy Because there is no external force, the system moves with constant velocity A coordinate system with the origin in the center of mass The total energy in terms of momentum The Hamiltonian operator The concept of quasi-particle The Hamiltonian of the quasi-particle in spherical coordinates The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum in the motion of the two-particle system The cole of angular momentum		oscillator	183
The molecular orientation and polarization  Chapter 13 Two-particle systems Introduction The Schrödinger equation for the internal motion The laboratory coordinate system The energy Because there is no external force, the system moves with constant velocity A coordinate system with the origin in the center of mass The total energy in terms of momentum The Hamiltonian operator The concept of quasi-particle The Hamiltonian of the quasi-particle in spherical coordinates The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum Supplement 13.1 The role of angular momentum in the motion of the two-particle system The ecolution of the angular momentum		The transition dipole	183
Chapter 13 Two-particle systems Introduction The Schrödinger equation for the internal motion The laboratory coordinate system The laboratory coordinate system The energy Because there is no external force, the system moves with constant velocity A coordinate system with the origin in the center of mass The total energy in terms of momentum The Hamiltonian operator The concept of quasi-particle The total energy of the angular momentum The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the angular momentum Supplement 13.1 The role of angular momentum in the motion of the two-particle system The evolution of the angular momentum		The molecular orientation and polarization	184
Chapter 13       Two-particle systems       1         Introduction       The Schrödinger equation for the internal motion       The laboratory coordinate system       1         The Schrödinger equation for the internal motion       The laboratory coordinate system       1         The Iaboratory coordinate system       The energy       Because there is no external force, the system moves with constant velocity       A coordinate system with the origin in the center of mass         The total energy in terms of momentum       The Hamiltonian operator       The concept of quasi-particle         The Hamiltonian of the quasi-particle       The Hamiltonian of the quasi-particle in spherical coordinates         The role of angular momentum in the motion of the two-particle system       Angular momentum in classical mechanics         The properties of angular momentum       The Schrödinger equation of the quasi-particle and the square of the angular momentum         Supplement 13.1       The role of angular momentum         The motion of the two-particle system       The colution of the angular momentum			
<ul> <li>Introduction</li> <li>The Schrödinger equation for the internal motion The laboratory coordinate system</li> <li>The energy</li> <li>Because there is no external force, the system moves with constant velocity</li> <li>A coordinate system with the origin in the center of mass</li> <li>The total energy in terms of momentum</li> <li>The Hamiltonian operator</li> <li>The concept of quasi-particle</li> <li>The Hamiltonian of the quasi-particle in spherical coordinates</li> <li>The role of angular momentum in the motion of the two-particle system</li> <li>Angular momentum in classical mechanics</li> <li>The properties of angular momentum</li> <li>The Schrödinger equation of the quasi-particle and the square of the angular momentum</li> <li>Supplement 13.1 The role of angular momentum</li> <li>in the motion of the two-particle system</li> </ul>	Chapter 13	Two-particle systems	187
<ul> <li>The Schrödinger equation for the internal motion The laboratory coordinate system The energy Because there is no external force, the system moves with constant velocity A coordinate system with the origin in the center of mass The total energy in terms of momentum The Hamiltonian operator The concept of quasi-particle</li> <li>The Hamiltonian of the quasi-particle in spherical coordinates</li> <li>The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum in the motion of the two-particle system The evolution of the two-particle system</li> </ul>		Introduction	187
The laboratory coordinate system The energy Because there is no external force, the system moves with constant velocity A coordinate system with the origin in the center of mass The total energy in terms of momentum The Hamiltonian operator The concept of quasi-particle The Hamiltonian of the quasi-particle in spherical coordinates The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum in the motion of the two-particle system Cupplement 13.1 The role of angular momentum in the motion of the angular momentum The ecolution of the angular momentum		The Schrödinger equation for the internal motion	189
The energy Because there is no external force, the system moves with constant velocity A coordinate system with the origin in the center of mass The total energy in terms of momentum The Hamiltonian operator The concept of quasi-particle The Hamiltonian of the quasi-particle in spherical coordinates The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum in the motion of the two-particle system The evolution of the two-particle system		The laboratory coordinate system	189
<ul> <li>Because there is no external force, the system moves with constant velocity</li> <li>A coordinate system with the origin in the center of mass</li> <li>The total energy in terms of momentum The Hamiltonian operator</li> <li>The concept of quasi-particle</li> <li>The Hamiltonian of the quasi-particle in spherical coordinates</li> <li>The role of angular momentum in the motion of the two-particle system</li> <li>Angular momentum in classical mechanics</li> <li>The properties of angular momentum</li> <li>The Schrödinger equation of the angular momentum</li> <li>Supplement 13.1 The role of angular momentum</li> <li>in the motion of the angular momentum</li> </ul>		The energy	190
with constant velocity A coordinate system with the origin in the center of mass The total energy in terms of momentum The Hamiltonian operator The concept of quasi-particle The Hamiltonian of the quasi-particle in spherical coordinates The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum Supplement 13.1 The role of angular momentum in the motion of the two-particle system The evolution of the angular momentum		Because there is no external force, the system moves	
<ul> <li>A coordinate system with the origin in the center of mass</li> <li>The total energy in terms of momentum The tamiltonian operator The Concept of quasi-particle</li> <li>The Hamiltonian of the quasi-particle in spherical coordinates</li> <li>The role of angular momentum in the motion of the two-particle system</li> <li>Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum</li> <li>Supplement 13.1 The role of angular momentum in the motion of the two-particle system The evolution of the angular momentum</li> </ul>		with constant velocity	191
of mass The total energy in terms of momentum The Hamiltonian operator The concept of quasi-particle The Hamiltonian of the quasi-particle in spherical coordinates The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum Supplement 13.1 The role of angular momentum in the motion of the two-particle system The evolution of the angular momentum		A coordinate system with the origin in the center	
The total energy in terms of momentum The Hamiltonian operator The concept of quasi-particle The Hamiltonian of the quasi-particle in spherical coordinates The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum Supplement 13.1 The role of angular momentum in the motion of the two-particle system The evolution of the angular momentum		of mass	194
The Hamiltonian operator The concept of quasi-particle The Hamiltonian of the quasi-particle in spherical coordinates The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum Supplement 13.1 The role of angular momentum in the motion of the two-particle system The evolution of the angular momentum		The total energy in terms of momentum	195
The concept of quasi-particleThe Hamiltonian of the quasi-particle in spherical coordinatesThe role of angular momentum in the motion of the two-particle systemAngular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentumSupplement 13.1 The role of angular momentum in the motion of the two-particle system The evolution of the angular momentum		The Hamiltonian operator	196
<ul> <li>The Hamiltonian of the quasi-particle in spherical coordinates</li> <li>The role of angular momentum in the motion of the two-particle system</li> <li>Angular momentum in classical mechanics</li> <li>The properties of angular momentum</li> <li>The Schrödinger equation of the quasi-particle and the square of the angular momentum</li> <li>Supplement 13.1 The role of angular momentum</li> <li>in the motion of the two-particle system</li> <li>The evolution of the angular momentum</li> </ul>		The concept of quasi-particle	197
coordinates The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum Supplement 13.1 The role of angular momentum in the motion of the two-particle system The evolution of the angular momentum		The Hamiltonian of the quasi-particle in spherical	
The role of angular momentum in the motion of the two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum Supplement 13.1 The role of angular momentum in the motion of the two-particle system The evolution of the angular momentum		coordinates	199
two-particle system Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum Supplement 13.1 The role of angular momentum in the motion of the two-particle system The evolution of the angular momentum		The role of angular momentum in the motion of the	
Angular momentum in classical mechanics The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum Supplement 13.1 The role of angular momentum in the motion of the two-particle system The evolution of the angular momentum		two-particle system	201
The properties of angular momentum The Schrödinger equation of the quasi-particle and the square of the angular momentum Supplement 13.1 The role of angular momentum in the motion of the two-particle system The evolution of the angular momentum		Angular momentum in classical mechanics	201
The Schrödinger equation of the quasi-particle and the square of the angular momentum Supplement 13.1 The role of angular momentum in the motion of the two-particle system The evolution of the angular momentum		The properties of angular momentum	201
and the square of the angular momentum Supplement 13.1 The role of angular momentum in the motion of the two-particle system The evolution of the angular momentum		The Schrödinger equation of the quasi-particle	
Supplement 13.1 The role of angular momentum in the motion of the two-particle system The evolution of the angular momentum		and the square of the angular momentum	205
in the motion of the two-particle system The evolution of the angular momentum		Supplement 13.1 The role of angular momentum	
The evolution of the angular momentum		in the motion of the two-particle system	207
		The evolution of the angular momentum	207

	A polar coordinate system	208
	The angular momentum in polar coordinates	210
	The energy in polar coordinates	210
Chapter 14	Angular momentum in quantum mechanics	213
	Introduction	213
	The operators representing the angular momentum in	-10
	quantum mechanics	215
	Angular momentum in classical mechanics	215
	The angular momentum operator in quantum	
	mechanics	216
	Angular momentum in spherical coordinates	217
	The operator $\hat{L}^2$	218
	The commutation relations between $\hat{L}^2$ and $\hat{L}_x$ , $\hat{L}_y$ , $\hat{L}_z$	218
	The eigenvalue equations for $\hat{L}^2$ and $\hat{L}_z$	220
	The eigenvalue problem for $\hat{L}^2$	221
	The eigenvalue problem for $\hat{L}_z$	222
	Spherical harmonics	222
	The physical interpretation of these eigenstates	225
	Supplement 14.1 A brief explanation of the procedure	
	for changing coordinates	226
Chapter 15	Two particle systems: the radial	
	and angular Schrödinger equations	231
	Introduction	231
	The Schrödinger equation in terms of $\hat{L}^2$	232
	The Hamiltonian of a two-particle system in terms	
	$of L^2$	232
	The radial and the angular Schrödinger equations	233
	The separation of variables in the Schrödinger	
	equation	233
	Additional physical conditions	234
	The integral over the angles	235
	The radial normalization	235

Chapter 16	The energy eigenstates of a diatomic molecule	239
	Introduction	239
	The harmonic approximation	240
	The form of the function $V(r)$	240
	The physics described by $V(r)$	241
	When the approximation is correct	244
	The harmonic approximation to $V(r)$	245
	The rigid-rotor approximation	247
	Physical interpretation	247
	The rigid-rotor approximation decouples vibrational	
	and rotational motion	248
	The eigenstates and eigenvalues of the radial Schrödinger equation in the harmonic and rigid-rotor	
	approximation	249
	The eigenvalues	249
	An improved formula for the energy	250
	The radial eigenfunctions	252
	The physical interpretation of the eigenfunctions	254
	The probability of having a given interatomic distance	055
	and orientation	255
	The probability of having a given bond length	256
	Turning point and tunneling	258
	The average values of $r - r_0$ and $(r - r_0)^2$	260
	The energy eigenstates and eigenvalues of a diatomic molecule	262
Chapter 17	Diatomic molecule: its spectroscopy	265
	Introduction	265
	Collect the necessary equations	269
	The frequencies of the absorbed photons	269
	Photon absorption and emission probabilities	271
	The wave function for the nuclear motion	272
	The electronic wave function	273

xiii

	The dipole moment of the molecule	274
	The separation of the transition dipole matrix	
	element into a rotational and vibrational	
	contribution	275
	The harmonic approximation for the dipole moment	277
	Physical interpretation	279
	The integral $\langle \ell_{\rm f}, m_{\rm f}   \cos(\theta)   \ell_{\rm i}, m_{\rm i} \rangle$	280
	Vibrational and rotational excitation by absorption of an	
	infrared photon	281
	The molecules in a gas have a variety of states	285
	The infrared absorption spectrum of a gas at a fixed	
	temperature	286
	The probability of $\wp(v, \ell, m; T)$	288
	The probability of various states in a gas: a numerical	
	study	289
	Back to the spectrum: the relative intensity of the	
	absorption peaks	291
	Numerical analysis	291
Chapter 18	The hydrogen atom	295
	Introduction	295
	The Schrödinger equation for a one-electron atom	296
	Why the properties of a one-electron atom are so	
	different from those of a diatomic molecule	297
	The solution of the Schrödinger equation for	
	a one-electron atom	299
	The eigenvalues	300

different from those of a diatomic molecule	297
The solution of the Schrödinger equation for	
a one-electron atom	299
The eigenvalues	300
The eigenfunctions	301
The energy	302
The magnitude of the energies	302
The energy scale $\varepsilon$ and the length scale a	304
The radial wave functions $R_{n,\ell}(r)$ and the mean values	
of various physical quantities	306
The probability of finding the electron at a certain	
distance from the nucleus	308

xiv

	The functions $R_{n,\ell}(r)$	310
	<i>Plots of</i> $R_{n,\ell}(r)$	311
	The mean values of $r$ , $r^2$ , Coulomb energy,	
	centrifugal energy, and radial kinetic energy	312
	The angular dependence of the wave function	317
	Some nomenclature	319
	The s-states	319
	The np orbitals	320
	The nd orbitals	323
	Hydrogen atom: absorption and emission spectroscopy	325
	The transition dipole	327
	The selection rules	328
	The radial integrals	330
	The wateria antibioted a product of wateries	
372	How to choose good orbitals un simuly	
Chapter 19	The spin of the electron and its role in	
	spectroscopy	331
	Introduction	331
	The spin operators	334
	Spin eigenstates and eigenvalues	335
	The scalar product	337
	The emission spectrum of a hydrogen atom in a	
	magnetic field: the normal Zeeman effect	339
	The experiment	340
	A modern (but oversimplified) version of the	
	Lorentz model	342
	The energy of the hydrogen atom in a magnetic field	343
	The emission frequencies	345
	The spectrum	347
	The role of spin in light emission by a hydrogen atom:	
	the anomalous Zeeman effect	348
	The interaction between spin and a magnetic field	348
	The energies of the electron in the hydrogen atom:	
	the contribution of spin	348
	Comments and warnings	350

xv

Chapter 20	The electronic structure of molecules: The H <sub>2</sub> molecule	353
	Introduction	353
	The Born–Oppenheimer approximation	355
	The electronic energies $E_n(\mathbf{R})$ are the potential	
	energies for the nuclear motion	358
	How to use the variational principle	363
	Application to the harmonic oscillator	363
	An application of the variational principle that	
	uses a basis set	366
	The many-body wave function as a product of orbitals	369
	The curse of multi-dimensionality	369
	The wave function as a product of orbitals	370
	How to choose good orbitals	372
	The electron wave function must be antisymmetric	372
	Indistinguishable particles	372
	The antisymmetrization of a product of orbitals	375
	How to generalize to more than two electrons	377
	The Pauli principle	379
	Which electrons should be antisymmetrized	380
	The molecular orbitals in a minimal basis set: $\sigma_u$ and $\sigma_g$	383
	The MO-LCAO method	383
	The minimal basis set	384
	Determine the molecular orbitals by using symmetry	384
	The molecular orbitals are normalized	385
	The symmetry of $\sigma_{\sigma}$ and $\sigma_{u}$	387
	The antisymmetrized products used in the configuration	
	interaction wave functions must be eigenfunctions of	
	$\hat{\mathbf{S}}^2$ and $\hat{\mathbf{S}}_z$	387
	The strategy for constructing the functions $\Phi_i(1,2)$	389
	The spin states	389
	The singlet state $ 0,0\rangle$	390
	The triplet states $ 1, m_s\rangle$	391

xvi

Pairing up the spin and the orbital functions to create	
antisymmetric configurations	391
The states $\Phi_1, \Phi_2$ , and $\Phi_6$	391
The states $\Phi_3, \Phi_4$ , and $\Phi_5$	392
The notations ${}^{1}\Sigma_{g+}$ , ${}^{1}\Sigma_{g-}$ , ${}^{3}\Sigma_{u,-1}$ , ${}^{3}\Sigma_{u,0}$ , ${}^{3}\Sigma_{u,1}$ , ${}^{1}\Sigma_{u,0}$	392
The configurations in terms of atomic orbitals: physical	
interpretation	393
The integrals required by the configuration interaction	
method	394
The overlap matrix is diagonal	395
Only the off-diagonal matrix elements $\langle \Phi_1     \hat{H}     \Phi_2  angle$	
and $\langle \Phi_2     \hat{H}     \Phi_1  angle$ differ from zero	395
The Hamiltonian matrix	396
The Hamiltonian in atomic units	396
Atomic units	397
The matrix elements in terms of atomic orbitals	397
Expression for the matrix elements	398
The overlap integral $S(R)$	399
The integral $J(R)$	399
The integral $K(R)$	401
The integral $J'(R)$	401
The integral $K'(R)$	402
The integral $L(R)$	404
The ground and excited state energies given by	
perturbation theory	405
Behavior of $H_{11}(R)$ at large R	407
The configuration interaction method	409
The variational eigenvalue problem: a summary	409
The eigenvalues and the eigen vectors of matrix $\overleftrightarrow{H}$	410
The coupling between configurations	411
When perturbation theory is accurate	412
The configuration interaction energies	412
The configuration interaction wave function of the	
ground state	414
Summary	416
A REAL PROPERTY OF THE REAL PARTY OF THE REAL PROPERTY OF THE REAL PROPE	

Chapter 21	Nuclear magnetic resonance and electron	
	spin resonance	421
	Introduction	421
	More information about spin operators and spin states	424
	The NMR spectrum of a system with one independent spin	428
	The energy of the spin states for non-interacting spins	428
	The energy levels	429
	The rate of energy absorption	430
	NMR notation and units	430
	The order of magnitude of various quantities	431
	Hot bands	432
	The chemical shift	434
	The magnetic field acting on a nucleus depends on	
	environment	434
	The NMR spectrum of a system of two	
	non-interacting nuclei having spin $rac{1}{2}$	436
	The Hamiltonian and the states of a system of two	
	non-interacting spin $\frac{1}{2}$ particles	436
	The order of magnitude of these energies	438
	The selection rules	438
	The frequencies of the allowed transitions	440
	The spin–spin interaction	441
	Spin–spin coupling	441
	The interaction between nuclear spins	442
	The spectrum of two distinguishable, interacting nuclei	443
	The energies of the spin states	443
	The Hamiltonian	444
	The states of the interacting spins	444
	The Galerkin method: how to turn an operator	
	equation into a matrix equation	446
	The matrix elements $H_{nm} = \langle \psi_n   \hat{H}   \psi_m \rangle$	447
	Perturbation theory	449
	The off-diagonal elements	450
	The lowest energy $E_1$ and eigenvector $ \phi_1\rangle$	451
	The eigenvalue $E_2$ and the spin state $ \phi_2\rangle$	452

453

	Why $ \phi_1\rangle$ and $ \phi_2\rangle$ are so different	453
	The physical meaning of $ \phi_2\rangle$	453
	The states $ \phi_3\rangle$ and $ \phi_4\rangle$ and the energies $E_3$ and $E_4$	455
	The orders of magnitude	456
	The NMR spectrum of two weakly interacting,	
	indistinguishable nuclei having spin $\frac{1}{2}$	457
	The states that satisfy the symmetry requirements	457
	Perturbation theory	459
	The selection rules	461
Appendices		463
	A1. Values of some physical constants	463
	A2. Energy conversion factors	464
	Further Reading	465
	Index	467