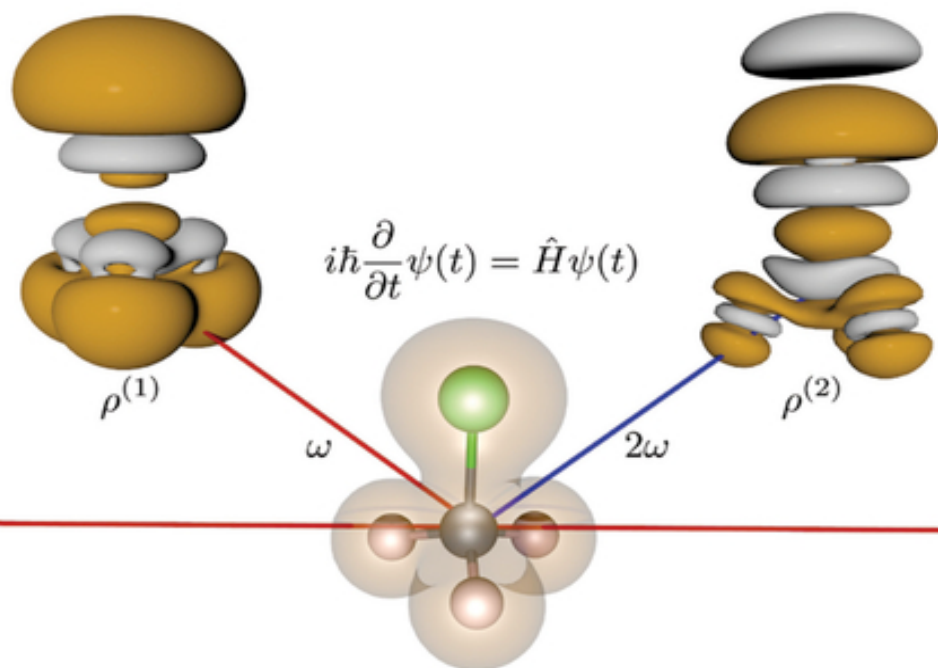


Patrick Norman, Kenneth Ruud,
Trond Saue

Principles and Practices of Molecular Properties

Theory, Modeling, and Simulations



**Principles and Practices of Molecular Properties:
Theory, Modeling, and Simulations**

Principles and Practices of Molecular Properties: Theory, Modeling, and Simulations

Patrick Norman

KTH Royal Institute of Technology, Stockholm, Sweden

Kenneth Ruud

University of Tromsø—The Arctic University of Norway, Norway

Trond Saue

CNRS/Université Toulouse III-Paul Sabatier, France

WILEY

This edition first published 2018

© 2018 John Wiley & Sons Ltd

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by law. Advice on how to obtain permission to reuse material from this title is available at <http://www.wiley.com/go/permissions>.

The right of Patrick Norman, Kenneth Ruud and Trond Saue to be identified as the author(s) of this work has been asserted in accordance with law.

Registered Office(s)

John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA

John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, UK

Editorial Office

9600 Garsington Road, Oxford, OX4 2DQ, UK

For details of our global editorial offices, customer services, and more information about Wiley products visit us at www.wiley.com.

Wiley also publishes its books in a variety of electronic formats and by print-on-demand. Some content that appears in standard print versions of this book may not be available in other formats.

Limit of Liability/Disclaimer of Warranty

In view of ongoing research, equipment modifications, changes in governmental regulations, and the constant flow of information relating to the use of experimental reagents, equipment, and devices, the reader is urged to review and evaluate the information provided in the package insert or instructions for each chemical, piece of equipment, reagent, or device for, among other things, any changes in the instructions or indication of usage and for added warnings and precautions. While the publisher and authors have used their best efforts in preparing this work, they make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives, written sales materials or promotional statements for this work. The fact that an organization, website, or product is referred to in this work as a citation and/or potential source of further information does not mean that the publisher and authors endorse the information or services the organization, website, or product may provide or recommendations it may make. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for your situation. You should consult with a specialist where appropriate. Further, readers should be aware that websites listed in this work may have changed or disappeared between when this work was written and when it is read. Neither the publisher nor authors shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

Library of Congress Cataloging-in-Publication Data

Names: Norman, Patrick 1968- author. | Ruud, Kenneth, 1969- author. | Saue, Trond, 1964- author.

Title: Principles and practices of molecular properties : theory, modeling and simulations / by Patrick Norman, Kenneth Ruud, Trond Saue.

Description: First edition. | Hoboken, NJ : John Wiley & Sons, 2018. | Includes bibliographical references and index. |

Identifiers: LCCN 2017041617 (print) | LCCN 2017047781 (ebook) | ISBN 9781118794838 (pdf) | ISBN 9781118794814 (epub) | ISBN 9780470725627 (cloth)

Subjects: LCSH: Molecules--Models. | Chemistry, Theoretical Chemistry, Physical.

Classification: LCC QD480 (ebook) | LCC QD480 .N67 2018 (print) | DDC 539/.12--dc23

LC record available at <https://lcn.loc.gov/2017041617>

Cover Design: Wiley

Cover Image: Courtesy of Patrick Norman

Set in 10/12pt WarnockPro by SPi Global, Chennai, India

Contents

Preface *xi*

1	Introduction	1
2	Quantum Mechanics	11
2.1	Fundamentals	11
2.1.1	Postulates of Quantum Mechanics	11
2.1.2	Lagrangian and Hamiltonian Formalisms	11
2.1.3	Wave Functions and Operators	18
2.2	Time Evolution of Wave Functions	22
2.3	Time Evolution of Expectation Values	25
2.4	Variational Principle	27
	Further Reading	29
3	Particles and Fields	31
3.1	Microscopic Maxwell's Equations	32
3.1.1	General Considerations	32
3.1.2	The Stationary Case	34
3.1.3	The General Case	38
3.1.4	Electromagnetic Potentials and Gauge Freedom	39
3.1.5	Electromagnetic Waves and Polarization	41
3.1.6	Electrodynamics: Relativistic and Nonrelativistic Formulations	45
3.2	Particles in Electromagnetic Fields	48
3.2.1	The Classical Mechanical Hamiltonian	48
3.2.2	The Quantum-Mechanical Hamiltonian	52
3.3	Electric and Magnetic Multipoles	57
3.3.1	Multipolar Gauge	57
3.3.2	Multipole Expansions	59
3.3.3	The Electric Dipole Approximation and Beyond	63
3.3.4	Origin Dependence of Electric and Magnetic Multipoles	64
3.3.5	Electric Multipoles	65
3.3.5.1	General Versus Traceless Forms	65
3.3.5.2	What We Can Learn from Symmetry	68
3.3.6	Magnetic Multipoles	69
3.3.7	Electric Dipole Radiation	70

3.4	Macroscopic Maxwell's Equations	72
3.4.1	Spatial Averaging	72
3.4.2	Polarization and Magnetization	73
3.4.3	Maxwell's Equations in Matter	77
3.4.4	Constitutive Relations	79
3.5	Linear Media	81
3.5.1	Boundary Conditions	82
3.5.2	Polarization in Linear Media	86
3.5.3	Electromagnetic Waves in a Linear Medium	92
3.5.4	Frequency Dependence of the Permittivity	96
3.5.4.1	Kramers–Kronig Relations	97
3.5.4.2	Relaxation in the Debye Model	98
3.5.4.3	Resonances in the Lorentz Model	101
3.5.4.4	Refraction and Absorption	105
3.5.5	Rotational Averages	107
3.5.6	A Note About Dimensions, Units, and Magnitudes	110
	Further Reading	111
4	Symmetry	113
4.1	Fundamentals	113
4.1.1	Symmetry Operations and Groups	113
4.1.2	Group Representation	117
4.2	Time Symmetries	120
4.3	Spatial Symmetries	125
4.3.1	Spatial Inversion	125
4.3.2	Rotations	127
	Further Reading	134
5	Exact-State Response Theory	135
5.1	Responses in Two-Level System	135
5.2	Molecular Electric Properties	145
5.3	Reference-State Parameterizations	151
5.4	Equations of Motion	156
5.4.1	Time Evolution of Projection Amplitudes	157
5.4.2	Time Evolution of Rotation Amplitudes	159
5.5	Response Functions	163
5.5.1	First-Order Properties	166
5.5.2	Second-Order Properties	166
5.5.3	Third-Order Properties	169
5.5.4	Fourth-Order Properties	174
5.5.5	Higher-Order Properties	179
5.6	Dispersion	179
5.7	Oscillator Strength and Sum Rules	183
5.8	Absorption	185
5.9	Residue Analysis	190
5.10	Relaxation	194
5.10.1	Density Operator	195

5.10.2	Liouville Equation	196
5.10.3	Density Matrix from Perturbation Theory	200
5.10.4	Linear Response Functions from the Density Matrix	201
5.10.5	Nonlinear Response Functions from the Density Matrix	204
5.10.6	Relaxation in Wave Function Theory	204
5.10.7	Absorption Cross Section	207
5.10.8	Einstein Coefficients	210
	Further Reading	211
6	Electronic and Nuclear Contributions to Molecular Properties	213
6.1	Born–Oppenheimer Approximation	213
6.2	Separation of Response Functions	216
6.3	Molecular Vibrations and Normal Coordinates	221
6.4	Perturbation Theory for Vibrational Wave Functions	225
6.5	Zero-Point Vibrational Contributions to Properties	227
6.5.1	First-Order Anharmonic Contributions	227
6.5.2	Importance of Zero-Point Vibrational Corrections	231
6.5.3	Temperature Effects	234
6.6	Pure Vibrational Contributions to Properties	235
6.6.1	Perturbation Theory Approach	235
6.6.2	Pure Vibrational Effects from an Analysis of the Electric-Field Dependence of the Molecular Geometry	238
6.7	Adiabatic Vibronic Theory for Electronic Excitation Processes	244
6.7.1	Franck–Condon Integrals	248
6.7.2	Vibronic Effects in a Diatomic System	250
6.7.3	Linear Coupling Model	252
6.7.4	Herzberg–Teller Corrections and Vibronically Induced Transitions	252
	Further Reading	253
7	Approximate Electronic State Response Theory	255
7.1	Reference State Parameterizations	255
7.1.1	Single Determinant	255
7.1.2	Configuration Interaction	263
7.1.3	Multiconfiguration Self-Consistent Field	266
7.1.4	Coupled Cluster	268
7.2	Equations of Motion	271
7.2.1	Ehrenfest Theorem	271
7.2.2	Quasi-Energy Derivatives	275
7.3	Response Functions	276
7.3.1	Single Determinant Approaches	276
7.3.2	Configuration Interaction	281
7.3.3	Multiconfiguration Self-Consistent Field	281
7.3.4	Matrix Structure in the SCF, CI, and MCSCF Approximations	281
7.3.5	Coupled Cluster	285
7.4	Residue Analysis	288
7.5	Relaxation	291
	Further Reading	293

8	Response Functions and Spectroscopies	295
8.1	Nuclear Interactions	296
8.1.1	Nuclear Charge Distribution	296
8.1.2	Hyperfine Structure	301
8.1.2.1	Nuclear Magnetic Dipole Moment	301
8.1.2.2	Nuclear Electric Quadrupole Moment	305
8.2	Zeeman Interaction and Electron Paramagnetic Resonance	310
8.3	Polarizabilities	317
8.3.1	Linear Polarizability	317
8.3.1.1	Weak Intermolecular Forces	321
8.3.2	Nonlinear Polarizabilities	325
8.4	Magnetizability	326
8.4.1	The Origin Dependence of the Magnetizability	328
8.4.2	Magnetizabilities from Magnetically Induced Currents	331
8.4.3	Isotropic Magnetizabilities and Pascal's Rule	332
8.5	Electronic Absorption and Emission Spectroscopies	335
8.5.1	Visible and Ultraviolet Absorption	338
8.5.2	Fluorescence Spectroscopy	343
8.5.3	Phosphorescence	344
8.5.4	Multiphoton Absorption	347
8.5.4.1	Multiphoton Absorption Cross Sections	348
8.5.4.2	Few-State Models for Two-Photon Absorption Cross Section	350
8.5.4.3	General Multiphoton Absorption Processes	351
8.5.5	X-ray Absorption	354
8.5.5.1	Core-Excited States	355
8.5.5.2	Field Polarization	358
8.5.5.3	Static Exchange Approximation	360
8.5.5.4	Complex or Damped Response Theory	362
8.6	Birefringences and Dichroisms	364
8.6.1	Natural Optical Activity	366
8.6.2	Electronic Circular Dichroism	372
8.6.3	Nonlinear Birefringences	375
8.6.3.1	Magnetic Circular Dichroism	376
8.6.3.2	Electric Field Gradient-Induced Birefringence	379
8.7	Vibrational Spectroscopies	381
8.7.1	Infrared Absorption	381
8.7.1.1	Double-Harmonic Approximation	381
8.7.1.2	Anharmonic Corrections	383
8.7.2	Vibrational Circular Dichroism	384
8.7.3	Raman Scattering	388
8.7.3.1	Raman Scattering from a Classical Point of View	388
8.7.3.2	Raman Scattering from a Quantum Mechanical Point of View	392
8.7.4	Vibrational Raman Optical Activity	402
8.8	Nuclear Magnetic Resonance	408
8.8.1	The NMR Experiment	408
8.8.2	NMR Parameters	413
	Further Reading	417

Appendices

A	Abbreviations	419
B	Units	421
C	Second Quantization	423
C.1	Creation and Annihilation Operators	423
C.2	Fock Space	425
C.3	The Number Operator	426
C.4	The Electronic Hamiltonian on Second-Quantized Form	427
C.5	Spin in Second Quantization	429
D	Fourier Transforms	431
E	Operator Algebra	435
F	Spin Matrix Algebra	439
G	Angular Momentum Algebra	441
H	Variational Perturbation Theory	445
I	Two-Level Atom	451
I.1	Rabi Oscillations	452
I.2	Time-Dependent Perturbation Theory	454
I.3	The Quasi-energy Approach	455
	Index	457

Preface

This book has grown out of an ambition to collect the basic theoretical foundations needed in our daily work as computational chemists with a focus on calculating molecular spectroscopic properties. The result is of course a product strongly influenced by our past experiences and will, as such, provide both a subjective and selective view of the field. It is subjective in the ways we choose to present the subject matter and it is selective in the inclusion of some topics but leaving out others that by many may be deemed just as important. But it is our hope that we provide a basic understanding of key concepts so as to enable further reading of research articles providing either a more detailed treatment of theoretical specifics and algorithmic implementations, or covering any one of the several spectroscopies not mentioned in the book.

Every chapter in this book expresses a balance between *principles* and *practices*. A principle (such as the variational principle) can typically be expressed in an extremely compact manner and governs the practices in a wide range of applications (such as a whole category of methods in electronic structure theory). After an introductory chapter aimed at getting the reader into the right mind-set, the second chapter (on the topic of *quantum mechanics*) almost exclusively deals with principles. It sets the stage and introduces much of the notation used in the remainder of the book. This chapter, as well as this book, is best appreciated after having completed a dedicated course on quantum mechanics¹ at the level of the second cycle in higher education. The third chapter is devoted to *electrodynamics* and here we attempt not only to provide principles but also practices in a form adapted to its use in theoretical chemistry. It represents a core chapter of this book and it should be possible to study it even without any particular background in the field. The fourth chapter is devoted to the topic of *symmetry* and it focuses on principles and is hardly the material for a first time encounter. We expect that the reader is well familiar with the use of molecular point groups and one finds here merely a brief recapitulation of this topic.² However, we have tried to provide a novel perspective that takes the reader a bit further than the standard presentation, which will help prepare the reader to handle not only spin-free nonrelativistic wave functions, but also systems where the two-component (or four-component) nature of electronic wave functions must be considered. In the fifth chapter of this book, we reach the core of the theoretical exposé and become familiar with molecular *response properties*. This is intended to be a self-contained chapter and it is followed by the sixth chapter that explains the *separation of electronic and nuclear degrees of freedom* and discusses nuclear contributions to molecular properties. The seventh chapter provides a glimpse into the vast amount of work devoted to implementing the ideas of *response theory in approximate-state theory*. This chapter treads somewhere right in between principles and practices. It treats with certain detail some wave function models but leaves out much of

1 A recommended textbook is *Quantum Mechanics* by B. H. Bransden and C. J. Joachain.

2 A recommended reading is *Group Theory and Chemistry* by D. M. Bishop.

the background in electronic structure theory.³ Our book is completed with the eighth chapter that illustrates the use of molecular response theory for the calculation of spectroscopic properties. We exemplify nuclear structure and spin properties, dispersive and absorptive electronic response properties, electronic birefringences and dichroisms, and vibrational spectroscopies. Needless to say, the list of examples in this final chapter could be made much longer, but we hope that our selection is diverse enough to provide compelling evidence for the impact and use of response theory in molecular modeling.

Before proceeding, let us note some notational conventions that will be used in this book. We will use the *Système International d'unités* (SI units). Vectors are typeset in boldface and operators are denoted by a hat, as for instance the molecular Hamiltonian $\hat{H}$. When referring to a specific matrix representation of an operator, we leave out the hat. We will indicate the real and imaginary parts of complex quantities by *Re* and *Im*, respectively. For compliance with the literature on electrodynamics, we will in Chapter 3 use **E** to denote the electric field. In the rest of the book, however, we will use **F** for the electric field in order to avoid confusion with the molecular energy that will be denoted by *E*. We will use implicit summation of repeated indices (the Einstein summation convention), such that

$$A_{\alpha\alpha} \Rightarrow \sum_{\alpha=x,y,z} A_{\alpha\alpha}.$$

Over the course of time spent in writing this book, we have discussed the material with a large number of people. We have organized several week-long courses where the manuscript has been used as teaching material and we have received numerous comments and corrections during these events. We are greatly indebted to all the enthusiastic students attending these schools on response theory, taking place in Chamonix and Luchon in France, as well as at Virginia Tech in the United States. The school at Virginia Tech has been co-organized with Daniel Crawford, who has provided excellent local arrangements and shared his expertise with us in a series of lectures. The U.S. variant of this school could never have been realized without his kind help. We have also benefited from the dedicated proof reading by several people, including Daniel Fries (Düsseldorf), Bin Gao (Tromsø), Michal Jaszuński (Warsaw), Marius Kadek (Tromsø), Nanna H. List (Stockholm), Roberto Di Remigio (Tromsø), and Magnus Ringholm (Tromsø).

A special thanks goes to the following persons for helpful discussions and exchange: Mats Aigner (Linköping), Radovan Bast (Tromsø), Hélène Bolvin (Toulouse), Richard A. Clarke (Surrey), David J. Griffiths (Reed), Trygve Helgaker (Oslo), John D. Jackson (Berkeley), Mathieu Linares (Stockholm), and Nanna H. List (Stockholm). We would also like to thank Barbara Helgaker for helping us iron out some language issues.

Things take longer time than one thinks, even when one takes into account that things take longer time than one thinks. Trond and Patrick would like to thank Hélène, Aurélien, and Sigurd and Dorthé, Jonathan, and Alexander, respectively, for their patience and understanding over the several years it has taken to complete this work.

Patrick Norman, Stockholm
Kenneth Ruud, Tromsø
Trond Saue, Toulouse

June, 2017

³ The most comprehensive treatment of today on this topic is found in *Molecular Electronic-Structure Theory* by T. Helgaker, J. Olsen, and P. Jørgensen.

1

Introduction

If you want to find the secrets of the universe, think in terms of energy, frequency and vibration.

Nicolas Tesla

This is a book about molecular properties, or to be more specific, molecular response properties. Response properties tell us about how molecules respond to electromagnetic fields. To understand these responses, we have to enter the microscopic world of atoms and molecules, governed by the laws of quantum mechanics. For that reason, the reader of this book can expect several intellectual challenges ranging from profound and conceptual cornerstones of quantum theory itself to trivial, yet mind-boggling, issues relating to the smallness of atomic sizes. Consider for instance the situation in which a collection of molecules are being exposed to the intense electric field of a laser, as illustrated in Figure 1.1. From a human perspective, the focal point of a laser is a dangerous place to be, but, from the atomic perspective, it is far less dramatic. In our example, there will be fewer photons than molecules, and, for instance, if the purpose is to protect the eye by efficient optical power limiting, only about every second molecule needs to absorb an incoming light quanta in order to reduce the energy in the transmitted light pulse to an eye-safe level. Furthermore, as strong as the electric field may appear to our eyes, to the individual electron it is several orders of magnitude smaller than the dominating forces exerted by the atomic nuclei and fellow electrons. To get an idea of magnitudes, one may note that the electric field below overhead power lines may reach 10^4 V m^{-1} and the maximum electric field strength possible in air without creating sparks is $3.0 \times 10^6 \text{ V m}^{-1}$. In contrast, at the Bohr radius a_0 in the hydrogen atom, the electric field strength is $5.1 \times 10^{11} \text{ V m}^{-1}$. This is a key point, namely, that we can expose molecules to fields that are strong enough so that we can detect the responses of their charges (nuclei and electrons) while at the same time the fields are weak enough to act as probes, not significantly perturbing the electronic and nuclear structure of the molecule.

Take a very simple example: What happens if a neutral atom (not even a molecule) is placed in a uniform electric field? An experimentalist will ask nature—that is, he or she may perform an experiment, where every macroscopic experiment relates to a very large number of probabilistic microscopic quantum events—by probing how the charge distribution of the atom is modified by the applied field. A theoretician will ask the wave function ψ . The quantum-mechanical equivalent to the outcome of the experiment is the expectation value

$$\langle \hat{\Omega} \rangle = \langle \psi | \hat{\Omega} | \psi \rangle, \quad (1.1)$$

where $\hat{\Omega}$ is the quantum-mechanical operator corresponding to the observable monitored by the experiment. Quantum mechanics is a probabilistic theory. The link between theory and

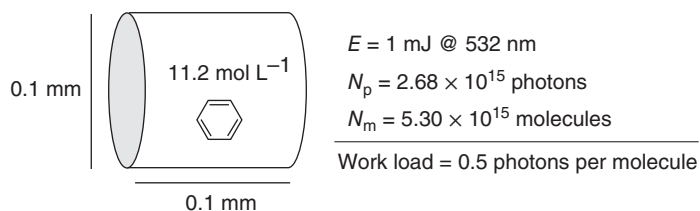


Figure 1.1 Liquid benzene in a small volume corresponding to the focal point of a laser operating at 532 nm and releasing pulses with an energy of 1 mJ.

experiment is made by considering a large number of systems prepared in the same state, prior to switching on the field. If we disregard measurement errors, then the possible outcomes of the individual quantum events are given by the eigenvalues $\{\omega_n\}$ of the operator $\hat{\Omega}$, defined by the eigenvalue equation

$$\hat{\Omega}\psi_n = \omega_n\psi_n. \quad (1.2)$$

Following the postulates of quantum mechanics, the operator $\hat{\Omega}$ is by necessity Hermitian, and the eigenvalues are thus real (corresponding to real-valued observables), and there is a probability $p_n = |\langle\psi_n|\psi\rangle|^2$ for the outcome ω_n in each of the single quantum events, leading to an expectation value that is

$$\langle\hat{\Omega}\rangle = \sum_n \omega_n p_n. \quad (1.3)$$

For example, indirect information about the charge distribution of the atom can be obtained from measurements of the electric dipole moment since the two quantities are connected through an expectation value of the form

$$\mu = \left\langle \psi \left| -e \sum_{i=1}^{N_e} \mathbf{r}_i \right| \psi \right\rangle = \int \mathbf{r} \rho(\mathbf{r}) d^3\mathbf{r}, \quad (1.4)$$

where N_e denotes the number of electrons and e is the elementary charge. However, the electronic charge density can in itself also be expressed as an expectation value

$$\rho(\mathbf{r}) = \left\langle \psi \left| -e \sum_{i=1}^{N_e} \delta(\mathbf{r} - \mathbf{r}_i) \right| \psi \right\rangle, \quad (1.5)$$

and it is possible to probe $\rho(\mathbf{r})$ in for instance X-ray diffraction experiments.

If the external electric field is weak compared to the internal atomic fields, we can expand the induced electronic charge density in a Taylor series with respect to field strength. In Figure 1.2, such a perturbation expansion is illustrated to fifth order for a neon atom. The electric field of strength F is applied along the vertical z -axis (directed upward in the figure) and will tend to pull the positive charge along the field and the negative charge in the opposite direction, resulting in an electronic charge density that can be expanded as

$$\rho(\mathbf{r}) = \rho^{(0)}(\mathbf{r}) + \rho^{(1)}(\mathbf{r})F + \frac{1}{2!}\rho^{(2)}(\mathbf{r})F^2 + \frac{1}{3!}\rho^{(3)}(\mathbf{r})F^3 + \frac{1}{4!}\rho^{(4)}(\mathbf{r})F^4 + \frac{1}{5!}\rho^{(5)}(\mathbf{r})F^5 + \dots. \quad (1.6)$$

The zeroth-order density $\rho^{(0)}$ refers to that of neon in isolation and integrates to $-10e$. It follows from charge conservation that the higher-order densities all integrate to zero. The first-order density $\rho^{(1)}$ shows the charge separation of a dipole, and we then get more and more complicated

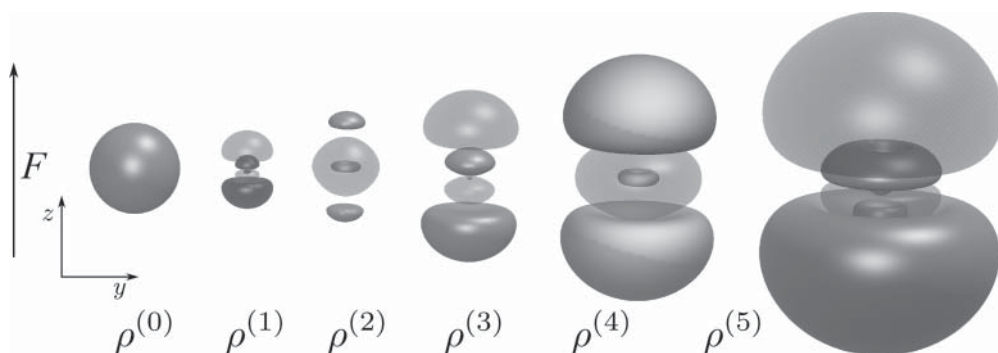


Figure 1.2 Electronic charge density of neon expanded in orders of the applied electric field F . Light and dark gray regions indicate positive and negative values, respectively.

structures with increasing order. It is also clear that the higher the order, the more diffuse the density becomes, and we can expect that an accurate description of higher-order responses put strong requirements on the wave function flexibility at large distances from the nucleus.

If we insert the expansion of the charge density into the expression for the dipole moment [Eq. (1.4)], even orders of the density will not contribute due to symmetry—this is a reflection of the fact that odd-order electric properties vanish in systems with a center of inversion. The resulting induced dipole moment, directed along the z -axis, becomes

$$\mu_z = \left[\int z \rho^{(1)}(\mathbf{r}) d^3\mathbf{r} \right] F + \frac{1}{3!} \left[\int z \rho^{(3)}(\mathbf{r}) d^3\mathbf{r} \right] F^3 + \frac{1}{5!} \left[\int z \rho^{(5)}(\mathbf{r}) d^3\mathbf{r} \right] F^5 + \dots \quad (1.7)$$

This expression defines a series of proportionality constants between the induced dipole moment and powers of the field. The linear and cubic coupling constants are known as the electric dipole polarizability and second-order hyperpolarizability, and they are conventionally denoted by Greek letters α and γ , respectively.¹ It is the focus of this book to understand how these and other molecular properties can be determined by means of quantum-chemical calculations.

When judging the quality of quantum-chemical calculations, one typically considers the choice of method and basis set. These two quantities combined constitute a theoretical model chemistry, that is, a certain approximation level reaching toward the exact solution of the electronic wave function equation. There exist hierarchical series of basis sets that allow for systematic convergence toward the complete one-particle basis set limit, as indicated in Figure 1.3. An increase in the cardinal number of the basis set, from double- to triple- ζ and so forth, improves the description of the ground-state wave function, whereas levels of augmentation with diffuse functions in the basis set are particularly important for the description of the excited electronic states, and therefore also for many molecular properties. Likewise, in conventional wave function-based electronic structure theory, the configuration interaction (CI) and coupled cluster (CC) expansions provide systematic ways to reach the complete N -particle limit. Increased complexity of the theoretical model chemistry comes, however, at a sometimes staggering computational cost. In general, the computational cost scales as n^y , where the base n represents the size of the one-particle basis set, and therefore implicitly scales with the system size, and the exponent y is associated with a given electronic

¹ Hyperpolarizability is a naming convention originally chosen on the basis of the presumed increase of the polarizability in the presence of a strong electric field, whereas hypopolarizability, a name not used any longer, was suggested for systems where there was a decrease.

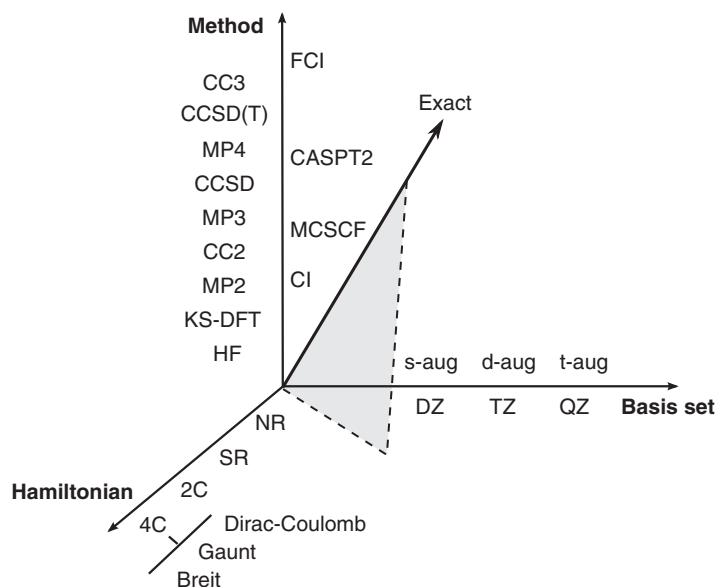


Figure 1.3 Hierarchy of quantum-chemical methods.

structure method. Starting from the Hartree–Fock (HF) method, which formally scales as n^4 , each excitation level treated variationally (perturbatively) increases the exponent by two units (one unit). Accordingly, CC and CI models that include single and double (SD) excitations, CCSD and CISD, respectively, scale as n^6 , but the CC expansion includes electron correlation in a more efficient manner than does CI and has other advantages such as size extensivity. Adding triple excitations perturbatively, as in CCSD(T), increases the exponent to seven. A great achievement of quantum chemistry has been to devise algorithms that significantly reduce these formal scalings.

Kohn–Sham density functional theory (KS-DFT) has become the most widely used method in quantum chemistry due to its efficient treatment of electron correlation at modest computational cost. It formally has the same scaling as HF theory as it also employs a single Slater determinant to describe the reference state of the fictitious noninteracting KS system, constrained to have the same electron density as the real interacting system. The similarity in the parametrization of the reference state has implications in the presentation of the time-dependent response approaches. Until the very final stages, we need not specify which of these two approaches we address, treating them instead in a uniform manner. We will present this formulation, common to time-dependent HF and KS-DFT theories, under the name self-consistent field (SCF) theory. At the end of the day, there is only one drawback that stands out as critical with the KS-DFT technique, and that is the lack of a systematic way to improve the exchange–correlation (XC) functional, which makes it impossible to provide a general ranking of DFT functionals. This leads to the necessity to benchmark the performance of different XC functionals, not only with respect to classes of molecular systems but also with respect to molecular properties.

Theoretical model chemistries are represented as points in the two-dimensional space spanned by the axis of electronic structure methods and that of the basis sets, as shown in Figure 1.3. Methods and basis sets should be chosen in a balanced manner. For instance, combining the HF method with a quadruple- ζ basis set is normally a waste of resources and time. On the other hand, in the 1980s, a widely used theoretical model chemistry was the CISD

method combined with double- ζ basis sets. With increased computational power, however, it was shown numerically that such a combination of methods and basis sets provided reasonable results largely due to a fortuitous cancellation of errors—by increasing the quality of basis sets, the theoretical results moved away from the experimental ones, revealing the intrinsic error of the method. In general, triple- ζ basis sets or better should be used with CC and CI methods to provide an adequate description of the electron–electron cusp region. It should also be noted that standard basis sets are, in most cases, optimized according to energy criteria and that basis set requirements therefore may (and usually do) change when calculating molecular properties. This is easily understood from Figure 1.2 that demonstrates how the induced charge densities governing molecular properties become increasingly more diffuse as compared to the unperturbed density governing the energy.

Since the 1980s, it has become increasingly clear that a theoretical model chemistry providing a balanced description of *all* elements of the periodic table requires the inclusion of relativistic effects. Relativistic effects are normally associated with particles moving at speeds close to the speed of light c , which is the case for electrons in the vicinity of heavy nuclei. The kinetic energy of a 1s-electron in a hydrogen-like ion is

$$K = \frac{Z^2 \hbar^2}{2m_e n^2 a_0^2}. \quad (1.8)$$

It is thus proportional to the square of the nuclear charge Z and ranges from 13.6 eV for hydrogen to about 10^5 eV for the heaviest elements with $Z \approx 100$. In Eq. (1.8), we have introduced the electron mass m_e , the Dirac constant $\hbar$, also known as the reduced Planck constant, and the quantum number n for the electron. For small kinetic energies, when

$$K = \frac{mv^2}{2}, \quad (1.9)$$

we thus expect a linear dependence between the electron speed and the nuclear charge Z , as illustrated in Figure 1.4(b). At high kinetic energies, on the other hand, this classical relation breaks down and we have instead

$$K = (\gamma - 1) mc^2, \quad (1.10)$$

where the Lorentz factor γ

$$\gamma = \frac{1}{\sqrt{1 - (v/c)^2}}, \quad (1.11)$$

will increasingly deviate from its nonrelativistic limiting value of 1, as illustrated in Figure 1.4(a). In the region of gold (atomic number 79) in the periodic table, the speed of 1s-electrons reaches values of about $0.6c$, corresponding to a Lorentz factor of about 1.15. The Lorentz factor appears in the expression for the relativistic mass increase $m = \gamma m_e$, and, since the Bohr radius is inversely proportional to the mass, we expect relativity to contract and stabilize orbitals.

One can of course argue, as did Dirac himself, that our focus on the 1s-orbitals is an extreme case for relativistic effects, and, because the 1s-electrons orbit very close to their respective nuclei, such relativistic effects will play an insignificant role in most of chemistry. However, relativistic effects propagate out to the valence through their modification of orbitals in the core region and, through the requirement of orthogonality, among all orbitals. An illustration of this aspect is given in Figure 1.4(c), in terms of the contraction of the valence ns -orbitals, which is seen to be particularly pronounced for the coinage metal atoms. The direct effect of relativity is to contract orbitals, but this contraction leads to increased screening of the nuclear charge, so there will be a competition between the direct and indirect effects of relativity. In practice, one finds that s - and p -orbitals tend to contract while d - and f -orbitals tend to expand.

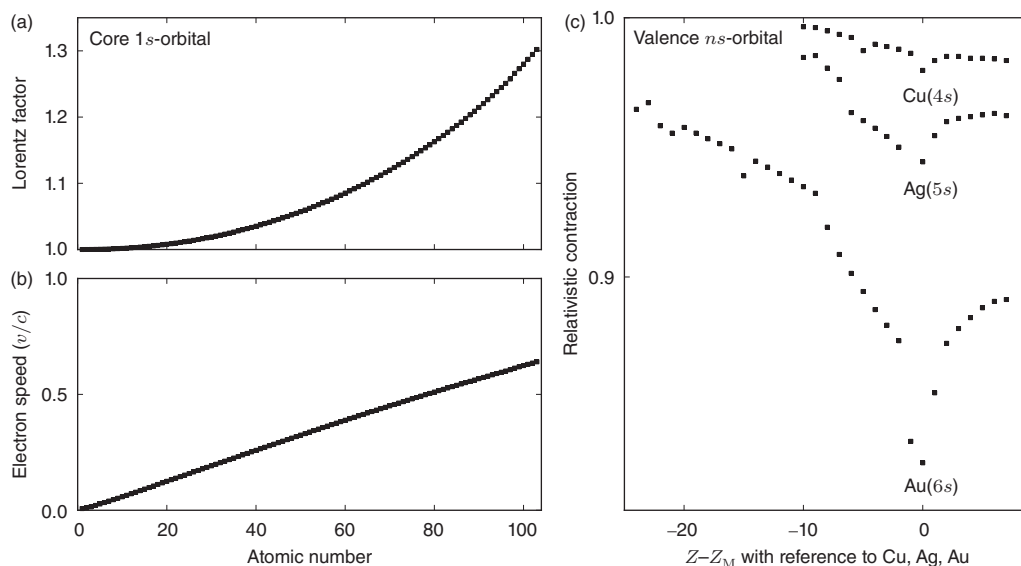


Figure 1.4 Speed of 1s-electrons relative to the speed of light (b) and the corresponding Lorentz factor (a) versus atomic number. Relativistic contractions (c), defined as ratio between relativistic and nonrelativistic HF radial expectation values, of valence ns -orbitals for elements of rows 4, 5, and 6 of the periodic table. Atomic numbers Z are given relative to atomic number Z_M of the coinage metal of each row ($M=\text{Cu, Ag, Au}$).

Relativistic effects associated with the relativistic mass increase of electrons discussed earlier are denoted scalar relativistic effects. A second relativistic effect is spin–orbit interaction. The name and typical operator form $\hat{h}_{\text{SO}} \sim \hat{\mathbf{s}} \cdot \hat{\mathbf{l}}$ suggests an interaction due to a coupling of the spin and angular momentum of the electron. However, this confuses the underlying physics that is simply magnetic induction. Spin–orbit coupling refers to the interaction of the electron spin with the magnetic fields generated by charged particles (nuclei or electrons) in relative motion. The orbital angular momentum operator $\hat{\mathbf{l}}$ appears in the operator describing the spin–orbit interaction induced by nuclei because it encodes the relative motion between the electron and the nucleus. Spin–orbit interactions constitute one of the several categories of intramolecular magnetic interactions that are unaccounted for in a nonrelativistic formulation, and they are often introduced in the nonrelativistic framework in an *ad hoc* manner, as they govern important phenomena in chemistry such as intersystem crossings and phosphorescence. Another example is given by electron paramagnetic resonance (EPR) spectroscopy where one of the parameters, the anisotropy of the molecular g tensor, is rooted in spin–orbit interactions. The spin–orbit interaction couples spin and spatial degrees of freedom, such that spin is no longer a good quantum number. Atomic orbitals will be characterized by their total angular momentum $\mathbf{j} = \mathbf{l} + \mathbf{s}$ with possible magnitude $j = l \pm 1/2$ and corresponding azimuthal quantum number $m_j = m_l + m_s$. As an example, the six degenerate p -orbitals split into two degenerate $p_{1/2}$ - and four degenerate $p_{3/2}$ -orbitals. The energy associated with the $p_{1/2}$ -orbitals is lowered as a consequence of an optimum orientation of electron spin in space, see Figure 1.5(a). This flexibility for the direction of the spin to vary between different points in space is not accounted for in the nonrelativistic realm, where orbitals are either pure α - or pure β -spin orbitals. Interestingly, this is also the case for the relativistic $p_{3/2}$ -orbital with $m_j = \pm 3/2$, as illustrated in Figure 1.5(b). The $m_j = 3/2$ orbital is pure α simply because β spin ($m_s = -1/2$) would require $m_l = 2$, which is not a valid quantum number for $l = 1$ angular functions.

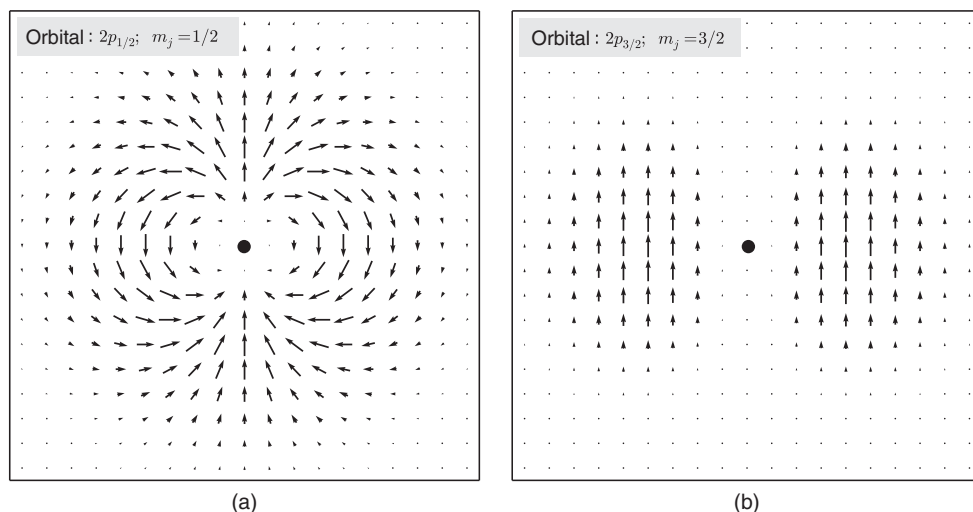


Figure 1.5 Hydrogen spin densities in the xz -plane for the (a) $2p_{1/2}$ ($m_j = 1/2$) and (b) $2p_{3/2}$ ($m_j = 3/2$) orbitals.

Dealing with elements from large parts of the periodic table thus corresponds to a situation in which conventional nonrelativistic calculations of the electronic structure may make little sense and relativistic modifications of the Hamiltonian are required, corresponding to the third axis in Figure 1.3. Scalar relativistic effects can be introduced without significant additional computational cost, whereas the inclusion of spin–orbit interactions requires Hamiltonians based on the four-component Dirac operator or two-component approximations to it. A simple way to introduce relativistic effects is to replace the relativistic core orbitals by effective core potentials, but this choice is only viable when is concerned with valence electron properties.

The choice of Hamiltonian is in principle one *independent* of the two other axes of our chart, which means that the conventional theoretical model chemistries known to us from the nonrelativistic realm can be extended to the relativistic domain. Another important consequence is that the choice of Hamiltonian only comes with a prefactor, independent of system size, to the overall computational cost.

At this point, some readers may feel that a lot of time has been spent discussing relativistic effects, especially if their focus is on molecular systems containing light atoms only. However, it should be kept in mind that a book about molecular properties is essentially about electromagnetic interactions, and electrodynamics—as elegantly summarized by Maxwell’s equations—is a relativistic theory. In the nonrelativistic limit, electrodynamics scales down to electrostatics; that is, in this limit not only do the effects of the finite speed of interactions vanish, but also all magnetic interactions, including magnetic induction. We will demonstrate that nonrelativistic calculations of magnetic properties are made possible by using a relativistic coupling of particles to fields. This is a perfectly valid, pragmatic approach, but implies a mixing of theories with different transformation properties and makes the underlying physics less transparent than a fully relativistic formulation.

Most quantum-chemical calculations describe molecules alone in the universe and at 0 K. This may be a good approximation for dilute gases, since intermolecular interactions are often negligible unless explicitly addressed in the experimental studies. However, the scope of applications for the computational chemist is far wider, including molecules in liquid and solid phases, as well as at interfaces. With molecular response approaches, we can address cases where the properties of the macroscopic system is predominantly determined by the properties

of the molecules, that is, one can regard the effects of the environment as perturbations. This is not, however, the same as saying that one employs the techniques of perturbation theory to account for these interactions; rather, self-consistent schemes are commonly adopted. Either way, the space is divided into regions treated at different levels of accuracy, where the core quantum region is large enough to encompass those parts of the electron density that give rise to the response signal in the experiment. The exterior of the core quantum region is treated by means of classical physics, either in terms of continuum dielectric medium models, such as the polarizable continuum model (PCM), or by the introduction of discrete charge multipole expansions representing the solvent molecules in molecular mechanics (MM) approaches. The latter of the two techniques can be rather straightforwardly combined with molecular dynamics (MD) simulations, be it classical or quantum MD, and it is a common procedure to extract snapshots from MD simulations and perform individual response theory calculations based on each of these snapshots. This is a way to sample the molecular configuration space under given experimental conditions of temperature, liquid, and chromophore densities, and the statistically averaged theoretical spectra represents the final result of the simulation. Figure 1.6 shows one such snapshot taken from simulations of luminescence properties of an oligothiophene chromophore used for optical probing of certain proteins. The partitioning of a solvent or a large molecular system into a target area treated accurately and with the remaining environment being treated in a more approximate manner is often referred to as focused models, and can be considered a computational equivalent of the chemical concept of active or functional regions in a complex molecular system.

This brief introduction aims to show that when the computational chemist needs to evaluate molecular response properties, a number of problems of computational and theoretical nature must be addressed, explicitly or at least assessed with respect to the expected relevance and importance. This book aims to be a valuable aid in this work, by introducing a response theory framework that is general enough to host the most commonly adopted model chemistries while leaving out most details of their implementations. The choice of basis set in the calculation is an obvious parameter that is not of much concern in the formulation of a theory, and, although less obvious, this holds largely true also for the choice of Hamiltonian. The reason for the latter simplification is that, before evaluating specific matrix elements, one can suppress the reference

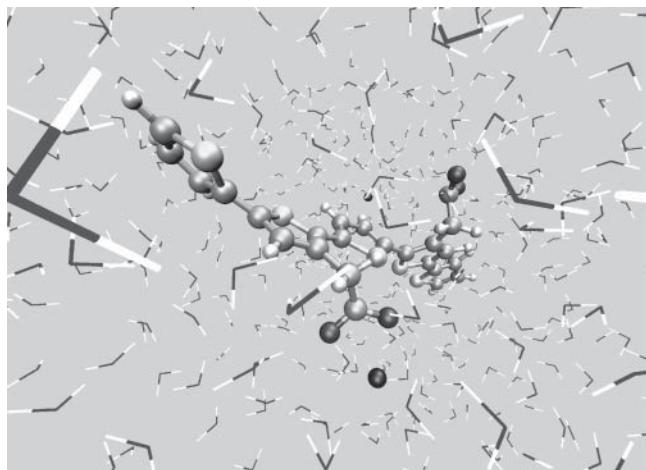


Figure 1.6 Anionic polythiophene acetic acid with sodium counterions in water solution.

to the explicit form of the Hamiltonian and write it in a general form, including summations of one-electron $\hat{h}(i)$ and two-electron $\hat{g}(i, j)$ terms—a form which is common to one-, two-, and four-component Hamiltonians. Even such a seemingly insurmountable complexity as that provided by the interactions with the surrounding environment can, from our perspective, be largely ignored. The key here is to define effective operators that will couple the external classical region to the core quantum region. Once this coupling is achieved, it can be viewed as a modification of the Hamiltonian that fits into our general framework. When it comes to the third axis in Figure 1.3—the electronic structure methods used in the model chemistries—the situation becomes substantially more complicated. In this case, care has to be taken already at the outset of the derivation of the response functions when choosing an equation of motion for the time evolution of the wave function. Although all formulations of exact-state wave mechanics give rise to identical time propagations of a given initial reference state, this is no longer true in approximate-state theories. We will discuss this issue at length and consider two fundamentally different formulations of time-dependent perturbation theory. These two formulations are referred to as the Ehrenfest and the quasi-energy approaches, respectively, and while the former is applicable only to variational electronic structure methods, the latter can also be applied to nonvariational methods.

2

Quantum Mechanics

Quantum mechanics, that mysterious, confusing discipline, which none of us really understands but which we know how to use. It works perfectly, as far as we can tell, in describing physical reality, but it is a ‘counter-intuitive discipline’, as social scientists would say. Quantum mechanics is not a theory, but rather a framework, within which we believe any correct theory must fit.

M. Gell-Mann (1980)

In this chapter we give a brief, and in many respects, an incomplete introduction to quantum mechanics, with a focus on the bare minimum of concepts that are central to the subsequent parts of the book. In addition to providing the necessary basis for the subsequent chapters, this chapter introduces much of the notation that will be used throughout the book.

2.1 Fundamentals

2.1.1 Postulates of Quantum Mechanics

The theory of quantum mechanics rests on a set of postulates as illustrated in Table 2.1 in the case of a single-particle system in one-dimensional (1D) motion. The precise knowledge of the system state and physical observables in the classical case has, in the quantum case, been turned into a situation where the values of observables can only be predicted probabilistically. The coordinate vectors $|x\rangle$ that are often used as a basis for the infinite-dimensional Hilbert space can be imagined (but not realized) as states of perfect particle localization $\langle x'|x\rangle = \delta(x - x')$, but in general the position of the quantum particle is described by the *probability density* (or simply the density)

$$n(x, t) = |\psi(x, t)|^2. \quad (2.3)$$

Changes in the density may be predictable and deterministic in accordance with Postulate D (the time-dependent Schrödinger equation), but they may also be indeterministic and associated with sudden “quantum jumps” to eigenstates of the operators $\hat{\Omega}$ in accordance with Postulate C.

2.1.2 Lagrangian and Hamiltonian Formalisms

From Postulate D, we see that the correspondence between classical and quantum mechanics goes through the Hamiltonian formalism. In order to better understand the construction of the Hermitian operators in quantum mechanics that are associated with physical observables, we

Table 2.1 Postulates in classical and quantum mechanics.

Classical mechanics	Quantum mechanics
<i>State of system</i> A The state of a particle at any given time is given by the two variables $x(t)$ and $p(t)$, that is, a point in a 2D phase space.	The state of a particle is represented by a state vector $\psi(t)\rangle$ of unit norm in a Hilbert space. The projection on the basis $x\rangle$ gives the wave function $\langle x \psi(t)\rangle = \psi(x, t)$ in coordinate space.
<i>Observables</i> B Every dynamical variable ω is a function of x and p: $\omega = \omega(x, p)$.	The independent variables x and p in classical mechanics are represented by the Hermitian operators $\hat{x}$ and $\hat{p}$ that obey the commutator relation $[\hat{x}, \hat{p}] = i\hbar.$ The operator that corresponds to the dynamical variable $\omega(x, p)$ is the Hermitian operator obtained from the substitution $\hat{\Omega}(\hat{x}, \hat{p}) = \omega(x \rightarrow \hat{x}, p \rightarrow \hat{p}).$
<i>Measurements</i> C A measurement of the variable ω on a particle in a state given by x and p gives a value $\omega(x, p)$. After the measurement, the state is left unchanged.	A measurement of the variable, corresponding to operator $\hat{\Omega}$, on a particle in a normalized state $\psi\rangle$ results in an eigenvalue ω with probability $P(\omega) = \langle \omega \psi\rangle ^2$. The state of the system is left in the associated eigenstate $\omega\rangle$ after the measurement.
<i>Equations of motion</i> D The state variables have a time dependence given by Hamilton's equations $\dot{x} = \frac{\partial H}{\partial p}; \quad \dot{p} = -\frac{\partial H}{\partial x}. \quad (2.1)$	The state vector $\psi(t)\rangle$ has a time dependence given by the time-dependent Schrödinger equation $i\hbar \frac{\partial}{\partial t} \psi(t)\rangle = \hat{H} \psi(t)\rangle, \quad (2.2)$ where $\hat{H}(\hat{x}, \hat{p}, t) = H(x \rightarrow \hat{x}, p \rightarrow \hat{p}, t)$ is the quantum mechanical Hamiltonian and H is the classical Hamiltonian.

need to take a closer look at Hamiltonian mechanics. In fact, in order to get the complete picture of quantization, we shall start from *Lagrangian mechanics*. A fascinating aspect of Lagrangian mechanics is that it allows us to derive the equations of motion of a dynamical system of N particles from a single scalar function, the Lagrangian. Let $x \equiv x(t)$ collectively denote the $3N$ coordinates of the particles in the system—mapping out a point in the *configuration space* of the system—with corresponding velocities given by their total time derivatives $\dot{x} \equiv dx/dt$. In particular, let $x(t_a)$ and $x(t_b)$ be the particle coordinates at times t_a and t_b , respectively. We next introduce the *action* S defined as

$$S[x] = \int_{t_a}^{t_b} L(x, \dot{x}, t) dt, \quad (2.4)$$

which is an example of a mathematical object known as a functional. In general, functionals map functions onto complex numbers, in contrast to functions that map sets into sets. In order to explore the possible values of the input function, a functional is often given as a definite

integral over the function variables, that is

$$F[y] = \int_{x_1}^{x_2} f(y(x), y'(x), \dots, x) dx. \quad (2.5)$$

The functional dependence of F on the function $y(x)$ is indicated by square brackets to separate it from arguments of a function that are kept inside parenthesis. In the calculus of variations, a central question is how the value of the functional depends on the variations of the function. For this purpose, the *first variation* of the functional F is defined as

$$\delta F = \lim_{\epsilon \rightarrow 0} \frac{F[y + \epsilon \delta y] - F[y]}{\epsilon}, \quad (2.6)$$

where δy is an unspecified test function that can be viewed as pointing out a direction in the function space along which one takes an infinitesimal step by means of the multiplication with ϵ . A variation δy in the input function is connected to the variation of the functional through the functional derivative

$$\delta F = \int_{x_1}^{x_2} \left(\frac{\delta F}{\delta y(x)} \right) \delta y(x) dx. \quad (2.7)$$

This can be compared to the corresponding relation for functions, where an infinitesimal change in the argument is connected to the change in the function through the (function) derivative

$$dy = \left(\frac{dy}{dx} \right) dx. \quad (2.8)$$

In our applications, the function y is typically to be replaced by either the wave function ψ or the electron charge density ρ , and we will be scanning the respective function spaces in the search for elements that yield zero first-order variations. Since the function variations δy are arbitrary, this implies that the functional derivative itself is zero. In the present case, the functional under study is the action S , which is a functional of the system trajectory $x(t)$ and expressed as an integral over the *Lagrangian* from an initial time t_a to a final time t_b , as seen in Eq. (2.4).

The *principle of stationary action* states that the actual path taken by the system between times t_a and t_b is the one for which an infinitesimal change in the trajectories leaves the action unchanged (stationary), or, in other words, the first variation of the action vanishes

$$\delta S = \int_{t_a}^{t_b} \left[\left(\frac{\partial L}{\partial x} \right) \delta x(t) + \left(\frac{\partial L}{\partial \dot{x}} \right) \delta \dot{x}(t) \right] dt = 0. \quad (2.9)$$

To find the corresponding functional derivative of S with respect to the trajectory $x(t)$ in configuration space, we compare the above expression with the defining relation

$$\delta S = \int_{t_a}^{t_b} \frac{\delta S}{\delta x(t)} \delta x(t) dt. \quad (2.10)$$

We see that the first, but not the second term of Eq. (2.9), has the desired form. In order to bring the latter into the correct form, we carry out an integration by parts

$$\int_{t_a}^{t_b} \left(\frac{\partial L}{\partial \dot{x}} \right) \delta \dot{x}(t) dt = \left(\frac{\partial L}{\partial \dot{x}} \right) \delta x(t) \Big|_{t_a}^{t_b} - \int_{t_a}^{t_b} \left(\frac{d}{dt} \frac{\partial L}{\partial \dot{x}} \right) \delta x(t) dt. \quad (2.11)$$

We now impose that the start- and endpoints of the trajectories are known and fixed such that

$$\delta x(t_a) = \delta x(t_b) = 0. \quad (2.12)$$

Then the first term on the right-hand side of Eq. (2.11) vanishes and we obtain a form of δS that allows us to extract the functional derivative. Setting the functional derivative to zero for all coordinates x_i gives

$$\frac{\delta S}{\delta x_i(t)} = \frac{\partial L}{\partial x_i} - \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{x}_i} \right) = 0; \quad i = 1, \dots, 3N. \quad (2.13)$$

These equations of motion are known as the Euler–Lagrange equations. The condition $\delta S = 0$ implies that functional derivatives for individual coordinates are zero only to the extent that the coordinates are linearly independent. It may be that there are constraints on the motions of the particles; for instance, that our particles are constrained to move on the surface of a sphere, in which case this condition no longer holds. However, if there are k constraints on the form

$$f_\alpha(x, t) = 0; \quad \alpha = 1, \dots, k, \quad (2.14)$$

then we may build them into our formalism by transforming to a set of $3N - k$ linearly independent *generalized coordinates* q_i , collectively denoted as q , which now defines our configuration space. In our derivations we will for simplicity ignore such constraints.

At this point it is important to note that the Lagrangian function is not given *a priori*, but should be chosen to give trajectories in accordance with the experiment. Building new Lagrangians therefore means building new physics. Generally, in the absence of dissipative forces such as friction, the Lagrangian has the form $L = T - U$ where T is the kinetic energy and $U = U(x, \dot{x}, t)$ is called the generalized potential. The kinetic energy is the Lagrangian of free particles, corresponding to the case $U = 0$. In the absence of any constraints, the kinetic energy is a function of velocities only and we may re-write the Euler–Lagrange equations, Eq. (2.13), in the form of Newton’s second law as

$$F_i = \frac{d}{dt} \left(\frac{\partial T}{\partial \dot{x}_i} \right); \quad i = 1, \dots, 3N, \quad (2.15)$$

where the generalized force F_i appears

$$F_i = -\frac{\partial U}{\partial x_i} + \frac{d}{dt} \left(\frac{\partial U}{\partial \dot{x}_i} \right). \quad (2.16)$$

Now let us consider the force $\mathbf{F}$ acting on a single particle. The work done by the force upon the particle along its trajectory between times t_1 and t_2 is given by a line integral

$$W = \int_{\mathbf{r}(t_1)}^{\mathbf{r}(t_2)} \mathbf{F} \cdot d\mathbf{r} = \int_{t_1}^{t_2} \mathbf{F} \cdot \mathbf{v} dt. \quad (2.17)$$

A first thing to note is that if we use Newton’s second law $\mathbf{F} = m\mathbf{a}$, we can show that the total work along the trajectory is equal to the change in kinetic energy $T = \frac{1}{2}mv^2$ between the end-points of the trajectory, that is,

$$W = \int_{\mathbf{r}(t_1)}^{\mathbf{r}(t_2)} \mathbf{F} \cdot d\mathbf{r} = \int_{t_1}^{t_2} m \frac{d\mathbf{v}}{dt} \cdot \mathbf{v} dt = \frac{1}{2}m \int_{t_1}^{t_2} \frac{d(v^2)}{dt} dt = \int_{T(t_1)}^{T(t_2)} dT = T(t_2) - T(t_1). \quad (2.18)$$

Let us assume that the force is monogenic, that is, derivable from a single potential function $U(\mathbf{r}, \mathbf{v}, t)$, as in Eq. (2.16). We can then write the infinitesimal work as

$$\begin{aligned} dW = \mathbf{F} \cdot d\mathbf{r} &= \left[-\left(\frac{\partial U}{\partial \mathbf{r}} \right) + \frac{d}{dt} \left(\frac{\partial U}{\partial \mathbf{v}} \right) \right] \cdot d\mathbf{r} \\ &= -dU + \left(\frac{\partial U}{\partial \mathbf{v}} \right) \cdot d\mathbf{v} + \left(\frac{\partial U}{\partial t} \right) dt + \frac{d}{dt} \left(\frac{\partial U}{\partial \mathbf{v}} \right) \cdot d\mathbf{r}, \end{aligned} \quad (2.19)$$

where, in the final step, we have used the total differential

$$dU = \left(\frac{\partial U}{\partial \mathbf{r}} \right) \cdot d\mathbf{r} + \left(\frac{\partial U}{\partial \mathbf{v}} \right) \cdot d\mathbf{v} + \left(\frac{\partial U}{\partial t} \right) dt, \quad (2.20)$$

of the generalized potential. In many situations, but *not* in the presence of electromagnetic forces, the potential function has no explicit dependence on velocities and time. In such a case, the work along the trajectory is given by the value of the potential function at the endpoints, that is,

$$W = U(t_1) - U(t_2). \quad (2.21)$$

The work is therefore path independent and will for instance be zero around any closed path. Combining the above result with Eq. (2.19) we have

$$T(t_1) + U(t_1) = T(t_2) + U(t_2), \quad (2.22)$$

and the force is said to be *conservative*.

Returning to the general case, let us consider the total time derivative of the work. Starting from Eq. (2.19), we obtain

$$\frac{dW}{dt} = -\frac{dU}{dt} + \left(\frac{\partial U}{\partial \mathbf{v}} \right) \cdot \frac{d\mathbf{v}}{dt} + \frac{\partial U}{\partial t} + \frac{d}{dt} \left(\frac{\partial U}{\partial \mathbf{v}} \right) \cdot \frac{d\mathbf{r}}{dt} = -\frac{dU}{dt} + \frac{d}{dt} \left[\left(\frac{\partial U}{\partial \mathbf{v}} \right) \cdot \mathbf{v} \right] + \frac{\partial U}{\partial t}. \quad (2.23)$$

Keeping in mind that $dW = dT$, we can rearrange this to

$$\frac{d}{dt} \left[T + U - \left(\frac{\partial U}{\partial \mathbf{v}} \right) \cdot \mathbf{v} \right] = \frac{\partial U}{\partial t}. \quad (2.24)$$

We identify the expression in square brackets with energy

$$E = T + V; \quad V = U - \left(\frac{\partial U}{\partial \mathbf{v}} \right) \cdot \mathbf{v}, \quad (2.25)$$

where V is the potential energy.¹ Eq. (2.24) therefore demonstrates that the total energy is conserved if the general potential has no explicit time dependence.

Let us now turn to Hamiltonian mechanics. Again, a scalar function, this time the *Hamiltonian*, takes center stage. It can be obtained from the Lagrangian by a *Legendre transformation*

$$H(x, p, t) = \sum_{j=1}^{3N} \dot{x}_j p_j - L(x, \dot{x}, t). \quad (2.26)$$

A crucial difference between the Hamiltonian and the Lagrangian is that the dependence on velocity $\dot{x}$ in the latter is replaced by dependence on momentum p in the former, achieved through the Legendre transformation. We can also use the Legendre transformation to find the general definition of momentum: The Hamiltonian does not depend on velocity and so by taking the partial derivative with respect to velocity $\dot{x}$ on both sides of Eq. (2.26), we obtain

$$\frac{\partial H}{\partial \dot{x}_i} = 0 \quad \Rightarrow \quad p_i = \frac{\partial L}{\partial \dot{x}_i} = \frac{\partial T}{\partial \dot{x}_i} - \frac{\partial U}{\partial \dot{x}_i}. \quad (2.27)$$

If the generalized potential does not depend on velocity, that is, for a conservative system, the momentum reduces to its usual (nonrelativistic) form $p_i = m\dot{x}_i$, denoted by the *mechanical momentum*. However, as discussed in Chapter 3, magnetic forces depend on particle velocities, and hence the need to start from the correct Lagrangian to get a proper definition of momentum for use in the Hamiltonian, both in classical and quantum mechanics.

1 C. Lanczos. *The Variational Principles of Mechanics*. University of Toronto Press, 1949.

Hamilton's equations, which appear in Postulate D in Eq. (2.1), can be obtained from the Legendre transformation, Eq. (2.26), as well. Taking the partial derivative with respect to momentum we obtain the first equation. Taking the partial derivative with respect to coordinate x and using the Euler–Lagrange equations, Eq. (2.13), gives the second equation. Finally, taking the total time derivative of the Hamiltonian using the chain rule, we obtain

$$\frac{dH}{dt} = \left(\frac{\partial H}{\partial x} \right) \dot{x} + \left(\frac{\partial H}{\partial p} \right) \dot{p} + \frac{\partial H}{\partial t}. \quad (2.28)$$

By using Hamilton's equations, we find that the first two terms cancel. The final result is

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}, \quad (2.29)$$

where the final step is obtained by taking the explicit time derivative of the Legendre transformation. If the Lagrangian has no explicit time dependence, the above expression shows that the Hamiltonian is time independent and thus a constant of motion. In fact, we can obtain Eq. (2.29) directly by taking the total time derivative of the Lagrangian. For a single particle, we get

$$\frac{dL}{dt} = \left(\frac{\partial L}{\partial \mathbf{r}} \right) \cdot \frac{d\mathbf{r}}{dt} + \left(\frac{\partial L}{\partial \mathbf{v}} \right) \cdot \frac{d\mathbf{v}}{dt} + \frac{\partial L}{\partial t} = \frac{d}{dt} \left[\left(\frac{\partial L}{\partial \mathbf{v}} \right) \cdot \mathbf{v} \right] + \frac{\partial L}{\partial t}, \quad (2.30)$$

where the final step is obtained using the Euler–Lagrange equation, Eq. (2.13). By rearrangement, we obtain

$$\frac{d}{dt} [\mathbf{p} \cdot \mathbf{v} - L] = -\frac{\partial L}{\partial t}. \quad (2.31)$$

We see that the Legendre transformation leading to the Hamiltonian function drops out directly in the above expression. We can even go one step further and show that it is equivalent to the energy expression of Eq. (2.25) by writing the Legendre transformation, Eq. (2.26), as

$$H = T + V = \mathbf{v} \cdot \frac{\partial L}{\partial \mathbf{v}} - L \quad (2.32)$$

and carrying it out separately for the components T and U of the Lagrangian. From the kinetic energy, we get

$$\frac{\partial T}{\partial \mathbf{v}} - T = T, \quad (2.33)$$

and from the generalized potential we get directly the potential energy. The Hamiltonian can therefore be identified with the total energy,² which is conserved if there is no explicit time dependence in the generalized potential.

Let us illustrate these concepts with a very simple, albeit not very chemical, example, namely that of the free particle. We can deduce the nonrelativistic (NR) form of this Lagrangian from some simple considerations: (i) for a free particle there is no preferred moment in time (homogeneity of time), so the Lagrangian cannot depend explicitly on time, and (ii) there is no preferred point or direction in space (homogeneity and isotropy of space) so the Lagrangian cannot depend explicitly on the position or the velocity direction. Based upon these considerations, we write the Lagrangian as proportional to the square of the velocity (or speed) of the particle

$$L_0^{\text{NR}} = T = \frac{1}{2} m \dot{x}^2, \quad (2.34)$$

² In the case of constrained motions [Eq. (2.14)], Eq. (2.33) does not hold if there is an explicit time dependence in the functions f_a expressing the constraints. The Hamiltonian can then not be identified with energy.

where the constant of proportionality is fixed by experiment. Using Eq. (2.27), we find that the momentum of the free particle is $p = m\dot{x}$. Next, we obtain the corresponding free-particle Hamiltonian by the Legendre transformation, Eq. (2.26),

$$H_0^{\text{NR}} = m\dot{x}^2 - \frac{1}{2}m\dot{x}^2 = \frac{p^2}{2m}. \quad (2.35)$$

Note that the intermediate expression, referred to as the energy function, does not represent a valid Hamiltonian since it is expressed in terms of the velocity. Only after the velocity is substituted by the momentum does the Hamiltonian become a function of *position and momentum* as required. The velocity in terms of momentum is provided by the first of Hamilton's equations, whereas the second takes the form $\dot{p} = 0$, corresponding to Newton's first law. We again stress the fact that the momentum is defined from the Lagrangian and will therefore hinge upon a correct definition of this function. This point will turn out to be crucial when considering the introduction of electromagnetic fields, as will be discussed in Chapter 3.

The final quantum-mechanical Hamiltonian is obtained by replacing the position and momentum variables by their corresponding operators. These should be chosen such that the canonical commutation relation

$$[x_i, p_j] = i\hbar\delta_{ij}, \quad (2.36)$$

is obeyed. In the *coordinate representation*, we use the substitutions

$$x_i \rightarrow \hat{x}_i = x_i; \quad p_i \rightarrow \hat{p}_i = -i\hbar \frac{\partial}{\partial x_i}. \quad (2.37)$$

Another option is the *momentum representation*

$$x_i \rightarrow \hat{x}_i = i\hbar \frac{\partial}{\partial p_i}; \quad p_i \rightarrow \hat{p}_i = p_i, \quad (2.38)$$

but it is less useful for localized systems such as molecules.

The relativistic (R) free-particle case is more complicated and the appropriate form of the Lagrangian is less evident. In fact, since there is no longer a universal time, we should not single out a specific infinitesimal of time dt in the action [Eq. (2.4)] but rather use the Lorentz-invariant *proper* time τ , which is the time in the reference frame moving with the particle. The variation of the action becomes

$$\delta S = \delta \int_{\tau_a}^{\tau_b} \Lambda(x_\mu, v_\mu, \tau) d\tau = 0; \quad c d\tau = \sqrt{c^2 dt^2 - dx^2}, \quad (2.39)$$

where the relativistic Lagrangian Λ is now a function of the four-position $x_\mu = (x, ict)$, four-velocity $v_\mu = \gamma(\dot{x}, ic)$, and the proper time τ . Following the same line of arguments as for the nonrelativistic free particle, it can be proposed that the relativistic Lagrangian should be proportional to the square of the four-velocity. In fact, the suitable form is $\Lambda = mv_\mu v_\mu = -mc^2$, which clearly is Lorentz invariant. We can go to a specific frame by noting that

$$c d\tau = c dt\gamma^{-1}, \quad (2.40)$$

where the Lorentz factor γ was defined in Eq. (1.11) and can be considered a diagnostic for relativistic effects. Relativistic effects will be important (and γ large) when the speed of the particle v is sizable compared to the speed of light, here denoted by c .

The action integral can now be re-expressed in its familiar form of Eq. (2.4) with the relativistic free-particle Lagrangian

$$L_0^{\text{R}} = -mc^2\gamma^{-1}. \quad (2.41)$$

At first sight, Eqs. (2.34) and (2.41) look very different, but if we expand the inverse Lorentz factor to second order in $(v/c)^2$, we obtain

$$L_0^R = -mc^2 + \frac{1}{2}mv^2 - \frac{1}{8}\frac{mv^4}{c^2}. \quad (2.42)$$

The first term, which does not contribute to the equation of motion since it is constant, is minus the rest mass, the second term is the nonrelativistic free-particle Lagrangian L_0^{NR} , Eq. (2.34), and the third term represents a relativistic correction known as the mass-velocity correction. Using Eq. (2.27), we obtain the relativistic momentum

$$p = \gamma mv, \quad (2.43)$$

which differs from the nonrelativistic definition by the Lorentz factor. The appearance of the Lorentz factor can be associated with a relativistic mass increase. A Legendre transformation of the Lagrangian in accordance with Eq. (2.26) gives

$$H_0^R = \dot{x}p - L_0^R = mc^2\gamma. \quad (2.44)$$

Before the identification of a valid Hamiltonian can be made, we must in this expression replace the velocity hidden in the Lorentz factor by the momentum. However, in order to carry out this replacement, we must proceed via a quadratic form and arrive at

$$(H_0^R)^2 = (pc)^2 + (mc^2)^2 \Rightarrow H_0^R = \pm \sqrt{m^2c^4 + c^2p^2}. \quad (2.45)$$

This is a problematic expression, for many reasons. One is that we face the possibility of free particles with negative sign. Another is that quantization is not straightforward because the momentum operator appears in the square root. We shall, however, postpone this discussion to Section 3.2.2.

2.1.3 Wave Functions and Operators

The wave function $\psi(x, t)$ associated with a single electron is, from a mathematical point of view, an element of a Hilbert space, which is a complete vector space equipped with a norm in the form of a scalar product. The probabilistic interpretation of the wave function implies that it should belong to the Hilbert space L^2 of square-integrable functions. More precisely, it can be enforced that

$$\|\psi\|^2 = \int_{\mathbb{R}^3} \psi^\dagger(x, t)\psi(x, t)d^3\mathbf{r} = 1; \quad \forall t. \quad (2.46)$$

Starting from the vector space $\mathbb{V}^0$ associated with the scalar orbital part, we may successively add further degrees of freedom through a sequence of direct products

$$\mathbb{V} = \mathbb{V}^0 \otimes \mathbb{V}^c \otimes \mathbb{V}^s. \quad (2.47)$$

The electron spin is typically added by multiplying the spatial orbital by spin functions α and β , but we may also proceed in a more formal manner by using their representations

$$(\alpha, \beta) \rightarrow \mathbb{V}^s = \left\{ \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right\}. \quad (2.48)$$

The corresponding representation of the spin operator $\hat{\mathbf{s}} = (\hat{s}_x, \hat{s}_y, \hat{s}_z)$ is given by $\hbar\boldsymbol{\sigma}/2$, where the Pauli spin matrices appear

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (2.49)$$

If we go all the way to the description of the electron provided by the Dirac equation, we also have to include a further two-dimensional part $\mathbb{V}^c$, now associated with the charge conjugation degrees of freedom (changing the sign of the charge but leaving other properties intact) because the Dirac equation describes both electrons and their antiparticles, the positrons. The four components of the Dirac wave function is constructed as

$$\begin{aligned} \psi^{L\alpha}(x, t) \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad \psi^{L\beta}(x, t) \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix}; \\ \psi^{S\alpha}(x, t) \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad \psi^{S\beta}(x, t) \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \end{aligned} \quad (2.50)$$

forming the general wave function as the sum of these four components to arrive at

$$\psi(x, t) = \begin{pmatrix} \psi^{L\alpha} \\ \psi^{L\beta} \\ \psi^{S\alpha} \\ \psi^{S\beta} \end{pmatrix}. \quad (2.51)$$

The label $s = \alpha, \beta$ of each component ψ^{cs} refers to spin. It is important to realize, though, that the label $c = L, S$, referring to large and small components, respectively, does not correspond directly to electronic or positronic degrees of freedom. The entire wave function is in fact either electronic or positronic, but related to that of its antiparticle through charge conjugation. Arriving at the full four-component form of the wave function, we note that the adopted ordering of vector spaces in Eq. (2.47), with $\mathbb{V}^c$ to the left of $\mathbb{V}^s$, leads to a collection of the two large (small) components in the upper (lower) half of the spinor.

In a two-component formalism, one suppresses the degrees of freedom associated with $\mathbb{V}^c$, and, in a one-component nonrelativistic formalism, one may also suppress the reference to $\mathbb{V}^s$ and instead introduce and manage electron spin in a more *ad hoc* manner, as described above. Because the nonrelativistic Hamiltonian is spin independent, one can always separate the spatial and spin parts of the wave function, but regardless of such simplifications in the representation and notation of the wave function, the true nature of the electronic wave function is described by Eq. (2.51), and we refer to such a wave function as a four-spinor.

The corresponding density is

$$n(x, t) = \psi^\dagger(x, t)\psi(x, t) = \sum_c \sum_s^{L, S} |\psi^{cs}(x, t)|^2. \quad (2.52)$$

We will, however, often use the simplified notation of the density as introduced in Eq. (2.3) regardless of the number of components in the wave function.

We extract information that can be related to experiment from wave functions by forming integrals

$$\langle \psi_i | \hat{\Omega} | \psi_j \rangle = \langle \psi_i | \hat{\Omega} \psi_j \rangle. \quad (2.53)$$

In particular, expectation values ($i = j$) connect to observables, whereas the squared norm of transition moments ($i \neq j$) connects to spectral intensities. The right-hand side of Eq. (2.53) stresses that the operator $\hat{\Omega}$ acts to the right, on the ket. The *adjoint* operator $\hat{\Omega}^\dagger$ is defined to give the same result when acting on the bra, that is

$$\langle \hat{\Omega}^\dagger \psi_i | \psi_j \rangle = \langle \psi_j | \hat{\Omega}^\dagger | \psi_i \rangle^* = \langle \psi_i | \hat{\Omega} \psi_j \rangle. \quad (2.54)$$

In more informal usage one writes

$$\langle \psi | \hat{\Omega} = \langle \hat{\Omega}^\dagger \psi |, \quad (2.55)$$

Table 2.2 A selection of quantum mechanical operators.

Operator	Symbol	$\hat{\Omega}^o$	$\hat{\Omega}^c$	$\hat{\Omega}^s$
Identity	$\hat{I}$	$\hat{I}$	I_2	I_2
Position	$\hat{x}$	x	I_2	I_2
Linear momentum	$\hat{p}_x$	$-i\hbar\partial/\partial x$	I_2	I_2
Orbital angular momentum	$\hat{L}_x$	$y\hat{p}_z - z\hat{p}_y$	I_2	I_2
Spin angular momentum	$\frac{\hbar}{2}\hat{\Sigma}_x$	$\hat{I}$	I_2	$\frac{\hbar}{2}\sigma_x$
Nonrelativistic velocity	$\hat{v}_x$	$\hat{p}_x/m$	I_2	I_2
Relativistic velocity	$c\hat{\alpha}_x$	$\hat{I}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$c\sigma_x$
Dirac β -matrix	$\hat{\beta}$	$\hat{I}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	I_2

Operators relating to Cartesian components y and z are obtained by straightforward generalization.

that is, an operator becomes its adjoint when acting to the left.³ Quantum-mechanical operators are selected to be self-adjoint ($\hat{\Omega}^\dagger = \hat{\Omega}$) such that expectation values are real. We usually refer to such operators as Hermitian, and we shall adhere to this usage, although there is a subtle difference between the two terms.⁴

Similar to what we discussed for wave functions, general electronic quantum-mechanical operators are written as a direct product between one part that acts in orbital space $\hat{\Omega}^o$, one that acts in spin space $\hat{\Omega}^s$, and one part associated with the charge conjugation degrees of freedom

$$\hat{\Omega} = \hat{\Omega}^o \otimes \hat{\Omega}^c \otimes \hat{\Omega}^s. \quad (2.56)$$

The formation of a product operator means that we take the product in each individual operator space in accordance with

$$\hat{\Omega}\hat{\Lambda} = \hat{\Omega}^o\hat{\Lambda}^o \otimes \hat{\Omega}^c\hat{\Lambda}^c \otimes \hat{\Omega}^s\hat{\Lambda}^s. \quad (2.57)$$

A small selection of operators is given in Table 2.2. In this table, only one of the Cartesian components is provided for the vectorial operators, but other components follow suit.

With *pure* spatial (or spin) operators, we refer to situations when only $\hat{\Omega}^s$ (or $\hat{\Omega}^o$) is different from the identity operator—the identity operator itself is both a pure spatial and a pure spin operator. It is common practice to allow for simplified notations of operators, for example, to omit the symbol for the direct product or, for pure operators, to omit the identity operators. We shall use such conventions whenever there is no risk of confusion. An example of a pure orbital operator where the identity operators in $\mathbb{V}^s$ and $\mathbb{V}^c$ have been left out is given by the nonrelativistic Hamiltonian in the form given in Eq. (2.35). In dealing with pure operators,

3 From a mathematical point of view this is sloppy, since operators always act to the right. Furthermore, it may be that $\hat{\Omega}$ and its adjoint $\hat{\Omega}^\dagger$ have different domains; see next footnote.

4 The difference between Hermitian and self-adjoint operators arises from the fact that operators are mathematically defined not only by their actions, but also by their domain $D(\hat{\Omega})$; that is, the function space they act on. Hermitian operators have the same action $\hat{\Omega}^\dagger\psi = \hat{\Omega}\psi$ for all functions $\psi \in D(\hat{\Omega})$, but it may be that $D(\hat{\Omega}^\dagger) \neq D(\hat{\Omega})$, contrary to self-adjoint operators. This distinction becomes particularly important for unbounded operators, of which both the position and momentum operators are examples. Bounded operators satisfy $\|\hat{\Omega}\psi\| \leq M \|\psi\|$ for positive constant M and for all functions $\psi \in D(\hat{\Omega})$. A good discussion of this and other subtle points has been discussed in F. Gieres. *Rep. Prog. Phys.*, 63:1893, 2000.

simplifications may be introduced in the notation, and it also makes it possible to separately treat symmetries in the vector and operator spaces. In the nonrelativistic domain, we do so for instance by the construction of spin-adapted wave functions and operators as well as by the use of symmetry-adapted spatial orbitals. In the relativistic domain, on the other hand, spin and spatial degrees of freedom are always coupled with the spin-orbit interactions and, as a consequence, it becomes impossible to separately treat spin and spatial symmetries.

The generalization of the vector space and the operators to a many-electron system is quite straightforward. For instance, the state vectors for two-electron systems are elements of a Hilbert space of the form

$$\mathbb{V} = \mathbb{V}^1 \otimes \mathbb{V}^2, \quad (2.58)$$

and the corresponding operators are given by

$$\hat{\Omega} = \hat{\Omega}'(1) \otimes \hat{\Omega}''(2). \quad (2.59)$$

For many-electron systems, we should keep in mind that electrons belong to the family of fermions and as such they obey the Pauli exclusion principle. This means that no two interacting electrons can be in the same quantum state, and the vector space $\mathbb{V}$ is therefore limited to include only antisymmetric two-particle vectors of the type

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_a(x_1) \otimes \psi_b(x_2) - \psi_b(x_1) \otimes \psi_a(x_2)] = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_a(x_1) & \psi_b(x_1) \\ \psi_a(x_2) & \psi_b(x_2) \end{vmatrix}. \quad (2.60)$$

In the last step we have made use of a determinant to write the antisymmetrized two-particle state, and we have also included an optional, explicit, normalization constant of $1/\sqrt{2}$ together with the assumption that the one-particle state vectors are individually normalized. Such a determinant is known as a Slater determinant in quantum chemistry, and one of the most notable properties of the Slater determinant is that when $a = b$, the wave function vanishes. The Slater determinant thus ensures that the Pauli principle is satisfied. It is clear that the set of all possible Slater determinants constructed from a complete set of one-particle states constitutes the natural basis of $\mathbb{V}$.

Another aspect to note—and which is a reminder in the handling of the vector as well as the operator spaces—is that there are vectors and operators that themselves may not be written as direct products. The general electronic wave function in Eq. (2.51) is one example as it is a sum of four direct product components, and for many-electron systems, a simple example is given by the coupled two-particle operator with a coordinate representation in terms of the Dirac delta function

$$\hat{\Omega} = \delta(x_1 - x_2). \quad (2.61)$$

Let us assume that $\{\psi_n\}$ forms a complete set of orthonormal one-particle functions. We then have

$$\delta(x_1 - x_2) = \langle x_2 | x_1 \rangle = \sum_n \langle x_2 | \psi_n \rangle \langle \psi_n | x_1 \rangle = \sum_n \psi_n^*(x_1) \psi_n(x_2), \quad (2.62)$$

which provides a resolution of $\hat{\Omega}$ into products of one-particle functions. Another and also very important example is given by an instantaneous Coulomb interaction operator. The Coulomb operator for a two-electron system takes the basic form

$$\hat{\Omega} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (2.63)$$

We may replace the orthogonality condition for the basis vectors with a condition of biorthogonality

$$\langle \psi_n | \phi_m \rangle = \delta_{nm}, \quad (2.64)$$

or, equivalently,

$$\sum_n \psi_n^*(\mathbf{r}_1) \phi_n(\mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (2.65)$$

where the operator $\hat{\Omega}$ relates the pairs of biorthogonal vectors

$$\phi_m(\mathbf{r}) = \int \frac{\psi_m(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}'. \quad (2.66)$$

We can then proceed to obtain a resolution of the Coulomb operator according to

$$\begin{aligned} \hat{\Omega} &= \sum_{n,m} \int \int \phi_n(\mathbf{r}_2) \psi_n^*(\mathbf{r}_2') \frac{1}{|\mathbf{r}_1' - \mathbf{r}_2'|} \psi_m(\mathbf{r}_1') \phi_m^*(\mathbf{r}_1) d^3 \mathbf{r}_1' d^3 \mathbf{r}_2' \\ &= \sum_n \phi_n^*(\mathbf{r}_1) \phi_n(\mathbf{r}_2), \end{aligned} \quad (2.67)$$

which provides a resolution of the Coulomb operator in a one-particle basis. Apart from providing a demonstration of how to decouple a two-particle interaction operator, it gives a glimpse into a family of techniques developed to achieve cost-efficient numerical treatments of two-electron integrals.

In this section, we have demonstrated how to construct wave functions and operators for many-electron systems. We emphasize that the foundations of quantum mechanics do not depend on the inclusion or exclusion of relativity, and to the extent possible, the aim has been to give a presentation that is valid in both situations. At the same time, it cannot be avoided that, at a certain level of detail, one must be specific about the choice of Hamiltonian (and other operators) and depending on that choice, there are particular and less general aspects to be explored and utilized in the calculations.

2.2 Time Evolution of Wave Functions

The time evolution of the state vector is given by the time-dependent Schrödinger equation, Postulate D, and is thus dictated by the Hamiltonian. Formally, we may describe the evolution of the wave function from some initial time t_0 by the introduction of a time evolution operator, or time propagator, according to

$$|\psi(t)\rangle = \hat{U}(t, t_0) |\psi(t_0)\rangle, \quad (2.68)$$

An equation of motion for the propagator is obtained by first inserting the above expression into the time-dependent Schrödinger equation. Since $|\psi(t_0)\rangle$ is independent of the time variable t , we obtain a resulting operator equation

$$i\hbar \frac{\partial}{\partial t} \hat{U}(t, t_0) = \hat{H} \hat{U}(t, t_0), \quad (2.69)$$

which is equivalent to the time-dependent Schrödinger equation. Expressions for the time evolution operator are now obtained by integrating this equation. Alternatively, we can proceed via an infinitesimal time evolution operator. For an infinitesimal time interval dt , we may Taylor

expand the wave function to first order and use the time-dependent Schrödinger equation to arrive at

$$|\psi(t_0 + dt)\rangle = |\psi(t_0)\rangle + dt \left. \frac{\partial}{\partial t} |\psi(t)\rangle \right|_{t=t_0} = |\psi(t_0)\rangle - \frac{i}{\hbar} dt \hat{H}(t_0) |\psi(t_0)\rangle, \quad (2.70)$$

which shows that the infinitesimal time evolution operator is

$$\hat{U}(t_0 + dt, t_0) = \hat{I} - \frac{i}{\hbar} dt \hat{H}(t_0). \quad (2.71)$$

Since we only retain the infinitesimal interval dt to first order and since the Hamiltonian is Hermitian, it follows that the infinitesimal time evolution operator is unitary

$$\hat{U}^\dagger(t_0 + dt, t_0) \hat{U}(t_0 + dt, t_0) = \left(\hat{I} + \frac{i}{\hbar} dt \hat{H}^\dagger(t_0) \right) \left(\hat{I} - \frac{i}{\hbar} dt \hat{H}(t_0) \right) = \hat{I}. \quad (2.72)$$

For a finite time interval, we may express the time evolution operator as a product of infinitesimal time evolution operators by dividing the time interval into sufficiently small pieces

$$t_k = t_0 + k \frac{t - t_0}{n}; \quad k = 0, \dots, n, \quad (2.73)$$

which yields a time propagator that reads as

$$\hat{U}(t, t_0) = \lim_{n \rightarrow \infty} \prod_{k=0}^{n-1} \hat{U}(t_{k+1}, t_k) = \lim_{n \rightarrow \infty} \prod_{k=0}^{n-1} \left[1 - \frac{i}{\hbar} \frac{(t - t_0)}{n} \hat{H}(t_k) \right]. \quad (2.74)$$

This product form of individually unitary operators shows that the time evolution for a finite interval is unitary as well. When the Hamiltonian is time independent, the time evolution operator attains a simple exponential form

$$\hat{U}(t, t_0) = \lim_{n \rightarrow \infty} \left[1 - \frac{i}{\hbar} \frac{(t - t_0)}{n} \hat{H} \right]^n = e^{-i\hat{H}(t-t_0)/\hbar}. \quad (2.75)$$

If the initial state happens to be an eigenstate of the Hamiltonian, the time dependence becomes an overall phase factor of the wave function. Let us assume that at time t_0 , the wave function is an eigenstate of $\hat{H}$ denoted by ψ_n with eigenvalue E_n . From Eq. (2.68), we get

$$\psi(x, t) = \psi_n(x) e^{-iE_n(t-t_0)/\hbar}, \quad (2.76)$$

and the particle density, Eq. (2.3), is thus in this case time independent

$$n(x) = |\psi_n(x)|^2. \quad (2.77)$$

For this reason, the eigenstates of the Hamiltonian are also referred to as the *stationary* states of the system and are characterized by being separable in space and time. It is important to note that even for a system in a stationary state there can be an associated nonzero linear momentum as illustrated by the case of the nonrelativistic free particle. The stationary states can in this case be written as

$$\psi_p(x, t) = e^{ipx/\hbar} e^{-iE_p(t-t_0)/\hbar}, \quad (2.78)$$

and the associated linear momentum is given by

$$\langle \hat{p} \rangle = p. \quad (2.79)$$

This corresponds to particle motion at a speed of $v = p/m$ for the stationary state. For a molecular system with bound electrons, a nonzero linear momentum may be found in orbitally degenerate states—such as the p -states in hydrogen, or the E -states in benzene—but the current

density is such that the particle flow into a probing infinitesimal volume ΔV equals the flow out of it.

In general, the initial state will not be an eigenstate of the Hamiltonian, and consequently the density of a system will be time dependent, even when its Hamiltonian is not. This can be illustrated by the nonrelativistic harmonic oscillator with a displaced Gaussian wave packet serving as the initial state at time $t_0 = 0$

$$\psi(x, 0) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-m\omega(x-x_0)^2/2\hbar}, \quad (2.80)$$

centered about $x = x_0$, and the initial wave packet corresponds to a translated ground-state harmonic oscillator wave function. We follow the propagation of the generally complex wave packet ψ and its amplitude $|\psi|$ in Figure 2.1. At the initial time, the phase of the wave function is independent of the spatial coordinate x —in fact the phase is equal to zero since the initial state is real—and the expectation value of the Hermitian, but imaginary linear momentum operator, must therefore vanish. In the initial state, $\langle \hat{p} \rangle = 0$ and $\langle \hat{x} \rangle = x_0$, corresponding to a classical turning point of the harmonic oscillator, as illustrated in the lowest curve plot in Figure 2.1. At a later time, the wave function is found by application of Eq. (2.68). After a short while, at $t = 0.002T$ ($T = 2\pi/\omega$), it will take the form illustrated in the second curve plot. Here it is visible that we plot not only the amplitude but also the complex value of the wave function. The z and y directions are used for plotting the real and imaginary parts of $\psi(x, t)$, respectively, and since we adopt a right-handed coordinate system with a z -axis directed upward, the positive y axis points into the plane of the paper. In this second curve plot, the phase starts to become negative for all values of x .

At a time equal to one quarter of the period time ($t = T/4$), the phase changes rapidly in space corresponding to a maximum in the linear momentum, and we may think of the complex wave function in terms of a corkscrew drilling its way through space. By the time the wave packet

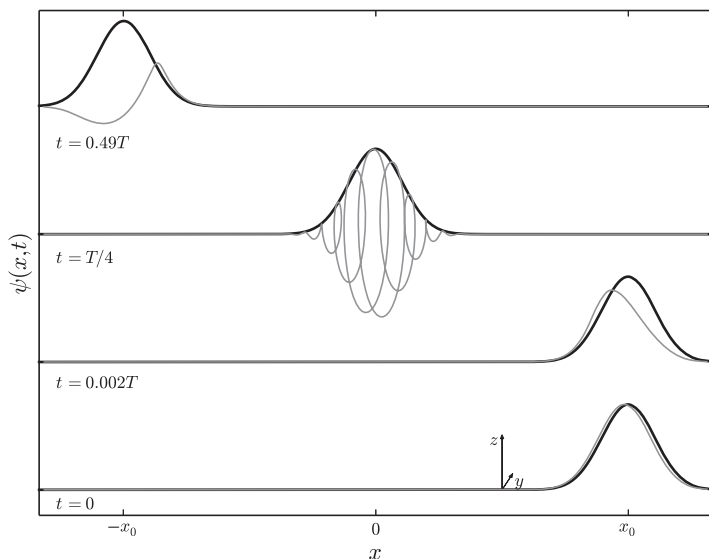


Figure 2.1 Time evolution of a wave packet $\psi(x, t)$ in a harmonic oscillator potential. The black line indicates the amplitude $|\psi|$ of the generally complex wave function. The full wave packet (gray line) has been traced in the complex plane normal to the x -axis; the orientation of the y imaginary axis and z real axis is indicated in the lower curve plot.

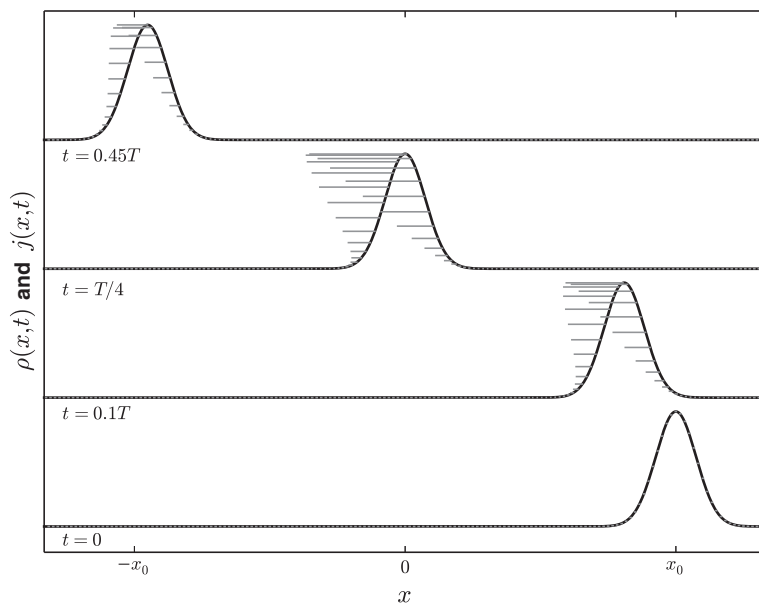


Figure 2.2 Time dependence of the probability current density for the harmonic oscillator.

reaches the other classical turning point, at time $t = T/2$, the phase again becomes independent of the spatial coordinate so that the linear momentum will be zero. The uppermost curve plot is a snapshot taken right before the turning point. This example illustrates that although the changes in the density function are not very dramatic—the density performs an oscillatory motion with a shape that is constant in time—the time and spatial dependencies of the phase function are all the more violent.

Associated with the time-dependent density there is a nonzero probability current density which is

$$j(x, t) = \text{Re} \left[\psi^*(x, t) \frac{\hat{p}}{m} \psi(x, t) \right]. \quad (2.81)$$

For the displaced harmonic oscillator, $j(x, t)$ is illustrated together with the density in Figure 2.2. Different points on the density curve are shown by lines pointing in the direction of the current and with lengths proportional to the size of the current. At the two turning points the current density vanishes since the linear momentum vanishes.

2.3 Time Evolution of Expectation Values

It is interesting to note molecular responses to electromagnetic fields and the time evolution of expectation values, since they correspond to observables such as electric and magnetic moments. The direct approach to this problem is to determine the time dependence of the reference wave function and then *subsequently* form the expectation value to determine the property. However, in a situation where the Hamiltonian depends on time, the direct integration of the Schrödinger equation cannot be carried out to form a simple propagator expression as in Eq. (2.68). Instead, we can establish an equation of motion for the expectation value itself, and from this equation determine the property of interest. The time derivative of

an expectation value takes the form

$$\frac{\partial}{\partial t} \langle \hat{\Omega} \rangle = \left\langle \frac{\partial \psi}{\partial t} | \hat{\Omega} | \psi(t) \right\rangle + \left\langle \psi(t) | \hat{\Omega} | \frac{\partial \psi}{\partial t} \right\rangle + \left\langle \psi(t) | \frac{\partial \hat{\Omega}}{\partial t} | \psi(t) \right\rangle = -\frac{i}{\hbar} \langle [\hat{\Omega}, \hat{H}] \rangle + \left\langle \frac{\partial \hat{\Omega}}{\partial t} \right\rangle, \quad (2.82)$$

where, in the last step, the substitution of the time derivative of the wave function is made with use of the time-dependent Schrödinger equation. This equation is known as the Ehrenfest theorem and it is equivalent to the Schrödinger equation in the sense that it provides neither more nor less information. As an example, we see that, for a system described by a time-independent Hamiltonian, we have

$$\frac{\partial}{\partial t} \langle \hat{H} \rangle = 0. \quad (2.83)$$

To the extent that the Hamiltonian can be identified with the energy as discussed in connection with Eq. (2.33), the above result demonstrates the conservation of energy of the quantum-mechanical system. An example of paramount importance to us is given by molecular systems subjected to external static electromagnetic fields, leading to well-defined, field-dependent energies that can be used as starting points to define molecular properties.

Another important application of the Ehrenfest theorem is provided by $\hat{\Omega} = \hat{I}$ that leads to

$$\frac{\partial}{\partial t} \langle \psi(t) | \psi(t) \rangle = 0, \quad (2.84)$$

showing that the time-dependent Schrödinger equation conserves the norm of the wave function. This implies that

$$\langle \psi(t) | \psi(t) \rangle = \langle \psi(t_0) | \hat{U}^\dagger(t, t_0) \hat{U}(t, t_0) | \psi(t_0) \rangle = \langle \psi(t_0) | \psi(t_0) \rangle, \quad (2.85)$$

which is another demonstration of the fact that the time-evolution operator is unitary.

If we insert the time evolution operator into the expectation value expression for a general operator, we can shift the time dependence of the wave function to the operator

$$\langle \hat{U}(t, t_0) \psi(t_0) | \hat{\Omega} | \hat{U}(t, t_0) \psi(t_0) \rangle = \langle \psi(t_0) | \hat{\Omega}_H(t) | \psi(t_0) \rangle, \quad (2.86)$$

where

$$\hat{\Omega}_H(t) = \hat{U}^\dagger(t, t_0) \hat{\Omega} \hat{U}(t, t_0). \quad (2.87)$$

This corresponds to going from the Schrödinger picture to the Heisenberg picture, a transformation which is indicated by a subscript H on the now generally time-dependent operator. Analogous to the Ehrenfest theorem, we can obtain an equation of motion for operators in the Heisenberg picture by using the equation for the time evolution operator Eq. (2.69). The resulting Heisenberg equation of motion takes the form

$$\frac{d\hat{\Omega}_H(t)}{dt} = -\frac{i}{\hbar} [\hat{\Omega}_H, \hat{H}]_H + \left(\frac{\partial \hat{\Omega}}{\partial t} \right)_H. \quad (2.88)$$

Choosing $\hat{\Omega}$ to be the position operator $\mathbf{r}$ leads to

$$\frac{d\mathbf{r}_H}{dt} = \frac{\hat{\mathbf{p}}_H}{m}. \quad (2.89)$$

In the nonrelativistic domain, this equation suggests that the velocity operator $\mathbf{v}_H$ is the momentum operator divided by the particle mass, which is reasonable. The relativistic result is more intriguing. The velocity operator, defined in Table 2.2, in the Heisenberg picture is denoted by

$\hat{\mathbf{v}}_H^R$ and becomes $c\boldsymbol{\alpha}_H$. Since the square of any of the Dirac $\boldsymbol{\alpha}$ matrices is the unit matrix, this suggests that each component of the particle velocity is on the order of the speed of light c , such that the speed of the particle is beyond c . We must remember, however, that we cannot independently probe the three velocity components in any conceivable experiment because the three Dirac $\boldsymbol{\alpha}$ matrices fail to commute. The curious form of the relativistic velocity operator is a manifestation of the particle motion proposed by Schrödinger, known as *Zitterbewegung*, that is, the highly oscillatory motion due to the interference of positive and negative energy states that is superimposed on the average trajectory of the relativistic electron.

2.4 Variational Principle

A fundamental property of the eigenfunctions $|\omega_n\rangle$ of a Hermitian operator $\hat{\Omega}$ is that they form a complete set and can be used for the formation of an orthonormal basis of our wave function space. The eigenstates and eigenvalues of Hermitian operators are of particular interest to us because they appear in connection with measurements as described in Postulate C in Table 2.1. An arbitrary wave function can be expanded in the basis of eigenstates

$$|\psi\rangle = \sum_n c_n |\omega_n\rangle, \quad (2.90)$$

where the expansion coefficient c_n is to be regarded as a projection coefficient of $|\psi\rangle$ onto the basis vector $|\omega_n\rangle$, that is

$$c_n = \langle\omega_n|\psi\rangle. \quad (2.91)$$

The change from one orthonormal basis $|n\rangle$ to another $|\omega_n\rangle$ represents a unitary transformation according to

$$|\omega_n\rangle = \hat{U}|n\rangle = \sum_k |k\rangle\langle k|\hat{U}|n\rangle = \sum_k |k\rangle U_{kn}, \quad (2.92)$$

and so, if the matrix representation of the operator $\hat{\Omega}$ is Ω in the basis $|n\rangle$, then we can diagonalize this matrix by means of the unitary transformation matrix U

$$D = U^\dagger \Omega U. \quad (2.93)$$

The matrix D now contains the eigenvalues of Ω as diagonal elements. This result provides us with a convenient way to evaluate the function of a matrix $f(\Omega)$ by employing $|\omega_n\rangle$ as an auxiliary basis. The explicit formula becomes

$$f(\Omega) = Uf(D)U^\dagger, \quad (2.94)$$

where $f(D)$ is a diagonal matrix with diagonal elements that are $f(\omega_n)$. A closely related result is that

$$f(\hat{\Omega})|\omega_n\rangle = f(\omega_n)|\omega_n\rangle. \quad (2.95)$$

If one could be granted access to the eigenfunctions (and eigenvalues) of a single Hermitian operator, the first choice would be to pick those of the Hamiltonian. Already from the eigenvalues, or, to be more precise, the differences between them, it is possible to compare the theoretical results to spectral peak positions arising from any of the several different available absorption spectroscopies. Additionally, the energy basis also stands out as one in which certain technical calculations can be performed with ease. Let us for instance assume that the wave

function at time t_0 is known and that we are interested in its time propagation. With the use of an expansion of $\psi(t_0)$ in the energy basis, the result can immediately be written as

$$|\psi(t)\rangle = \hat{U}(t, t_0) \sum_n c_n(t_0) |\psi_n\rangle = \sum_n c_n(t_0) |\psi_n\rangle e^{-iE_n t/\hbar}, \quad (2.96)$$

where the time propagator, being a function of the Hamiltonian, acts on the energy eigenstates in analogy with Eq. (2.95).

As attractive as these results may be, they represent a detour from our destination in this section since the true eigenstates of the Hamiltonian are rarely accessible to us in practical calculations. But the mere fact that the energy basis does exist and that an arbitrary ket vector can *in principle* be expanded in this basis allows for an important conclusion with practical implications in approximate-state theory. Any wave function in approximate-state theory ψ^A can also be expanded in the energy basis according to

$$|\psi^A\rangle = \sum_n c_n^A |\psi_n\rangle. \quad (2.97)$$

The energy E^A associated with the wave function ψ^A is given by the expectation value of the Hamiltonian. For this expectation value, we conclude that

$$E^A = \langle \psi^A | \hat{H} | \psi^A \rangle = \sum_n |c_n^A|^2 E_n \geq E_0, \quad (2.98)$$

where E_0 is the lowest eigenvalue of the Hamiltonian, corresponding to the ground state.⁵ This result is known as the *variational principle*, and it is often used as a measure of the quality of approximate-state wave functions. The wave function ψ^A includes a set of parameters, such as for example, molecular orbital coefficients, and the best values of these parameters are defined as those minimizing the energy E^A . This approach is directly applicable to the optimization of ground-state wave functions, but with some constraints it can also be adopted for the optimization of wave functions representing excited states.

In Eq. (2.98), it is natural to consider E^A as a mapping of wave functions to real numbers. This turns out to represent an example of a functional as introduced in Eq. (2.5). With respect to wave functions, the simplest functional of interest to us is the norm of the wave function

$$N[\psi] = \langle \psi | \psi \rangle. \quad (2.99)$$

This functional is special in the sense that it maps *all* wave functions onto the real number 1, and it is clear that the first variation of N vanishes for all allowed ψ . We can also formulate this as a requirement on the test function $\delta\psi$ (or variations in ψ) that results in

$$\delta N[\psi] = \langle \delta\psi | \psi \rangle + \langle \psi | \delta\psi \rangle = 0. \quad (2.100)$$

This means that, when we move from ψ to $\psi + \varepsilon \delta\psi$ in function space, we are restricted to move in directions given by

$$|\delta\psi\rangle = |\delta\psi^\perp\rangle + i\eta|\psi\rangle; \quad \eta \in \mathcal{R}, \quad (2.101)$$

where $\delta\psi^\perp$ is strictly orthogonal to ψ .

Next we consider the stationary states in quantum mechanics which, as we have seen, are separable in space and time variables. The spatial parts of these particular solutions to the Schrödinger equation fulfill the eigenvalue equation of the Hamiltonian

$$\hat{H}\psi_n(x) = E_n\psi_n(x), \quad (2.102)$$

⁵ This assumes that the Hamiltonian is bounded from below, which is true for the nonrelativistic, but not for the relativistic, case.

often referred to as the time-independent Schrödinger equation. We can isolate the energy E_n in Eq. (2.102) by the multiplication with a bra vector

$$\langle \psi_n | \hat{H} | \psi_n \rangle = E_n. \quad (2.103)$$

It is clear that the multiplication with a vector belonging to the orthogonal complement yields

$$\langle \psi_n^\perp | \hat{H} | \psi_n \rangle = 0. \quad (2.104)$$

For allowed variations of the form given in Eq. (2.101), by using Eq. (2.104) we can conclude that the first variation in the energy functional vanishes

$$\delta E_n = \langle \delta \psi_n | \hat{H} | \psi_n \rangle + \langle \psi_n | \hat{H} | \delta \psi_n \rangle = 0. \quad (2.105)$$

All eigenstates of the Hamiltonian are characterized by having a zero electronic gradient.

In many cases, the Hamiltonian carries a dependence on a parameter F (such as an external static field amplitude), and we can trace the dependence of the eigenfunctions of the Hamiltonian on this parameter. Due to the normalization condition, it is clear that

$$\frac{d}{dF} \langle \psi_n(F) | \psi_n(F) \rangle = \left\langle \frac{d\psi_n}{dF} | \psi_n(F) \right\rangle + \left\langle \psi_n(F) | \frac{d\psi_n}{dF} \right\rangle = 0, \quad (2.106)$$

which tells us that $\delta \psi_n = d\psi_n/dF$ is an allowed variation of the wave function in accordance with Eq. (2.100). The derivative of the energy with respect to the parameter F thereby becomes

$$\begin{aligned} \frac{dE_n}{dF} &= \left\langle \frac{d\psi_n}{dF} | \hat{H} | \psi_n \right\rangle + \left\langle \psi_n | \hat{H} | \frac{d\psi_n}{dF} \right\rangle + \left\langle \psi_n | \frac{\partial \hat{H}}{\partial F} | \psi_n \right\rangle \\ &= \delta E_n + \left\langle \psi_n | \frac{\partial \hat{H}}{\partial F} | \psi_n \right\rangle \\ &= \left\langle \psi_n | \frac{\partial \hat{H}}{\partial F} | \psi_n \right\rangle, \end{aligned} \quad (2.107)$$

where, the last step is based on the fact that the first-order variation in the energy vanishes for all eigenfunctions of the Hamiltonian [see Eq. (2.105)]. The resulting equation is known as the *Hellmann-Feynman theorem*, and it holds as long as the wave function is variationally optimized with respect to the Hamiltonian. As can be seen in Chapter 5, this theorem is highly relevant, since it provides a bridge between energy derivatives and molecular properties, through the left- and right-hand sides of the equation, respectively.

Further Reading

- 1 J. E. Baggott. *Beyond Measure: Modern Physics, Philosophy, and the Meaning of Quantum Theory*. Oxford University Press, 2004.
- 2 B. H. Bransden and C. J. Joachain. *Quantum Mechanics*. Pearson Education, 2000.
- 3 C. Cohen-Tannoudji, B. Diu, and F. Laloë. *Quantum Mechanics*. Wiley, 1977.
- 4 K. G. Dyall and K. Fægri Jr. *Introduction to Relativistic Quantum Chemistry*. Oxford University Press, 2007.
- 5 W. Greiner. *Relativistic Quantum Mechanics*, volume 3. Springer, 1990.
- 6 E. Merzbacher. *Quantum Mechanics*. Wiley, 1998.
- 7 D. J. Tannor. *Introduction to Quantum Mechanics*. University Science Books, 2007.

3

Particles and Fields

From a long view of the history of mankind, seen from, say, ten thousand years from now, there can be little doubt that the most significant event of the nineteenth century will be judged as Maxwell's discovery of the laws of electrodynamics.

R. Feynman

The overall theme of this book is the behavior of molecules when subject to combinations of electromagnetic fields. We therefore need to know how to introduce external electromagnetic fields into our molecular or electronic Hamiltonian. The same procedure can also be used to introduce internal fields not normally taken into account in our unperturbed Hamiltonian, such as those associated with nuclear magnetic moments.

For a system of particles and fields we can generally write the total Hamiltonian as

$$\hat{H} = \hat{H}_p + \hat{H}_{\text{int}} + \hat{H}_f, \quad (3.1)$$

where $\hat{H}_p$, $\hat{H}_f$, and $\hat{H}_{\text{int}}$ describe particles, fields, and their interactions, respectively. In practice one never employs the full Hamiltonian, containing all degrees of freedom associated with both particles and fields. Usually, the external fields are considered fixed and enter the Hamiltonian as parameters rather than as variables. This means that the fields do not react to the particle motion so that the field term $\hat{H}_f$ becomes a constant and contributes a mere shift of the energy that can be neglected. In the framework of classical mechanics, such a constant term will disappear from the equations of motion because they only involve derivatives of the Hamiltonian with respect to the variables (see Postulate D in Chapter 2). It is also possible to go to the other extreme and fix the particle motion, such that the particle term $\hat{H}_p$ disappears from the equations of motion. The particles are now simply sources of electromagnetic fields and the resulting equations of motion in classical electrodynamics are Maxwell's equations.

The latter view is often the perspective of the experimentalist, who will probe a molecular sample with electromagnetic fields and monitor their changes. A simple example is optical activity where the experimentalist observes the rotation of the plane of polarization as light passes through the sample. We thus have, on the one hand, the theoretician studying the responses of the molecular charge density and, on the other hand, the experimentalist studying the responses of the electromagnetic fields. A further distinction to keep in mind is that the theoretician starts from a microscopic description of the system, whereas the experimentalist necessarily, due to the size of the measuring apparatus, works at a macroscopic level. Connecting theory and experiment therefore means that the response of molecules and fields as well as the microscopic and macroscopic descriptions of phenomena must be reconciled.

3.1 Microscopic Maxwell's Equations

3.1.1 General Considerations

Classical electrodynamics is summarized by the celebrated Maxwell's equations. These are first-order differential equations consisting of a homogeneous and an inhomogeneous pair. The homogeneous pair, with right-hand sides being equal to zero, reads as

$$\nabla \cdot \mathbf{B} = 0, \quad (3.2)$$

$$\nabla \times \mathbf{E} + \partial_t \mathbf{B} = \mathbf{0}, \quad (3.3)$$

and thus involves only the electric $\mathbf{E}$ and magnetic $\mathbf{B}$ fields. In the above equations, ∂_t represents the derivative with respect to time, while ∇ is the gradient, or del, operator, which in Cartesian coordinates takes the form

$$\nabla = \partial_x \mathbf{e}_x + \partial_y \mathbf{e}_y + \partial_z \mathbf{e}_z = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right). \quad (3.4)$$

The inhomogeneous pair, with right-hand sides different from zero, is given by

$$\nabla \cdot \mathbf{E} = \rho / \epsilon_0, \quad (3.5)$$

$$\nabla \times \mathbf{B} - \frac{1}{c^2} \partial_t \mathbf{E} = \mu_0 \mathbf{j}, \quad (3.6)$$

in which appear the electric and magnetic constants ϵ_0 and μ_0 , respectively, also known as the permittivity and permeability of free space. These constants are connected to the vacuum speed of light c through the relation

$$\mu_0 \epsilon_0 = \frac{1}{c^2}. \quad (3.7)$$

The inhomogeneous pair adds the sources of the fields, that is, the charge density ρ and current density $\mathbf{j}$. For a classical point charge with charge q , as depicted in Figure 3.1, the charge density reduces to charge times a Dirac delta function fixing the instantaneous position to the trajectory $\mathbf{r}(t)$ of the particle whereas the current density is charge times the instantaneous velocity, or, equivalently,

$$\rho(\mathbf{r}', t) = q \delta(\mathbf{r}' - \mathbf{r}(t)); \quad \mathbf{j}(\mathbf{r}', t) = q \dot{\mathbf{r}}(t) \delta(\mathbf{r}' - \mathbf{r}(t)). \quad (3.8)$$

Maxwell's equations determine the electric and magnetic fields given a set of sources. Equation (3.5) is known as Gauss' law, and by analogy Eq. (3.2) is sometimes called Gauss' law of magnetism. Equation (3.3) corresponds to Faraday's law and describes electromagnetic induction, that is, the generation of an electric field by a magnetic field varying in time.

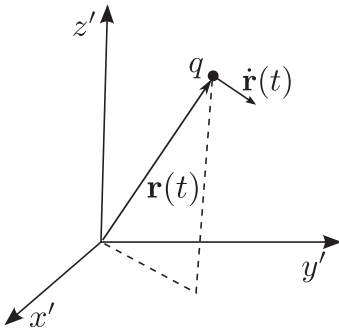


Figure 3.1 A classical point charge in motion.

Equation (3.6) is known as the Ampère–Maxwell equation and enounces that a magnetic field can be generated from currents (Ampère’s law) and time-varying electric fields. The latter effect, pointed out by Maxwell, is important and leads to a relation between the charge and current density as follows:

For a general vector field $\mathbf{F}$, the divergence of its curl vanishes, or in other words,

$$\nabla \cdot (\nabla \times \mathbf{F}) = 0. \quad (3.9)$$

By taking the divergence of Eq. (3.6), we are thereby led to conclude

$$-\frac{1}{c^2} \partial_t (\nabla \cdot \mathbf{E}) = \mu_0 (\nabla \cdot \mathbf{j}), \quad (3.10)$$

and, with further use of Eqs. (3.5) and (3.7), we arrive at

$$(\nabla \cdot \mathbf{j}) + \partial_t \rho = 0. \quad (3.11)$$

This important relation is known as the *continuity equation*, and it expresses the conservation of charge, as will become clear by the consideration to follow.

The integral of the divergence of a vector function $\mathbf{F}$ over some volume V is related to its *flux* through the surface S enclosing the volume according to the *divergence theorem*¹

$$\int_V (\nabla \cdot \mathbf{F}) dV = \int_S (\mathbf{F} \cdot \mathbf{n}) dS. \quad (3.12)$$

On the right-hand side of Eq. (3.12), $\mathbf{n}$ is a unit vector normal to the surface that, by convention, points outward from the surface at each point and dS is an infinitesimal surface element. The right-hand integral thus represents a surface summation of the component of the vector function $\mathbf{F}$ perpendicular to the surface, which in turn encloses the entire volume. An example of the use of the divergence theorem is to recast the continuity equation, Eq. (3.11), in integral form

$$\int_V (\nabla \cdot \mathbf{j}) dV = \int_S (\mathbf{j} \cdot \mathbf{n}) dS = - \int_V \partial_t \rho dV = -\partial_t Q. \quad (3.13)$$

The surface integral represents the charge flowing out of the enclosed volume and it is equal to the negative time derivative of the total charge Q inside the volume, showing that the continuity equation expresses charge conservation.

Correspondingly, by the *curl theorem*², the integral of the outward component of the curl of a vector function over some surface S is related to its *circulation* around a curve C enclosing the surface

$$\int_S (\nabla \times \mathbf{F}) \cdot \mathbf{n} dS = \oint_C (\mathbf{F} \cdot \mathbf{t}) dl. \quad (3.14)$$

On the right-hand side of Eq. (3.14), $\mathbf{t}$ is a unit vector tangential to the curve at each point and dl is an infinitesimal line element such that the line integral samples the tangential component of the vector function along the curve. If the normal vector $\mathbf{n}$ points toward the reader, the line integration follows the tangential vector $\mathbf{t}$ in a counterclockwise sense around the curve.

We can derive a specific form of the divergence theorem by considering the vector function

$$\mathbf{F} = f \mathbf{m}, \quad (3.15)$$

where $\mathbf{m}$ is a constant vector. Its divergence is

$$\nabla \cdot \mathbf{F} = \mathbf{m} \cdot \nabla f. \quad (3.16)$$

1 Other names are Gauss’ theorem, Ostrogradsky’s theorem, and Gauss–Ostrogradsky theorem.

2 Also known as Stokes’ theorem.

From the divergence theorem it then follows that

$$\int_V \nabla f \, dV = \int_S f \mathbf{n} \, dS, \quad (3.17)$$

which is useful when integration by parts is to be done in vector calculus. For a product function with a vanishing surface integral, we have

$$0 = \int_V \nabla(fg) \, dV = \int_V g \nabla f \, dV + \int_V f \nabla g \, dV. \quad (3.18)$$

We can alternatively define the divergence of a vector function $\mathbf{F}$ in a point by a limiting process in which the surrounding volume in Eq. (3.12) tends toward zero, that is

$$\nabla \cdot \mathbf{F} = \lim_{\Delta V \rightarrow 0} \frac{1}{\Delta V} \int_S (\mathbf{F} \cdot \mathbf{n}) \, dS. \quad (3.19)$$

In the same manner, we can define the curl of a vector function $\mathbf{F}$ in a point and in the direction normal to some surface by a limiting process in which the surface area in Eq. (3.14) tends toward zero, that is

$$(\nabla \times \mathbf{F}) \cdot \mathbf{n} = \lim_{\Delta S \rightarrow 0} \frac{1}{\Delta S} \oint_C (\mathbf{F} \cdot \mathbf{t}) \, dl. \quad (3.20)$$

These limiting values are independent of the shape of the corresponding volumes and surfaces.

3.1.2 The Stationary Case

Let us now explore the physical content of Maxwell's equations. We begin by a treatment of the *stationary case* in which the electric and magnetic fields are time independent. Under such circumstances, Maxwell's equations simplify to

$$\begin{aligned} \nabla \cdot \mathbf{B} &= 0; & \nabla \cdot \mathbf{E} &= \rho/\epsilon_0; \\ \nabla \times \mathbf{E} &= \mathbf{0}; & \nabla \times \mathbf{B} &= \mu_0 \mathbf{j}. \end{aligned} \quad (3.21)$$

This restriction on the electric and magnetic fields also implies restrictions on the sources: Taking the divergence of the last relation, we obtain $\nabla \cdot \mathbf{j} = 0$, which corresponds to *steady* currents and, from the continuity equation, time-independent charge densities. In other words, steady current implies that there is no net transport of charge. As a further restriction, if there exist no currents ($\mathbf{j} = \mathbf{0}$), we obtain the *static case*.

The left-hand sides of the stationary Maxwell equations involve the divergence and curl of the electric and magnetic fields. Let us therefore first look at these vector operations in more detail. We note that the sources determine directly the curl and divergence of the fields, but not the fields themselves. *Boundary conditions* must be added to uniquely determine the fields for a given set of sources. The conventional boundary condition is to let $\mathbf{E}$ and $\mathbf{B}$ go to zero at infinite distance from the sources.

As an example, consider the case where there are no sources. Equation (3.21) shows that the divergence and the curl of the electric and magnetic fields are zero everywhere in space. But both vector fields $\mathbf{F}_1 = (0, 0, 0)$ and $\mathbf{F}_2 = (yz, zx, xy)$ have zero divergence and curl and it is not until we impose the boundary condition that we can conclude that $\mathbf{F}_1$ is the only acceptable solution of the two. Can there be additional acceptable solutions? In order to address this question, we employ the vector field identity

$$\nabla^2 \mathbf{F} = \nabla(\nabla \cdot \mathbf{F}) - \nabla \times (\nabla \times \mathbf{F}), \quad (3.22)$$