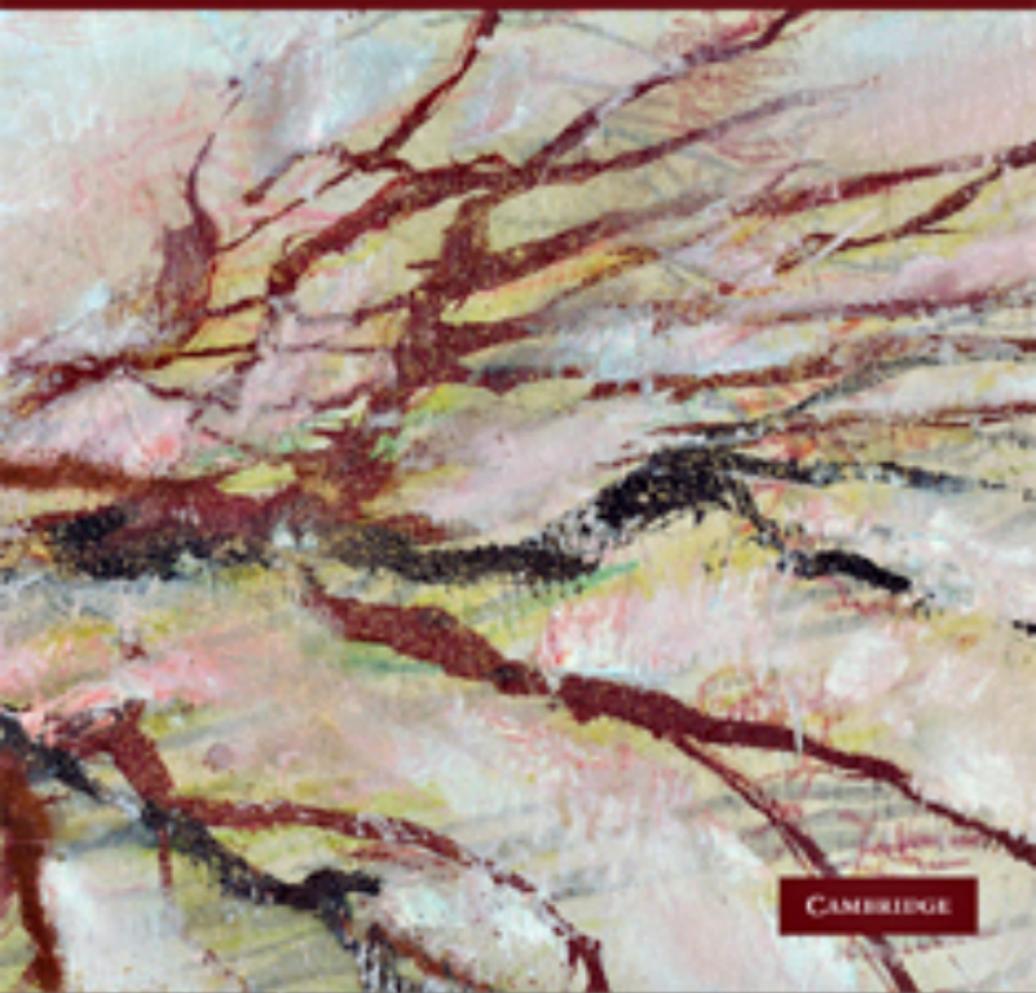


Quantum Statistical Mechanics

William C. Schieve and Lawrence P. Horwitz



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QUANTUM STATISTICAL MECHANICS

Many-body theory stands at the foundation of modern quantum statistical mechanics. It is introduced here to graduate students in physics, chemistry, engineering and biology. The book provides a contemporary understanding of irreversibility, particularly in quantum systems. It explains entropy production in quantum kinetic theory and in the master equation formulation of non-equilibrium statistical mechanics.

The first half of the book focuses on the foundations of non-equilibrium statistical mechanics with emphasis on quantum mechanics. The second half of the book contains alternative views of quantum statistical mechanics, and topics of current interest for advanced graduate level study and research.

Uniquely among textbooks on modern quantum statistical mechanics, this work contains a discussion of the fundamental Gleason theorem, presents quantum entanglements in application to quantum computation and the difficulties arising from decoherence, and derives the relativistic generalization of the Boltzmann equation. Applications of statistical mechanics to reservoir ballistic transport are developed.

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QUANTUM STATISTICAL MECHANICS

Perspectives

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Contents

<i>Preface</i>	<i>page</i> xi
1 Foundations of quantum statistical mechanics	1
1.1 The density operator and probability	1
1.2 The Gleason theorem and consequences	6
1.3 Calculation of averages of observables	9
Appendix 1A: Gleason theorem	12
References	18
2 Elementary examples	19
2.1 Introduction	19
2.2 Harmonic oscillator	19
2.3 Spin one-half and two-level atoms	27
Appendix 2A: the Fokker–Planck equation	34
References	35
3 Quantum statistical master equation	37
3.1 Reduced observables	37
3.2 The Pauli equation	39
3.3 The weak coupling master equation for open systems	42
3.4 Pauli equation: time scaling	46
3.5 Reservoir states: rigorous results and models	53
3.6 The completely positive evolution	54
Appendix 3A: Chapman–Kolmogorov master equation	57
References	59
4 Quantum kinetic equations	61
4.1 Introduction	61
4.2 Reduced density matrices and the B.B.G.Y.K. hierarchy	61
4.3 Derivation of the quantum Boltzmann equation	63
4.4 Phase space quantum Boltzmann equation	66
4.5 Memory of initial correlations	76

4.6	Quantum Vlasov equation	79
	Appendix 4A: phase space distribution functions	80
	References	83
5	Quantum irreversibility	85
5.1	Quantum reversibility	85
5.2	Master equations and irreversibility	87
5.3	Time irreversibility of the generalized master and Pauli equations	87
5.4	Irreversibility of the quantum operator Boltzmann equation	89
5.5	Reversibility of the quantum Vlasov equation	90
5.6	Completely positive dynamical semigroup: a model	92
	Appendix 5A: the quantum time reversal operator	94
	References	96
6	Entropy and dissipation: the microscopic theory	98
6.1	Introduction	98
6.2	Macroscopic non-equilibrium thermodynamics	98
6.3	Dissipation and the quantum Boltzmann equation	105
6.4	Negative probability and the quantum ξ theorem	111
6.5	Entropy and master equations	113
	Appendix 6A: quantum recurrence	120
	References	121
7	Global equilibrium: thermostatics and the microcanonical ensemble	123
7.1	Boltzmann's thermostatic entropy	124
7.2	Thermostatics	125
7.3	Canonical and grand canonical distribution of Gibbs	126
7.4	Equilibrium fluctuations	129
7.5	Negative probability in equilibrium	131
7.6	Non-interacting fermions and bosons	132
7.7	Equilibrium limit theorems	136
	References	139
8	Bose–Einstein ideal gas condensation	141
8.1	Introduction	141
8.2	Continuum box model of condensation	142
8.3	Harmonic oscillator trap and condensation	145
8.4	^4He : the λ transition	148
8.5	Fluctuations: comparison of the grand canonical and canonical ensemble	150
8.6	A master equation view of Bose condensation	152
	Appendix 8A: exact treatment of condensate traps	155
	References	158

9	Scaling, renormalization and the Ising model	159
9.1	Introduction	159
9.2	Mean field theory and critical indices	160
9.3	Scaling	167
9.4	Renormalization	169
9.5	Renormalization and scaling	172
9.6	Two-dimensional Ising model renormalization	174
	References	177
10	Relativistic covariant statistical mechanics of many particles	178
10.1	Introduction	178
10.2	Quantum many-particle dynamics: the event picture	180
10.3	Two-event Boltzmann equation	183
10.4	Some results of the quantum event Boltzmann equation	187
10.5	Relativistic quantum equilibrium event ensembles	191
	References	197
11	Quantum optics and damping	199
11.1	Introduction	199
11.2	Atomic damping: atomic master equation	199
11.3	Cavity damping: the micromaser: detection	206
11.4	Detection master equation for the cavity field	207
	Appendix 11A: the field quantization and interaction	214
	References	219
12	Entanglements	221
12.1	Introduction	221
12.2	Entanglements: foundations	221
12.3	Entanglements: Q bits	224
12.4	Entanglement consequences: quantum teleportation, the Bob and Alice story	226
12.5	Entanglement consequences: dense coding	228
12.6	Entanglement consequences: quantum computation	228
12.7	Decoherence: entanglement destruction	231
12.8	Decoherence correction (error correction)	235
	Appendix 12A: entanglement and the Schmidt decomposition	236
	References	238
13	Quantum measurement and irreversibility	240
13.1	Introduction	240
13.2	Ideal quantum measurement	241
13.3	Irreversibility: measurement master equations	243
13.4	An open system master equation model for measurement	246

13.5	Stochastic energy based collapse	248
	References	251
14	Quantum Langevin equation and quantum Brownian motion	253
14.1	Introduction	253
14.2	Quantum Langevin equation	254
14.3	Quantum Langevin equation with measurement	260
	References	262
15	Linear response: fluctuation and dissipation theorems	264
15.1	Introduction	264
15.2	Quantum linear response in the steady state	266
15.3	Linear response, time dependent	269
15.4	Fluctuation and dissipative theorems	272
15.5	Comments and comparisons	277
	References	279
16	Time-dependent quantum Green's functions	281
16.1	Introduction	281
16.2	One- and two-time quantum Green's functions and their properties	282
16.3	Analytic properties of Green's functions	284
16.4	Connection to linear response theory	288
16.5	Green's function hierarchy truncation	289
16.6	Keldysh time-loop path perturbation theory	297
	References	302
17	Decay scattering	303
17.1	Basic notions and the Wigner–Weisskopf theory	303
17.2	Wigner–Weisskopf method: pole approximation	306
17.3	Wigner–Weisskopf method and Lee–Friedrichs model with a single channel	312
17.4	Wigner–Weisskopf and multichannel decay	318
17.5	Wigner–Weisskopf method with many-channel decay: the Lee–Friedrichs model	321
17.6	Gel'fand triple	332
17.7	Lax–Phillips theory	335
17.8	Application to the Stark model	354
	References	362
18	Quantum statistical mechanics, extended	365
18.1	Intrinsic theory of irreversibility	365
18.2	Complex Liouvillian eigenvalue method: introduction	366
18.3	Operators and states with diagonal singularity	367
18.4	Super operators and time evolution	369

18.5	Subdynamics and analytic continuation	371
18.6	The Pauli equation revisited	375
	References	378
19	Quantum transport with tunneling and reservoir ballistic transport	379
19.1	Introduction	379
19.2	Pauli equation and boundary interaction	380
19.3	Ballistic transport	383
19.4	Green's function closed-time path theory to transport	385
	References	389
20	Black hole thermodynamics	390
20.1	Introduction to black holes	390
20.2	Equilibrium thermodynamic analogies: the first law	394
20.3	The second law of thermodynamics and black holes	397
20.4	Extended entropy principle for black holes	399
20.5	Acausal evolution: extended irreversible dynamics in black holes	401
	References	402
A	Problems	404
A.1	Comments on the problems	404
A.2	"Foundations" problems	404
A.3	Kinetic dynamics problems	407
A.4	Equilibrium and phase transition problems	409
	References	410
	<i>Index</i>	411

Preface

This book had its origin in a graduate course in statistical mechanics given by Professor W. C. Schieve in the Ilya Prigogine Center for Statistical Mechanics at the University of Texas in Austin.

The emphasis is *quantum* non-equilibrium statistical mechanics, which makes the content rather unique and advanced in comparison to other texts. This was motivated by work taking place at the Austin Center, particularly the interaction with Radu Balescu of the Free University of Brussels (where Professor Schieve spent a good deal of time on various occasions). Two Ph.D. candidate theses at Austin, those of Kenneth Hawker and John Middleton, are basic to Chapters 3 and 4, where the master equations and quantum kinetic equations are discussed. The theme there is the dominant and fundamental one of quantum irreversibility. The particular emphasis throughout this book is that of open systems, i.e. quantum systems in interaction with reservoirs and not isolated. A particularly influential work is the book of Professor A. McLennan of Lehigh University, under whose influence Professor Schieve first learned non-equilibrium statistical mechanics.

An account of relatively recent developments, based on the addition in the Schrödinger equation of stochastic fluctuations of the wave function, is given in Chapter 13. These methods have been developed to account for the collapse of the wave function in the process of measurement, but they are deeply connected as well with models for irreversible evolution.

The first six chapters of the present work set forth the theme of our book, particularly extending the entropy principle that was first introduced by Boltzmann, classically. These, with equilibrium quantum applications (Chapters 7, 8, 9 and possibly also Chapters 14 and 15), represent a one-semester advanced course on the subject.

As frequently pointed out in the text, quantum mechanics introduces special problems to statistical mechanics. Even in Chapter 1, written by the coauthor of this work, Professor Lawrence P. Horwitz of Tel Aviv, the idea of a *density operator* is required which is *not* a probability distribution, as in the classical case. The idea of the density operator lies at the very foundations of the quantum theory, providing a description of a quantum state in the most general way. Statistical mechanics requires this full generality. We give a proof of the Gleason theorem, stating that in a Hilbert space of three or more real dimensions, a general quantum state has a representation as a density operator, based on an elegant construction of C. Piron. This structure gives the quantum \mathfrak{H} theorem, a content which is essentially different from the classical one. This makes the subject surely interesting and important, but difficult.

Quantum entanglements are quite like magic, so to speak. It is necessary and important to see these modern developments; they are described in Chapter 15. This is one chapter that might be used in the extension of the course to a second semester. One- and two-time Green's functions, introduced by Kadanoff and Baym, might be included in the extended treatment, since they are popular but difficult. This is included in Chapter 16 with an application in Chapter 19.

An extension to special relativity is described in Chapter 10. This is a new derivation of a many-body *covariant* kinetic theory. The Boltzmann-like kinetic equation outlined here was derived in collaboration by the authors. The covariant picture is an event dynamics controlled by an abstract time variable first introduced by both Feynman and Stueckelberg and obtains a covariant scalar many-body wave function parameterized by the new time variable. The results of this event picture are outlined in Chapter 10.

Another arena of activity utilizing quantum kinetic equations for open systems is the extensive development in quantum optics. This has been a personal interest of one of the authors (WCS). This interest was a result of a Humboldt Foundation grant to the Max Planck Institute in Munich and later to Ulm, under the direction of Professors Herbert Walther, Marlon Scully and Wolfgang Schleich. The particular area of interest is described in the results outlined in Chapter 11. This material can be included as an introduction to quantum optics in an extended two-semester course.

The idea of spontaneous decay in a quantum system goes back to Gamov in quantum mechanics. This irreversible process seems intrinsic, introducing the notion of the Gel'fand triplet and rigged Hilbert spaces states. The coauthor (LPH) has made personal contributions to this fundamental change in the wave function picture. It is very appropriate to include an extensive discussion of this, which is the content of Chapter 17, describing, among other things, the Wigner–Weisskopf method and the Lax–Phillips approach to enlarging the scope of quantum wave

functions. All of this requires a more advanced mathematical approach than the earlier discussions in this book. However, it is necessary that a well-grounded student of quantum mechanics know these things, as well as acquire the mathematical tools, and therefore it is very appropriate here in a discussion of quantum statistical mechanics.

Chapter 18 is in many ways an extension of Chapter 17. It is an outline of what has been called extended statistical mechanics. Ilya Prigogine and his colleagues in Brussels and Austin, in the past few years, have attempted to formulate many-body dynamics which is intrinsically irreversible. In the classical case this may be termed the complex Liouville eigenvalue method. As an example, the Pauli equation is derived again by these nonperturbative methods. This is not an open-system dynamics but rather, like the previous Chapter 17 discussion, one of closed isolated dynamics. This effort is not finished, and the interested student may look upon this as an introductory challenge.

The final chapter of this book is in many ways a diversion, a topic for personal pleasure. The remarkable objects of our universe known as black holes apparently exist in abundance. These super macroscopic objects obey a simple equilibrium thermodynamics, as first pointed out by Bekenstein and Hawking. Remarkably, the area of a black hole has a similarity to thermodynamic entropy. More remarkable, the S -matrix quantum field theoretic calculation of Hawking showed that the baryon emission of a black hole follows a Planck formula. Hawking introduced a superscattering operator which is analogous to the extended dynamical theory of Chapter 18.

To complete these comments, we would like to thank Florence Schieve for support and encouragement over these last years of effort on this work. She not only gave passive help but also typed into the computer several drafts of the book as well as communicating with the coauthor and the editorial staff of the publisher. The second coauthor wishes also to thank his wife Ruth for her patience, understanding, and support during the writing of some difficult chapters.

We also acknowledge the help of Annie Harding of the Center here in Austin. Three colleagues at the University of Texas—Tomio Petrosky, George Sudarshan and Arno Bohm—also made valuable technical comments. WCS also thanks the graduate students who, over many years of graduate classes, made enlightened comments on early manuscripts.

We recognize the singular role of Ilya Prigogine in creating an environment in Brussels and Austin in which the study of non-equilibrium statistical mechanics was our primary goal and enthusiasm.

Finally, WCS thanks the Alexander von Humboldt Foundation for making possible extended visits to the Max Planck Institute of Quantum Optics in Garching and later in Ulm. LPH thanks the Center for Statistical Mechanics and Complex

Systems at the University of Texas at Austin for making possible many visits over the years that formed the basis for his collaboration with Professor Schieve, and the Institute for Advanced Study at Princeton, particularly Professor Stephen L. Adler, for hospitality during a series of visits in which, among other things, he learned of the theory of stochastic evolution, and which brought him into proximity with the University of Texas at Austin.

1

Foundations of quantum statistical mechanics

1.1 The density operator and probability

Statistical mechanics is concerned with the construction of methods for computing the expected value of observables important for characterizing the properties of physical systems, generally containing many degrees of freedom. Starting with a formally complete detailed description for these many degrees of freedom, probability theory is used to obtain effective procedures. Quantum statistical mechanics makes use of *two* types of probability theory. One of these is the set of natural probabilities associated with the quantum theory which emerges from its structure as a Hilbert space. For example, the Born probability is associated with the square of a wave function. The second is the essentially classical probability associated with an ensemble of separate systems, each with an *a priori* probability assigned by the frequency of occurrence in the ensemble. The quantity which describes both types of probability in an efficient, convenient way is the density operator.

As an example which illustrates many of the basic ideas, consider a beam of particles with spin $\frac{1}{2}$. We shall repeat the resulting definitions later in complete generality.

The spin states of these particles are represented by two-dimensional spinors which we denote by the Dirac kets $|\sigma_z\rangle$ for $\sigma_z = \pm 1$, corresponding to the z component of the spin σ of the particle. If we perform a filtering measurement to select a particle of spin σ' with spin $\sigma'_z = \pm 1$ in the z direction, the outcome of the measurement on a beam of particles with spin σ_z is

$$|\langle \sigma'_z | \sigma_z \rangle|^2 = \delta_{\sigma'_z, \sigma_z}.$$

This result can be written as

$$|\langle \sigma'_z | \sigma_z \rangle|^2 = \text{Tr} P_z(\sigma') P_z(\sigma),$$

where the projection operator $P_z(\sigma) = |\sigma_z\rangle\langle\sigma_z|$ represents the state of the beam of particles with spin σ of definite value σ_z , and the projection operator $P_z(\sigma')$ represents the experimental question of which value, ± 1 , this set of particles has.

If we measure instead a different component of spin and, for example, ask for the fraction of particles in the ensemble with spin in the $\pm x$ direction, the measurement is represented by a projection operator $P_x(\sigma) = |\sigma_x\rangle\langle\sigma_x|$, with $\sigma_x = \pm 1$. In terms of the eigenvectors of σ_z ,

$$|\sigma_x = \pm 1\rangle = \frac{1}{\sqrt{2}}(|+1\rangle \pm |-1\rangle).$$

It is true (for any of the values of σ_x and σ_z) that

$$|\langle\sigma_x | \sigma_z\rangle|^2 = \frac{1}{2}.$$

We can write this result as

$$|\langle\sigma_x | \sigma_z\rangle|^2 = \text{Tr}(P_x(\sigma) P_z(\sigma)).$$

Let us now consider a beam of spin $\frac{1}{2}$ particles with a fraction γ_+ with spin up and γ_- with spin down in the z direction ($\gamma_+ + \gamma_- = 1$). The probability to find spin up as the outcome of the experiment is

$$\begin{aligned} P_+ &= |\langle\sigma'_z = +1 | \sigma_z = +1\rangle|^2 \gamma_+ + |\langle\sigma'_z = +1 | \sigma_z = -1\rangle|^2 \gamma_- \\ &= \gamma_+, \end{aligned}$$

since the second term vanishes. If $\gamma_+ = \frac{1}{2}$, the result is indistinguishable from the probability to find a spin $\pm\frac{1}{2}$ in the x direction in a beam of particles with definite spin in the z direction.

We can write the result of the second example as

$$\begin{aligned} P_+ &= \gamma_+ \text{Tr}(P(\sigma'_z = +1) P(\sigma_z = +1)) + \gamma_- \text{Tr}(P(\sigma'_z = +1) P(\sigma_z = -1)) \\ &= \text{Tr}(\rho P(\sigma'_z = +1)) \end{aligned}$$

for

$$\rho \equiv \gamma_+ P(\sigma_z = +1) + \gamma_- P(\sigma_z = -1).$$

The operator ρ is called the *density operator*, representing a state consisting of a *mixture* of components with spin up and spin down in the ensemble of possibilities. We see that, with a slight generalization of the procedure used above with $\rho_z \rightarrow \rho_0$, no matter what direction 0 we test in the experiment, the outcome P_0 (a linear combination of γ_+ , γ_- with coefficients less than unity) can never reach unity if γ_+ or γ_- is not unity. In the first example, where we have a beam with definite

σ_z , the state is represented by a *vector*, and the measurement of the spin in the z -direction can yield probability one. For a general choice of γ_{\pm} , there is *no* vector that can represent the state. In the first case the state is called *pure*, and it can be represented by a projection into a one-dimensional subspace (in the previous example, $P_{\sigma_z} = |\sigma_z\rangle\langle\sigma_z|$). This is equivalent to specifying the vector, up to a phase, corresponding to the one-dimensional subspace. In the second case, it is called *mixed* and does not correspond to a vector in the Hilbert space.

It is clear from the discussion of these examples that the *a priori* probabilities γ_{\pm} are essentially classical, reflecting the composition of the beam that was prepared in the macroscopic laboratory.

Although a density operator ρ of the type that we have defined in this example appears to be a somewhat artificial construction, it is actually a fundamental structure in quantum statistical mechanics (Dirac, 1958). It enables one to study a complex system in the framework of an ensemble and in fact occurs on the most fundamental level of the axioms of the quantum theory.

It was shown by Birkhoff and von Neumann (1936) that both quantum mechanics and classical mechanics can be formulated as the description of a set of questions for which the answer, as a result of experiment, is “yes” or “no.” Such a set, which includes the empty set ϕ (questions that are absurd, e.g. the statement that the system does not exist) and the trivial set I (the set of all sets, e.g. the statement that the system exists), and is closed with respect to intersections and unions, is called a lattice. A lattice that satisfies the distributive law

$$a \cap (b \cup c) = (a \cap b) \cup (a \cap c),$$

where \cup represents the union and \cap the intersection, is called Boolean. These operations have the physical meaning of “or” (the symbol \cup), in which one or the other of the propositions is true, and “and” (the symbol \cap), for which both must be true for the answer of the compound measurement to be “yes.” An example of such a lattice may be constructed in terms of two-dimensional closed regions on a piece of paper. This is discussed again in the appendix to this chapter.

Both classical and quantum theories may be associated with lattices in terms, respectively, of the occupancy of cells in phase space or states in the subspaces of the Hilbert space. The questions a correspond, in the first case, to the phase space cells (with answer corresponding to occupancy) and in the second to the projection operators P_{α} associated with a subspace M_{α} , with the answer corresponding to the values ± 1 which a projection operator can have. These values correspond to evaluating the projection operator on vectors which lie within or outside the subspace.

Birkhoff and von Neumann asserted that the fundamental difference between classical and quantum mechanics is that the lattices corresponding to classical

mechanics are Boolean, and those corresponding to quantum mechanics *are not*. The non-Boolean structure of the quantum lattice is associated with the lack of commutativity of the projection operators associated with different subspaces:

$$a \cap (b \cup c) \neq (a \cap b) \cup (a \cap c). \quad (1.1)$$

This is a fundamental difference between classical and quantum statistics.

Let us illustrate this point by a simple example, again using the spin $\frac{1}{2}$ system. Each of the Pauli spin matrices has eigenvalues ± 1 and is therefore associated with a set of projection operators of the form

$$P_i = \frac{1}{2} (1 \pm \sigma_i)$$

for $i = x, y, z$. Let us consider three closed linear subspaces associated with the projections into the subspaces with the σ_i positive, i.e. with the P_i defined as above with positive signs. We call these subspaces M_x, M_y, M_z ; they correspond to propositions which are not compatible, i.e. the corresponding projection operators do not commute. We shall show explicitly, for this simple example, that

$$M_z \cap (M_x \cup M_y) \neq (M_z \cap M_x) \cup (M_z \cap M_y),$$

that is, this set of propositions is not Boolean. The construction is interesting in that it illustrates the special structure of the topology of Hilbert spaces as well as the notion of the non-Boolean lattice.

We start by constructing the union of the manifolds M_x and M_y by their joint linear span. Taking the standard definition of the Pauli matrices,

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

the projection operators into the subspaces with positive eigenvalues are

$$\begin{aligned} P_x &= \frac{1}{2} (1 + \sigma_x) = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \\ P_y &= \frac{1}{2} (1 + \sigma_y) = \frac{1}{2} \begin{pmatrix} 1 & -i \\ i & 1 \end{pmatrix} \\ P_z &= \frac{1}{2} (1 + \sigma_z) = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}. \end{aligned}$$

The corresponding eigenvectors are given by projecting a generic vector v into the respective subspaces. For

$$v = \begin{pmatrix} v_1 \\ v_2 \end{pmatrix},$$