Molecular Spectroscopy and Quantum Dynamics

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Preface

Molecular Spectroscopy and Quantum Dynamics: Molecules in Motion

> *That everything changes is an unescapable fact which from time immemorial has moved poets, exercised metaphysicians and excited the curiosity of natural philosophers.*
> (C.N. Hinshelwood)

Ever since Max Planck introduced "quanta" in the year 1900 in order to explain the spectral distribution of thermal black body radiation by a "quantum statistical" theory and Bohr's quantum theoretical interpretation of atomic line spectra in 1913, there has been a close relation between spectroscopy and quantum theory. This relation became even closer – one might speak of a fruitful marriage – with the advent of quantum mechanics in 1925. Indeed, quantum mechanics resulted in the discovery of the completely new world of microscopic dynamics, very different from the old world of classical mechanics describing so well the macroscopic dynamics of our daily life including celestial dynamics, which in the old world defined even our quantitative notion of time in terms of hours, days, months, and years. Today quantum dynamics provides an understanding of microscopic phenomena ranging from elementary particle physics to nuclei, atoms, and molecules.

As far as molecular spectroscopy and quantum mechanics are concerned it is probably fair to say that during much of the 20th century the analysis of spectra was dominated by the time-independent "structural" point of view in terms of stationary states, their energies, and wavefunctions. The three classic volumes on "Molecular Spectra and Molecular Structure" published by Gerhard Herzberg between 1939 and 1966 provide beautiful examples for this view with the quantum mechanical analysis of molecular spectra carrying an enormous information content. Further such examples can be found in many other books and the scientific journal literature during these decades. Also the three volumes of the "Handbook of High Resolution Spectroscopy" published in 2011, reporting many great and more recent advances both in theory and experiment, are dominated by a majority of chapters dealing with this stationary state point of view, although time-dependent molecular phenomena are dealt with as well to some extent.

On the other hand, the time-dependent phenomena of molecular kinetics during much of the 20th century were largely understood using the statistical point of view in terms of rate constants, for instance, in the framework of transition state theory, where quantum mechanics plays an important but subordinate, not truly "dynamical" role. This situation changed dramatically during the last decades of the 20th century, driven by the availability of strong, coherent laser radiation allowing for the observation of phenomena such as coherent infrared multiphoton excitation of polyatomic molecules, coherent control, and femtosecond kinetics. The now historical First Conference on "Femtosecond Chemistry" in Berlin 1993 is reflected by a special issue in the Journal of Physical Chemistry (Vol. 97, No. 48, pp. 12423–12649) and the two monumental volumes on "Femtosecond Chemistry" edited by Jörn Manz and Ludger Wöste (VCH, Weinheim 1995). While in Chapter 1 of these volumes the Lord George Porter as a pioneer in the field starting with microsecond to nanosecond kinetics claimed (on page 3) that with the "femtosecond timescale … chemists are near the end of the race against time" the outlook of the last Chapter 27 by another author (on page 781) stated that "considering the possible time scales of molecular processes, it becomes clear that femtosecond (fs) resolution can only be a short time intermediate level in research and our goal must be to approach the yoctoseconds (10^{-9} fs) and beyond". Possibilities for this were outlined establishing the relation between molecular dynamics and the symmetries of high energy physics.

Indeed, it turned out that with the year 2000 vigorous developments in molecular spectroscopy and quantum dynamics on the attosecond time scale became a reality. Truly time-dependent dynamics with "Molecules in Motion" was the theme of a summarizing article in 2001 and recently also of the COST action MOLIM (2014–2019) combining efforts from numerous laboratories in many countries. It thus seemed timely to provide by 2020 a book summarizing some of these recent advances. No single author today can claim adequate expertise of the diverse fields related to these advances and it was therefore the strategy of the present book to collect contributions from leading authors in the field covering theory as well as experiment. Chapter 1 provides an introductory survey of the theoretical foundations by the editors of the book, starting from the basic concepts and dealing with some of the essential theoretical methods of treating time dependent quantum dynamics, including also a discussion of the important role of symmetries. Chapter 2 by Császár, Fábri, and Szidarovszky presents exact numerical methods for stationary state molecular quantum mechanics of polyatomic molecules. This provides the basis for an exact analysis of molecular spectra as also a starting point for many of the approaches towards time-dependent molecular quantum dynamics.

Chapter 3 by Braun, Bayer, Wollenhaupt, and Baumert reports on 2-Dimensional Strong Field Spectroscopy as applied to ultrafast phenomena in electronic dynamics and control schemes for molecules. Chapter 4 by Baykusheva and Wörner provides an overview of the state-of-the-art of experiments in attosecond molecular spectroscopy and dynamics and their theoretical description, including also photoionization and the dynamics of ions and further applications.

Chapter 5 by Gokhberg, Kuleff, and Cederbaum outlines the theoretical description of electronic decay cascades and interatomic Coulombic decay processes in chemical environments after excitation with high energy photons. Chapter 6 by Vaníček and Begušić provides, on the other hand, the theory of vibrationally resolved electronic spectra of polyatomic molecules by means of ab initio semiclassical methods with thawed Gaussians. Chapter 7 by Quack and Seyfang aims at an overview over Atomic and Molecular Tunnelling Processes in Chemistry, one of the central quantum effects in molecular dynamics, where the motion of "heavy" particles are involved (i.e., atoms or nuclei from protons, perhaps also muons or Muonium, to heavy atoms, but not electrons).

Chapter 8 by Ando, Iwasaki, and Yamanouchi demonstrates in beautiful experiments how Ultrafast Femtosecond Dynamics and the High Resolution Spectroscopy of Molecular Cations can be connected. Chapter 9 by Cvitaš and Richardson finally reports results on the quantum dynamics of water clusters as central systems in chemistry. This forms the basis for our spectroscopic and quantum dynamical understanding of the "liquid of life", for which many theoretical and experimental advances have been made in recent years.

To conclude we mention a further aspect of the timeliness of quantum dynamics today: The year 2019 has seen the introduction of important changes to the International System of Units, the SI (Système International). For the first time in the history of mankind, the units of measurements in science as in daily life are based on fundamental natural constants, including the quantum of action h. This concludes finally a development, which started with the atomic Cesium clock as standard (accepted at the 13ième Conférence Générale des Poids et Mesures, 1967) defining the second (as time unit s) through an atomic motion based on a hyperfine structure interval in the ground state of Cs, whereas formerly the second had been defined by an astronomical time interval with the planetary motion of the earth as an appropriate fraction of the tropical year 1900 (31 556 925.9747 s). Later the meter (m) as a unit of length was defined using a definition of the universal speed of light in vacuo, c, and the distance traveled in 1 s. Finally, according to the resolutions of the 26th Conference of Weights and Measures in Paris (2019) the unit for electric current was defined by fixing the value of the elementary charge (e) by definition, and the unit of mass, the kilogram kg, by fixing the Planck constant to a defined value. There is really a spectroscopic idea behind this. Given the relation of the meter and the second, and the definition of the latter through the Cs atom period or its inverse, the frequency ν, the mass m can be related to the frequency via the fundamental equations

$$\nu = \Delta m\, c^2/h,$$

or

$$\Delta m = h\,\nu/c^2.$$

One can thereby obtain a definition of the kg, because one has for the unit of action $1\ \mathrm{J\,s} = 1\ \mathrm{m^2\,kg/s}$, and m and s are already defined. While the experiment to realize such a definition is more complicated, one might say that the relativistic mass of the photon emitted in the hyperfine transition of Cs, or equivalently the mass difference between the Cs atom in the lower state and in the upper state of the transition, is an appropriate fraction of the kg (through $\Delta m \approx 6.777265\ 10^{-41}$ kg), thereby defining the kilogram by "spectroscopy and quantum dynamics". In this sense our current century has become the true quantum century relating the microscopic and macroscopic quantities in terms of their units. These relations might perhaps remain in use for the millennium, in principle.

Thus to complement our preface, we add for the convenience of the readers a brief summary of the new "quantum dynamical" SI and a table of the new values for the fundamental constants, and further constants useful for molecular quantum dynamics and spectroscopy.

We should also conclude with our thanks to the authors contributing to this volume and many colleagues who gave us advice and support, too numerous to mention all of them individually, but they can be found cited in the references of individual chapters, and we give our particular thanks to Frédéric Merkt and Jürgen Stohner, and last but not least also to Regina and Roswitha.

Roberto Marquardt and Martin Quack

Strasbourg and Zurich
July 2020

Summary of the SI (excerpt from the SI Brochure, “The International System of Units (SI)”, Bureau International des Poids et Mesures, 9th edition, 2019)

The SI defines all base units by means of fixed, defined values of certain natural constants.

TABLE 1
The seven defining constants and the corresponding units they define.

Defining constant	Symbol	Numerical value	Unit
hyperfine transition frequency of Cs	$\Delta\nu_{\mathrm{Cs}}$	9 192 631 770	Hz
speed of light in vacuum	c	299 792 458	$\mathrm{m\,s^{-1}}$
Planck constant	h	$6.626\,070\,15 \times 10^{-34}$	J s
elementary charge	e	$1.602\,176\,634 \times 10^{-19}$	C
Boltzmann constant	k	$1.380\,649 \times 10^{-23}$	$\mathrm{J\,K^{-1}}$
Avogadro constant	N_{A}	$6.022\,140\,76 \times 10^{23}$	$\mathrm{mol^{-1}}$
luminous efficacy	K_{cd}	683	$\mathrm{lm\,W^{-1}}$

TABLE 2
The definition of the base units.

The second (s) 1 s = 1 Hz^{-1}	$1\ \mathrm{Hz} = \dfrac{\Delta\nu_{\mathrm{Cs}}}{9\,192\,631\,770} \quad 1\ \mathrm{s} = \dfrac{9\,192\,631\,770}{\Delta\nu_{\mathrm{Cs}}}$
The meter (m)	$1\ \mathrm{m} = \dfrac{c\ \mathrm{s}}{299\,792\,458} = \dfrac{9\,192\,631\,770}{299\,792\,458}\ \dfrac{c}{\Delta\nu_{\mathrm{Cs}}}$
The kilogram (kg)	$1\ \mathrm{kg} = \dfrac{h\ \mathrm{s\,m^{-2}}}{6.626\,070\,15 \times 10^{-34}} = \dfrac{(299\,792\,458)^2}{6.626\,070\,15 \times 10^{-34} \times 9\,192\,631\,770}\ \dfrac{h\,\Delta\nu_{\mathrm{Cs}}}{c^2}$
The ampere (A)	$1\ \mathrm{A} = \dfrac{e\ \mathrm{s^{-1}}}{1.602\,176\,634 \times 10^{-19}} = \dfrac{1}{1.602\,176\,634 \times 10^{-19} \times 9\,192\,631\,770}\ \Delta\nu_{\mathrm{Cs}}\, e$
The kelvin (K)	$1\ \mathrm{K} = \dfrac{1.380\,649 \times 10^{-23}\ \mathrm{kg\,m^2\,s^{-2}}}{k} = \dfrac{1.380\,649 \times 10^{-23}}{6.626\,070\,15 \times 10^{-34} \times 9\,192\,631\,770}\ \dfrac{h\,\Delta\nu_{\mathrm{Cs}}}{k}$
The mole (mol)	$1\ \mathrm{mol} = \dfrac{6.022\,140\,76 \times 10^{23}}{N_{\mathrm{A}}}$
The candela (cd)[a]	$1\ \mathrm{cd} = \dfrac{K_{\mathrm{cd}}\ \mathrm{kg\,m^2\,s^{-3}\,sr^{-1}}}{683} = \dfrac{1}{6.626\,070\,15 \times 10^{-34} \times (9\,192\,631\,770)^2 \times 683}\ h\,\Delta\nu_{\mathrm{Cs}}^2\, K_{\mathrm{cd}}\ \mathrm{sr^{-1}}$

[a] The definition of the candela implies a definition of the numerical value of the luminous efficacy K_{cd}, see the SI Brochure for details.

TABLE 3
SI prefixes for decimal multiples and submultiples of SI units.

Factor	Name	Symbol	Factor	Name	Symbol
10^{1}	deca	da	10^{-1}	deci	d
10^{2}	hecto	h	10^{-2}	centi	c
10^{3}	kilo	k	10^{-3}	milli	m
10^{6}	mega	M	10^{-6}	micro	μ
10^{9}	giga	G	10^{-9}	nano	n
10^{12}	tera	T	10^{-12}	pico	p
10^{15}	peta	P	10^{-15}	femto	f
10^{18}	exa	E	10^{-18}	atto	a
10^{21}	zetta	Z	10^{-21}	zepto	z
10^{24}	yotta	Y	10^{-24}	yocto	y

TABLE 4
Useful physical constants[a].

Quantity	Symbol	Value
magnetic constant	μ_0	1.256 637 062 12(19) $\times 10^{-6}$ N A^{-2}
electric constant	$\varepsilon_0 = 1/\mu_0 c_0{}^2$	8.854 187 8128(13) $\times 10^{-12}$ F m^{-1}
electron mass	m_e	9.109 383 7015(28) $\times 10^{-31}$ kg
proton mass	m_p	1.672 621 923 69(51) $\times 10^{-27}$ kg
neutron mass	m_n	1.674 927 498 04(95) $\times 10^{-27}$ kg
atomic mass constant	$m_\mathrm{u} = 1\ \mathrm{u} = 1\ \mathrm{Da}$	1.660 539 066 60(50) $\times 10^{-27}$ kg
molar mass constant	M_u	0.999 999 999 65(30) $\times 10^{-3}$ kg mol^{-1}
Faraday constant	$F = N_\mathrm{A}\, e$	9.648 533 212... $\times 10^{4}$ C mol^{-1} (exact)
molar gas constant	$R = N_\mathrm{A}\, k$	8.314 462 618... J K^{-1} mol^{-1} (exact)
zero of the Celsius scale		273.15 K (defined)
molar volume of ideal gas, $p = 100$ kPa, $t = 0\,°\mathrm{C}$	V_m	22.710 954 64... dm^3 mol^{-1} (exact)
fine-structure constant	$\alpha = \mu_0 e^2 c_0/2h$	7.297 352 5693(11) $\times 10^{-3}$
	α^{-1}	137.035 999 084(21)
Bohr radius	$a_0 = \varepsilon_0 h^2/\pi m_\mathrm{e} e^2$	5.291 772 109 03(80) $\times 10^{-11}$ m
Hartree energy	$E_\mathrm{h} = h^2/4\pi^2 m_\mathrm{e} a_0{}^2$	4.359 744 722 2071(85) $\times 10^{-18}$ J
Rydberg constant	$R_\infty = E_\mathrm{h}/2hc_0$	1.097 373 156 8160(21) $\times 10^{7}$ m^{-1}
electron volt	eV	1.602 176 634 $\times 10^{-19}$ J (exact)
atomic unit of time	$h/(2\pi\, E_\mathrm{h})$	2.418 884 326 5857(47) $\times 10^{-17}$ s
Bohr magneton	$\mu_\mathrm{B} = eh/4\pi m_\mathrm{e}$	9.274 010 0783(28) $\times 10^{-24}$ J T^{-1}
electron magnetic moment	μ_e	−9.284 764 7043(28) $\times 10^{-24}$ J T^{-1}
Landé g-factor for the free electron	$g_\mathrm{e} = 2\mu_\mathrm{e}/\mu_\mathrm{B}$	−2.002 319 304 362 56(35)
nuclear magneton	$\mu_\mathrm{N} = eh/4\pi m_\mathrm{p}$	5.050 783 7461(15) $\times 10^{-27}$ J T^{-1}
Stefan–Boltzmann constant	$\sigma = 2\pi^5 k^4/15h^3 c_0{}^2$	5.670 374 419... $\times 10^{-8}$ W m^{-2} K^{-4} (exact)
first radiation constant	$c_1 = 2\pi hc_0{}^2$	3.741 771 852... $\times 10^{-16}$ W m^2 (exact)
second radiation constant	$c_2 = hc_0/k$	1.438 776 877... $\times 10^{-2}$ m K (exact)
Newtonian constant of gravitation	G	6.674 30(15) $\times 10^{-11}$ m^3 kg^{-1} s^{-2}
standard acceleration of gravity	g_n	9.806 65 m s^{-2} (defined)
Josephson constant	$K_\mathrm{J} = 2e/h$	483 597.848 4... 10^{9} Hz V^{-1} (exact)
von Klitzing constant	$R_\mathrm{K} = h/e^2$	25 812.807 45... Ω (exact)
Fermi coupling constant	G_F	1.435 8510(8) $\times 10^{-62}$ J m^3
Weak mixing parameter	$\sin^2(\theta_\mathrm{W})$	0.2229(3)

[a] According to the view of https://physics.nist.gov/cuu/Constants/ as per July 31, 2020. The symbol c_0 is an alternative for the symbol of the speed of light in vacuum, c. The value of the weak mixing parameter $\sin^2(\theta_\mathrm{w})$ depends on the scheme used and upon momentum transfer. In the divisions all symbols to the right of the division sign are implied to be in the denominator, thus a/b c d corresponds to: a/(b c d). Defined constants are given in Table 1. Constants which can be calculated exactly from the defined constants are given with a finite number of digits followed by ..., implying more digits than given here. Standard uncertainties are stated for the other constants in parentheses in terms of the last specified digits.

CHAPTER 1

Foundations of Time Dependent Quantum Dynamics of Molecules Under Isolation and in Coherent Electromagnetic Fields

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Abstract

We discuss the foundations of molecules in motion as treated by time-dependent quantum dynamics from very short to long time scales. We consider molecules in isolation, as well as under the influence of coherent electromagnetic radiation, as relevant in many current time-dependent spectroscopic experiments.

1.1 INTRODUCTION

Starting with the analysis by Planck of thermal black body radiation using quantization (Planck, 1900a,b) and the photon concept introduced for the understanding of the photoelectric effect (Einstein, 1905), it was particularly Bohr's work on the analysis of atomic spectra, notably the hydrogen atom and the Balmer formula (Balmer, 1885a,b), which led to an early atomic and molecular "quantum" dynamics in relation to spectroscopy (Bohr, 1913a,b,c; Sommerfeld, 1919). In Bohr's picture of quantum dynamics, stationary atomic and molecular states corresponding to quantized energies, say, E_i and E_f, could undergo radiative transitions by emission of monochromatic radiation of frequency ν_{fi} satisfying the Bohr condition with Planck's constant h:[1]

$$\left|\Delta E_{fi}\right| = \left|E_f - E_i\right| = h\nu_{fi}. \tag{1.1}$$

The corresponding radiative "quantum jump" by emission or absorption of radiation was treated by Einstein quantitatively using statistical concepts (Einstein, 1916a,b, 1917). This was complemented by the more fundamental "quantum mechanics" (Heisenberg, 1925) and "wave mechanics" (Schrödinger, 1926a,b,c,d,e, see also the work of de Broglie, 1926 and Dirac, 1927, 1929), where also the stationary states and transitions between them were central concepts for understanding atomic and molecular spectra and structure (Herzberg, 1945, 1950, 1966). Indeed, high resolution spectroscopy has remained one of the most important tools in understanding atomic and molecular quantum dynamics until today (Merkt and Quack, 2011a,b). It is probably fair to say that during the first half of the 20th century the structural stationary state aspects of spectroscopy were dominant.

In the second half of the 20th century, much driven by the development of the MASER and LASER, the time-dependent aspects of molecular spectroscopy and quantum dynamics have become increasingly important. The dynamics on ever shorter time scales have become accessible experimentally, from microseconds to nanoseconds, to picoseconds and femtoseconds. Today the attosecond (10^{-18} s) time scale is the subject of intense investigations as exemplified by several chapters of the present book. And even the yoctosecond (10^{-24} s) from high energy physics can be shown to be of some relevance for molecular quantum dynamics (Quack, 1994, 1995a,b, 2001, 2006, 2011a,b), as we shall also briefly discuss here in Section 1.2. In parallel to the experimental developments, theoretical approaches were developed for treating explicitly time dependent molecular quantum dynamics, "molecules in motion" (Quack, 2001), which has been also the title

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[1] According to Resolution 1 of the 26th Conference of Weights and Measures (International Bureau of Weights and Measures, 2019), as of 20 May 2019, the Planck constant has the fixed value of $6.626\,070\,15 \cdot 10^{-34}$ Js.

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TABLE 1.1
Summary of currently known elementary (pointlike) particles with their approximate masses and the charges Q in multiples of the elementary charge[a].

Standard model of particle physics: particles				
Leptons ($S = \hbar/2$, fermions)				
	ν_e	ν_μ	ν_τ	$Q = 0e$
Mass m/(GeV c^{-2})	$<2 \times 10^{-9}$	$<2 \times 10^{-4}$	$<2 \times 10^{-2}$	
	e^-	μ^-	τ^-	$Q = -1e$
Mass m/(GeV c^{-2})	5×10^{-4}	0.1	1.8	
Quarks ($S = \hbar/2$, fermions)				
	u_1, u_2, u_3	c_1, c_2, c_3	t_1, t_2, t_3	$Q = 2/3\,e$
Mass m/(GeV c^{-2})	5×10^{-3}	1.3	174	
	d_1, d_2, d_3	s_1, s_2, s_3	b_1, b_2, b_3	$Q = -1/3\,e$
Mass m/(GeV c^{-2})	10^{-2}	0.2	4.3	

[a] After Groom et al., 2000, Perkins, 2000.
The essence of experimental data from high-energy physics can be accounted for by these particles. To each particle, one has an antiparticle of opposite charge (not listed here Schopper, 1999, after Quack and Stohner, 2005, see also Quack, 2006, 2011a and CERN reference cited therein). The recent observations of neutrino oscillations indicate that also $m(\nu_\tau, \nu_\mu)\,c^2 < 2$ eV.

of a most recent transnational and transdisciplinary research effort (COST action "Molecules in Motion").

The goal of the present review is to provide a broad overview of various theoretical aspects and methods of time-dependent molecular quantum dynamics including also some of the foundations of the underlying physics. We shall take here the practical approach to time dependent quantum dynamics, where "time" is simply a parameter to be measured experimentally by some clock (say, an atomic clock) and "measurements" are considered to provide spectroscopically observed quantities. This approach circumvents some problems related to the foundations of time-dependent quantum mechanics. At this point, we thus take the theory as being used like a heuristic model describing and predicting experiments qualitatively and quantitatively (using in essence the "Copenhagen interpretation"). This is not to imply that there are no remaining basic conceptual problems, such as those considered by Bell (2004), Primas (1981), as well as by Fröhlich and Schnubel (2012). We shall return to some of the basic questions in conclusion, but they have no influence on the remainder of the review. We shall start out in Section 1.2 by a brief summary of the current theory of microscopic matter in terms of the standard model of particle physics (SMPP) and time dependent classical and quantum molecular dynamics, with a focus on the time evolution operator approach to time dependent quantum dynamics. In Section 1.3 we discuss in some detail various methods for solving the time-dependent Schrödinger equation (see also Tannor, 2007). Section 1.4 provides a brief discussion of relevant Hamiltonians, Section 1.5 deals with coordinates. In Section 1.6 we treat quite explicitly the time dependent quantum dynamics with excitation by coherent monochromatic radiation. In the concluding Section 1.7 we discuss the role of symmetries, constants of the motion and some related fundamental questions.

1.2 FOUNDATIONS OF MOLECULAR QUANTUM DYNAMICS BETWEEN HIGH ENERGY PHYSICS, CHEMISTRY AND MOLECULAR BIOLOGY

1.2.1 The Standard Model of Particle Physics (SMPP) as a Theory of Microscopic Matter Including the Low Energy Range of Atomic and Molecular Quantum Dynamics

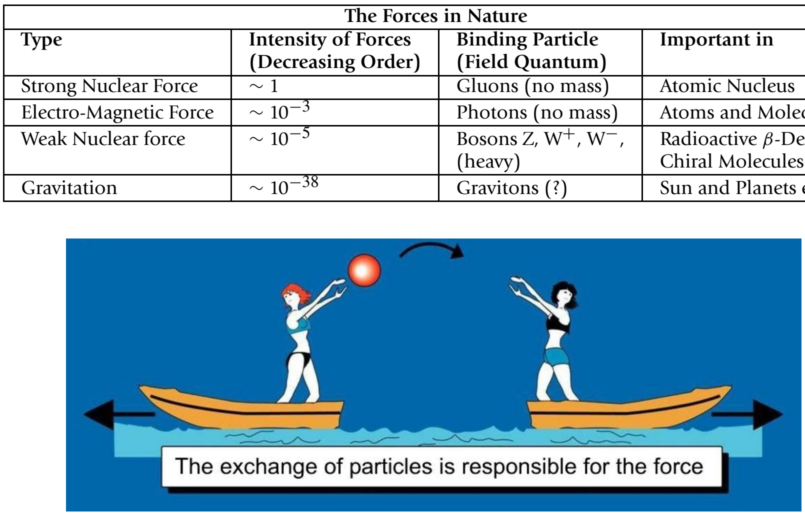
The current theoretical understanding of microscopic matter is summarized in the so-called "Standard Model of Particle Physics". In spite of its modest name, "Model", it is really a fairly comprehensive theory of microscopic matter, particles, and fields, from high energy particle physics to atomic and molecular physics. Microscopic matter is built from elementary particles, which interact by four fundamental forces. These are summarized in Tables 1.1 and 1.2.

Fig. 1.1 summarizes the modern view of the origin of the fundamental interactions as publicized on the web-

TABLE 1.2
Summary of interactions and field particles[a].

Interactions and field particles	Strong	Electromagnetic	Weak	Gravitation
	SU(3)	SU(2) $\otimes$ U(1)		
Relative Strength	1	1/137	$\approx 10^{-5}$	$\approx 10^{-38}$
Range	0.1–1 fm	(∞)	<0.1 fm	(∞)
Gauge bosons ($S = 1\hbar$) (except graviton)	Gluons g_1–g_8	Photon γ	$W^{\pm}$, Z^0	(Still hypothetical), (graviton G, $S = 2\hbar$)
Mass $m/(\text{GeV}\,c^{-2})$	$<10^{-2}$	$<10^{-24}$	≈ 80, ≈ 91	
Acting on particles	Hadrons	Charged	Hadrons, leptons	All
Important in	Atomic nucleus	Atoms and molecules	Radioactive β-decay (neutrons), chiral molecules	Sun, planets, spacecraft, etc.

[a] After Quack and Stohner, 2005, see also Quack, 2006, 2011a.



The Forces in Nature			
Type	**Intensity of Forces (Decreasing Order)**	**Binding Particle (Field Quantum)**	**Important in**
Strong Nuclear Force	~ 1	Gluons (no mass)	Atomic Nucleus
Electro-Magnetic Force	$\sim 10^{-3}$	Photons (no mass)	Atoms and Molecules
Weak Nuclear force	$\sim 10^{-5}$	Bosons Z, W^+, W^-, (heavy)	Radioactive β-Decay, Chiral Molecules
Gravitation	$\sim 10^{-38}$	Gravitons (?)	Sun and Planets etc.

FIG. 1.1 Forces in the standard model of particle physics (SMPP) and important effects. This is taken from the CERN website (CERN, 1992), but the importance of the weak interaction for chiral molecules has been added here from our work following Quack (2006) and by permission of CERN in public domain. We also note (while not mentioned by CERN) that the motif of lightly dressed ladies throwing a ball has been presented in a mosaic at Piazza Armerina, Sicily, 4th Century AD.

site of a large accelerator facility (CERN). According to this view, the electromagnetic force, which is included in the "Dirac-like" ordinary quantum chemistry, leads to the Coulomb repulsion, say, between two electrons in a molecule by means of photons as field particles. In the picture, the two electrons are compared to the ladies on two boats throwing a ball. If we do not see the exchange of the ball, we will observe only the motion of the boats resulting from the transfer of momentum in throwing the ball, and we could interpret this as resulting from a repulsive "force" between the two ladies on the boats. Similarly, we interpret the motion of the electrons resulting from "throwing photons as field particles" as arising from the Coulomb law, which forms the basis of ordinary quantum chemistry. The Coulomb force with the $1/r$ potential energy law is of long range. The other forces arise similarly. The strong force with very short range (0.1 to 1 fm) mediated by the gluons as field particles is important in nuclear physics but has only indirect influence in chemistry by providing the structures of the nuclei, which enter as parameters in chemistry, but there is otherwise usually no need to retain the strong force explicitly in chemistry. The weak force, on the other hand, is mediated by the $W^{\pm}$ and Z^0 bosons as field particles of very high mass (98 dalton for the Z^0 boson, with $m_0 c^2 = 91$ GeV) and short lifetime (0.26 yoctoseconds $= 0.26 \cdot 10^{-24}$ s). This force is thus very weak and of very short range (< 0.1 fm) and one might therefore think that similar to the even weaker gravitational force (mediated by the still hypothetical graviton of spin 2) it should not contribute significantly to the forces between the particles in molecules (nuclei and electrons). Indeed, the weak force, because of its short range, becomes effective in molecules, when the electrons penetrate the nucleus, and then it leads only to a very small perturbation on the molecular dynamics, which ordinarily might be neglected completely. It turns out, however, that because of the different symmetry groups of the electro-magnetic and the electroweak Hamiltonians there arises a fundamentally important, new aspect in the dynamics of chiral molecules, which we therefore have added in our Fig. 1.1 different from the figure from CERN, where this was not originally included.

When applying the standard model of particle physics (SMPP) to the low energy phenomena of atomic and molecular physics, one can do so at several levels of approximation. Firstly, the effects from the fundamental particles and the strong force generating the atomic nuclei are all incorporated in the properties of the specific nucleus, which are its mass, intrinsic angular momentum (usually called "nuclear spin" although it is not a pure spin but has contributions from the orbital motions of the nucleons within the nucleus) parity, magnetic dipole moment, nuclear quadrupole moment, etc. The nuclei as given by these parameters are thus the "effective elementary particles" of atomic and molecular physics, and neither the true elementary particles nor the strong nuclear force mediated by the gluons have to be considered explicitly in the usual approximations. The electrons are retained as elementary particles and interact with the nuclei through the electromagnetic force and the weak force. The gravitational force between electrons and nuclei is sufficiently weak to be neglected except for large assemblies of particles, with a large total mass. The weak nuclear force is frequently neglected, although it can be of importance under special circumstances, particularly in chiral molecules, to which we return in Section 1.7. Usually, quantum chemistry and quantum molecular dynamics retain only the electromagnetic force. One can then introduce further approximations in several steps.

Quantum chemistry in principle treats the quantum dynamics of atoms and molecules by solving the equations of motion for electrons and nuclei to obtain quantum states of atoms (see, for instance, Yamaguchi and Schaefer (2011) as well as Reiher and Wolf (2009)). In molecules one can introduce as a further step the Born–Oppenheimer approximation (or similar "adiabatic" approximations for the electronic structure), which provides effective potentials for the motions of nuclei or "atoms" as effective elementary particles, the dynamics of which is treated in a space of dimension $3N$, where N is the number of atoms, whereas the space of the complete atomic and molecular dynamics would be $3N + 3n$ where n is the often large number of electrons. Cederbaum (2004) presents a particularly clear account of the theory, which is also discussed in more detail in Section 1.4 below. The Born–Oppenheimer potential hypersurfaces defining the forces between atoms are given in a space of dimension $3N - 6(5)$ noting the 3 translational and 3(2) rotational degrees of freedom where the numbers in parentheses apply to linear diatomic molecules. Molecular quantum dynamics can often be treated with these approximations quite successfully in applications to molecular spectroscopy and kinetics (Carrington, 2011; Marquardt and Quack, 2011; Breidung and Thiel, 2011; Tennyson, 2011), see also Chapter 2 of the present book (Császár et al., 2020).

For a wide range of applications one introduces as a further approximation the use of the classical ("Newtonian") equations of motion for the atoms under the influence of the Born–Oppenheimer electronic potentials or other approximate potentials or force fields (Karplus, 2014; van Gunsteren et al., 2006; Car and Parrinello, 1985; Bunker, 1971, 1977; Hase, 1976, 1981, 1998) , see also Chapter 6 (Vaníček and Begušić, 2020).

We shall briefly summarize in the following subsections the foundations of the classical and quantum equations of motion.

1.2.2 Classical Mechanics and Quantum Mechanics

We follow here almost literally the presentation by Merkt and Quack (2011b). Many systems in both classical and quantum mechanics can be described by the motion of interacting point particles, where the physical "particles" are replaced by points of mass m_k with position at the center of mass of the particle. For planetary systems, the "particles" would be the sun and planets with their moons (plus planetoids and artificial satellites, etc.). For atomic and molecular systems the "point particles" can be taken to be the nuclei and electrons to within a very good approximation or the "atoms" within the less good Born–Oppenheimer approximation.

In classical dynamics one describes such an N particle system by a point in the mathematical phase space, which has dimension $6N$ with $3N$ coordinates (for instance, Cartesian coordinates x_k, y_k, z_k for each particle "k") and $3N$ momenta p_{x_k}, p_{y_k}, p_{z_k}. Such a point in phase space moving in time contains all mechanically relevant information of the dynamical system. In the 19th century Hamiltonian formulation of classical mechanics, one writes the Hamiltonian function H as a sum of the kinetic (T) and potential (V) energy,

$$H = T + V, \tag{1.2}$$

in terms of generalized coordinates q_k and their conjugate momenta p_k (Landau and Lifshitz, 1966; Goldstein, 1980; Iro, 2002). Following Hamilton, one obtains the canonical Hamiltonian differential equations of motion accordingly

$$\frac{\mathrm{d}q_k}{\mathrm{d}t} = \dot{q}_k = \left(\frac{\partial H}{\partial p_k}\right), \tag{1.3}$$

$$\frac{\mathrm{d}p_k}{\mathrm{d}t} = \dot{p}_k = -\left(\frac{\partial H}{\partial q_k}\right). \tag{1.4}$$

The dynamics of the classical system is thus obtained from the solution of $6N$ coupled differential equations. Provided that one knows some exact initial condition for one point in phase space, all future and past states of the system in terms of the set $\{q_k(t), p_k(t)\}$ can be calculated exactly. Further considerations arise if the initial state is not known exactly, but we shall not pursue this further.

One approach to quantum dynamics replaces the functions H, p_k, q_k by the corresponding quantum mechanical operators ($\hat{H}$, $\hat{p}_k$, $\hat{q}_k$) or their matrix representations ($\boldsymbol{H}$, $\boldsymbol{p}_k$, $\boldsymbol{q}_k$) resulting in the Heisenberg equations of motion (Heisenberg, 1925; Dirac, 1958):

$$\frac{\mathrm{d}\hat{q}_k}{\mathrm{d}t} = \frac{2\pi}{\mathrm{i}h}\left[\hat{q}_k, \hat{H}\right], \tag{1.5}$$

$$\frac{\mathrm{d}\hat{p}_k}{\mathrm{d}t} = \frac{2\pi}{\mathrm{i}h}\left[\hat{p}_k, \hat{H}\right], \tag{1.6}$$

which involve now Planck's quantum of action (or constant) h, and $\mathrm{i} = \sqrt{-1}$. Following Dirac (1958), these equations are the quantum-mechanical equivalent of the Poisson-bracket formulation of classical mechanics, and one can, in fact, derive the corresponding classical equations of motion from the Heisenberg equations of motion, if one uses quantum mechanics as the more fundamental starting point, as discussed by Sakurai (1985), for instance. Eqs. (1.5) and (1.6) contain the commutator of two operators $\hat{A}$ and $\hat{B}$ in general notation,

$$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}. \tag{1.7}$$

As quantum mechanical operators and their matrix representations do not in general commute, this introduces a new element into quantum mechanics as compared to classical mechanics. For instance, in Cartesian coordinates the coordinate operator x_k is simply multiplicative, while the momentum operator $\hat{p}_{x_k}$ is given by the differential operator

$$\hat{p}_{x_k} = \frac{h}{2\pi\mathrm{i}}\frac{\partial}{\partial x_k}, \tag{1.8}$$

leading to the commutator

$$\left[\hat{x}_k, \hat{p}_{x_k}\right] = \mathrm{i}h/(2\pi) \tag{1.9}$$

and the corresponding Heisenberg uncertainty relation (Messiah, 1961)

$$\Delta x_k \Delta p_{x_k} \geq h/(4\pi) \tag{1.10}$$

where Δx_k and Δp_{x_k} are defined as the root mean square deviations of the corresponding ideal measurement results for the coordinates x_k and momenta p_{x_k}. Similar equations apply to y_k, z_k with p_{y_k}, p_{z_k}, etc., for all particles labeled by their index k. It is thus impossible in quantum mechanical systems to know experimentally the position of the "point in phase space" to better than allowed by the Heisenberg uncertainty relation in a quantum mechanical state. In classical mechanics, on the other hand, x_k and p_{x_k}, etc., commute, and the point in phase space can be defined and measured with arbitrary accuracy, in principle.

A somewhat more complex reasoning leads to a similar "fourth" uncertainty relation for energy E and time t,

$$\Delta E \Delta t \geq h/(4\pi). \tag{1.11}$$

We note that Eqs. (1.10) and (1.11) are strictly *inequalities*, not equations in the proper sense. Depending on the system considered, the uncertainty can be *larger* than what would be given by the strict equation. If the equality sign in Eqs. (1.10), (1.11) applies, one speaks of a "minimum uncertainty state or wavepacket[2]" (see below). The commutators in Eqs. (1.5), (1.6) are readily obtained from the form of the kinetic energy operator in Cartesian coordinates:

$$\hat{T} = \frac{1}{2}\sum_{k=1}^{N}\left(\frac{\hat{p}_{x_k}^2}{m_k} + \frac{\hat{p}_{y_k}^2}{m_k} + \frac{\hat{p}_{z_k}^2}{m_k}\right) \tag{1.12}$$

and

$$\hat{H} = \hat{T} + \hat{V} \tag{1.13}$$

if the potential energy $\hat{V}$ is a multiplicative function of the coordinates of the particles (for instance, with the Coulomb potential for charged particles).

While this so-called Heisenberg representation of quantum mechanics is of use for some formal aspects and also certain calculations, frequently the "Schrödinger representation" turns out to be useful in spectroscopy and quantum dynamics.

1.2.3 Time Evolution Operator Formulation of Quantum Dynamics

The time dependence of the operators $\hat{p}_k$ and $\hat{q}_k$ in the Heisenberg equations of motion and, indeed, the time dependence of every operator $\hat{Q}$ in the Heisenberg representation is given by Eq. (1.14),

$$\hat{Q}(t) = \hat{U}^{\dagger}(t,t_0)\hat{Q}(t_0)\hat{U}(t,t_0). \tag{1.14}$$

Here t_0 is the initial time and t the time after some evolution. The operator $\hat{U}$ satisfies the differential equation

$$\mathrm{i}\frac{h}{2\pi}\frac{\partial\hat{U}(t,t_0)}{\partial t} = \hat{H}\hat{U}(t,t_0). \tag{1.15}$$

Thus, in general one has to solve this differential equation in order to obtain $\hat{U}(t,t_0)$. If, however, $\hat{H}$ does not depend upon time, $\hat{U}(t,t_0)$ is given by the equation

$$\hat{U}(t,t_0) = \exp\left[-\frac{2\pi\mathrm{i}}{h}\hat{H}\cdot(t-t_0)\right]. \tag{1.16}$$

The exponential function of an operator $\hat{Q}$, as well as that of a matrix representation of this operator, is given by Eq. (1.17),

$$\exp(\hat{Q}) = \sum_{n=0}^{\infty}\frac{\hat{Q}^n}{n!}, \tag{1.17}$$

$\hat{U}(t,t_0)$ thus "propagates" the operators $\hat{p}_k$, $\hat{q}_k$, etc., from time t_0 to time t and is often called "propagator". Also $\hat{U}$ provides the solution for the time-dependent Schrödinger equation for the wave function[2] Ψ,

$$\mathrm{i}\frac{h}{2\pi}\frac{\partial\Psi(x_1,y_1,z_1,\ldots,x_n,y_n,z_n,t)}{\partial t} = \hat{H}\,\Psi(x_1,y_1,z_1,\ldots,x_n,y_n,z_n,t). \tag{1.18}$$

In the Schrödinger formulation of quantum mechanics ("wave mechanics"), one introduces the "wave function" $\Psi(x_1,y_1,z_1,\ldots x_n,y_n,z_n,t)$ depending on the particle coordinates and time, and satisfying the differential equation (time-dependent Schrödinger equation, Eq. (1.18)).

The physical significance of the wave function Ψ (also called state function) can be visualized by the probability density

$$\begin{aligned} P(x_1,y_1,z_1,\ldots,x_n,y_n,z_n,t) &= \Psi(x_1,\ldots,z_n,t)\Psi^*(x_1,\ldots,z_n,t) \\ &= |\Psi(x_1,\ldots,z_n,t)|^2 \end{aligned} \tag{1.19}$$

where P is real, positive or zero, whereas Ψ is, in general, a complex-valued function. Moreover, $P(x_1,y_1,z_1,\ldots,z_n\,t)\,\mathrm{d}x_1\mathrm{d}y_1\mathrm{d}z_1\cdots\mathrm{d}z_n$ gives the probability of finding the quantum mechanical system of point particles in the volume element $(\mathrm{d}x_1\cdots\mathrm{d}z_n)$ at position $(x_1,\ldots,z_n)$ at time t.

The differential operator in Eq. (1.18) is sometimes called energy operator $\hat{E}$,

$$\hat{E} = \mathrm{i}\frac{h}{2\pi}\frac{\partial}{\partial t}, \tag{1.20}$$

thus one can write

$$\hat{E}\,\Psi(r,t) = \hat{H}\,\Psi(r,t), \tag{1.21}$$

where we introduce the convention that r represents in general a complete set of space (and spin) coordinates and includes the special case of systems depending only on one coordinate which then can be called r.

The solution of Eq. (1.18) has the form

$$\Psi(r,t) = \hat{U}(t,t_0)\Psi(r,t_0). \tag{1.22}$$

One of the most important properties of Ψ is that it satisfies the principle of linear superposition. If $\Psi_1(r,t)$

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[2] In this book, these terms are written in a single word 'wavepacket', 'wavefunction' or in separate words 'wave packet', 'wave function'; while the separate form is more frequently found, and is also sometimes separated by a hyphen, all forms are currently being used and are accepted.

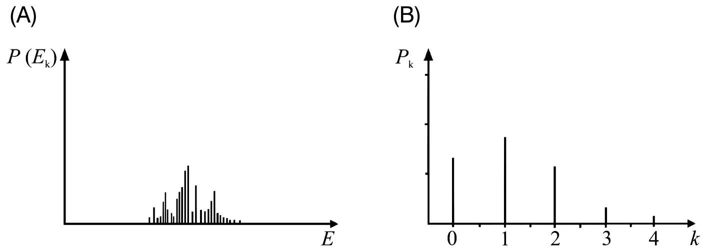

FIG. 1.2 Spectral decomposition schemes: Illustration of spectral decomposition of a time-dependent state where $p_k(E_k) = |c_k|^2$ is the probability of measuring the eigenvalue E_k in the time-dependent state given by $\Psi(r,t)$: (A) irregular spectrum and distribution; (B) harmonic oscillator with a Poisson distribution (after Merkt and Quack, 2011b).

and $\Psi_2(r,t)$ satisfy Eq. (1.18) as possible representations of the dynamical state of the system, then the linear superposition

$$\Psi(r,t) = c_1\Psi_1(r,t) + c_2\Psi_2(r,t) \tag{1.23}$$

is also a possible dynamical state satisfying Eq. (1.18), as is readily shown, given that $\hat{H}$ is a linear operator and c_1, c_2 are complex coefficients. However, $\Psi(r,t)$, in general, is not an eigenstate of $\hat{H}$. In the special case of stationary states leading to the time-independent Schrödinger equation, we assume that $\hat{H}$ does not depend on time. We consider the special case where $\Psi_k(r,t)$ is an eigenfunction of $\hat{H}$ with eigenvalue E_k. Thus

$$\hat{H}\,\Psi_k(r,t) = \hat{E}\Psi_k(r,t) = E_k\Psi_k(r,t). \tag{1.24}$$

The solution for this special case is given by Eq. (1.25),

$$\mathrm{i}\frac{h}{2\pi}\frac{\partial\Psi_k(r,t)}{\partial t} = E_k\Psi_k(r,t) = E_k\psi_k(r)\exp(-2\pi\mathrm{i}\frac{E_k t}{h}), \tag{1.25}$$

where, $\hat{H}$ being independent of time, one can divide both sides in Eq. (1.24) by $\exp(-2\pi\mathrm{i}E_k t/h)$ and obtain

$$\hat{H}\,\psi_k(r) = E_k\psi_k(r). \tag{1.26}$$

The eigenfunctions of $\hat{H}$ are called *stationary states*,

$$\Psi_k(r,t) = \psi_k(r)\exp(-2\pi\mathrm{i}\frac{E_k t}{h}). \tag{1.27}$$

The name for stationary states is related to the time independence of the corresponding probability density

$$P(r,t) = \Psi_k(r,t)\,\Psi_k^*(r,t) = |\Psi_k(r,t)|^2 = |\psi_k(r)|^2\,. \tag{1.28}$$

The time-independent Schrödinger equation (1.26) is thus derived as a special case from the time-dependent Schrödinger equation.

Making use of the superposition principle (Eq. (1.23)), the general solution of the Schrödinger equation results as follows:

$$\Psi(r,t) = \sum_k c_k\psi_k(r)\exp(-2\pi\mathrm{i}\frac{E_k t}{h}) = \sum_k c_k\Psi_k(r,t). \tag{1.29}$$

If $\hat{H}$ does not depend on time, such as in the case of isolated atomic and molecular systems, the coefficients c_k are time independent, generally complex coefficients. According to the principle of spectral decomposition, the probability of measuring energy E_k in the time-dependent state given by Eq. (1.29) is

$$p_k\,(E_k) = |c_k|^2 = c_k c_k^*. \tag{1.30}$$

Thus, with time-independent $\hat{H}$, the p_k are independent of time, as is also the expectation value of the energy

$$\langle E(t)\rangle = \sum |c_k|^2\,E_k. \tag{1.31}$$

Fig. 1.2 illustrates the spectral decomposition for two types of spectra. The energy in a time-dependent state is therefore not a well-defined quantity but is characterized by a statistical distribution given by p_k in Eq. (1.30). This distribution satisfies the uncertainty relation given by Eq. (1.11). For further discussion and the numerical approaches to realize solutions of the Schrödinger equation, we refer to Section 1.3.

We conclude this section by mentioning the special limiting case of scattering theory and S-matrix theory used therein. Formally, the S-matrix in a collision between two (or more) collision partners can be considered to be a limiting case of the matrix representation of the time evolution operator in the basis of the scattering channels related to the quantum states of the scattering partners at infinite distance "i" before and "f" after the collision), i.e.,

$$S_{fi} = U_{fi}(t = +\infty, t = -\infty). \tag{1.32}$$

For a more detailed introduction of collision and S-matrix theory, we refer to the books of Newton (1966), Clary (1986), and Schatz and Ratner (1993).

1.2.4 Further Approaches to Quantum Mechanics and Molecular Dynamics

The Schrödinger and Heisenberg approaches are certainly the most widely used approaches towards time dependent and time independent quantum dynamics (often introduced as the Schrödinger and Heisenberg "pictures" of quantum mechanics). We shall briefly mention here a few further approaches to molecular quantum dynamics which have found wider use. Apart from the entirely classical molecular dynamics approaches, which we have already mentioned, there are also the so-called "semiclassical" methods of quantum dynamics, which have their historical roots in the "old quantum theory" of Bohr (1913a,b,c). One of these is the Wentzel (1926), Kramers (1926), and Brillouin (1926) (abbreviated WKB) approximation to quantum mechanics, which has found wide use, for instance, also for quantum mechanical tunneling problems, as discussed in Chapters 7 (Quack and Seyfang, 2020) and 9 of this book (Cvitaš and Richardson, 2020). A more recent development is the semiclassical limit quantum mechanics by Miller (1974, 1975b). Another, in principle rigorous approach is the so-called path integral quantum mechanics, which is commonly attributed to Feynman (1948), but has its historical origin in the early work of Gregor Wentzel (1924) (the successor of Schrödinger in Zürich in 1928, see also Freund et al., 2009; Antoci and Liebscher, 1996). Path integral quantum mechanics with its important numerical implementations has been extremely fruitful in recent times as an alternative approach to quantum dynamics, and substantial books have been written on this approach (Feynman and Hibbs, 1965; Kleinert, 2009). Marx and Parrinello (1996), Tuckerman et al. (1996) as well as Chapters 6 (Vaníček and Begušić, 2020) and 9 (Cvitaš and Richardson, 2020) in the present book refer also to path integral methods. Numerical implementations of path integral methods were published in computer code packages (Ceriotti et al., 2010, 2014; Kapil et al., 2019).

Finally, Diffusion Quantum Monte Carlo (DQMC) methods have found much recent application as a rigorous approach to numerically solve the time-independent Schrödinger equation as a first step towards solving then also the time-dependent Schrödinger equation. DQMC follows an idea originally attributed to Fermi (Metropolis and Ulam, 1949) and introduced into quantum chemistry as a numerically practical approach in the algorithmic implementation by Anderson (1975, 1976). DQMC makes use of the interesting isomorphism between the N-body time-dependent Schrödinger equation propagated in an imaginary time equivalent $\tau = 2\pi i t/h$ with dimensions of a reciprocal energy and a $3N$ dimensional transport equation (with diffusion and source/sink terms) in Cartesian coordinate space,

$$\frac{\partial \Psi}{\partial \tau} = -\hat{H}\Psi, \tag{1.33}$$

$$\hat{H} = \hat{T} + \hat{V} = -\sum_{k=1}^{N} \frac{\nabla_k^2}{2m_k} + V. \tag{1.34}$$

Here $\hat{H}$ is a time-independent Hamiltonian with kinetic energy $\hat{T}$ and potential energy $\hat{V}$, having eigenvalues $E_0 \leq E_1 \leq \cdots \leq E_k$ and eigenfunctions Ψ_0, Ψ_1, etc. By numerically simulating a diffusion process as a quasi-statistical process, one can converge towards obtaining the ground state energy and wavefunction, as well as, with appropriate techniques making use of symmetry and nodal properties, also excited state results. The approach is conceptually and numerically interesting as it provides statistical upper *and* lower bounds on the energies E_0 (possibly E_1, etc). It has been used for both electronic structure and vibrational–rotational dynamics (Anderson, 1975, 1976; Reynolds et al., 1982; Ceperley and Alder, 1986; Coker and Watts, 1986; Garmer and Anderson, 1988; Bernu et al., 1990; Quack and Suhm, 1991; Lewerenz and Watts, 1994; Quack and Suhm, 1998; Tanaka et al., 2012). The possibility of simulating the quantum mechanics of a relatively large number of particles, as well as the upper and lower bound property of the solutions, is of interest. Limitations arise in obtaining excited state energies and wavefunctions, although this is possible as well, as discussed in Chapter 7 of this book (Quack and Seyfang, 2020) in applications to tunneling.

1.2.5 Time-Dependent Quantum Statistical Dynamics

When one wishes to consider the time evolution of a physical system, the initial state of which might be characterized by a statistical distribution of a mixture of different "pure quantum states", it is useful to define a density operator given by Eq. (1.35) (Messiah, 1961;

Sakurai, 1985):

$$\hat{\rho}(t) = \sum_n p_n \left|\Psi_n\right\rangle \left\langle\Psi_n\right| \tag{1.35}$$

satisfying the Liouville–von Neumann equation

$$\mathrm{i}\frac{h}{2\pi}\frac{\mathrm{d}\hat{\rho}(t)}{\mathrm{d}t} = \left[\hat{H}, \hat{\rho}(t)\right] \tag{1.36}$$

with the solution

$$\hat{\rho}(t) = \hat{U}(t, t_0)\hat{\rho}(t_0)\hat{U}^{\dagger}(t, t_0). \tag{1.37}$$

This equation is of particular importance for statistical mechanics.

In many applications one can usefully introduce reduced density matrices, which describe only a subsystem of the total quantum statistical mechanical system, with the understanding that only the knowledge of the time-dependent behavior of this small subsystem is of interest in an experiment. Often one uses then simple kinetic models for the matrix representation of the reduced operator. For instance, for the simple reduced density matrix with just two states, the diagonal elements (P_{11}, P_{22}) describe the time-dependent populations of the two levels and the off-diagonal elements their "coherences" (P_{12}, P_{21}). The time-dependent relaxation of the populations towards equilibrium might be assumed to be exponential with a relaxation time τ_1, whereas the coherences (P_{12}, P_{21}) decay to zero with a relaxation time τ_2. Of course, there is no guarantee that such a simple model will be a good approximation, and there is no need to restrict to just two states. In any case the idea of the reduced density matrix description is to treat a problem of small size (perhaps matrices of the order of 1000), whereas the complete quantum statistical system might have to be described by matrices easily exceeding 10^{1000}. These reduced density matrix approaches are widely used in magnetic resonance (Ernst et al., 1987; Schweiger and Jeschke, 2001), but also more generally (Blum, 1981). In principle, one can also simulate statistical behavior by random ensembles of solutions of the Schrödinger equation (Marquardt and Quack, 1994).

Another approach to simplify the quantum dynamical treatment of large microscopic or "mesoscopic", or even macroscopic systems, by statistical methods goes back to Pauli (1928). Here one starts from the time-dependent Schrödinger equation of the complete system involving a very large number of quantum states but considers only coarse-grained sums (or averages) of individual state populations p_k to derive coarse-grained level populations

$$p_K = \sum_k{}' p_{k(K)} = \sum_{k=x+1}^{x+N_K} b_{k(K)} b^*_{k(K)}. \tag{1.38}$$

By a nontrivial reasoning, which considers the emergence of simple structures for such average (or summed coarse grained) quantities, one obtains Master Equations of low dimension (Quack, 1981, 2014a,b):

$$\frac{\mathrm{d}\boldsymbol{p}(t)}{\mathrm{d}t} = \boldsymbol{K}\,\boldsymbol{p}(t), \tag{1.39}$$

$$\boldsymbol{p}(t) = \boldsymbol{Y}(t, t_0)\,\boldsymbol{p}(t_0), \tag{1.40}$$

$$\boldsymbol{Y}(t, t_0) = \exp[\boldsymbol{K}(t - t_0)]. \tag{1.41}$$

The sums $\sum{}'$ in Eq. (1.38) with $p_{k(K)}$ and $b_{k(K)}$ are implied to be restricted to quantum "states" k, ranging between some counting index $x + 1$ and $x + N_k$ and belonging to the "level" K, with N_k being the number of such states, which may possibly be very large. The rate coefficient matrix $\boldsymbol{K}$ has matrix elements K_{MN} which can be derived from quantum-mechanical perturbation theory or by other methods. In recent times classical trajectory calculations (i.e., classical molecular dynamics) have been proposed and used to calculate the "rate coefficient matrix" K_{MN} (Nüske et al., 2014), following otherwise similar lines of thinking as in Quack (1978, 1979, 1981), where a calculation of K_{MN} by means of quantum mechanical perturbation theory or other quantum approaches was implied.

Using a theorem originally due to Frobenius (von Mises, 1931), one can further simplify the mathematics by considering the rapid convergence of the solutions of Eq. (1.39) with only a small number of eigenvalues $(\lambda_1, \lambda_2, \lambda_3, \ldots)$ of $\boldsymbol{K}$. For some of the earlier discussion of these approaches, we refer to Quack (1979, 1981, 1982). We also note that the differential equation (1.39) can be of the "Pauli Master equation" type (Pauli, 1928, case B in Quack, 1978) or of a more general nature (cases A, B, C, D in Quack, 1978), where the "case A" is the well known "Fermi Golden Rule" and is a very special long known case (Wentzel, 1927, 1928) (some historical aspects are discussed by Merkt and Quack, 2011a), which has been rigorously derived for a model of electronic relaxation in large molecules by Bixon and Jortner (1968), and Jortner et al. (1969).

This "Fermi Golden Rule" (case A) can be considered as a "statistical" case because the product state populations are summed following Eq. (1.38). We can note here also that classical molecular dynamics by classical trajectories can be considered to be a statistical approximation to quantum dynamics when averaging over the initial conditions corresponding to a pure quantum state, when the latter is simulated by a statistical distribution in phase space (Quack and Troe, 1981). Although one might assume that statistical averages in classical dynamics might be a better approximation to quantum dynamics than just a straight phase space trajectory, there are, of course, quantum phenomena such as tunneling, which are not "averaged out" by statistical averaging (Quack and Seyfang, 2020, Chapter 7 of this book). Sometimes in classical molecular dynamics simulations of biomolecular systems such as proteins (Karplus, 2014; van Gunsteren et al., 2006), it is argued that, while the motion of the light H-atoms in the protein may well be quantum-like, the motion of the "heavy atom" framework (C, N, O, etc.) of the protein behaves classically. However, simulations of processes involving essential motion of even heavier atoms such as fluorine in the dissociation of the dimer $(HF)_2$ indicate large differences between quantum and classical results (Manca et al., 2008). Sometimes one might consider a combination of classical trajectory calculations for a part of the problem with a quantum statistical theory such as the statistical adiabatic channel model (Quack and Troe, 1981, 1998; Troe et al., 2005; Troe, 2006). Of course, the ultimate quantum statistical limit widely used in reaction kinetics is transition state theory for which various quantum dynamical versions have been formulated, such as the statistical adiabatic channel model (SACM, Quack and Troe, 1974, 1998) or semiclassical and quantum transition state theory (Miller, 1975a, 2014) beyond the original theory for thermal rate constants both in the classical mechanical and quantum mechanical versions (for the historical references see Chapter 7 in the present book, Quack and Seyfang, 2020).

In the debate on the validity of classical dynamics for describing the atomic motions on quantum Born–Oppenheimer potential hypersurfaces, it is often argued that the high degree of averaging in thermal situations justifies the use of classical mechanics. This point of view can be rejected with an argument given by Quack and Troe (1981): If we calculate the forward and backward rates of a thermal reaction by classical dynamics, the ratio of the rate constants results in the classical statistical thermodynamic limit for the equilibrium constant, which is known to be highly inaccurate by comparison with the easily accessible quantum statistical equilibrium constants. Thus the individual rate constants cannot be accurate.

1.3 METHODS FOR SOLVING THE TIME-DEPENDENT SCHRÖDINGER EQUATION

In this section we write the time-dependent Schrödinger equation in the form

$$\mathrm{i}\frac{h}{2\pi}\frac{\partial|\Psi(t)\rangle}{\partial t} = \hat{H}\,|\Psi(t)\rangle \tag{1.42}$$

where $|\Psi(t)\rangle$ represents the time dependent state of the system under investigation. Following the mathematical foundations of quantum mechanics (von Neumann, 2018), states are vectors, for which Dirac's notation is used here and essentially throughout the following section, where methods to solve Eq. (1.42) will be reviewed. The specific form of the molecular Hamiltonian is addressed in Section 1.4, and appropriate choices of coordinates used to describe the position of the particles composing a molecule are discussed in Section 1.5.

To solve Eq. (1.42) in practice, in particular to obtain numerical solutions for it, states and operators are represented in a finite set of states $\mathbb{L}_N = \{|\chi_1\rangle, \ldots, |\chi_N\rangle\}$ that is well defined in advance, and for which a scalar product $\langle\chi_n|\chi_m\rangle$ can also be defined; these states can always be defined to be orthonormal, i.e., $\langle\chi_n|\chi_m\rangle = \delta_{nm}$, where δ_{nm} is the Kronecker symbol (Cohen et al., 2007).

The state $|\Psi(t)\rangle$ is then represented by a time-dependent vector $\boldsymbol{b}(t)$, the so-called *state vector*, the components of which are the projections $b_n(t) = \langle\chi_n|\Psi(t)\rangle$:

$$|\Psi(t)\rangle = \sum_{n=1}^{N} b_n(t)\,|\chi_n\rangle. \tag{1.43}$$

Operators are represented by matrices, i.e., $\hat{H}$ is represented by a matrix $\boldsymbol{H}$; the element H_{nm} is given by the scalar product of $\langle\chi_n|$ with $\hat{H}|\chi_m\rangle$, $H_{nm} = \langle\chi_n|\hat{H}|\chi_m\rangle$. In this representation, Eq. (1.42) becomes

$$\mathrm{i}\frac{h}{2\pi}\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{b}(t) = \boldsymbol{H}\,\boldsymbol{b}(t). \tag{1.44}$$

The set $\mathbb{L}_N$ is a subspace of the entire linear space in which the quantum mechanical states exist. Because of the finiteness of N, the representation given by Eqs. (1.43) and (1.44) is normally an approximation of the true physical situation, which can be improved systematically, the larger N is made. The symbols $|\Psi(t)\rangle$ and $\boldsymbol{b}(t)$ denote two different types of vectors: the former is defined in the actual space of quantum states, the latter is defined in the dual space of the linear subspace $\mathbb{L}_N$; mathematically the former is a *covariant* vector, the latter a *contravariant* vector. It is important to note that, while a quantum mechanical state $|\Psi\rangle$ is basis set independent, the state vector is a contravariant vector, and as such dependent on the specific choice made for the basis states used to set up $\mathbb{L}_N$. A more detailed notation for it would therefore be $\boldsymbol{b}^{(\chi)}$; if a different basis of orthonormal states is used, say $\mathbb{L}_N = \{|\eta_1\rangle, \ldots, |\eta_N\rangle\}$, the corresponding state vector would be $\boldsymbol{b}^{(\eta)}$. However, for the sake of simplicity, and when any ambiguity can be discarded, we drop the specific indication to the chosen basis in the notation.

If the system under investigation is isolated, i.e., the Hamiltonian does not depend on time, $\hat{H}(t') = \hat{H}(t'')$, for all t' and t'', its total energy is conserved, and Eq. (1.42) has the special solutions

$$|\Psi_n\rangle(t) = |\psi_n\rangle \exp\left(-2\pi \mathrm{i} \frac{E_n}{h} t\right) \tag{1.45}$$

where the states $|\psi_n\rangle$ are the solutions of the time-independent Schrödinger equation

$$\hat{H} \, |\psi_n\rangle = E_n \, |\psi_n\rangle \tag{1.46}$$

at the specific energies E_n. Mathematically they are the eigenstates of $\hat{H}$ and the E_n are their energies; they describe the *spectroscopic states* of the isolated system, and energy differences $E_n - E_m$ correspond to potentially observable spectral lines $\nu_{nm} = (E_n - E_m)/h$. Because of their simple time dependence, as noted from Eq. (1.45), spectroscopic states are also called stationary states. Eq. (1.45) is indeed equivalent to Eq. (1.27), because $\Psi_k(r,t) = \langle r|\Psi_k(t)\rangle$ and $\psi_k(r) = \langle r|\psi_k\rangle$. And so are Eqs. (1.46) and (1.42) equivalent to Eqs. (1.21) and (1.18), respectively.

For isolated systems, Eq. (1.44) may be solved formally, by setting $\boldsymbol{b}(t) = \boldsymbol{U}(t,t_0)\,\boldsymbol{b}(t_0)$, where

$$\boldsymbol{U}(t,t_0) = \exp\left(-\mathrm{i}\frac{2\pi}{h}\,\boldsymbol{H}\,(t-t_0)\right) \tag{1.47}$$

is the matrix representation of the time evolution operator (see also Eq. (1.16)). For time-dependent Hamiltonians, the formal integration is more complex. For instance, in the so-called Magnus expansion (Magnus, 1954), as reviewed by Quack (1978, 1982) and Blanes et al. (2009), the integration involves nested commutators of the Hamiltonian at different times, see also Eq. (1.100), Section 1.6.3.

1.3.1 Spectral Decomposition Method

When the Hamiltonian is independent of time, the natural method suggested by Schrödinger (1926a,b,c,d,e) to solve Eq. (1.42) is to determine prior solutions of Eq. (1.46) and use an appropriate finite subset of solutions $\mathbb{L}_N = \{|\psi_1\rangle, \ldots, |\psi_N\rangle\}$. The time-dependent wave function may then be given such as in Eq. (1.43), see also Eq. (1.29),

$$|\Psi(t)\rangle = \sum_{n=1}^{N} b_n(t)\,|\psi_n\rangle \tag{1.48}$$

with

$$b_n(t) = b_n(0)\,\exp(-2\pi \mathrm{i}\,E_n\,t/h) \tag{1.49}$$

and $b_n(0) = \langle\phi_n|\Psi(0)\rangle$

However, it is difficult to know the stationary states in advance (see also Chapter 2 of this book (Császár et al., 2020)). It is reasonable to conjecture, that an approximate knowledge of these states could help simplify the calculation and interpretation of molecular quantum dynamics.

In practice, the direct way in this case is to solve Eq. (1.46) by first representing $\hat{H}$ in a given basis set $\mathbb{L}_N = \{\chi_1, \ldots, \chi_N\}$ and diagonalizing the thus obtained matrix $\boldsymbol{H}$. The time evolution operator is then given as

$$\boldsymbol{U}(t-t_0) = \boldsymbol{Z}\,\boldsymbol{U}^{(\mathrm{d})}(t-t_0)\,\boldsymbol{Z}^{\dagger} \tag{1.50}$$

where $\boldsymbol{U}^{(\mathrm{d})}(t-t_0)$ is a diagonal matrix,

$$U^{(\mathrm{d})}_{nm}(t-t_0) = \begin{cases} \exp(-2\pi \mathrm{i} E_n (t-t_0)/h), & n = m, \\ 0, & n \neq m, \end{cases} \tag{1.51}$$

E_n are the eigenvalues of $\boldsymbol{H}$, and the matrix $\boldsymbol{Z}$ is composed of N column vectors $z_1, \ldots, z_N$, which are the representations of the eigenvectors of $\boldsymbol{H}$ in $\mathbb{L}_N$. Eq. (1.52) is the corresponding representation of Eq. (1.46),

$$\boldsymbol{H}\,z_n = E_n\,z_n. \tag{1.52}$$

The number of floating point operations involved in the diagonalization with full determination of all eigenstates increases with N^3. Currently, diagonalization algorithms in standard linear algebra program libraries straightforwardly handle matrices with ranks up to $N = 50\,000$, although computation time and storage space of vectors and matrices increase rapidly with the rank.

In multidimensional spaces, the linear space of wave functions can be represented by a simple tensor product of one-dimensional spaces. Let d be the number of dimensions to be considered and let M be the average number of one-dimensional basis functions; then $N = M^d$, and the number of floating point operations is M^{3d}. For $d > 5$, typically, the spectral decomposition method becomes essentially impractical, unless some special measures are taken to optimize the size of the original representation basis, e.g., by suitably compressing basis vectors, or by applying collocation methods (Avila and Carrington, 2015). This issue is also discussed in Chapter 2 of this book (Császár et al., 2020).

These technical drawbacks are the only serious disadvantages of the spectral decomposition method. Whenever possible, this method should be given preference to other methods discussed below for three main reasons: Firstly, one can compare the calculated energy values with those derived from high-resolution spectroscopy, which are frequently available with very high accuracy, and thus test some of the underlying approximations, for instance, the potential energy surface (PES) used for the nuclear dynamics; other observables, such as the transition dipole moments, can also be directly compared. Secondly, it is very easy to vary the initial condition of the dynamical calculation with almost no additional computational effort. Finally, with the spectral decomposition method, one can design suitable approximations, such as the quasiresonant approximation for coherent excitation (see Section 1.6 below), which allows for accurate long-time propagation that is not easily accessible with the direct approaches to be discussed in the following sections.

1.3.2 Linearization

The operational simplest method to obtain the time evolution operator is to consider the Taylor expansion of the exponential function in Eq. (1.47). For "small" displacements along the time axis, $\Delta t = t - t_0$, the operator in Eq. (1.47) may be approximated by the linearized operator

$$\boldsymbol{U}_{\text{lin}}(\Delta t) = \boldsymbol{I} - \mathrm{i}\,\frac{2\pi}{h}\,\boldsymbol{H}\,\Delta t. \tag{1.53}$$

Here, $\boldsymbol{I}$ is the identity matrix. Hence, the state vector at time $t_k = k\,\Delta t + t_0$ $(k > 0)$ is given as a linear function of the state vector at time t_{k-1},

$$\boldsymbol{b}(t_k) = \boldsymbol{b}(t_{k-1}) - \mathrm{i}\,\frac{2\pi}{h}\Delta t\,\boldsymbol{H}\,\boldsymbol{b}(t_{k-1}). \tag{1.54}$$

There is an error of the order Δt^2 at each time step, and the integrated error increases with the total evolution time by error propagation. Following the uncertainty relation Eq. (1.11), appropriate time step sizes should satisfy the condition $\Delta t \ll h/\Delta E$, where ΔE is a typical transition or coupling energy.

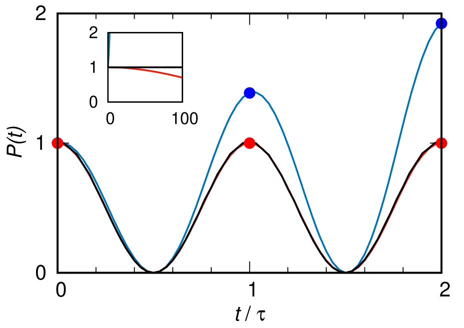

FIG. 1.3 Population evolution $P(t) = \cos^2(\pi t/\tau)$ of an initially 100% populated level in a simple scheme of two isoenergetic levels coupled by an interaction energy $V = h/(2\tau)$ (black line). The blue line yields the result from the simple linearized formula in Eq. (1.54) with a propagation step $\Delta t = 0.033\,\tau$. The red line is from the second order formula in Eq. (1.55) – it essentially overlaps with the black line in the main figure. The dots are the results at times $t_n = n \times \tau$ $(n = 0, 1, 2, \ldots)$ and their collection is displayed in the insert by lines in the corresponding color – the blue line is hardly seen because of the fast increase of the propagation error, the black line is the exact solution.

What is typically a sufficiently small Δt? This question seems odd, in particular in studies of ultrafast processes, as one might naively think that the process will be over before error has accumulated significantly. Fig. 1.3 shows, as an example, a simple two-level dynamics, where a quantum state is coupled resonantly via a coupling constant V to a second, isoenergetic quantum state – this is the simplest model of a quantum mechanical tunneling motion and can also be used to discuss the monochromatic excitation between two quantum states, see Section 1.6.6 below. The exact evolution $P(t) = \cos^2(\pi t/\tau)$ of the population of the initial state is shown there as a black line; $\tau = h/2V$ is the typical evolution time. The blue line shows the same evolution calculated via Eq. (1.54). Quite impressively, the accrued propagation error becomes as large as 30% after just one period of the evolution, if Δt is only 3% of the typical evolution time τ. There is also error propagation in terms of the phases of the time evolving state vector, which is not shown here.

As can be seen from the figure, the error increases rapidly and is already 100% after just two periods because of error propagation. The strong increase of the population goes inline with a severe nonconservation of the norm, which is an unacceptable nonphysical behavior. The error can be much reduced via the use of a second order formula which relies on the evaluation of the wave function at two earlier time steps t_k and t_{k-1} (Kosloff and Kosloff, 1983a) – this formula is related to the Crank–Nicholson method (Bachau et al., 2001):

$$\boldsymbol{b}(t_{k+1}) = \boldsymbol{b}(t_{n-1}) - \mathrm{i}\,\frac{4\pi}{h}\Delta t\, \boldsymbol{H}\, \boldsymbol{b}(t_n). \tag{1.55}$$

The corresponding evolution is given in Fig. 1.3 by the red line. Even if the error can be much reduced by the second-order linear formula in the case of the simple example discussed here, it can still be quite important at a longer time evolution, as shown by the insert of Fig. 1.3 or in more complex situations where many states with different sizes of couplings are involved. The sole remedy for this simple algorithm is to reduce drastically the linear evolution time step Δt, at the cost of having a huge number of sequential matrix vector multiplications to perform if a longer time evolution is needed.

A very detailed discussion on error accumulation was given by Marquardt and Quack (1989) on the basis of an exactly solvable model for femtosecond multiphoton excitation in the infrared (see also Section 1.6 below).

Despite the important error propagation inherent to the linearized propagator, the simplicity of the method is appealing, in particular when the system is very complex. In such cases even a simple matrix–vector multiplication as that of Eq. (1.54) can become highly time consuming because the dimension of the linear space becomes very large. Therefore the simpler the algorithm, the easier its implementation. More advanced methods exist, however. Sophisticated predictor–corrector algorithms are typically employed to solve nonlinear ordinary differential equations (Gear, 1971; Shampine and Gordon, 1975; Beck et al., 2000) and may be implemented to optimize dynamically the time step and in this way contribute to reduce error accumulation. Such algorithms are used in the MCTDH program package discussed below.

1.3.3 The “Chebychev” Method

Some methods make explicit use of higher order expansions of the propagator. As an alternative to expanding the exponential function in Eq. (1.47) in terms of powers of the argument, it may be expanded in terms of polynomials.

Tal-Ezer and Kosloff (1984) used an expansion in terms of Chebychev polynomials $T_k(z)$ (Courant and Hilbert, 1968), which are defined for $-1 \le z \le 1$. Light and Carrington (2000) and Beck et al. (2000) discuss several characteristic properties of these polynomials, relevant for the application in quantum dynamics. This method has since then been used in varied forms mainly in scattering quantum dynamics.

This method works as follows: First, upper ($E_{\max}$) and lower ($E_{\min}$) bounds for the largest and lowest eigenvalues of $\boldsymbol{H}$, respectively, need to be known, at least approximately. These may be estimated straightforwardly for finite matrix representations (Carrington, 2011). Then, the time evolution operator may be written as (Tal-Ezer and Kosloff, 1984)

$$\begin{aligned} \boldsymbol{U}_{\mathrm{cheb}}(t+\Delta t, t) &= \exp\left(\mathrm{i}\,\frac{2\pi}{h}\,E_{\mathrm{S}}\,\Delta t\right) \\ &\times \sum_{k=0}^{k_{\max}} (2-\delta_{k0})\, J_k\left(\frac{2\pi}{h}\,E_{\mathrm{D}}\,\Delta t\right) T_k\left(\frac{2\pi}{h}\,\boldsymbol{H}\,\Delta t\right) \end{aligned} \tag{1.56}$$

where $E_{\mathrm{S}} = 1/2(E_{\max} + E_{\min})$, $E_{\mathrm{D}} = 1/2(E_{\max} - E_{\min})$, and J_k are Bessel functions of the first kind of order k (Courant and Hilbert, 1968). To evaluate the Chebychev polynomial of degree k on the state vector, the recursion formula

$$T_k\,(\boldsymbol{M}) = 2\,\boldsymbol{M}\,T_{k-1}\,(\boldsymbol{M}) + T_{k-2}\,(\boldsymbol{M}) \tag{1.57}$$

is used, with $T_0(\boldsymbol{M}) = \boldsymbol{I}$ and $T_1(\boldsymbol{M}) = \boldsymbol{M}$. The Bessel functions of the first kind have the property that $J_k(x) \approx 0$ for $k \ge x$. If the maximal order considered in Eq. (1.56) is chosen such that $k_{\max} \ge 2\pi E_{\mathrm{D}}\,\Delta t/h$, the propagation error can be made as small as desired.

The Chebychev method has been recently applied in the scattering quantum dynamics of triatomic (Zhou and Xie, 2015) and tetraatomic systems (Song and Guo, 2015), in full-dimensional rovibrational quantum dynamics of ammonia isotopomers (Fábri et al., 2019), but also in spin noise calculations of semiconductor quantum dots (Hackmann and Anders, 2014), in the hydrodynamical formulation of quantum mechanics (Cruz-Rodriguez et al., 2016), and in continuous time quantum walks (Izaac and Wang, 2015). The method was also extensively reviewed by Kosloff (1994).

1.3.4 “Short-Iterative” Lanczos Method

Quite often, only a rather small number of spectroscopic states is effectively involved in the representation of the time evolution operator during a given time interval Δt. This means that, if $|\Psi(t_j)\rangle$ is the solution of Eq. (1.42) at time t_j, it can be decomposed in a limited set of states $\{|\tilde{\psi}_1\rangle, \ldots, |\tilde{\psi}_{N(t_j)}\rangle\}$,

$$|\Psi(t_j)\rangle = \sum_{n=1}^{N(t_j)} b_n(t_j)\,|\tilde{\psi}_n\rangle \tag{1.58}$$

with

$$b_n(t_j) = \langle \tilde{\psi}_n | \Psi(t_j) \rangle \tag{1.59}$$

such that

$$\sum_{n=1}^{N(t_j)} |b_n(t_j)|^2 \approx 1 \tag{1.60}$$

with a hopefully rather small value of $N(t_j)$. Since the method described here may also apply to potentially time-dependent Hamiltonians $\hat{H}(t)$ and corresponding pseudoeigenvalues $E_n(t)$, the notation is here such that $|\tilde{\psi}_n\rangle$ are pseudoeigenstates, for which

$$\hat{H}(t_j)\,|\tilde{\psi}_n\rangle = E_n(t_j)\,|\tilde{\psi}_n\rangle \tag{1.61}$$

holds at the given time step t_j, and $N(t_j)$ is the number of pseudoeigenstates contributing importantly to the dynamics at time t_j. This number can vary smoothly as a function of time.

Following an idea formulated by Park and Light (1986), we consider here the integration step from a time t_j to a time $t_{j+1} = t_j + \Delta t$. The Hamiltonian at time t_j is diagonalized within the Lanczos method (Cullum and Willoughby, 1985), such as to yield a limited number of pseudoeigenstates $|\tilde{\psi}_n\rangle$ and corresponding energies $E_n(t_j)$. The Lanczos iteration is started from the state $|\Psi(t_j)\rangle$, which helps ensure that the set of calculated pseudoeigenfunctions includes all eigenfunctions $\tilde{\psi}_n$ that contribute significantly to the dynamics at this particular time step, i.e., for which the overlap integrals $b_n(t_j)$ fulfill the condition of Eq. (1.60). With this method, $N(t_j)$ varies typically between 20 and 30.

The state at time t_{j+1} is then calculated from a restricted expansion of the type of Eq. (1.48):

$$|\Psi(t_{j+1})\rangle = \sum_{n}^{N(t_j)} b_n(t_j) \exp\left(-\mathrm{i}\frac{2\pi}{h}\, E_n(t_j)\,\Delta t\right) |\tilde{\psi}_n\rangle. \tag{1.62}$$

The sum in Eq. (1.62) is restricted to the subset of pseudoeigenstates obtained within the Lanczos algorithm that satisfy Eq. (1.60) within a given accuracy threshold. With this recipe, the solution of Eq. (1.42) can then be obtained by iteration. The accrued propagation error depends clearly on the iteration time step Δt used, but it can be largely reduced depending on the threshold used to verify Eq. (1.60).

The Lanczos method to solve Eq. (1.42) has been reviewed more recently from an applied mathematical (Lubich, 2015) and physical prospective (Bader et al., 2018), and also applied in the context of qubit dynamics (Cangemi et al., 2018).

1.3.5 "Split-Operator" Technique

Another method that makes use of higher order expansions of the propagator is the *split-operator* method (Feit et al., 1982). Let $\boldsymbol{H} = \boldsymbol{H}_0 + \boldsymbol{H}_1$ be such that the norms of these Hamiltonians satisfy $||\boldsymbol{H}_1|| \ll ||\boldsymbol{H}_0||$. The quantity E_D defined in Section 1.3.3, is one possible norm of a matrix. The time evolution operator

$$\boldsymbol{U}_\mathrm{split}(t+\Delta t, t) = \exp\left(-\mathrm{i}\,\frac{\pi}{h}\,\boldsymbol{H}_0\,\Delta t\right) \times \exp\left(-\mathrm{i}\,\frac{2\pi}{h}\,\boldsymbol{H}_1\,\Delta t\right) \exp\left(-\mathrm{i}\,\frac{\pi}{h}\,\boldsymbol{H}_0\,\Delta t\right) \tag{1.63}$$

is an approximation to $\boldsymbol{U}(t+\Delta t, t)$ and, compared to the latter, has quadratic convergence in Δt (Bandrauk and Shen, 1993).

The Hamiltonian used in Eq. (1.63) can often be considered to be split into the kinetic and potential energy part $\boldsymbol{H} = \boldsymbol{T} + \boldsymbol{V}$, with either $\boldsymbol{H}_0 = \boldsymbol{T}$ and $\boldsymbol{H}_1 = \boldsymbol{V}$, or vice versa, depending on which operator satisfies the aforementioned norm condition better. It is then possible and even appropriate to evaluate $\boldsymbol{U}_\mathrm{split}$ in two steps involving the momentum and space representations of the time evolving quantum state. Let $\boldsymbol{H}_0 = \boldsymbol{T}$.

The state at time t is first represented in the momentum space. When the kinetic energy is evaluated in Cartesian coordinates, the action of the first factor on the right-hand side of Eq. (1.63) is to add the angle $-(2\pi t/h)\sum_k p_k^2/2m_k$ to the phase of the state's wave function in momentum space.

Then the representation is switched to a space representation by a Fourier transformation and the central factor in Eq. (1.63) adds a phase $-(2\pi t/h)\,V(\boldsymbol{x})$ to the state's wave function.

Finally, this function is back-transformed into momentum space and its phase is incremented by the same angle as in the first step.

The split operator technique takes advantage of available routines that perform fast Fourier transformations (Kosloff and Kosloff, 1983a,b) and has since then been much used to solve Eq. (1.42) (see, for instance, Kolba et al., 1992 and, for recent applications and developments, Sun et al., 2015, Greene and Batista, 2017, Blanes et al., 2017 for nuclear dynamics and Sabzyan and Jenabi, 2016 for electron transfer processes). This method can be applied also when $\boldsymbol{H}_1$ is an explicit function of time, supposing that the variation of $\boldsymbol{H}_1$ with time t is itself of order Δt^3 in the time interval between t and

$t + \Delta t$. In this context, "commutator-free" propagators have been discussed recently, by which the performance can be significantly improved (Bader et al., 2018).

One interesting aspect of the split operator technique is to chose a representation basis for the dynamics that diagonalizes the kinetic energy. The advantage of the fast Fourier transform is then lost, however. The numerical effort of such a procedure has been tested (Quack and Stohner, 1993).

1.3.6 The "Multiconfigurational Time-Dependent Hartree" Method

Quantum dynamics are in general multidimensional. The time dependent quantum state $|\Psi(t)\rangle$ contains simultaneously information on all particles involved in a system, each particle being essentially characterized by its position in the three-dimensional space. In molecules, one considers as particles the nuclei of the atoms composing these systems and the electrons surrounding them.

Accordingly, the quantum state has to be studied with respect to its projections on the spaces of the different particles. If the total dimension to be considered is d, the quantity to be determined is the d-dimensional wave function $\Psi(x_1, \ldots, x_d; t) = \langle x_1, \ldots, x_d | \psi(t) \rangle$.

Similarly to the idea underlying the short iterative Lanczos method explained above, one exploits the fact that the number of states that strongly participate at the dynamics in a given time interval Δt is normally small. In the time-dependent Hartree method (Jungwirth and Gerber, 1999), the time dependent, d-dimensional wave function is set up as a product of d one-dimensional, time dependent *single particle functions* $\varphi_j(x_j, t)$,

$$\Psi(x_1, \ldots, x_d; t) = \varphi_1(x_1, t) \cdots \varphi_d(x_d, t).$$

The single particle functions can be obtained as solutions of nonlinear coupled partial differential equations, which can be rigorously derived from the Dirac–Frenkel variational principle (see Beck et al., 2000, and references therein).

Alike the configuration interaction expansion in electronic structure theory, it is possible to improve the accuracy of the description via a Hartree product by considering a "multiconfigurational" expansion ("MCTDH", Meyer et al., 1990)

$$\Psi(x_1, \ldots, x_d; t) = \sum_{I=1}^{N_{\mathrm{MCTDH}}} b_I(t)\, \Phi_I(x_1, \ldots, x_d; t). \tag{1.64}$$

The number I is a superindex that counts set of indexes $i_1, \ldots, i_d$. It defines a particular configuration of single particle functions $\Phi_I(x_1, \ldots, x_d, t) = \varphi_{i_1}^{(1)}(x_1, t) \cdots \varphi_{i_d}^{(d)}(x_d, t)$. The quantities $b_I(t)$ are time-dependent coefficients. For the numerical evaluation, single particle functions are expanded in terms of time-independent *primitive functions* $\xi_1^{(k)}, \ldots, \xi_{n_k}^{(k)}$:

$$\varphi_i^{(k)}(x_k, t) = \sum_{j=1}^{n_k} c_{ji}^{(k)}(t)\, \xi_j^{(k)}(x_k). \tag{1.65}$$

The maximal number of single particle functions of coordinate x_k is n_k. The equations of motion for the expansion coefficients $c_{ji}^{(k)}(t)$ and $b_I(t)$ can again be rigorously obtained from the Dirac–Frenkel variational principle. The number n_k of primitive functions can quite often be chosen sufficiently small for converged calculations. The number $N_{\mathrm{MCTDH}} = n_1 \cdots n_d$ of configurations participating in the expansion Eq. (1.64) can hence be made considerably smaller than the number N of stationary states needed such as in Eq. (1.43).

While the idea underlying the MCTDH method allows us to solve high-dimensional problems that would otherwise not be solvable, in practice it has a serious conceptual drawback: the linearity originally embedded in Eq. (1.44) (or Eq. (1.42), or Eq. (1.18)) has to be given up. The equations of motion are nonlinear, ordinary differential equations that can be solved by any integration method, in principle, with variable efficiency and accuracy, which depends strongly on the precise predictor–corrector algorithm used (see Beck et al., 2000 and references given therein; a specific algorithm with step size control was also devised for MCTDH). Also, as for all initial value problems, the integration has to be restarted from time t_0 for each new initial condition. In contrast to this, the spectral decomposition scheme described in the previous subsections yields a universal time evolution operator $\boldsymbol{U}(t, t_0)$ which holds for all initial conditions $\boldsymbol{b}(t_0)$.

The great advantage of the MCTDH approach in high dimensional problems is, however, that it simply renders these problems treatable, as $N_{\mathrm{MCTDH}} \ll N$. A second, more technically oriented advantage of the method is related to the implicit product form of the wave function. As a consequence, multidimensional integrals related to practical evaluation of scalar products may be carried out as products of one dimensional integrals, if the operators can also be written in the form of sums of products of one dimensional operators. While this condition can be met quite generally by specially devised forms of the potential energy operators, a more judicious choice of the coordinates used is necessary to ensure that the kinetic energy operator is of this form. Such coordinates are, for instance, polyspherical coordinates. The MCTDH method has meanwhile been applied to a plethora of systems. Both method and applications were reviewed by Gatti (2014) and Gatti et al. (2017).

Marquardt et al. (2010) give a detailed comparison between results obtained with the MCTDH and URIMIR codes of the time evolution of populations and relative phases of a state vector defined in a four-dimensional vibrational subspace in ammonia. The URIMIR code discussed in Section 1.6 below allows us to also obtain numerically exact solutions of Eq. (1.42) under the influence of an external radiation field.

1.3.7 Specific Methods for the Electronic Motion

Electronic motion can in principle be assessed by all methods discussed in the previous sections. Several problems hamper the straightforward implementation of the equations, however. One problem is connected with the representation of the Hamiltonian: Basis sets need to be very large, as the long range Coulomb potential leads to interactions in very much extended regions of space. A second problem arises in the correct time dependent treatment of the fermionic character of the electrons. Some approaches are related to the MCTDH method, described above, where the total, time-dependent electronic function is described as a multiconfigurational expansion of completely antisymmetric configuration functions, very much like in the configuration interaction method of static electronic structure calculations (Kato and Kono, 2004; Caillat et al., 2005; Nest, 2006); contrary to the static case, the orbitals used to compose the time dependent electronic wave function are time-dependent, however. These "MCTDHF" called methods allow us also to calculate excited state properties (Nest et al., 2005). However, they still have a limited domain of applications.

In most cases treated so far, the solutions of Eq. (1.42) are given for the electronic motion alone in the so-called "sudden" approximation, in which the nuclei are essentially frozen at their positions during the actual interaction time of a few tens or hundreds of attoseconds. Additionally, methods used so far are generally based on the *single active electron* (SAE) approximation. This approximation is used to simulate processes involved in high harmonic generation (Farrell et al., 2011) and attosecond molecular dynamics (Wörner and Corkum, 2011), see also Chapter 4 (Baykusheva and Wörner, 2020) of this book.

Related, highly specific methods have been used for instance to discuss $He^{2+} + H_2$collisions (Sisourat et al., 2011), or the interaction of atoms and molecules with high intensity radiation, as reviewed by Maquet and Grobe (2002) and Salières et al. (2012), where the *strong field approximation* (SFA) is made. The latter consists essentially in describing the wave function of the "active" electron in terms of analytic Gordon–Volkov solutions for Eq. (1.42), to describe the quantum dynamics of an electron in the presence of a strong laser field (Reiss, 1992). Lorin et al. (2007) solved the Maxwell–Schrödinger equation numerically for H_2^+ in a four-dimensional space; here, the time propagation was evaluated via a modified version of Eq. (1.55).

In Chapter 5 of this book (Gokhberg et al., 2020), methods are described for the theoretical treatment of several fast electronic processes involving molecular ionization and charge migration in molecular aggregates. They rely on the calculation of a time dependent hole density using the Heisenberg representation (Eq. (1.14)) and the short iterative Lanczos technique explained in Section 1.3.4 above. For the calculation of the hole density matrix the algebraic diagrammatic construction scheme was used, a Green's function formalism. For more details on this technique, we refer to Kuleff et al. (2005), Sansone et al. (2012), Kuleff (2019), and the references cited therein, as well as to Chapter 5.

Theoretical methods used in attosecond molecular dynamics were reviewed in the book edited by Vrakking and Lépine (2019). We also refer to the work by Ambrosek et al. (2004), Barth and Manz (2007), Bredtmann et al. (2015) and Jia et al. (2019) on femtosecond and attosecond electron and nuclear quantum fluxes and currents in molecular compounds. The sub-fs electronic time scale for charge migration in small peptides was discussed by Remacle and Levine (2006).

1.4 HAMILTONIANS

In nonrelativistic quantum mechanics the molecular Hamiltonian is indeed set up as the sum of the Coulomb potential energy terms between the charged nuclei and the electrons as point masses, as well as the kinetic energy of these particles expressed in the usual way in terms of the Cartesian coordinates of these points and their masses (see Eqs. (1.12) and (1.13)). Solving for the complete molecular dynamics within this general scheme is very difficult and limited to small systems, such as the H_2^+ cation, for which the full three-body problem was solved numerically by Chelkowski et al. (1995) and Lorin et al. (2007) (see also the references cited therein).

The focus of current theoretical developments is still based on the Born–Huang expansion of the molecular state (Born and Huang, 1954),

$$|\Psi(t)\rangle = \sum_k |\Psi_k^{(\mathrm{n})}(t)\rangle \otimes |\psi_k^{(\mathrm{e})}\rangle. \tag{1.66}$$

The symbol $|\Psi^{(\mathrm{n})}(t)\rangle \otimes |\psi^{(\mathrm{e})}\rangle$ means a tensor product of "nuclear" and "electronic states".

The "electronic state" $|\psi^{(\mathrm{e})}\rangle$ is supposed to be time independent, while the "nuclear state" $|\Psi^{(\mathrm{n})}(t)\rangle$ contains the information on the time dependence of the molecular state. Variations of Eq. (1.66) have been suggested (Cederbaum, 2008; Abedi et al., 2010), in which the electronic state is of the form $|\Psi_k^{(\mathrm{e})}(t)\rangle$, i.e., it also contains an explicit time dependence. While this ansatz is legitimate and interesting from a fundamental point of view, so far it yields no practical method for the solution of Eq. (1.42) for the combined nuclear and electronic motions in molecules. In practice, all electronic states $|\psi_k^{(\mathrm{e})}\rangle$ are set to depend parametrically on the nuclear coordinates, as will be discussed below, and the product ansatz does not correspond to a true separation of the dynamics.

The expansion in Eq. (1.66) is usually interpreted as corresponding to a representation of the molecular state in a specific, countable basis of electronic states $|\psi_1^{(\mathrm{e})}\rangle, |\psi_2^{(\mathrm{e})}\rangle, \ldots$ Clearly, this interpretation provides only an approximate description of ionization processes, where the state of the dissociated electron belongs to a continuum of states.

The time-dependent Schrödinger equation, Eq. (1.42), then reads

$$\mathrm{i}\frac{h}{2\pi}\frac{\partial}{\partial t}\begin{pmatrix} |\Psi_1^{(\mathrm{n})}(t)\rangle \\ |\Psi_2^{(\mathrm{n})}(t)\rangle \\ \vdots \end{pmatrix} = \begin{pmatrix} \hat{H}_{11}^{(\mathrm{n})} & \hat{H}_{12}^{(\mathrm{n})} & \cdots \\ \hat{H}_{21}^{(\mathrm{n})} & \hat{H}_{22}^{(\mathrm{n})} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}\begin{pmatrix} |\Psi_1^{(\mathrm{n})}(t)\rangle \\ |\Psi_2^{(\mathrm{n})}(t)\rangle \\ \vdots \end{pmatrix}. \tag{1.67}$$

The matrix in Eq. (1.67) is a representation of the total Hamiltonian in the chosen basis of electronic states $|\psi^{(\mathrm{e})}\rangle$. Its matrix elements are Hamiltonian operators $\hat{H}_{ik}^{(\mathrm{n})}$ that act exclusively on the nuclear degrees of freedom:

$$\hat{H}_{ik}^{(\mathrm{n})} = \langle\psi_i^{(\mathrm{e})}||\hat{H}||\psi_k^{(\mathrm{e})}\rangle = \begin{cases} \hat{T} + V_k & (i = k), \\ \hat{H}_{ik}^{(\mathrm{non-a})} & (i \neq k). \end{cases} \tag{1.68}$$

In this equation, the symbol $\langle\cdot||\cdot||\cdot\rangle$ means a scalar product involving the electronic states only; V_k is normally a function of the relative positions of the nuclei in the molecular complex and is interpreted as the "potential energy surface" for the motion of the nuclei in the electronic state k; $\hat{T}$ is an adequate representation of the operator for the kinetic energy in the coordinate space of the nuclei and does generally not depend on any specific electronic state. Such representations will be addressed in the following section. It will be shown that $\hat{T}$ is essentially a derivative operator, which might depend on the position of the nuclei, however.

Potential energy surfaces can be obtained from electronic structure calculations. In these calculations the electronic wave functions $\psi_k^{(\mathrm{e})}(\boldsymbol{x}^{(\mathrm{e})}) = \langle\boldsymbol{x}^{(\mathrm{e})}||\psi_k^{(\mathrm{e})}\rangle$ are obtained as eigenstates of the time independent molecular Schrödinger equation in the so-called *clamped nuclei approximation* (see Cederbaum, 2004), i.e., by fixing the position of the nuclei and neglecting their kinetic energy. Here $\boldsymbol{x}^{(\mathrm{e})}$ is a generalized electronic position vector. The functions obtained in this way depend parametrically on the positions of the nuclei (see above). The eigenvalue corresponding to a state $|\psi_k^{(\mathrm{e})}\rangle$ yields the multidimensional potential energy (hyper-)surface $V_k(\boldsymbol{x}^{(\mathrm{n})})$, where $\boldsymbol{x}^{(\mathrm{n})}$ is a generalized nuclear position vector. The states $|\psi_k^{(\mathrm{e})}\rangle$ obtained in the clamped approximation are called *adiabatic* electronic states, as the electrons are supposed to follow adiabatically the motion of the nuclei.

Many methods exist today in electronic structure theory with a variety of applications. Some benchmark calculations have been discussed by Schreiber et al. (2008). The status of methods used in electronic structure calculations to obtain potential energy surfaces for electronically excited states has been reviewed by González et al. (2012) and, in particular in reference to transition metal complexes by Daniel (2002, 2015a,b) and Penfold et al. (2018).

The clamped nuclei technique enforces a point-wise determination of the functions. In molecular dynamics and spectroscopy, the knowledge of potential energy surfaces is essential and often it is desirable to have analytical representations of these surfaces that are global, i.e., that are physically well defined in the entire space of nuclear coordinates. Methods for deriving global analytical representations of potential energy surfaces from electronic structure calculations and from spectroscopic data are discussed by Marquardt and Quack (2011). It is worth mentioning that the very first analytical representations of molecular potential energy surfaces were derived from spectroscopic experiments prior to modern quantum mechanics (Bjerrum, 1914). The use of permutation symmetry of identical nuclei in the formulation of analytical potential hypersurfaces was discussed by Marquardt and Quack (1998) and Qu et al. (2018) (see also Fábri et al., 2017).

The operators $\hat{H}_{ik}^{(\mathrm{non-a})}$ occurring in Eq. (1.68) represent the *nonadiabatic* couplings between the adiabatic electronic states. They account for the coupling between the adiabatic states and therefore play an important role in the description of ultrafast processes that may occur mainly in electronically excited molecules (González et al., 2012; Daniel, 2002, 2015a; Vrakking and Lépine, 2019), see also Chapter 6 of this book (Vaníček and Begušić, 2020).

Eq. (1.67) is in principle an exact representation of Eq. (1.42), whenever the expansion in Eq. (1.66) can be considered exact. It cannot be considered exact, as explained above, in processes involving the ionization of molecules. To solve this equation in a general case is difficult, however, and one has normally to resort to several approximations, as discussed in Section 1.3.7 above.

In the *Born–Oppenheimer approximation*, the action of the nonadiabatic couplings is neglected with respect to that of the diagonal operators. This approximation is adequate, even excellent in many cases, as long as the energies of two electronic states are not too close one to the other, i.e., as long as $|V_k(\boldsymbol{x}^{(\mathrm{n})}) - V_i(\boldsymbol{x}^{(\mathrm{n})})| \gg 0$. These terms can hardly be neglected, when the potential energy surfaces of two electronic states cross, such as at conical intersections (Domcke et al., 2004; Domcke and Yarkony, 2012). These are the regions of the nuclear configuration space where the multidimensional potential energy surfaces of two or more electronic states intersect, even if they belong to the same irreducible representation space of the molecular symmetry group (Teller, 1937; Herzberg and Longuet-Higgins, 1963). The mathematical foundations of conical intersections are clearly explained by Longuet-Higgins (1975).

The exact evaluation of the nonadiabatic couplings is difficult for several reasons (Cederbaum, 2004): as for potential energy surfaces, these terms need to be evaluated in pointwise electronic structure calculations in the space of nuclear configurations, there are generally no global analytical representations of these operators; furthermore, they may become singular, in particular at conical intersections.

Singularities may theoretically be removed by performing an appropriate unitary basis transformation (Cederbaum, 2004):

$$|\tilde{\Psi}_k^{(\mathrm{n})}(t)\rangle = \sum_l Y_{lk}^* \, |\Psi_l^{(\mathrm{n})}(t)\rangle, \tag{1.69}$$

$$|\tilde{\psi}_k^{(\mathrm{e})}\rangle = \sum_l Y_{kl} \, |\psi_l^{(\mathrm{e})}\rangle, \tag{1.70}$$

where $\sum_k Y_{lk}^* Y_{kl'} = \delta_{ll'}$. The unitarity of the matrix $\boldsymbol{Y}$ ensures the invariance of the Born–Huang expansion in Eq. (1.66). Because the basis of electronic states depends parametrically on the relative nuclear position vectors $\boldsymbol{x}^{(\mathrm{n})}$, it is expected that the matrix $\boldsymbol{Y}$ will also depend on $\boldsymbol{x}^{(\mathrm{n})}$.

It can be shown that, under appropriate conditions, the singularities expected to occur in the derivative coupling terms $\hat{H}_{ik}^{(\mathrm{non-a})}$ in the adiabatic basis representations can be made to vanish and be replaced by multiplicative, generally nonsingular coupling operators (Cederbaum, 2004). The states $|\tilde{\psi}_k^{(\mathrm{e})}\rangle$ introduced by this procedure are called *diabatic*; in practice this technique leads only to an approximate treatment of the coupling, since the transformation runs over a finite number of countable states. A quite valuable technique to obtain nonadiabatic couplings uses a block diagonalization of the electronic Hamiltonian (Pacher et al., 1988). These operators may then be represented by an analytical Taylor expansion limited to the vicinity of the conical intersection, at which they were derived. This method leads to the *vibronic coupling Hamiltonian*, which may be used for the study of the ultrafast dynamics in this limited region of configuration space (González et al., 2012; Daniel, 2015a), also in competition with the spin–orbit coupling prominent in transition metal complexes (Penfold et al., 2018).

Many theoretically fundamental or methodological articles on nonadiabatic couplings and conical intersections, as well as the dynamics resulting from them and examples of applications, can be found in the book by Domcke et al. (2004) or in the reviews by Chu et al. (2006), Matsika and Krause (2011) or Domcke and Yarkony (2012).

Vibrational wave packet dynamics associated with ultrafast electron transfer reactions in a condensed phase environment has been studied by Thoss et al. (2004). A special issue of the *Journal of Chemical Physics* has been devoted to nonadiabatic molecular dynamics (see the keynote article by Tully (2012)).

For systems involving more than 5 atoms, typically, finding accurate solutions of Eq. (1.67) outside the vibronic coupling Hamiltonian approach becomes truly difficult, and classical or semiclassical approaches for the motion of the nuclei are considered instead, as discussed in Chapter 6 of this book (Vaníček and Begušić, 2020). In order to describe the transfer of population from one adiabatic state to the other, many of these approaches use a *surface hopping* idea, such as that proposed by Tully (1990), or variations thereof (Tully, 2012, and the references given therein). However, one must not consider these classical or semiclassical treatments as actual approximations of the quantum dynamics. Rather, they yield a classical picture of a process that can be quite misleading, indeed, due to the wave mechanical nature of the actual dynamics that they cannot fully recover.

One way to simplify the great complexity of the Hamiltonian for multidimensional molecular motion is a quasiadiabatic separation of vibrational degrees of freedom. For instance, one may treat the Hamiltonian quite explicitly in one coordinate (the "reaction path") or perhaps a small subset of coordinates, whereas all other coordinates are treated implicitly by their effect on this selected subset. This is the idea of the "Reaction Path Hamiltonian" (RPH, Miller et al., 1980) and the extension to the quasiadiabatic channel RPH approach (Quack and Suhm, 1991; Fehrensen et al., 1999, 2007). These approaches are discussed in more detail in Chapter 7 of this book (Quack and Seyfang, 2020).

1.5 COORDINATES

Cartesian coordinates defined in a space fixed reference frame give the simplest spatial representation of the quantum mechanical kinetic energy operator. As in classical mechanics, the Cartesian coordinates of all particles can be used to describe the internal molecular dynamics. However, in addition to the latter, they do also describe the center of mass motion and the overall rotation of the molecular system, which are constant quantities in the absence of external forces or torques. In order to separate external from internal motions, two types of coordinate transformations can be performed. In the first, linear type of transformation, the center of mass is separated by the definition of space fixed relative position vectors of the atoms. The second, nonlinear transformation defines a reference frame that rotates with the molecule.

Despite linearity, the kinetic energy operator becomes more complicated and nonseparable when expressed in the space fixed relative position vectors which are obtained, when the center of mass is separated. There is a class of *orthogonal relative position vectors*, the definition of which depends on the masses of the particles, and in which the kinetic energy operator becomes maximally separable. These are three dimensional vectors represented by the symbol $\vec{r}_n$. The issue is discussed very pedagogically by Mladenović (2000). For N particles, there are $N-1$ orthogonal relative position vectors $\vec{r}_n$. Examples of such vectors are Jacobi and Radau vectors. When each of the three-dimensional position vectors is described in terms of its polar coordinates r_n, ϑ_n and φ_n, one obtains a representation of the molecular system in polyspherical coordinates (Nauts and Chapuisat, 1987; Gatti et al., 1998). For a system of N particles, the kinetic energy operator then gains the following general, very compact form,

$$^{(\mathrm{SF})}\hat{T} = \sum_{n=1}^{N-1} \left\{ -\frac{h^2}{8\pi^2 \mu_n} \left(\frac{\partial^2}{\partial {r_n}^2} + \frac{2}{r_n}\frac{\partial}{\partial r_n} \right) + \frac{h^2}{8\pi^2 \mu_n r_n^2}\,^{(\mathrm{SF})}\hat{\Lambda}_n \right\}, \tag{1.71}$$

where

$$^{(\mathrm{SF})}\hat{\Lambda} = -\left(\frac{1}{\sin(\vartheta_n)}\frac{\partial}{\partial \vartheta_n}\sin(\vartheta_n)\frac{\partial}{\partial \vartheta_n} + \frac{1}{\sin^2(\vartheta_n)}\frac{\partial^2}{\partial {\varphi_n}^2} \right). \tag{1.72}$$

The quantities μ_n $(n = 1, \ldots, N-1)$ are appropriately defined reduced masses (Mladenović, 2000; Gatti et al., 1998; Gatti and Iung, 2009). In principle, N can be the total number of particles in the molecule, i.e., electrons and nuclei. In practice, electronic motion has usually been separated adiabatically from the nuclear motion, as discussed in the previous section, before the actual nuclear dynamics is treated, and only the nuclei are considered for the definition of orthogonal relative position vectors; $N = N_\mathrm{a}$ is then the number of atoms. Note that, in this case, an error is introduced, as the electrons are generally not considered in the definition of the center of mass. This error, which is typically smaller than the error usually made by applying the Born–Oppenheimer approximation with well separated electronic states, was discussed by Kutzelnigg (2007).

The kinetic operator in Eq. (1.71) has singularities at $r_n = 0$ and $\vartheta_n = 0$ or π. The singularity at $r_n = 0$ can easily be removed. Those in terms of ϑ_n can be removed in the evaluation of matrix elements using nonseparable bases such as spherical harmonics in ϑ_n and φ_n, or using special *discrete variable representations* (DVR) (Light and Carrington, 2000; Beck et al., 2000) derived from these functions. Using nonseparable basis functions may render calculations longer.

In order to transform the space fixed coordinates into molecule fixed coordinates that rotate with the molecule, a direction-cosine matrix is used in connection with the three Euler angles α, β and γ (Zare, 1988). In order to define these angles, the body fixed axes system ${}^{(\mathrm{BF})}z$, ${}^{(\mathrm{BF})}y$ and ${}^{(\mathrm{BF})}x$ has to be defined. Formerly (see, e.g., Wilson et al., 1955), the system of principal axes of the instantaneous inertia tensor was usually chosen. In more recent work, an *embedding idea* following Tennyson and Sutcliffe (1982) has been adopted, which consists of using two of the orthogonal relative position vectors to define the body fixed reference axis system (see also Tennyson, 2011). The highest indexed vector $\vec{r}_{N_\mathrm{a}-1}$ may be chosen to define the body fixed z-axis. Hence, we identify the Euler angles $\alpha = \varphi_{N_\mathrm{a}-1}$ and $\beta = \vartheta_{N_\mathrm{a}-1}$. Then, $\vec{r}_{N_\mathrm{a}-2}$ is chosen to define the body fixed xz-plane. The rotation angle γ about the body fixed axis ${}^{(\mathrm{bf})}z$ as well as all remaining angles can be determined analytically (Mladenović, 2000) from the space fixed angles. The corresponding transformation equations, which are nonlinear and transcendental, however, lead to a transformation among angles alone:

$$\underbrace{\vartheta_{N_\mathrm{a}-1},\varphi_{N_\mathrm{a}-1},\dots,\vartheta_1,\varphi_1}_{2\times(N_\mathrm{a}-1)\ \text{angles}}$$
$$\longrightarrow \underbrace{\alpha,\beta,\gamma,\theta_{N_\mathrm{a}-2},\theta_{N_\mathrm{a}-3},\phi_{N_\mathrm{a}-3},\dots,\theta_1,\phi_1}_{2\times(N_\mathrm{a}-1)\ \text{angles}}.$$

In the body fixed system, since $\vec{r}_{N_\mathrm{a}-2}$ lies in the body fixed xz-plane, the azimuthal angle $\phi_{N_\mathrm{a}-2}$ is fixed (usually to π), and does not appear as a dynamical variable. Note also that this transformation does not alter the lengths of the orthogonal relative position vectors.

The set of $(3 \times N_\mathrm{a} - 6)$ internal coordinates composed of $(N_\mathrm{a} - 1)$ radii and $(2 \times (N_\mathrm{a} - 1) - 3)$ angles,

$$r_{N_\mathrm{a}-1},\dots,r_1,\theta_{N_\mathrm{a}-2},\theta_{N_\mathrm{a}-3},\phi_{N_\mathrm{a}-3},\dots,\theta_1,\phi_1,$$

defines a set of *polyspherical coordinates*.

Polyspherical coordinates are a good choice for multidimensional dynamics, as the expression of the kinetic operator can be rendered quite simple. Additionally, the differential volume element, which is given as the Jacobian determinant of the nonlinear transformation, will always be separable. This has two important aspects: First, multidimensional integrals can always be evaluated as products of one-dimensional integrals; secondly, reduced dimensionality treatments can easily be defined, as the integration domains have no mutual dependencies. We may mention here also the use of "polar normal coordinates" in treating anharmonic Fermi resonances (Lewerenz and Quack, 1988; Luckhaus and Quack, 1992) who used this efficiently in contraction schemes in conjunction with DVR techniques (Bačić et al., 1988).

Such coordinates were used to describe a multidimensional tunneling motion in the femtosecond time domain in vibrationally highly excited ammonia (Marquardt et al., 2010) and methane vibrational states (Zhao et al., 2018), in the proton transfer dynamics in malonaldehyde (Joubert-Doriol et al., 2012), and even in the complex ring-opening dynamics of indolinobenzospiropyran (Joubert-Doriol et al., 2014).

Because of the nonlinear transformation between the space fixed and the body fixed reference system, the body-fixed form of the kinetic energy operator will in general be more complicated than the expression in Eq. (1.71). However, it is possible to show that it can always be written in terms of a sum of products of one dimensional operators (see the review by Gatti and Iung, 2009), which facilitates its use in particular in connection with the MCTDH method for solving Eq. (1.42).

Polyspherical coordinates will generate technical problems when chemical reaction are to be described, during which the set of orthogonal relative position vectors enabling the separation of reactant spaces in the entrance channel is not the same as that enabling the separation of product spaces in the exit channel. In order to evaluate expectation values such as scattering matrix elements, for instance, complicated coordinate transformations need to be applied, in such cases. Elegant solutions to this problem have been proposed by Xiao et al. (2011). An alternative would be to use hyperspherical coordinates (Nauts and Chapuisat, 1987; Kuppermann, 1996; Aquilanti and Cavalli, 1997; Aquilanti et al., 1999). The latter would allow us to obtain a more balanced treatment of entrance and exit channels in a collision, and the calculation of integrals become more easy. One disadvantage of using hyperspherical coordinates is the increased number of angular variables. As can be followed from inspection of Eq. (1.72), angular variables are accompanied by singularities in the kinetic energy operator, the number of which will hence increase. The necessity to use a larger number of nonseparable bases to avoid these singularities is a drawback.

1.6 QUANTUM DYNAMICS UNDER EXCITATION WITH COHERENT MONOCHROMATIC RADIATION

1.6.1 Introductory Remarks

The excitation with coherent monochromatic (or nearly monochromatic) radiation is an important special case of molecular spectroscopy and quantum dynamics to be discussed in more detail in this section. While, in principle, any of the direct integration schemes for the time dependent Schrödinger equation discussed in Section 1.3 might be used, we concentrate here on the approach where the electromagnetic field is treated classically and the stationary states of the field free molecule are obtained in a first step by solving the time independent Schrödinger equation for the isolated molecule, as described in Chapter 2 of this book (Császár et al., 2020).

In a second step one then solves the time dependent Schrödinger equation in the basis of these molecular eigenstates. The advantages of this two-step approach have been pointed out for the case of coherent infrared excitation by Quack (1978, 1989b), and in Fábri et al. (2019) (see also Section 1.3.1). One important advantage of this approach is the possibility to check the theoretical results of the first step against very accurate experimental results from high resolution spectroscopy (Merkt and Quack, 2011a). The division of the approach in two steps has been called a divide-and-rule (divide et impera, DEI)-Ansatz by Fábri et al. (2019).

We follow here closely the treatment given in Quack (1998) and Merkt and Quack (2011a), in part even literally. One should note, however, that some of the advantages of this DEI approach are lost when one considers very short excitation times, very strong fields and very high radiation frequencies (VUV, Röntgen, etc.) where some of the approximations in the starting point of the approach are lost.

1.6.2 General Aspects of Atomic and Molecular Systems in Electromagnetic Field

High-power coherent laser light sources allow for a variety of phenomena ranging from coherent single-photon transitions to multiphoton transitions of different types. Fig. 1.4 provides a summary of mechanisms for such transitions.

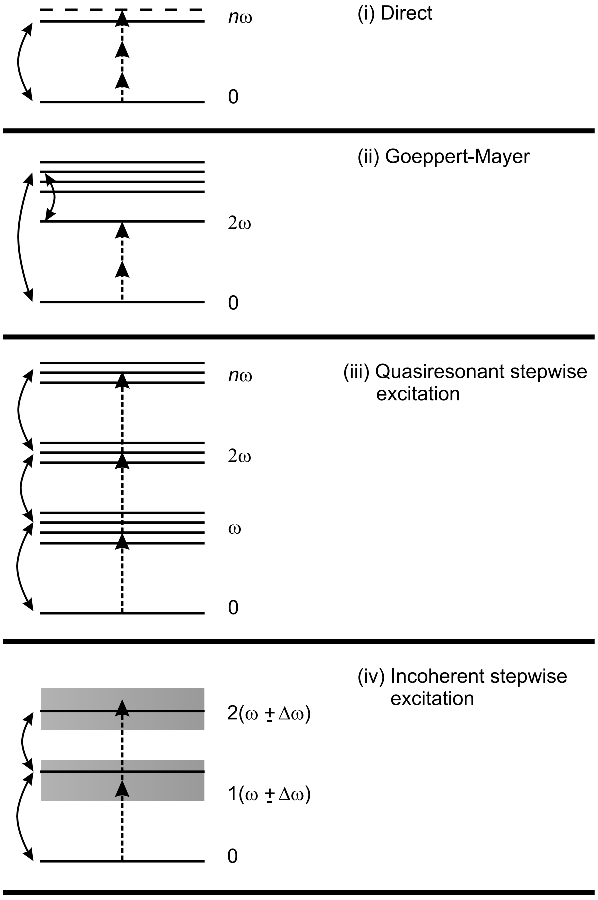

FIG. 1.4 Mechanisms for radiative excitation [after Quack, 1998]. Dotted lines give the transitions, curved full lines the dipole coupling.

While excitation with incoherent light can be based on a statistical treatment (Einstein, 1916a,b, 1917; Merkt and Quack, 2011b), excitation with coherent light can be handled by means of quantum dynamics. Intense, coherent laser radiation as also electromagnetic radiation in the radiofrequency domain used in nuclear magnetic resonance (NMR) spectroscopy (Ernst et al., 1987) can be treated as a classical electromagnetic wave satisfying the general wave equations (1.73) and (1.74) resulting from Maxwell's theory:

$$\nabla^2 \vec{E} = \mu\mu_0\varepsilon\varepsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2}, \tag{1.73}$$

$$\nabla^2 \vec{B} = \mu\mu_0\varepsilon\varepsilon_0 \frac{\partial^2 \vec{B}}{\partial t^2}, \tag{1.74}$$

where $\vec{E}$ is the electric field vector and $\vec{B}$ the vector of the magnetic induction, μ, μ_0, ε, ε_0 are the usual field constants, see (Cohen et al., 2007), with $\varepsilon = \mu = 1$ in vacuo. In Eqs. (1.73) and (1.74), $\nabla^2 = \vec{\nabla}^2$, and the nabla operator $\vec{\nabla}$ is defined in Eq. (1.75):

$$\vec{\nabla} = \vec{e}_x \frac{\partial}{\partial x} + \vec{e}_y \frac{\partial}{\partial y} + \vec{e}_z \frac{\partial}{\partial z} \tag{1.75}$$

where $\vec{e}_x$, $\vec{e}_y$, $\vec{e}_z$ are the unit vectors in a (right-handed) Cartesian coordinate system. The classical electromagnetic wave can be understood as the coherent state description of the quantum field in the limit of very large average number $\langle n \rangle$ of quanta per field mode (Glauber, 1963a,b; Perelomov, 1986). Coherent laser radiation and also radiofrequency radiation are frequently charac-

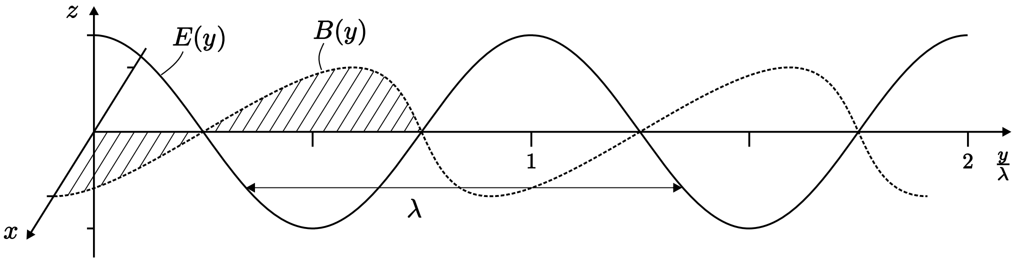

FIG. 1.5 Schematic representation of a z-polarized monochromatic wave (after Merkt and Quack, 2011b).

terized by $\langle n\rangle > 10^{10}$. Thus the classical approximation to the electromagnetic field is excellent. The situation of weak thermal light sources in the optical domain is very different ($\langle n\rangle < 1$), requiring a quantum statistical treatment.

We consider here, for simplicity, the special case of a classical z-polarized electromagnetic wave propagating in vacuo in the y-direction with slowly varying (or constant) field amplitudes $E_0(t)$ and $B_0(t)$ (see Fig. 1.5):

$$E_z(y,t) = |E_0(t)|\cos(\omega t + \eta' - k_\omega y), \tag{1.76}$$

$$B_x(y,t) = |B_0(t)|\cos(\omega t + \eta' - k_\omega y), \tag{1.77}$$

$\omega = 2\pi\nu$ is the angular frequency, $k_\omega = 2\pi/\lambda$ the angular wavenumber, $\nu = c/\lambda$ the ordinary frequency, and λ the wavelength. At a given position y, the phase η' can be combined with the phase $-k_\omega y$ to an overall phase ($\eta = k_\omega y - \eta'$).

The extension to more general cases is straightforward (see also Quack, 1998). The intensity of the radiation is, in general,

$$I(y,t) = |E_z(y,t)|^2\sqrt{\frac{\varepsilon\varepsilon_0}{\mu\mu_0}}, \tag{1.78}$$

and averaging over time with $\left\langle \cos^2 x\right\rangle = 1/2$, one has from Eqs. (1.76) and (1.78)

$$I(t) = \frac{1}{2}|E_0(t)|^2\sqrt{\frac{\varepsilon\varepsilon_0}{\mu\mu_0}}. \tag{1.79}$$

For the speed of light, one has in some medium with refractive index n_m

$$c_m = (\mu\mu_0\varepsilon\varepsilon_0)^{-1/2} = c/n_m \tag{1.80}$$

and in vacuo ($\mu = \varepsilon = 1$)

$$c = (\mu_0\varepsilon_0)^{-1/2}. \tag{1.81}$$

We can mention here some practical equations for calculating electric and magnetic field strengths when irradiating with monochromatic radiation of given intensity I:

$$\left|\frac{E_0}{\mathrm{V\ cm^{-1}}}\right| \simeq 27.44924\sqrt{\frac{I}{\mathrm{W\ cm^{-2}}}}, \tag{1.82}$$

$$\left|\frac{B_0}{\mathrm{T}}\right| \simeq 9.156\cdot 10^{-6}\sqrt{\frac{I}{\mathrm{W\ cm^{-2}}}}. \tag{1.83}$$

A further quantity characterizing the irradiation over some period of time t is the fluence $F(t)$ defined by Eq. (1.84) as

$$F(t) = \int_0^t I(t')\mathrm{d}t'. \tag{1.84}$$

For wavelengths $\lambda > 100$ nm, one can assume $\vec{E}$ and $\vec{B}$ to vary little over the extension of the atomic or molecular system ($\Delta y < 1$ nm) at any given time, which leads to the dipole approximation for the interaction energy between molecule and field,

$$\hat{V}_{\mathrm{el.dipole}} = -\hat{\vec{\mu}}_{\mathrm{el}}\cdot\vec{E}, \tag{1.85}$$

where $\hat{\vec{\mu}}_{\mathrm{el}}$ is the electric dipole operator vector given by Eq. (1.86), with charges q_i for the particles with position operator vector $\hat{\vec{r}}_i$,

$$\hat{\vec{\mu}}_{\mathrm{el}} = \sum_i q_i\hat{\vec{r}}_i. \tag{1.86}$$

Similarly, one has the interaction energy with a magnetic dipole operator vector $\hat{\vec{\mu}}_{\mathrm{magn}}$,

$$\hat{V}_{\mathrm{magn.dipole}} = -\hat{\vec{\mu}}_{\mathrm{magn}}\cdot\vec{B}. \tag{1.87}$$

For the present quantum dynamical treatment of coherent excitation, we restrict our attention to electric dipole transitions in a field given by Eq. (1.76), and therefore we can write, with the z-component $\hat{\mu}_z$ of the electric dipole operator vector (and abbreviating $\eta = k_\omega y - \eta'$), as follows:

$$\hat{V}_{\text{el.dipole}} = -\hat{\mu}_z E_z(y,t) = -\hat{\mu}_z \left|E_0(t)\right| \cos(\omega t - \eta). \tag{1.88}$$

The extension to magnetic dipole transitions is straightforward. We give here only a brief summary and refer to Quack (1978, 1982, 1998) for more details.

1.6.3 Time-Dependent Quantum Dynamics in an Oscillatory Electromagnetic Field

Consider now the time-dependent Schrödinger equation (1.18) (or Eq. (1.42)) with a time-dependent Hamiltonian

$$\hat{H}(t) = \hat{H}_{\text{Mol}} - \hat{\mu}_z \left|E_0(t)\right| \cos(\omega t - \eta), \tag{1.89}$$

with $\hat{H}_{\text{Mol}}$ being the time-independent Hamiltonian for the isolated molecule in the absence of fields and the interaction Hamiltonian being a time-dependent, oscillatory function. We assume the solution of the time-independent Schrödinger equation for the isolated molecule to be given by Eq. (1.90) with $\hbar = h/2\pi$,

$$\hat{H}_{\text{Mol}}\varphi_k = E_k\varphi_k = \hbar\omega_k\varphi_k, \tag{1.90}$$

and write the solution of the time-dependent Schrödinger equation in the basis φ_k of molecular eigenstates with time-dependent coefficients as

$$\Psi(r,t) = \sum_k b_k(t)\varphi_k(r). \tag{1.91}$$

Here r stands again for a set of molecular coordinates, as in Eq. (1.21). Inserting this into Eq. (1.18), we obtain a set of coupled differential equations:

$$i\hbar\frac{\mathrm{d}b_j}{\mathrm{d}t} = \sum_k H_{jk}b_k(t), \tag{1.92}$$

or in matrix notation,

$$i\hbar\frac{\mathrm{d}\boldsymbol{b}(t)}{\mathrm{d}t} = \boldsymbol{H}(t)\boldsymbol{b}(t). \tag{1.93}$$

This is again, in essence, a matrix representation of the original Schrödinger equation (see Section 1.3 and Eq. (1.44)). Assuming molecular states of well-defined parity, the diagonal electric dipole matrix elements vanish and we have the diagonal elements of $\boldsymbol{H}(t)$,

$$H_{ii} = E_i = \left\langle \varphi_i \middle| \hat{H}_{\text{Mol}} \middle| \varphi_i \right\rangle \equiv \hbar\omega_i. \tag{1.94}$$

For other situations such as for chiral molecules or if parity violation were important (see Quack, 2011a), one would have also a diagonal contribution from the electric dipole interaction energy. Disregarding such cases here, the electric dipole interaction energy leads to time-dependent off-diagonal matrix elements

$$H_{kj}(t) = \left\langle \varphi_k \middle| \hat{V}_{\text{el.dipole}}(t) \middle| \varphi_j \right\rangle. \tag{1.95}$$

Dividing H_{kj} by $\hbar\cos(\omega t - \eta)$, we obtain a matrix element V_{kj}, which is independent of time, if we can assume $|E_0(t)|$ to be sufficiently slowly varying in time that it can be taken to be constant for the time period under consideration, as we shall do, replacing $E_0(t)$ by E_0 leads to

$$V_{kj} = \frac{H_{kj}}{\left[\hbar\cos(\omega t - \eta)\right]} = -\left\langle \varphi_k \left| \hat{\mu}_z \right| \varphi_j \right\rangle \frac{|E_0|}{\hbar} = V^*_{jk}. \tag{1.96}$$

We then obtain a set of coupled differential equations in matrix notation:

$$\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{b}(t) = \{\boldsymbol{W} + \boldsymbol{V}\,\cos(\omega t - \eta)\}\,\boldsymbol{b}(t) \tag{1.97}$$

where we have defined the diagonal matrix $\boldsymbol{W}$ by the matrix elements $W_{kk} \equiv \omega_k$.

This is still a practically exact representation of the original time-dependent Schrödinger equation for the physical situation considered here. Because of the essential time dependence in $\boldsymbol{V}\cos(\omega t - \eta)$, in general there is no simple closed expression in the form of the exponential function analogous to Eqs. (1.16), (1.22) or (1.47) and (1.50), with a few exceptions, such as the harmonically driven harmonic oscillator (see Marquardt and Quack, 1989, and the references cited therein, as discussed at the end of this section). Apart from numerical, stepwise solutions discussed by Quack (1998), one can make use of series expansions such as the Magnus expansion. This solves Eq. (1.93) by means of the following series for $\boldsymbol{U}(t,t_0)$, with the unit matrix $\boldsymbol{I}$:

$$\boldsymbol{b}(t) = \boldsymbol{U}(t,t_0)\,\boldsymbol{b}(t_0), \tag{1.98}$$

$$\boldsymbol{U}(t_0,t_0) = \boldsymbol{I}, \tag{1.99}$$

$$\boldsymbol{U}(t,t_0) = \exp\left(\sum_{n=0}^{\infty} \boldsymbol{C}_n\right). \tag{1.100}$$

The first two terms are given by the following expressions:

$$\mathrm{i}\hbar \boldsymbol{C}_0 = \int_{t_0}^{t} \boldsymbol{H}(t')\mathrm{d}t', \tag{1.101}$$

$$\mathrm{i}\hbar \boldsymbol{C}_1 = -\frac{1}{2}\int_{t_0}^{t} \left\{ \int_{t_0}^{t''} \left[\boldsymbol{H}(t'), \boldsymbol{H}(t'')\right] \mathrm{d}t' \right\} \mathrm{d}t''. \tag{1.102}$$

Higher terms contain more complex combinations of commutators of the type $\left[\boldsymbol{H}(t'), \boldsymbol{H}(t'')\right]$. From this, one recognizes that the series terminates after the first term given by Eq. (1.78), if $\boldsymbol{H}(t')$ and $\boldsymbol{H}(t'')$ commute at all t', t'', which is true if $\boldsymbol{H}$ does not depend on time, resulting in the exponential solutions already discussed. There are other (rare) cases of time-dependent $\boldsymbol{H}(t)$, but with $\left[\boldsymbol{H}(t'), \boldsymbol{H}(t'')\right] = 0$. One can, however, also make use of the periodicity of the field using Floquet's theorem (Quack, 1978, 1998).

1.6.4 Floquet Solution for Hamiltonians With Strict Periodicity

With $\boldsymbol{H} = \hbar\{\boldsymbol{W} + \boldsymbol{V}\cos(\omega t - \eta)\}$ from Eq. (1.74), one has obviously

$$\boldsymbol{H}(t + \tau) = \boldsymbol{H}(t) \tag{1.103}$$

with period $\tau = 2\pi/\omega$.

Making use of the Floquet theorem (or Floquet–Liapunoff theorem, see Quack, 1978, 1998 and Quack and Sutcliffe, 1985 for the historical references), one has the following form for the time-evolution matrix (with some integer n):

$$\boldsymbol{U}(t, t_0) = \boldsymbol{F}(t, t_0)\exp\left(\boldsymbol{A}(t - t_0)\right), \tag{1.104}$$

$$\boldsymbol{F}(t_0, t_0) = \boldsymbol{I}, \tag{1.105}$$

$$\boldsymbol{F}(t + n\tau) = \boldsymbol{F}(t), \tag{1.106}$$

$$\boldsymbol{A}(t') = \boldsymbol{A}(t'') \qquad (\text{all } t', t''). \tag{1.107}$$

It is then sufficient to integrate Eq. (1.93) numerically over one period τ using methods discussed in Section 1.3, and then obtain the evolution for all times by matrix multiplications according to Eqs. (1.104)–(1.107). In particular, at multiples of the period τ, one finds (with $t_0 = 0$):

$$\boldsymbol{U}(\tau) = \exp(\boldsymbol{A}\tau), \tag{1.108}$$

$$\boldsymbol{U}(n\tau) = [\boldsymbol{U}(\tau)]^n. \tag{1.109}$$

There has been considerable literature making use of Floquet's theorem for the treatment of coherent excitation and there also exist computer program packages (Quack and Sutcliffe, 1986; Quack, 1998; Marquardt et al., 2019). We shall discuss here a further useful approximation.

1.6.5 Weak-Field Quasiresonant Approximation (WF-QRA) for Coherent Monochromatic Excitation

We consider a level scheme for coherent excitation with levels near the resonance as shown in Fig. 1.6. One can then associate with each molecular level of energy $E_k = \hbar\omega_k$ an integer photon number n_k for near-resonant excitation such that

$$\omega_k = n_k\omega + x_k \tag{1.110}$$

where x_k is a frequency mismatch for exact resonance at the best choice of n_k.

Under the conditions that (i) there is a sequential near-resonant excitation path, (ii) only levels with a general resonance mismatch satisfying $|x_k| \ll \omega$ contribute effectively to excitation (quasiresonant condition), and (iii) the coupling matrix elements satisfy $|V_{kj}| \ll \omega$ (weak-field condition), one can approximately derive a set of coupled equations with an effective Hamiltonian that does not depend on time. For this purpose, one makes the simple substitution (Quack, 1978, 1998), namely

$$a_k = \exp(\mathrm{i}n_k\omega t)b_k, \tag{1.111}$$

resulting in the set of differential equations

$$\mathrm{i}\frac{\mathrm{d}a_k}{\mathrm{d}t} = x_k a_k + \frac{1}{2}\sum_{j\neq k} V_{kj}a_j, \tag{1.112}$$

or in matrix form (with the diagonal matrix $\boldsymbol{X}$ and $X_{kk} = x_k$)

$$\mathrm{i}\frac{\mathrm{d}\boldsymbol{a}}{\mathrm{d}t} = \left\{\boldsymbol{X} + \frac{1}{2}\boldsymbol{V}'\right\}\boldsymbol{a}. \tag{1.113}$$

where $\boldsymbol{V}'$ differs from $\boldsymbol{V}$ by explicitly setting all V_{kj} equal to zero if the levels E_k and E_j are far off resonance, e.g. if they are not adjacent quasiresonant levels.

One can interpret this equation by means of an "effective Hamiltonian"

$$\boldsymbol{H}_{\text{eff}}^{(a)} = \hbar\left\{\boldsymbol{X} + \frac{1}{2}\boldsymbol{V}'\right\} \tag{1.114}$$

and the corresponding effective time-evolution matrix

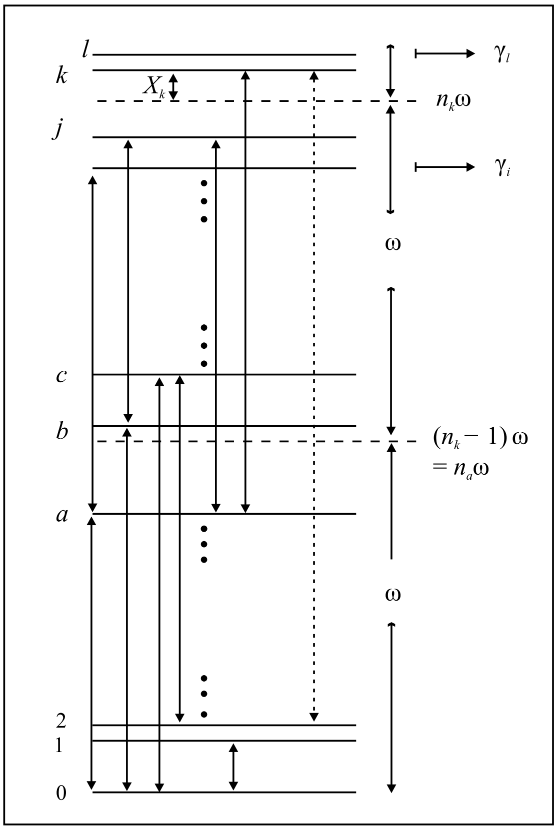

FIG. 1.6 Energy-level scheme [after Quack, 1982]. The molecular energy levels are marked as horizontal full lines. The horizontal dashed lines correspond to the energies $E_0 + n_k\hbar\omega$ of the ground state (E_0) plus the energy of n_k photons.

$$\boldsymbol{U}_{\text{eff}}^{(a)}(t,t_0) = \exp\left[-2\pi\mathrm{i}\frac{\boldsymbol{H}_{\text{eff}}^{(a)}(t-t_0)}{h}\right] = \exp\left[-\mathrm{i}\left(\boldsymbol{X} + \frac{1}{2}\boldsymbol{V}'\right)(t-t_0)\right], \tag{1.115}$$

$$\boldsymbol{a}(t) = \boldsymbol{U}_{\text{eff}}^{(a)}(t,t_0)\,\boldsymbol{a}(t_0). \tag{1.116}$$

It is sometimes useful to describe decay phenomena by adding an imaginary energy contribution, for instance, $E_l = \Re(E_l) - \mathrm{i}\gamma_l/2$ as indicated, where $\Re(z)$ designates the real part of the complex number z (see Quack, 1982 and Quack and Sutcliffe, 1984). The introduction of an imaginary part to the energy of a spectroscopic state introduces into the field of non-Hermitian quantum mechanics.

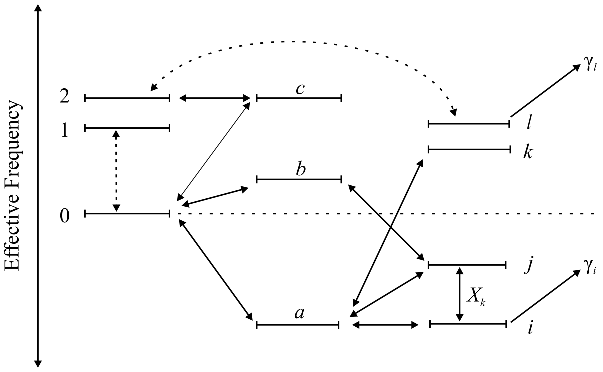

FIG. 1.7 Effective-frequency scheme corresponding to the energy-level scheme of Fig. 1.6 [after Quack, 1982].

Non-Hermitian quantum mechanics is covered in great detail in the book of Moiseyev (2011) (see also Hehenberger et al., 1974). In principle exponential decay can be derived also with the aid of Hermitean quantum mechanics, as exemplified by the Bixon-Jortner model (Bixon and Jortner, 1968). Related to exponential decay are quasi-Lorentzian lineshapes with a lower energy bound which were shown to arise from Hermitean quantum mechanics in an analytical exact solution of the time dependent Schrödinger equation (Marquardt, 2019). Various aspects of exponential decay and the related spectroscopic lineshapes were discussed by Merkt and Quack (2011b), were one can also find a critical discussion of the incorrect but frequently used "textbook" derivation of exponential decay lineshapes from the uncertainty relation Eq. (1.11), which often is presented as "didactically useful" but in fact is quite fallacious.

The result in Eqs. (1.113)–(1.116) is quite remarkable as it corresponds to replacing the molecular energies E_k by new effective energies $\hbar X_{kk}$ and the couplings V_{kj} by new effective couplings $(V_{kj}/2)$ for near-resonant levels (and implicitly by zero for far off-resonant levels). We can therefore use the time independent $\boldsymbol{V}'/2$ rather than $\boldsymbol{V}\cos(\omega t - \eta)$ for the general coupling matrix in Eq. (1.97). This is graphically shown in Fig. 1.7 for the same level scheme as in Fig. 1.6, but with effective energies that are "on the same energy shell" and thus effective couplings between levels of similar effective energy. We note the close analogy to the dressed atom (dressed molecule) picture by Cohen-Tannoudji et al. (1992) and Haroche (2012), which uses, however, a different derivation. We note that the quasiresonant transformation as given in Quack (1978, 1998) can be written in matrix notation:

$$\boldsymbol{a} = \boldsymbol{S}\,\boldsymbol{b}, \tag{1.117}$$

with the diagonal matrix

$$S_{kk} = \exp(\mathrm{i}n_k\omega t). \tag{1.118}$$

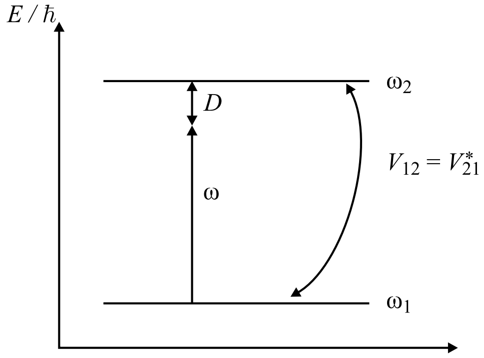

FIG. 1.8 Two-level scheme for coherent radiative excitation with frequency ω [after Merkt and Quack, 2011b].

Similarly, a transformation for the density matrix $\boldsymbol{P}^{(a)}$ from $\boldsymbol{P}^{(b)}$ can be derived in this approximation, resulting in the solution of the Liouville–von Neumann equation for $\boldsymbol{P}(t)$ by

$$\boldsymbol{P}^{(a)}(t) = \boldsymbol{S}\,\boldsymbol{P}^{(b)}\,\boldsymbol{S}^{\dagger}, \tag{1.119}$$

$$\boldsymbol{P}^{(a)}(t) = \boldsymbol{U}_{\mathrm{eff}}^{(a)}(t,t_0)\,\boldsymbol{P}^{(a)}(t_0)\,\boldsymbol{U}_{\mathrm{eff}}^{(a)\dagger}(t,t_0). \tag{1.120}$$

For details, we refer to Quack (1978, 1982, 1998) and the discussions in Donley et al. (2001), Marquardt et al. (2019), Quack and Sutcliffe (1984, 1985) as well as in Whaley and Light (1984). We turn now to a simple application to the special case of coherent radiative excitation connecting just two quantum states.

1.6.6 Coherent Monochromatic Excitation Between Two Quantum States

If only two quantum states are considered, one obtains a scheme for the coherent monochromatic radiative excitation as shown in Fig. 1.8.

Eq. (1.93) simplifies to the set of just two coupled differential equations:

$$\mathrm{i}\frac{\mathrm{d}b_1}{\mathrm{d}t} = \omega_1 b_1 + V_{12}\cos(\omega t - \eta)\; b_2, \tag{1.121}$$

$$\mathrm{i}\frac{\mathrm{d}b_2}{\mathrm{d}t} = V_{21}\cos(\omega t - \eta) b_1 + \omega_2 b_2. \tag{1.122}$$

One might think that this rather simple set of coupled differential equations has a simple solution, but, in fact, it seems that until today no simple general analytical solution in the form of a closed expression is known (see the discussion in Quack (1978, 1998), also for special cases). Of course, one can write down series expansions (Sections 1.3.2 and 1.3.3) or quite easily solve the equations numerically, by other methods discussed in Section 1.3.

However, following the discussion of Section 1.6.5, an analytical solution in the form of a closed expression can be derived in the weak-field quasiresonant approximation (WF-QRA). The most general solution in terms of the time-evolution matrix $\boldsymbol{U}_{\mathrm{eff}}^{(a)}$ is given by the matrix elements, omitting the index "eff" to simplify the notation, and taking a real $V_{12} = V_{21}^* = V$ as parameter,

$$U_{11}^{(a)} = \exp(-\mathrm{i}\lambda_1 t)\left[x^2 + y^2\exp(\mathrm{i}\omega_R t)\right], \tag{1.123}$$

$$U_{22}^{(a)} = \exp(-\mathrm{i}\lambda_1 t)\left[y^2 + x^2\exp(\mathrm{i}\omega_R t)\right], \tag{1.124}$$

$$U_{12}^{(a)} = U_{21}^{(a)} = \exp(-\mathrm{i}\lambda_1 t)xy\left[1 - \exp(\mathrm{i}\omega_R t)\right], \tag{1.125}$$

where we have used the following parameters as abbreviations:

$$D = \omega_2 - \omega_1 - \omega, \tag{1.126}$$

$$\omega_R = (\lambda_1 - \lambda_2) = \sqrt{V^2 + D^2} = \frac{2\pi}{\tau_R}, \tag{1.127}$$

$$\lambda_1 = \frac{1}{2}\left(D + \sqrt{V^2 + D^2}\right), \tag{1.128}$$

$$\lambda_2 = \frac{1}{2}\left(D - \sqrt{V^2 + D^2}\right), \tag{1.129}$$

$$x = \left[\frac{1}{2} - \frac{D}{2\omega_R}\right]^{1/2}, \tag{1.130}$$

$$y = \left[\frac{1}{2} + \frac{D}{2\omega_R}\right]^{1/2}. \tag{1.131}$$

We note that in Quack (1998) some of the expressions where misprinted, and these are corrected here (see also Merkt and Quack, 2011b). We also give the explicit form of the effective Hamiltonian corresponding to Eq. (1.114):

$$\frac{\boldsymbol{H}_{\mathrm{eff}}^{(a)}}{\hbar} = \begin{pmatrix} 0 & 0 \\ 0 & D \end{pmatrix} + \frac{1}{2}\begin{pmatrix} 0 & V \\ V & 0 \end{pmatrix} \tag{1.132}$$

$$= \boldsymbol{X} + \frac{1}{2}\boldsymbol{V}. \tag{1.133}$$

In the two-level case, the distinction between V and V' is not necessary.

Now $\boldsymbol{U}_{\mathrm{eff}}^{(a)}$ is explicitly derived by means of the eigenvalues and eigenstates of $\boldsymbol{H}_{\mathrm{eff}}^{(a)}$ (see Section 1.3.1 and Quack, 1998) as

$$\boldsymbol{Z}^{-1}\left(\boldsymbol{X} + \frac{1}{2}\boldsymbol{V}\right)\boldsymbol{Z} = \boldsymbol{\Lambda} = \boldsymbol{Diag}(\lambda_{1,}\lambda_2), \tag{1.134}$$

$$\boldsymbol{U}_{\mathrm{eff}}^{(a)}(t - t_0) = \boldsymbol{Z}\exp\left[-\mathrm{i}\boldsymbol{\Lambda}(t - t_0)\right]\boldsymbol{Z}^{-1}. \tag{1.135}$$

In Eq. (1.134) $\boldsymbol{\Lambda}$ is a diagonal matrix with eigenvalues λ_1 and λ_2.

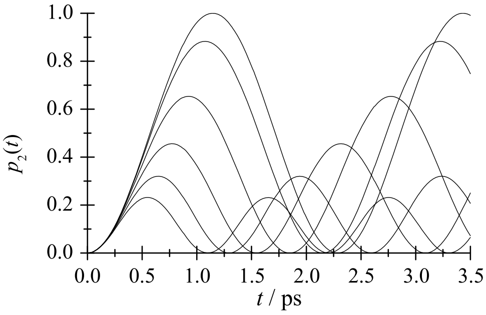

FIG. 1.9 Time-dependent level populations from Eq. (1.136). The population p_2 of the upper level in the scheme of Fig. 1.8 is shown with different resonant defects $D = (0, 1, 2, 3, 4, 5) \times 10^{12}$ s^{-1} for an electric dipole transition with the laser wave number $\tilde{\nu} = 1000$ cm^{-1}, intensity $I = 1$ GW cm^{-2} and transition moment $|\mu_{21}| = \langle\varphi_2|\hat{\mu}_z|\varphi_1\rangle =$ 1 Debye [after Merkt and Quack, 2011b].

While these general equations can be used to derive numerous properties of the coherent monochromatic excitation in the two-level problem, we conclude here with the result for the time-dependent population of the excited level $p_2(t)$, if, initially, at time zero, only the ground state is populated ($p_1(t=0) = 1$).

One obtains Eq. (1.136) for the population of the upper level:

$$p_2(t) = |b_2(t)|^2 = \frac{V^2}{V^2 + D^2}\left[\sin\left(\frac{t}{2}\sqrt{V^2 + D^2}\right)\right]^2$$
$$= 1 - p_1(t). \tag{1.136}$$

This is a periodic exchange of population between ground and excited states with a period

$$\tau_R = \frac{2\pi}{\sqrt{V^2 + D^2}}. \tag{1.137}$$

This period is called the *Rabi period*, with ω_R being the *Rabi frequency*, as these equations were derived on the basis of the so-called rotating wave approximation by Rabi (1937) (see also Rabi et al., 1938) in the context of early NMR experiments (in beams, with a magnetic dipole transition matrix element V, of course).

The rotating wave approximation becomes identical with the quasiresonant approximation for the special case of a two-level problem. Eq. (1.136) is frequently called the *Rabi formula*.

Fig. 1.9 shows the time-dependent level populations for a fairly typical case. With increasing resonant defect D, the amplitude of the oscillation decreases, but the frequency of oscillation increases. The initial time evolution is independent of the resonant defect as is readily seen from the series expansion of the $\sin(x)$ function for small arguments x ($\sin(x) = x + \cdots$) giving at sufficiently small times

$$p_2(t) \simeq V^2 t^2/4 \quad (\text{small } t). \tag{1.138}$$

One can also consider the time-averaged population $\langle p_2(\omega)\rangle_t$ as a function of the exciting laser frequency ω at fixed resonance frequency $\omega_{12} = \omega_2 - \omega_1$. Because $\left\langle \sin^2(x)\right\rangle_x = 1/2$, one has

$$\langle p_2(\omega)\rangle_t = \frac{1}{2}\frac{V^2}{V^2 + (\omega - \omega_{12})^2} \tag{1.139}$$

so that $\langle p_2(\omega)\rangle$ is proportional to the average absorbed energy as a function of frequency ω, and one can interpret this expression as the effective absorption lineshape under intense coherent excitation. Indeed, Eq. (1.139) corresponds to a Lorentzian lineshape with full width at half-maximum $\Gamma_{\text{FWHM}} = 2V$. This effect is called *power broadening* because $V \propto \sqrt{I}$ (cf. Eqs. (1.82) and (1.96), sometimes the term *intensity broadening* is used as well). We have neglected here effects from spontaneous emission or collisions, as is obviously appropriate for the timescales applicable to Fig. 1.9, but not necessarily always so.

We may finally conclude with an estimate of errors arising when the conditions of the WF-QRA are not fulfilled. The special case of the degenerate two-level problem has been solved exactly (Quack, 1978). In this case, one has $\omega_1 = \omega_2$ and therefore $D^2 = \omega^2$. The Rabi formula Eq. (1.136) thus would give

$$p_2^{\text{Rabi}}(t) = \frac{V^2}{V^2 + \omega^2}\left[\sin\left(\frac{t}{2}\sqrt{V^2 + \omega^2}\right)\right]^2. \tag{1.140}$$

The exact solution (Quack, 1978) is

$$p_2^{\text{ex}}(t) = \left\{\sin\left[\left(\frac{V}{\omega}\right)\sin(\omega t)\right]\right\}^2. \tag{1.141}$$

One can consider the limit $|V| \ll \omega$ because this must be assumed for the validity of the Rabi formula, and considering this limit, one obtains

$$p_2^{\text{Rabi}}(t) = \frac{V^2}{\omega^2}\left[\sin\left(\frac{\omega t}{2}\right)\right]^2, \tag{1.142}$$

$$p_2^{\text{ex}}(t) = \frac{V^2}{\omega^2}[\sin(\omega t)]^2. \tag{1.143}$$

Thus the exact solution gives the same amplitude as the Rabi formula, but the period differs by a factor of 2 and the short time limit for the population p_2 differs by a factor of 4. Of course, the second condition for the validity of the WF-QRA is not satisfied, as one cannot have $|D| \ll \omega$ (rather by definition of the special case, one has $|D| = \omega$). If $|D| \ll \omega$, the Rabi formula gives a very good approximation, as one can show numerically. We may note here that closed analytical expressions for the solutions are available for the excitation of the harmonic oscillator both with the exact treatment (Eq. (1.93)) and within the WF-QRA (Eq. (1.113)), taking an infinite number of levels into account, which may, perhaps, seem surprising. The derivation has been given by Marquardt and Quack (1989) and leads to a further estimate of the ranges of validity and uncertainties introduced by the WF-QRA, both for populations and phases, in this case for a many-level system. A very interesting simple situation for a two-level population transfer by a three-level mechanism which can be treated with the QRA or Floquet approximation is STIRAP (Stimulated Raman Adiabatic Passage) reviewed recently by Bergmann et al. (2019).

1.7 CONCLUDING REMARKS

> *We measure time by motion and motion by time (Aristotle, as cited and translated in Quack (2004a,b)).*
>
> *Time is what you read from your clock ("Zeit ist das, was man an der Uhr abliest", Einstein, 1922, as cited and translated in Quack (1999, 2004a,b)).*

We shall conclude here with some general considerations on time as defined by atomic and molecular clocks and the important role of symmetries and approximate or exact constants of the motion in molecular quantum dynamics. We follow here Quack (2011a), see also Quack and Hacker (2016) for the role of symmetries in a broader context.

1.7.1 Time-Dependent Quantum Motion, Spectroscopy and Atomic and Molecular Clocks

Simple periodic quantum motions can be considered to be the basis of atomic and molecular clocks as special cases of general intramolecular dynamics. Indeed, the general quantum dynamics of isolated molecules are described by Eqs. (1.18) and (1.26) (or the formally equivalent Eqs. (1.42) and (1.46)). The quantities ψ_k and E_k are obtained from the solution of the stationary Schrödinger equation (1.26). The eigenfunctions ψ_k depend only on space (and spin) coordinates, and the energy eigenvalues E_k can be subject to spectroscopic observation by means of the Bohr condition from Eq. (1.1), $|\Delta E_{jk}| = |E_k - E_j| = h\nu_{jk}$, with the transition frequency ν_{jk}. If we consider just two levels as equally populated, we obtain a periodic motion simplified to some time-dependent probability function:

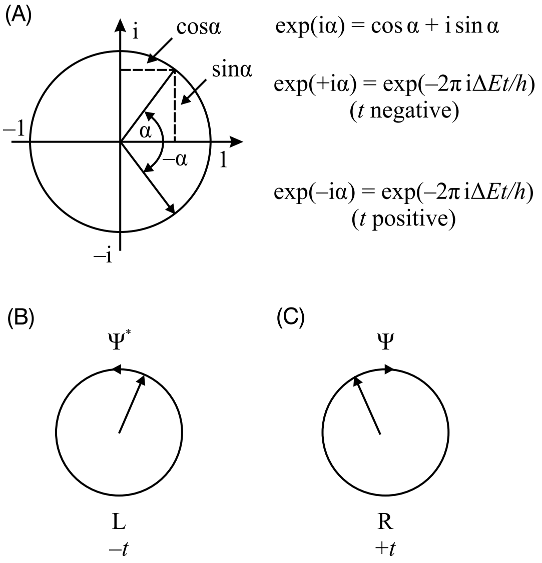

FIG. 1.10 Explanation of the phase factor of the complex, time-dependent wavefunction for the atomic and molecular clock. (A) The phase factor is graphically depicted as an arrow in the Gaussian plane (α is taken to be positive). For positive times t, one obtains $\exp(-i\alpha)$, the hand of the clocklike phase factor turns in the clockwise direction, in the sense of increasingly negative α. (B) and (C) These illustrate the wavefunction Ψ and its complex conjugate Ψ^*, which both describe a symmetrically equivalent solution of the Schrödinger equation, given time-reversal symmetry. The picture also describes the corresponding orbits of planets around the Sun, symmetric under time reversal. These can move in a clockwise as well as counterclockwise direction, providing acceptable solutions to the classical equations of motion [after Quack, 1999 by permission].

$$p(t) = |a + b\,\exp(-2\pi \mathrm{i}\,|\Delta E_{jk}|\,t/h)|^2. \qquad (1.144)$$

The time dependence of such an atomic or a molecular clock is fully described by a time-dependent, complex periodic phase factor exp(iα) represented graphically in Fig. 1.10 in terms of the complex Gaussian plane. The hand of the clock, figuratively speaking, is given by the vector describing exp(iα) in the plane that moves clockwise for positive time and counterclockwise for negative time. The period of the clock

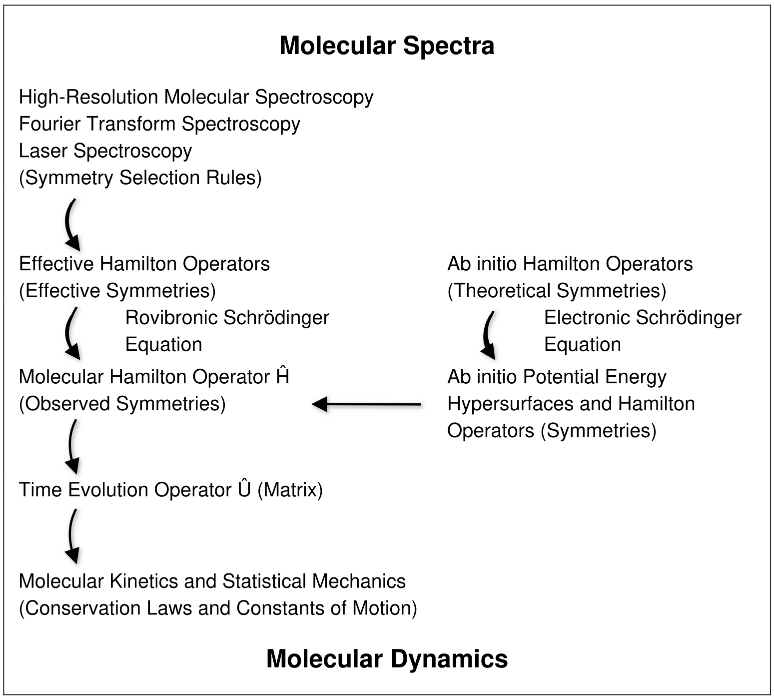

FIG. 1.11 Spectroscopic approach to intramolecular kinetics (see also Quack, 1997, 2003).

is given by one energy interval $|\Delta E_{jk}|$. The modern definition of the second is given by the separation ΔE_{jk} of the two hyperfine levels in ^{133}Cs (total angular momenta $F = 4$ and $F = 3$ resulting from combining nuclear spin $I = 7/2$ and electron spin $s = 1/2$) ($\Delta E_{jk} \approx 0.306\,633\,1899$ hc cm^{-1}) such that 1 s $= 9\,192\,631\,770\,\tau$ exactly, with $\tau = h/\Delta E_{jk}$ (see Stohner and Quack, 2011).

Combining Eq. (1.144) for the atomic clock, and the analysis of molecular spectra in terms of solutions of the time-independent Schrödinger equation for energies and wave functions and the solution of the time-dependent Schrödinger equation in terms of these wavefunctions and energies as well, this can be made the basis of a spectroscopic approach to intramolecular kinetics following the scheme in Fig. 1.11.

We have discussed elsewhere how this spectroscopic approach can be used to obtain deep insights into intramolecular processes with time resolution starting from about 200 attoseconds (Quack, 1990, 2003, 2004a) (see also Albert et al., 2011 and Hippler et al., 2011). Here, we shall furthermore address the relation to the breaking and violation of symmetries and various time scales for atomic and molecular primary processes.

1.7.2 Hierarchy of Interactions and Hierarchy of Timescales for the Successive Breaking of Approximate Dynamical Symmetries in Intramolecular Primary Processes

The hierarchy of time scales for symmetry breaking can be related to the size of contributions in the molecular Hamiltonian. For instance, one might write the Hamiltonian in the following practical order of contributions to a sum, which decrease (roughly) in the following order (Quack, 1983):

$$\begin{aligned} \hat{H} = \hat{T}_{\mathrm{e}} + \hat{V}_{\mathrm{nn}} + \hat{V}_{\mathrm{ne}} + \hat{V}_{\mathrm{ee}} \\ + \hat{T}_{\mathrm{n}} \\ + \hat{H}_{\mathrm{SO}} + \hat{H}_{\mathrm{SS}} + \hat{H}_{\mathrm{rel}} \\ + \hat{H}_{\mathrm{hfs}} \\ + \hat{H}_{\mathrm{mol,rad}} + \hat{H}_{\mathrm{mol,environment}} \\ + \hat{H}_{\mathrm{weak}} + \hat{H}_{\mathrm{gravitational}} + \cdots \end{aligned} \tag{1.145}$$

where $\hat{T}_{\mathrm{e}}$ and $\hat{T}_{\mathrm{n}}$ are the kinetic energy operators for electrons and nuclei and $\hat{V}_{\mathrm{nn}}$, $\hat{V}_{\mathrm{ne}}$ and $\hat{V}_{\mathrm{ee}}$ are nucleus–nucleus, nucleus–electron, and electron–electron Coulomb potentials. The contributions to the Hamiltonian can be characterized by their underlying symmetry groups. For instance, the initial terms in Eq. (1.145) all show "parity symmetry". $\hat{H}_{\text{weak}}$ would be, in the example of parity violation, the relevant term contributing to the dynamical symmetry breaking in an intramolecular process as discussed by Quack (1986, 2011a), on the timescale of about 1 s; $\hat{H}_{\text{so}}$, $\hat{H}_{\text{ss}}$ are spin–orbit and spin–spin, $\hat{H}_{\text{hfs}}$ is the hyperfine coupling and $\hat{H}_{\text{rel}}$ contains other relativistic contributions to the Hamiltonian, with obvious notation for the other terms. However, one could also separate the molecular Hamiltonian into other types of contributions, according to what one considers a practical separation of the Hamiltonian, in some abstract manner, say

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2 + \hat{H}_3 + \hat{H}_4 + \cdots . \tag{1.146}$$

In such an abstract description, a large $\hat{H}_0$ may show some (very high) symmetry, corresponding to a symmetry group of high order; $\hat{H}_1$ may be smaller (in terms of contributions to total energy), but might have a lower symmetry (smaller subgroup of the symmetry group of $\hat{H}_0$). Thus, considering $\hat{H}_1$, some of the symmetries of $\hat{H}_0$ will be violated or broken, and so forth with $\hat{H}_2$, $\hat{H}_3$, etc. The formal aspects of the time evolution with more or less symmetry can be summarized by just a few equations.

A dynamical variable represented by the operator $\hat{Q}$ satisfies the Heisenberg equation of motion, Eq. (1.14)).

If for a certain dynamical variable corresponding to the operator $\hat{C}$, one has the commutation relation (for an isolated system, $\hat{H}$ being time-independent)

$$\hat{C}\hat{H} = \hat{H}\hat{C}. \tag{1.147}$$

It follows with Eq. (1.16) that $\hat{U}$, being a function of $\hat{H}$, commutes with $\hat{C}$ as well,

$$\hat{U}\hat{C} = \hat{C}\hat{U}, \tag{1.148}$$

and therefore,

$$\begin{aligned}\hat{C}(t) &= \hat{U}^{\dagger}(t,t_0)\,\hat{C}(t_0)\,\hat{U}(t,t_0) = \hat{U}^{\dagger}(t,t_0)\,\hat{U}(t,t_0)\,\hat{C}(t_0)\\ &= \hat{C}(t_0).\end{aligned} \tag{1.149}$$

Thus, in the Heisenberg representation, $\hat{C}$ does not depend on time and is a "constant of the motion" or constant of evolution. Considered as transformations acting on $\hat{H}$ the $\hat{C}$ form a group, the symmetry group of $\hat{H}$ (and $\hat{U}$). One can readily see (Quack, 1983) that with the Liouville–von Neumann equation (1.37) for the density operator $\hat{P}$ or the corresponding density matrix $\boldsymbol{P}$ the expectation value of $\hat{C}$ is constant,

$$\langle \hat{C}(t) \rangle = \mathrm{Tr}(\hat{P}\hat{C}) = \langle \hat{C}(t_0) \rangle, \tag{1.150}$$

and also if $\Psi(t)$ is an eigenfunction $\zeta_n(t)$ of $\hat{C}$ with eigenvalue C_n, one has

$$\langle \hat{C}(t) \rangle = \langle \zeta_n(t) | \hat{C} | \zeta_n(t) \rangle = C_n. \tag{1.151}$$

The C_n are "good quantum numbers", which do not change in time with the evolution.

These equations can be applied in an analogous fashion to each part of the Hamiltonian in Eq. (1.146), i.e., successively to $\hat{H}_0$, $\hat{H}_1$, $\hat{H}_2, \ldots$, etc. A constant of the motion $\hat{C}_0$ of $\hat{H}_0$ will be strictly independent of time at the level of description corresponding to $\hat{H}_0$, which may be the largest contribution to the total energy. If then a smaller contribution $\hat{H}_1$ has a lower symmetry, some of the constants of motion $\hat{C}_0$ may show a time dependence due to this symmetry breaking term. If $\hat{H}_1$ contributes only a small part to the total energy, the time evolution of $\hat{C}_0$ will happen on correspondingly longer time scales and so forth for even smaller contributions due to $\hat{H}_2$, $\hat{H}_3$, $\hat{H}_4, \ldots$.

Indeed, we have made this abstract approach a basis for understanding the separation of timescales in intramolecular processes as derived from spectroscopy, and Table 1.3 provides a summary of such results for intramolecular kinetics.

For instance, if $\hat{H}_0$ is taken to correspond to a description of an N-atomic nonlinear molecule by $3N-6$ uncoupled harmonic oscillators and separable rotation, all quantum numbers v_k for the individual harmonic oscillators correspond to conserved "good" quantum numbers or constants of the motion.

As this is not a very good approximation, the anharmonic coupling terms (corresponding then to $\hat{H}_1$) are quite large and will lead to symmetry breaking on a very short timescale (depending on the case ranging from 10 fs to 10 ps as shown in Table 1.3 in the top group of processes). One can then introduce a number of successive coupling terms $\hat{H}_k$ that lead to further symmetry breaking and specific timescales for primary processes. The case of parity violation appears in group 4 counted from the top of Table 1.3 and the time evolution of parity as a kinetic primary process is one of the current frontiers in molecular quantum dynamics – interestingly on long timescales (Quack, 1986, 1994, 2001, 2011a,b). This example is also useful for illustrating another related concept arising for tunneling stereomutation in chiral molecules, as discussed in Chapter 7 of this book

TABLE 1.3
Timescales for intramolecular primary processes as successive symmetry breaking[a].

Symmetric state	Coupling and symmetry breaking	Timescale
Conservation of separable vibrational quantum numbers (for harmonic oscillators of normal modes)	Selective vibrational CH-stretch-bend-Fermi-Resonance in R_3CH (Marquardt et al., 1986; Marquardt and Quack, 1991; Quack, 1990; Quack and Stohner, 1993; Quack, 1995b; Beil et al., 1996a,b, 2000; Pochert et al., 2000)	10–200 fs
	Ordinary nonselective anharmonic couplings in CF_3R, Δl coupling in asymmetric $R_1R_2R_3CH$ (Quack, 1990; Pochert et al., 2000; He et al., 2002; Albert et al., 2017)	500 fs to 10 ps
Uncoupled oscillators (nearly adiabatically separable)	Adiabatically decoupled dynamics R–C≡C–H (Quack and Stohner, 1993; Quack, 1995b; von Puttkamer et al., 1983; Lehmann et al., 1994); $(HF)_2$ (Quack and Suhm, 1998; von Puttkamer and Quack, 1989; Quack, 2001, 2003); Δl coupling in C_{3v}-symmetric R_3CH (Luckhaus and Quack, 1993; Kushnarenko et al., 2018)	10 ps to 1 ns
Separable rotation-vibration-nuclear spin states (conservation of nuclear spin symmetry)	Violation of nuclear spin symmetry (nuclear spin–rotation–vibration coupling) (Quack, 1977, 1983; Chapovsky and Hermans, 1999)	1 ns to 1 s
Space inversion symmetry Parity conservation P	Parity violation (Quack, 1986, 1989a; Bakasov et al., 1996, 1998; Bakasov and Quack, 1999; Berger and Quack, 2000; Quack, 2002, 2006; Quack and Stohner, 2005; Prentner et al., 2015; Dietiker et al., 2015)	1 ms to 1 ks
Time-reversal symmetry T	T-violation in chiral and achiral molecules (Quack, 1997; Luckhaus and Quack, 1993; Luckhaus et al., 1993)	Molecular timescale not known
CPT symmetry	Hypothetical *CPT* violation (Quack, 1994, 1995a, 2003, 2008)	∞ (?)

[a] After Quack et al., 2008, see also Quack, 1990, Marquardt and Quack, 2001, Quack, 1995a, 2001, 2003, 2007.

(Quack and Seyfang, 2020). In the case of a very high barrier (tunneling splitting $\Delta E_{\pm} \approx 0$), the ground state of a chiral molecule is twofold degenerate because of space inversion symmetry, but this degeneracy is lifted by parity violation, resulting in a parity-violating energy difference $\Delta_{\mathrm{pv}}E$, which can be interpreted as the "splitting" of the degenerate levels by a symmetry-violating contribution $\hat{H}_{\mathrm{pv}}$ arising from H_{weak} to the Hamiltonian. The smallness of the symmetry-violating splitting of the degeneracy is directly related to the long timescale (1 ms to 1 ks, depending on the molecular example) for the dynamical, time-dependent symmetry breaking, simply by the equation for the general period of motion $\Delta\tau$:

$$\Delta\tau = h/\Delta E \tag{1.152}$$

which can be called the *elementary timescale for the symmetry breaking*. The ordering of the Hamiltonian in Eq. (1.146) by contributions from terms of different magnitude and different symmetry has one further aspect: It allows one to determine small contributions separately from large contributions, like weighing a captain directly and not as a difference of weights of ship with captain and ship without the captain. This is important in experimental and theoretical approaches.

The examples of Table 1.3 are largely drawn from the work of the Zurich group with emphasis on the connection between symmetries, approximate constants of the motion and time scales for intramolecular processes arising from various symmetry breakings. Of course, if one just considers time scales in kinetics, there is an enormous body of work from worldwide efforts. Particularly noteworthy for the remainder of the book is the "short time frontier", which would continue the table at the top end toward the attosecond range and shorter. There is considerable early history (Manz and Wöste, 1995; Quack, 2003, 2014c) and a nice personal account of the history of short time quantum dynamical processes from the early days of electronic relaxation in molecules to cluster Coulomb explosion and table top nuclear fusion ending with the question "How fast is ultrafast?" can be found in Jortner (2003). The various chapters in the present book provide beautiful examples of current work by these authors in the field addressing and in part also answering such questions.

A brief note is also useful concerning the role of relativistic effects. As is well known, these are important for the dynamics of electron motion, whenever the heavier elements are involved in the molecules considered. These effects can be calculated by relativistic quantum chemistry (Reiher and Wolf, 2009; Mastalerz and Reiher, 2011) and can lead, indeed, to dramatic changes in the effective Born–Oppenheimer potential hypersurfaces for molecular quantum dynamics, for example. Once these effects are included, the motion of atoms and molecules can be computed and understood in very much the same way using the Schrödinger equation as discussed for nonrelativistic potentials. If the molecules move at relativistic speeds, one has to consider the changes in the definition of time which is then to be measured by an atomic clock moving at relativistic speed. Indeed, one then has the well understood (and, in fact, experimentally observed) relativistic effects, such as an atomic and molecular "twin paradox" due to Einstein (1922). Further considerations arise when considering violations of time reversal symmetry and possibly a hypothetical violation of *CPT* symmetry, and we refer to Quack (2011a,b) where one can also find a discussion of the "42 open problems", some of which are related to the measurement and definition of time, time reversal symmetry, *CPT* symmetry and time-dependent entropy in statistical mechanics and molecular quantum dynamics. The investigation of possible violations of *CPT* symmetry is clearly one of the frontiers of fundamental physics (Quack, 1994, 2003; Gabrielse, 2016; Ahmadi et al., 2020) and cosmology (Boyle et al., 2018).

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