Cambridge University Press
978-1-107-00649-2 - Thermal Physics: Concepts and Practice
Allen L. Wasserman
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1 Introducing thermodynamics

> The atomistic nature of matter as conceptualized by the Greeks had, by the 19th century, been raised by scientists to a high probability. But it was Planck's law of radiation that yielded the first exact determination of the absolute size of atoms. More than that, he convincingly showed that in addition to the atomistic structure of matter there is a kind of atomistic structure to energy, governed by the universal constant h.
>
> This discovery has almost completely dominated the development of physics in the 20th century. Without this discovery a workable theory of molecules and atoms and the energy processes that govern their transformations would not have been possible. It has, moreover, shaken the whole framework of classical mechanics and electrodynamics and set science the fresh task of finding a new conceptual basis for all of physics. Despite partial success, the problem is still far from solved.
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> Albert Einstein, "Max Planck memorial service" (1948).
> Original image, Einstein Archives Online, Jerusalem
> (trans. A. Wasserman)

1.1 The beginning

Thermodynamics has exceeded the scope and applicability of its utile origins in the industrial revolution to a far greater extent than other subjects of physics' classical era, such as mechanics and electromagnetism. Unquestionably this results from over a century of synergistic development with quantum mechanics, to which it has given and from which it has gained clarification, enhancement and relevance, earning for it a vital role in the modern development of physics as well as chemistry, biology, engineering, and even aspects of philosophy.

The subject's fascinating history is intertwined with seminal characters who contributed much to its present form – some colorful and famous with others lesser known, maligned or merely ignored.

"Atomism" (i.e. molecular models), a source of early conflict, seems to have had Daniel Bernoulli as its earliest documented proponent when in 1738 he hypothesized

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a kinetic theory of gases.[1] Although science – thermodynamics in particular – is now unthinkable without such models, Bernoulli's ideas were largely ignored and for nearly a century little interest was shown in matter as based on microscopic constituents. Despite a continuing atmosphere of suspicion, particle models occasionally reappeared[2,3] and evolved, shedding some of their controversy (Joule 1851) while moving towards firm, accepted hypotheses (Kronig 1856). Adoption of kinetic models by the respected Rudolf Clausius (1857) began to erode the skeptics' position and encourage the new statistical theories of Maxwell (1859) and Boltzmann (1872). At about the same time van der Waals (1873), theorizing forces between *real* atoms and molecules, developed a successful equation of state for *non-ideal* gases.[4] Nevertheless, as the 20th century dawned, controversy continued only slightly abated. J. J. Thomson's discovery of the electron (1897) should have finally convinced remaining doubters of matter's microscopic essence – but it didn't. The argument continued into the 20th century stilled, finally, by the paradigm shift towards "quantized" models.

It all started with Max Planck who in 1900[5,6] introduced quantized energy into theories of electromagnetic radiation – and Einstein[7] who used quantized lattice vibrations in his ground-breaking heat capacity calculation. But it would be another 25 years before the inherently probabilistic, microscopic theory of matter – quantum mechanics – with its quantum probabilities and expectation values – would completely reshape the scientific landscape and permanently dominate most areas of physics, providing a basis for deeper understanding of particles, atoms and nuclei while grooming thermodynamics for its essential role in modern physics.

Thermodynamics is primarily concerned with mechanical, thermal and electromagnetic interactions in *macroscopic* matter, i.e. systems with huge numbers of microscopic constituents ($\sim 10^{23}$ particles). Although thermodynamic descriptions are generally in terms of largely intuitive macroscopic variables, most macroscopic behaviors are, at their root, quantum mechanical. Precisely how the classical

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[1] D. Bernoulli, *Hydrodynamica* (1738).

[2] J. Herapath,"On the causes, laws and phenomena of heat, gases, gravitation", *Annals of Philosophy* **9** (1821). Herapath's was one of the early papers on kinetic theory, but rejected by the Royal Society, whose reviewer objected to the implication that there was an absolute zero of temperature at which molecular motion ceased.

[3] J.J.Waterston,"Thoughts on the mental functions" (1843). This peculiar title was a most likely cause of its rejection by the Royal Society as "nothing but nonsense". In recognition of Waterston's unfairly maligned achievement, Lord Rayleigh recovered the original manuscript and had it published as "On the physics of media that are composed of free and perfectly elastic molecules in a state of motion", *Philosophical Transactions of the Royal Society A* **183**, 1 (1892), nearly 10 years after Waterston's death.

[4] Van der Waals' work also implied a molecular basis for critical points and the liquid–vapor phase transition.

[5] Max Planck,"Entropy and temperature of radiant heat", *Ann. der Physik* **1**, 719 (1900).

[6] Max Planck, "On the law of distribution of energy in the normal spectrum", *Ann. der Physik* **4**, 553 (1901).

[7] A. Einstein, "Planck's theory of radiation and the theory of specific heat", *Ann. der Physik* **22**, 180 (1907).

measurement arises from quantum behavior has been a subject of some controversy ever since quantum theory's introduction. But it now seems clear that macroscopic systems are quantum systems that are particularly distinguished by always being entangled (however weakly) with an environment (sometimes referred to as a reservoir) that is also a quantum system. Although environmental coupling may be conceptually simple and even uninteresting in detail, it has enormous consequences for quantum-based descriptions of macroscopic matter, i.e. thermodynamics.[8]

1.2 Thermodynamic vocabulary

A few general, large-scale terms are used in describing objects and conditions of interest in thermodynamics.

- **System:** A macroscopic unit of particular interest, especially one whose thermal properties are under investigation. It may, for example, be a gas confined within physical boundaries or a rod or string of elastic material (metal, rubber or polymer). It can also be matter that is magnetizable or electrically polarizable.
- **Surroundings:** Everything physical that is not the system or which lies outside the system's boundaries is regarded as "surroundings". This may be external weights, an external atmosphere, or static electric and magnetic fields. The system plus surroundings comprise, somewhat metaphorically, "the universe".
- **Thermal variables:** A set of macroscopic variables that describe the state of the system. Some variables are intuitive and familiar, such as pressure, volume, elongation, tension, etc. Others may be less intuitive and even abstract – such as temperature – but, nevertheless, also play important roles in thermodynamics. These will be discussed in detail in this and later chapters.
- **Thermal equilibrium:** The final state attained in which thermal state variables that describe the macroscopic system (pressure, temperature, volume, etc.) no longer change in time.[9] It is only at thermal equilibrium that thermodynamic variables are well defined. The time elapsed in attaining equilibrium is largely irrelevant.

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[8] Macroscopic behavior can be quite different from the behavior of individual constituents (atoms, molecules, nuclei, etc.) As an example, the appearance of spontaneous bulk magnetism in iron (at temperatures below some critical temperature T_c) is not a property of individual iron atoms but arises from large numbers of interacting iron atoms behaving collectively.

[9] There are, nevertheless, small departures from equilibrium averages, referred to as *fluctuations*, whose values are also part of any complete thermodynamic description.

1.3 Energy and the First Law

James Joule's classic contribution on the mechanical equivalent of heat and his theory of energy reallocation between a system and its surroundings[10] (referred to as energy conservation) led Rudolph Clausius[11] to the historic *First Law of Thermodynamics*:

$$\Delta\mathcal{U} = \mathcal{Q} - \mathcal{W}. \tag{1.1}$$

Here $\mathcal{W}$ is *mechanical work* done *by* the system and $\mathcal{Q}$ is *heat* (thermal energy) *added to* the system, both of which are classical quantities associated with surroundings. In Clausius' time controversy about reality in atomic models left $\mathcal{U}$ with no definitive interpretation. But being the maximum *work* which could be theoretically extracted from a substance it was initially called "intrinsic energy". As kinetic (atomic) models gained acceptance (Clausius having played an influential role) $\mathcal{U}$ became the *mean kinetic energy* of the system's microscopic constituents or, more generally, as *internal energy*. Although the *change* in internal energy, $\Delta\mathcal{U}$, is brought about by mechanical and thermal, i.e. classical, interactions, quantum mechanics provides a clear and specific meaning to $\Delta\mathcal{U}$ as an *average* change in energy of the *macroscopic system as determined from kinetic, potential and interaction energies of its microscopic constituents*, clearly distinguishing it from other energy contributions. The precise meaning and interrelation of this with similar *macroscopic averages* provides the basis for thermodynamics.[12]

1.3.1 Thermodynamic variables defined

Some thermodynamic concepts and macroscopic variables are familiar from classical physics while others arise simply from operational experience. Moving beyond this, quantum mechanics provides definitions and context for not only *internal* energy $\mathcal{U}$, but for other *macroscopic* (thermodynamic) variables, placing them within a microscopic context that adds considerably to their meaning and their role within thermal physics. The First Law, in arraying $\mathcal{Q}$ and $\mathcal{W}$ (both classical) against $\Delta\mathcal{U}$ (quantum mechanical), highlights this intrinsic partitioning of macroscopic variables into "classical"(C) vis-à-vis quantum (Q).

Examples of Q-*variables* – macroscopic variables having microscopic origins[13] – are:

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[10] James P. Joule, "On the existence of an equivalent relation between heat and the ordinary forms of mechanical power", *Phil. Mag.* **27**, 205 (1850).

[11] R. Clausius, "On the moving force of heat, and the laws regarding the nature of heat", *Phil. Mag.* **2**, 1–21, 102–119 (1851).

[12] Macroscopic "averages" will be discussed in Chapter 2.

[13] These are defined by quantum operators.

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- internal energy: $\mathbf{h}_{op}$ (energy of the system's microscopic constituents – kinetic plus potential);
- pressure: $\boldsymbol{p}_{op} = -\left(\frac{\partial\, \mathbf{h}_{op}}{\partial V}\right)$ (pressure arising from a system's internal constituents);
- electric polarization: $\mathcal{P}_{op}$;
- magnetization: $\boldsymbol{M}_{op}$;
- elongation (length): $\boldsymbol{\chi}_{op}$;
- particle number: $\mathcal{N}_{op}$.[14]

Examples of *C-variables* – classical (macroscopic) variables that exist apart from microscopic mechanics[15] – are:

- temperature: T;
- volume: V;
- *static* magnetic fields: $\mathcal{B}$ or H;
- *static* electric fields: $\mathcal{E}$ or $\mathcal{D}$;[16]
- elastic tension: τ;
- chemical potential: μ.[17]

Interaction energy

Most Q-variables listed above appear from interaction terms added to $\mathbf{h}_{op}$. The following are examples of such variables and their interactions.

a. Tension $\boldsymbol{\tau}$ applied to an elastic material produces a "conjugate" elongation $\boldsymbol{\chi}$, as described by an interaction operator[18]

$$\mathcal{H}^{\chi}_{op} = -\boldsymbol{\tau}\cdot\boldsymbol{\chi}_{op}. \tag{1.2}$$

b. A static magnetic induction field $\boldsymbol{\mathcal{B}}_{\mathbf{0}}$ contributes an interaction operator (energy)

$$\mathcal{H}^{\mathcal{M}}_{op} = -\boldsymbol{m}_{op}\cdot\boldsymbol{\mathcal{B}}_{\mathbf{0}}. \tag{1.3}$$

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[14] Variable particle number is essential for thermodynamic descriptions of phase transitions, chemical reactions and inhomogeneous systems. However, the particle number operator is not a part of Schrödinger's fixed particle number theory, though it appears quite naturally in quantum field theories. Implementing variable particle number requires operators to create and destroy them and operators to count them.

[15] These are not defined by quantum operators.

[16] Electromagnetic *radiation* fields are, on the other hand, representable by quantum field operators $\mathcal{B}_{op}$ and $\mathcal{E}_{op}$ obtained from a quantum electromagnetic vector potential operator $\mathcal{A}_{op}$. This will be discussed in Chapter 14, on radiation theory.

[17] μ is an energy per particle and is associated with processes having varying particle number.

[18] The tension $\boldsymbol{\tau}$ is said to be *conjugate* to the elongation $\boldsymbol{\chi}$. The variable and its conjugate comprise a thermodynamic energy.

Here $\boldsymbol{m}_{op}$ represents a magnetic moment *operator* for elementary or composite particles. The sum[19,20]

$$\boldsymbol{M}_{op} = \sum_i \boldsymbol{m}_{op}(i), \tag{1.4}$$

represents the total magnetization operator.

c. A static electric field $\boldsymbol{\mathcal{E}}_{\mathbf{0}}$ can contribute an interaction operator (energy)

$$\mathcal{H}_{op}^{\mathcal{P}} = -p_{op} \cdot \boldsymbol{\mathcal{E}}_{\mathbf{0}}, \tag{1.5}$$

where p_{op} represents an electric dipole moment *operator* and

$$\mathcal{P}_{op} = \sum_i p_{op}(i) \tag{1.6}$$

represents the total polarization.[21]

d. An energy associated with creating "space" for the system is

$$\mathcal{H}_{op}^{\mathcal{W}} = \boldsymbol{p}_{op} V, \tag{1.7}$$

with $\boldsymbol{p}_{op}$ representing the system pressure and V the displaced volume.

e. An "open system" energy associated with particle creation and/or destruction is

$$\mathcal{H}_{op}^{\mathcal{N}} = -\mu \mathcal{N}_{op}, \tag{1.8}$$

where the chemical potential μ (an energy per particle) is conjugate to a particle number *operator* $\mathcal{N}_{op}$. Chemical reactions, phase transitions and other cases with variable numbers of particles of different species are examples of open systems.[22]

1.4 Quantum mechanics, the "mother of theories"

As out of place as rigorous quantum ideas might seem in this introduction to thermodynamics, it is the author's view that they are an essential topic for an approach that strives to bring unity of structure and calculable meaning to the subject.

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[19] The field $\boldsymbol{\mathcal{B}}_{\mathbf{0}}$ conjugate to $\boldsymbol{m}_{op}$ is the field present prior to the insertion of matter. Matter itself may be magnetized and contribute to an effective $\mathcal{B}$.

[20] There are ambiguities in the thermodynamic roles of static fields, e.g. Maxwell's local magnetic average $\boldsymbol{\mathcal{B}}$ vs. an external $\boldsymbol{\mathcal{B}}_{\mathbf{0}}$ and Maxwell's local electric average $\boldsymbol{\mathcal{E}}$ vs. external $\boldsymbol{\mathcal{E}}_{\mathbf{0}}$.

[21] The field $\boldsymbol{\mathcal{E}}_{\mathbf{0}}$ is conjugate to the electric dipole operator p_{op}.

[22] Variable particle number is intrinsic to thermal physics even though it may be suppressed for simplicity when particle number is assumed constant.

1.4.1 Introduction

Macroscopic variables such as pressure p, magnetization $\boldsymbol{M}$, elastic elongation $\boldsymbol{\chi}$, particle number N, etc. – any (or all) of which can appear in thermodynamic descriptions of matter – have microscopic origins and should be obtainable from quantum models. The question is: "How?"

Investigating the means by which microscopic models eventually lead to macroscopic quantities is the aim of Chapters 2 and 6. Preliminary to that goal, this chapter reviews postulates, definitions and rules of quantum mechanics for typical *isolated* systems.[23] Particular attention is given to probabilities and expectation values of dynamical variables (*observables*).[24] This provides the basic rules, language and notation to carry us into Chapter 2 where the question "What is thermodynamics?" is raised, and then to Chapter 6 where the ultimate question "How does it arise?" is addressed.

In achieving this goal Chapter 2 will diverge somewhat from the familiar "wave mechanics" of introductory courses and focus on a less-familiar but closely related quantum mechanical object called the *density operator*, ρ_{op}. This quantity, although derived from a quantum state function, goes beyond state function limitations by adding the breadth and flexibility critical for answering most of our questions about thermodynamics. It is a "Yellow Brick Road" that will guide us from the land of the Munchkins to the Emerald City[25] – from the microscopic to the macroscopic – from quantum mechanics to thermodynamics.

1.4.2 A brief review

The review starts with Schrödinger's famous linear equation of non-relativistic quantum mechanics:

$$\mathcal{H}_{op}\psi\left(\mathbf{x},t\right)=i\hbar\frac{\partial\psi\left(\mathbf{x},t\right)}{\partial t}\,. \tag{1.9}$$

The solution to Eq. 1.9 is the time-evolving, complex, scalar *wavefunction* $\psi\left(\mathbf{x},t\right)$, which describes the *quantum* dynamics of an *isolated, fixed particle number, microscopic* system.

In the widely used (and preferred) Dirac notation, Eq. 1.9 is identical with

$$\mathcal{H}_{op}\left|\Psi\right\rangle=i\hbar\frac{\partial}{\partial t}\left|\Psi\right\rangle, \tag{1.10}$$

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[23] These are the systems described by Schrödinger theory.

[24] Most of this review material is likely to be familiar from an earlier course in modern physics. If not, it is recommended that you work alongside one of the many books on introductory quantum mechanics.

[25] L. Frank Baum, *Wizard of Oz*, Dover Publications, New York (1996).

where $|\Psi\rangle$ is the time-dependent state function, or "ket", corresponding to the wavefunction $\psi(\mathbf{x}, t)$, i.e.

$$\langle \mathbf{x} \mid \Psi \rangle \equiv \psi(\mathbf{x}, t)\,. \tag{1.11}$$

Here $|\mathbf{x}\rangle$ is an "eigen-ket" of the position operator with $\mathbf{x} \equiv \mathbf{x_1}, \mathbf{x_2}, \ldots, \mathbf{x_N}$ the coordinates of an N-particle system. As indicated in Eq. 1.11, the wavefunction $\psi(\mathbf{x}, t)$ is merely the "ket" $|\Psi\rangle$ in a coordinate representation.[26] $\mathcal{H}_{op}$ is the hamiltonian operator (inspired by classical dynamics). A hamiltonian operator for a case with only internal particle dynamics may, for example, be written

$$\mathbf{h}_{op} = \mathcal{T}_{op} + \mathcal{V}_{op}, \tag{1.12}$$

where $\mathcal{T}_{op}$ and $\mathcal{V}_{op}$ are kinetic energy and potential energy operators, respectively.[27] Additional interaction terms $\mathcal{H}_{op}^{int}$ such as Eqs. 1.2 → 1.8 may appear, depending on the physical situation, in which case

$$\mathcal{H}_{op} = \mathbf{h}_{op} + \mathcal{H}_{op}^{int}\,. \tag{1.13}$$

The quantum state function $|\Psi\rangle$ (see Eq. 1.11) has no classical counterpart and is, moreover, not even a measurable! But it is nevertheless interpreted as the generating function for a statistical description of the quantum system – including probabilities, statistical averages (expectation values) and fluctuations about these averages. It contains, in principle, all that is knowable about the isolated, microscopic system.[28]

Devising an arbitrary but reasonable quantum knowledge scale, say

$$1 \Rightarrow \textit{all knowledge}, \tag{1.14}$$

$$0 \Rightarrow \textit{no knowledge}, \tag{1.15}$$

and using this scale to calibrate "information", Schrödinger's quantum state function has information value 1.[29] Unless there is some quantum interaction with the surroundings (i.e. the system is no longer isolated) $|\Psi\rangle$ will retain information value 1 indefinitely.[30,31]

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[26] The "ket" $|\Psi\rangle$ is an abstract, representation-independent object. Its only dependence is t, time.

[27] $\mathcal{V}_{op}$ is assumed to also include particle–particle interactions.

[28] Whereas probabilities are derivable from the system state function, the reverse is not the case – state functions $|\Psi\rangle$ cannot be inferred from measurement.

[29] In Chapter 2 we will introduce a more solidly based mathematical measure of "information", extending this arbitrary scale.

[30] The isolated system state function is a quantity of maximal information. The system's isolation assures that no information will "leak" in or out.

[31] Macroscopic complexity has relaxed absolute reliance on a detailed many-body quantum description of a macroscopic system. Even at this early point we can foresee that exact (or even approximate) knowledge of the macroscopic (many-body) quantum state function (even if that were possible, which it is not) is unnecessary for macroscopic descriptions.

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An energy expectation value – an observable – is defined (in terms of the wavefunction) by

$$\langle \mathcal{H}(t) \rangle = \int \mathrm{d}\mathbf{x} \psi^*(\mathbf{x}, t)\, \mathcal{H}_{op} \psi(\mathbf{x}, t)\,, \tag{1.16}$$

where $\psi^*(\mathbf{x}, t)$ is the complex conjugate of the wavefunction $\psi(\mathbf{x}, t)$. In the more convenient Dirac notation

$$\langle \mathcal{H} \rangle = \langle \Psi | \mathcal{H}_{op} | \Psi \rangle, \tag{1.17}$$

where $\langle \Psi |$, the conjugate to $| \Psi \rangle$, is called a “bra”. The energy expectation value (sometimes called average value) is often a measurable[32] of physical interest.

But neither Eq. 1.16 nor Eq. 1.17 represent thermodynamic state variables. In particular, $\langle \mathbf{h} \rangle = \langle \Psi | \mathbf{h}_{op} | \Psi \rangle$ is *not* macroscopic internal energy $\mathcal{U}$, the centerpiece of the First Law. This is a *crucial* point that will be further addressed in Chapter 2 when we inquire specifically about thermodynamic variables.

In quantum mechanics, each of nature’s dynamical observables (e.g. momentum, position, energy, current density, magnetic moment, etc.) is represented by an hermitian operator. (An *hermitian operator* satisfies the condition $\Omega_{op}^{\dagger} = \Omega_{op}$, where † is the symbol for hermitian conjugation. In matrix language *hermiticity* means $\Omega^{\dagger} = (\Omega^*)^T = \Omega$, where $(\Omega^*)^T$ is the complex conjugate-transpose of the matrix Ω.)[33]

The quantum theory postulates an auxiliary eigenvalue problem for Ω_{op} (which represents a typical hermitian operator)

$$\Omega_{op} \,|\omega_n\rangle = \omega_n \,|\omega_n\rangle\,, \tag{1.18}$$

with $n = 1, 2, 3, \ldots$, from which the spectrum of allowed quantum observables ω_n (called eigenvalues) is derived. The ω_n are real numbers[34] and $|\omega_n\rangle$ are their corresponding set of complex eigenfunctions. (For simplicity we assume the eigenvalues are discrete.) The specific forms required for dynamical hermitian operators will be introduced as the models require.

1.5 Probabilities in quantum mechanics

According to the Great Probability Postulate of quantum mechanics, the Schrödinger state function $|\Psi\rangle$ is a generator of *all probability information* about an isolated

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[32] The value of this measurable is the average of a very large number of identical measurements on identical systems with identical apparatus.

[33] In the following discussion Ω_{op} is used as a generic symbol for operators representing observables.

[34] The hermitian property of quantum mechanical operators assures that the eigenvalues will be real numbers.

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quantum system with fixed number of particles.[35] Using the complete orthonormal set of eigenfunctions determined from Eq. 1.18, a state function $|\Psi\rangle$ can be expressed as a linear coherent superposition[36]

$$|\Psi\rangle = \sum_n |\omega_n\rangle\langle\omega_n|\Psi\rangle, \tag{1.19}$$

where the coefficients

$$p(\omega_n, t) = \langle\omega_n|\Psi\rangle \tag{1.20}$$

are complex probability amplitudes. *Coherence* as used here implies phase relations among the terms in the sum which leads to characteristic quantum interference effects.

The probability that a measurement outcome will be ω_n is given by

$$\mathcal{P}(\omega_n, t) = |\langle\omega_n|\Psi\rangle|^2 \tag{1.21}$$

$$= \langle\omega_n|\Psi\rangle\langle\Psi|\omega_n\rangle\,. \tag{1.22}$$

The eigenfunction $|\omega_n\rangle$ acts, therefore, as a statistical projector in the sense that with some appropriate measuring device it projects out from the state function $|\Psi\rangle$ the statistical probability of measuring ω_n. The probabilities $\mathcal{P}\,(\omega_n, t)$ are normalized in the usual probabilistic sense, i.e.

$$\sum_n \mathcal{P}\,(\omega_n, t) = 1, \tag{1.23}$$

which corresponds to state function normalization

$$\langle\Psi|\Psi\rangle = 1\,. \tag{1.24}$$

1.5.1 Expectation values

If the probability of observing the measurable value ω_n is $\mathcal{P}\,(\omega_n, t)$, then its expectation (average) value $\langle\omega\rangle$ is, as in ordinary statistics,

$$\langle\omega\rangle = \sum_n \omega_n \mathcal{P}\,(\omega_n, t) \tag{1.25}$$

$$= \sum_n \omega_n \langle\omega_n|\Psi\rangle\langle\Psi|\omega_n\rangle\,. \tag{1.26}$$

For the important special case of energy of an isolated (microscopic) system, where

$$\mathcal{H}_{op}|E_n\rangle = E_n|E_n\rangle, \tag{1.27}$$

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[35] The state function $|\Psi\rangle$ depends on time t so that all quantities calculated from it will – in principle – also depend on time.

[36] This is the famous *linear superposition theorem.*