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THERMODYNAMICS OF QUANTUM COLLISIONS

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Abstract

In this thesis, we show how the thermodynamic concepts of heat and work arise at the level of a quantum collision. We consider the collision of a particle travelling in space, described by a wave packet, with a fixed system having internal energy states. Our main finding is that the energy width of the wave packet, which can be narrow or broad with respect to the system energies, plays a crucial role in identifying energy exchanges due to collisions as heat or work. While heat is generated by narrow wave packets effusing with thermal momenta, work is generated by fast and broad wave packets. We compare our results with models of repeated interactions, which despite being inspired by quantum collisions, still present shortcomings when used as a basis for a thermodynamic theory. We show how these difficulties are circumvented by a proper application of quantum scattering theory.

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Author Contributions

This thesis contains the following manuscripts which I authored or co-authored:

- S. L. Jacob, M. Esposito, J. M. R. Parrondo and F. Barra. Thermalization induced by quantum scattering. *PRX Quantum*, 2(2):020312, 2020.
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- S. L. Jacob, M. Esposito, J. M. R. Parrondo and F. Barra. Quantum scattering as a work source. *arXiv:2109.10620*, submitted.

A fourth manuscript is being written [S. L. Jacob, M. Esposito, J. M. R. Parrondo and F. Barra, in preparation] whose results were not included in this thesis.

I chose a quote from the french writer Antoine de Saint-Exupéry, which I interpret both as a wise statement about life and a praise to the microscopic world.

> *L'essentiel est invisible pour les yeux.*

Preface

The purpose of this thesis is to understand how the concepts of heat and work arise from a collision between quantum systems. This involves putting together two different research fields - thermodynamics and quantum mechanics. Although historically linked since the beginning of the XXth century, these two fields are conceptually quite different. Chapter 1 provides a general introduction of these fields. In Secs. 1.1 and 1.2, we review the history and concepts of thermodynamics and quantum mechanics, respectively. In Sec.1.3, we show how thermodynamics can be formulated quantum mechanically in the language of open quantum systems, as developed in the later half of the century. This theory describes how quantum systems evolve irreversibly, over very long times, into classical states by changing heat with an environment in thermal equilibrium. The environment is pictured here to be very large and in permanent contact with the open system — a picture which is clearly at odds with short time events such as collisions. In Sec. 1.4, we introduce models of repeated interaction, where the environment is pictured as being divided into sub-systems, called of units, which interact sequentially and for a short time with a quantum system. Since the units can be prepared in a non equilibrium state, these models capture the essence of modern experiments with matter and light, being a promising avenue to study thermodynamics of quantum systems out of equilibrium. Despite being inspired by collisions, there is no notion of space or momentum in these models; instead, the system-unit interaction is modelled by a time-dependent function. This leads to problems when these models are used as a basis for thermodynamics — related to thermalization and work — which are discussed at the end of Chapter 1. In Chapter 2, we tackle the problems from the perspective of quantum scattering theory, where particles move freely in space long before and after they collide. Their quantum state of motion is described by wave packets, which are groups of waves that travel together in a quantum superposition. As a first step towards thermodynamics, Sec. 2.1 presents a treatment of a thermal gas in terms of wave packets and a comparison with traditional approach based on plane waves. This treatment is important in order to establish the notion of heat in scattering theory. In Sec. 2.2 we introduce the mathematical formalism of quantum scattering theory based on the scattering operator. Having the necessary tools, we present our results in Sec. 2.3 over three manuscripts, where we formulate the notions of heat and work using scattering theory. The central result is that the wave packet plays a crucial role in identifying heat and work sources. Our approach overcomes many of the limitations of repeated interactions models. The conclusions of this thesis are presented in Chapter 3, where we discuss limitations and open perspectives in the light of our results.

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Chapter 1

Introduction

1.1 Classical Thermodynamics

In this section, we give an overview of thermodynamics for classical systems in thermal equilibrium. Summarizing, the first law of thermodynamics splits energy changes into heat and work. The second law of thermodynamics splits entropy changes into a reversible contribution related to heat and an irreversible contribution called entropy production. In the absence of work, an open system exchanges heat with a thermal reservoir and produces entropy, until it reaches thermal equilibrium. This state is represented statistically by the Boltzmann distribution, corresponding to the state of maximum entropy.

1.1.1 Historical Perspective

Born in the XIX$^{\text{th}}$ century, thermodynamics was motivated by the technological progress brought about by the Industrial Revolution. At the center of the revolution is the heat engine, whose basic principle of operation was eventually understood to be the conversion of heat, the energy flow between systems at different temperatures, into work, the energy flow that generates motion.

Carnot Engine

The first step in understanding this principle was given in 1824 by Sadi Carnot, who introduced an abstract model of the heat engine [1]. Carnot's heat engine is reversible: it can extract work by making heat flow from a hot reservoir to a cold one, but it can spend the same amount of work to make heat flow from a cold reservoir to a hot one. By operating the engine in a cyclic fashion — in such a way that the engine returns to its initial state after a sequence of operations — he showed that no engine can extract more work than the reversible heat engine. This limit on the efficiency of work extraction, known as Carnot efficiency, is very general since it depends only on the temperatures of the reservoirs which exchange the heat and not on the details of the engine. Carnot achieved this at a time when heat was still thought to be an indestructible substance called caloric, that can be exchanged but never created or destroyed.

Heat, Work and Entropy

This view on the nature of heat was overturned two decades later by James Joule, which showed experimentally that mechanical energy can be used to increase the temperature of matter, thereby generating heat. In other words, heat and work are both forms of energy which can be interconverted. Around the same time, the work of Robert Mayer and Hermann von Helmholtz on the principle of energy conservation helped to establish the first law of thermodynamics: the energy change in a given system is the sum of heat and work [2, 3]. Then, in 1865, Rudolph Clausius explained the efficiency of the reversible engine in terms of a quantity called entropy: a system which exchanges heat with a reservoir in a reversible fashion produces no entropy, thus allowing for maximal work extraction [4]. Conversely, irreversible heat exchanges

produce entropy and decrease the amount of extracted work. This became known as the second law of thermodynamics: irreversible processes are characterized by entropy production. In Subsec. 1.1.2, we present the mathematical form of these fundamental laws.

1.1.2 The Laws of Thermodynamics

Thus thermodynamics was born as a theory about energy conversion in macroscopic systems. The prime example of such a system is a gas of particles, whose state is characterized by a small number of macroscopic parameters called state variables, namely volume V, number of particles N, temperature T and pressure P. The state of the gas can be changed by changing the state variables, e.g. compressing or expanding it with a piston, heating or cooling it with a thermal reservoir. The energy $E = E(V,N,T)$ and entropy $S = S(V,N,T)$ of the system, which form the basis for the laws of thermodynamics introduced below, are functions of these variables called state functions. Their change ΔE and ΔS, due to changes in some state variables, depends only on the initial and final states of the gas.

In general, the system interacts with its exterior through the boundary of the volume V. We take the number of particles to be conserved within the system and say that a system is isolated if it cannot exchange energy with its exterior; otherwise, it is called open.[1] For an isolated system, the fact that a single temperature can be defined for the whole system is what we mean by thermal equilibrium. In the same way, two open systems are in thermal equilibrium with each other (they have the same temperature) if they do not exchange heat: a statement known as the zeroth law of thermodynamics [2, 3, 5].

First Law of Thermodynamics

Denote by ΔE the change in energy of the system after an arbitrary change of state variables. Then the first law of thermodynamics is given by

$$\Delta E = Q + W\,, \tag{1.1}$$

where Q and W are the heat and work exchanged, respectively. We use the convention that $Q > 0$ if heat is absorbed by the system and equivalently for work. Note that if $\Delta E = 0$ it follows $Q = -W$. This happens for an isolated system due to energy conservation, or for an open system undergoing any cyclic transformation (because E is a state function). It is worth noting that heat and work are not state functions, but only processes by which energy is exchanged.

[1] The traditional nomenclature in classical thermodynamics calls a system open if it exchanges matter and energy with the exterior, and closed if only energy is exchanged. In this section, we adopt a different nomenclature and substitute closed by open for consistency with quantum theory introduced later.

Second Law of Thermodynamics

The second law relates the entropy to the heat exchanged with a thermal reservoir at temperature T. According to Clausius, the entropy change in the system ΔS is an upper bound on the reversible heat exchanged [4]

$$\Delta S \geq \frac{Q}{T}\,, \tag{1.2}$$

where the equality holds for reversible processes, achieved by very slow transformations such that thermal equilibrium is never disrupted. A contemporary formulation of the second law writes the last inequality as an equality [3, 6]

$$\Delta S = \Sigma + \frac{Q}{T}\,. \tag{1.3}$$

The quantity Q/T, which can be positive or negative, is called the entropy flow and represents the entropy change associated to reversible heat exchanges with the thermal reservoir. Accordingly, the entropy production $\Sigma \geq 0$ is a measure of the irreversibility of the processes within the system. Since the entropy flow is minus the change in entropy of the reservoir $\Delta S_E = -Q/T$, we can write the second law as

$$\Delta S + \Delta S_E \geq 0\,, \tag{1.4}$$

with the usual interpretation that the entropy of the universe (system and exterior) always increases. Since S is a state function, for an open system undergoing a cyclic process we have $\Delta S = 0$ and thus $Q/T \leq 0$. Due to irreversible processes, the system can never return to its initial state without increasing the entropy of the exterior by the expulsion of heat.

1.1.3 Statistical Mechanics

The laws of classical thermodynamics are general because they make no reference to the microscopic state of the system which, according to classical mechanics, would involve specifying the energy, momenta or positions of the particles that compose it. However, with the advent of statistical mechanics in the second half of the XIX$^{\text{th}}$ century, it became possible to understand macroscopic properties (such as temperature, pressure and entropy) in terms of microscopic states [7, 8, 9, 10, 11]. Joseph Willard Gibbs introduced the concept of an ensemble as a collection of identical systems, each one representing a different microscopic state compatible with the macroscopic state of the system. In statistical mechanics, these microscopic states are assigned a probability distribution and the macroscopic state corresponds to certain averages over this distribution.

The Boltzmann Distribution

For this thesis, the canonical ensemble is the most relevant ensemble, describing an open system exchanging energy with a thermal reservoir at temperature T. In this case, the probability that the system has energy E is always proportional to $\exp(-\beta E)$ where $\beta \equiv (k_B T)^{-1}$ has units of inverse energy and

$k_B = 1.38 \times 10^{-23}$ J K^{-1} is the Boltzmann constant. Since the system is in thermal equilibrium with the reservoir, its average energy $\langle E \rangle$ is conserved. Below, we overview the canonical ensemble for systems with discrete and continuous energy states.

Discrete Energies. The first case of interest is when the energies of the system are discrete $\{E_i\}_{i=1}^N$, with N being the total number of energy microscopic states. This case is specially relevant for quantum systems discussed in Secs. 1.2 and 1.3. Then the probability P_i that the system has energy E_i is given by the Boltzmann or Gibbs distribution

$$P_i = Z^{-1} \exp(-\beta E_i) \quad \text{with} \quad Z = \sum_{i=1}^{N} \exp(-\beta E_i)\,, \tag{1.5}$$

where Z is called the partition function. Under the macroscopic constraints of average energy $\langle E \rangle = \sum_{i=1}^N P_i E_i$, the Boltzmann distribution can be derived as the distribution maximizing the quantity

$$S = -k_B \sum_{i=1}^{N} P_i \log P_i \geq 0\,, \tag{1.6}$$

which is called the Gibbs entropy [8] or more recently the Shannon entropy [12, 13]. From the point of view of information theory, the Shannon entropy in Eq. (1.6) can be interpreted as a measure of the ignorance about the microscopic state of the system, or equivalently as the information gained if we were to know this state with certainty [13]. In this sense, the equilibrium distribution in Eq. (1.5) has the least information possible about the microscopic state of the system and is thus maximally random.

Continuous Energies. The second case of interest is when the energies of the system are continuous, as is the case for a particle with mass m belonging to a gas. This case is specially relevant when we study a thermal gas of wave packets in Sec. 2.1. Since the main results of this thesis are formulated in one dimension, we consider the gas to be confined to a length $L = V^{1/3}$. For a low density gas, we can ignore potential energy due to very rare collisions so that the energy of a particle is purely kinetic and independent of position $E = p^2/2m$, where p is the momentum. The Boltzmann distribution is then given by

$$\rho(p) = \frac{\mu_{\text{MB}}(p)}{L} \quad \text{with} \quad \mu_{\text{MB}}(p) = \frac{1}{\sqrt{2\pi m/\beta}} \exp\Big(-\frac{\beta p^2}{2m}\Big)\,, \tag{1.7}$$

where the probability density is normalized over the length L and all momenta. The momentum probability density $\mu_{\text{MB}}(p)$ is called Maxwell-Boltzmann distribution.[2] By computing the average kinetic energy

[2] We can also write the distribution as $\rho(p) = (2\pi\hbar Z)^{-1} \exp(-\beta p^2/2m)$, where $Z = L/\lambda$ is the partition function and $\lambda = \hbar\sqrt{2\pi\beta/m}$ is the thermal wavelength. The constant $\hbar$ has the units of action (momentum times length) and is most naturally identified with the Planck constant to be introduced below in Sec. 1.2.

$\langle E \rangle = k_B T/2$, one can understand temperature in terms of average particle motion in the gas. Regarding the entropy, we simply note that Boltzmann showed, from its famous transport equation, that the Maxwell-Boltzmann distribution maximizes a continuous analog of the Shannon entropy in Eq. (1.6) under the constraints of average energy of the gas particle [7, 9, 11].

Thermalization

Suppose that a system in a non equilibrium state, i.e. described by some probability distribution other than the Boltzmann distribution, is put in contact with a thermal reservoir. In the absence of work sources, the first law in Eq. (1.1) implies that only heat is exchanged, while the second law in Eq. (1.3) that entropy is produced. Eventually the system reaches thermal equilibrium, i.e. it is described by the Boltzmann distribution, where its entropy is maximal and no longer produced. Thus $Q = \Delta S = 0$ and the second law reads $\Sigma = 0$. This irreversible evolution towards thermal equilibrium is called thermalization. The problem faced by statistical mechanics is to reconcile this irreversible behaviour with the underlying reversible microscopic laws, either for classical or quantum systems [14, 15, 16]. We discuss thermalization in quantum systems in Sec. 1.3 and from a quantum scattering perspective in Sec. 2.3.

1.2 Quantum Mechanics

We introduce quantum mechanics for closed and isolated systems. The state of a quantum system is given by a state vector in Hilbert space or by an ensemble of such vectors represented by a density operator. Its state evolves unitarily in time as a superposition of observable states, each assigned with a probability of occurrence. For a quantum particle moving freely in space, its state is represented as a wave packet, which form the basis of the results of Chapter 2. Importantly, the entropy of a closed or isolated quantum system does not change under unitary evolution.

1.2.1 Historical Perspective

Until the end of the XIX$^{\text{th}}$ century, most natural phenomena was explained on the basis of classical physics, comprising of three fields: thermodynamics, classical mechanics and electromagnetism. Thermodynamics holds macroscopically and was discussed in Sec. 1.1. Microscopically, one has classical mechanics and electromagnetism, the first describing the motion of matter and the second describing light in terms of electromagnetic waves. Put together, these last two fields provide a classical picture of how matter and light interact that is relevant even nowadays [17, 18].

Planck's Relation

Despite the many successes of classical physics, it failed to explain light emitted from a blackbody in thermal equilibrium.[3] In 1901, Max Planck solved the problem by postulating that matter and light could only exchange energy in discrete amounts or quanta [19]. This was in stark contrast to continuous energy exchanges allowed by the classical theory of electromagnetism. According to Planck, the quantum of energy E exchanged between a matter oscillator in equilibrium with thermal light is given by $E = \hbar\omega$ where $\hbar = 1.05\times10^{-34}$ J s is Planck's constant and ω is the angular frequency of the oscillator. Drawing on the work of Planck, Albert Einstein postulated in 1905 that light is composed of particles, called photons, obeying Planck's relation [20]. This view on light was used to explain the photoelectric effect, which hitherto lacked theoretical basis, and later found experimental support in the Compton effect [21, 22]. Moreover, after the discovery of the atomic nucleus in 1911 by Ernest Rutherford, it became clear that classical physics could neither describe the stability of the atom, whose electrons should lose energy by radiation and eventually fall into the nucleus, nor the discreteness of the atomic spectra. This was remedied in 1913 when Niels Bohr proposed his model of the atom, where the orbits of the electrons are quantized and stable except for jumps between orbits induced by absorption or emission of photons. The work of the aforementioned

[3] A blackbody absorbs and emits all radiation at all frequencies.

scientists made clear that the quantum nature of light and matter was necessary to explain many phenomena in microscopic physics.

de Broglie's Relation

In the early 1920s, Louis de Broglie postulated that the wave-particle duality should not only apply to light, but to matter as well. Thus, to every particle with momentum p there is an associated wave vector k, defined through the relation $p = \hbar k$ where $\lambda = 2\pi/k$ is called the de Broglie wavelength [23]. It did not take long for de Broglie's hypothesis to be confirmed through scattering experiments of electrons by crystals and through double-slit experiments with electrons. The latter experiments showed that single electrons behave as waves, in the sense that they pass through both slits in a superposition (much like classical waves), thus displaying interference patterns when detected on a screen. However, the interference pattern is not observed if the experimenter has a way to infer through which slit the electron has gone. The double-slit experiments (which can also be performed with light) and many others showed that measurement destroys the wave nature of particles [21, 22, 24].

The Superposition Principle

By the end of the 1920s, the bits and pieces of non-relativistic quantum mechanics were put together in a cohesive picture by Erwin Schrödinger and Werner Heisenberg [25, 26], while the mathematical framework in its most abstract form was put forth by Paul Dirac [27] and later by von Neumann [28]. In this formalism, the state of a quantum system is described as a superposition of observable states, each assigned with a probability of being measured. Thus, a particle bound by some potential, such as an electron in an atom, can be described as a wave in a superposition of discrete energy states. In contrast, a free particle is described by wave in a superposition of continuous energy or momentum states, a so-called wave packet. The formalism presented below includes both of these cases.

1.2.2 The Schrödinger Equation

In quantum mechanics, the state of a system is given by a vector in a complex, separable Hilbert space $|\psi\rangle \in \mathscr{H}$ with inner product $\langle\phi|\psi\rangle = \langle\psi|\phi\rangle^*$ for any $|\phi\rangle \in \mathscr{H}$.[4] For physical purposes, the state vector is normalized according to $\langle\psi|\psi\rangle = 1$. Transformations of state vectors are effected by linear operators, say A, so that if $|\psi\rangle = \alpha_1|\psi_1\rangle + \alpha_2|\psi_2\rangle$ is a linear combination of state vectors with $\alpha_1, \alpha_2 \in \mathbb{C}$ then $A|\psi\rangle = \alpha_1 A|\psi_1\rangle + \alpha_2 A|\psi_2\rangle$.[5] The adjoint of an operator A, denoted $A^\dagger$, is defined through the inner product by

[4] A Hilbert space is separable if it admits a countable, dense and orthonormal basis.

[5] Transformations can also be effected by anti-linear operators B, which act as $B|\psi\rangle = \alpha_1^* B|\psi_1\rangle + \alpha_2^* B|\psi_2\rangle$. This is the case for the time-reversal operator discussed in the publications. Unless stated otherwise, all operators are linear.

$\langle\phi|A|\psi\rangle = \langle\psi|A^\dagger|\phi\rangle^*$ and an operator is called self-adjoint if $A = A^\dagger$.

Spectral Decomposition

Observables of the system such as energy, position and momentum are represented by self-adjoint operators. We usually express state vectors in the eigenbasis of the energy operator H called the Hamiltonian, which can have both discrete and continuous spectrum. In this section, we always assume the discrete spectrum to not be degenerate. In this case we have $H|i\rangle = e_i|i\rangle$ where $\{|i\rangle\}_{i=1}^N$ is a discrete orthonormal basis $\langle j|i\rangle = \delta_{ji}$ and $\dim(\mathscr{H}) = N$. For its continuous spectrum we have $H|\lambda\rangle = E_\lambda|\lambda\rangle$, where $\{|\lambda\rangle\}$ is a continuous orthogonal basis satisfying $\langle\lambda'|\lambda\rangle = \delta(\lambda-\lambda')$. Such a continuous basis is called an improper basis, since it has infinite norm when $\lambda = \lambda'$, but can nevertheless be used to build proper (normalized) state vectors. Any self-adjoint can be expressed in terms of projection operators onto the subspace associated to each eigenvalue [28, 29, 30]. This is the spectral decomposition, which for the Hamiltonian reads

$$H = \sum_{i=1}^{N} e_i\,|i\rangle\langle i| + \int_{-\infty}^{\infty} E_\lambda\,|\lambda\rangle\langle\lambda|\,d\lambda\,, \tag{1.8}$$

where $|i\rangle\langle i|$ and $|\lambda\rangle\langle\lambda|$ are projection operators. An important case is obtained by considering the identity operator $\mathbb{I} = \sum_{i=1}^N |i\rangle\langle i| + \int_{-\infty}^{\infty}|\lambda\rangle\langle\lambda|\,d\lambda$, which simplifies to the sum or integral term if the spectrum is purely discrete or purely continuous, respectively.

Time Evolution

The time evolution of the state vector $|\psi(t)\rangle$ is found by solving the Schrödinger equation

$$\frac{d\,|\psi(t)\rangle}{d\,t} = -\frac{iH(t)}{\hbar}|\psi(t)\rangle\,, \tag{1.9}$$

where $H(t) = H^\dagger(t)$ is the Hamiltonian which in general can be time-dependent. It specifies the total energy of the system considered. For quantum systems, we say that the system is closed if its Hamiltonian is time-dependent, otherwise it is called isolated. The expectation value of the energy at time t can be found by $\langle H(t)\rangle \equiv \langle\psi(t)|H(t)|\psi(t)\rangle$ and similarly for other observables. The formal solution to Eq. (1.9) is given by

$$|\psi(t)\rangle = U(t,t_0)|\psi(t_0)\rangle \tag{1.10}$$

where $U(t,t_0)$ is the evolution operator obeying $U(t,t_0)U^\dagger(t,t_0) = U^\dagger(t,t_0)U(t,t_0) = \mathbb{I}$ and $\mathbb{I}$ is the identity operator. All unitary operators obey the last relation, which imply that the inner product and norm are preserved under such transformations. Note that the evolution operator has an inverse for all times $U^\dagger(t,t_0) = U^{-1}(t,t_0)$, implying that unitary dynamics in $\mathscr{H}$ is always reversible. The evolution operator

admits the general expression

$$U(t,t_0) = \mathrm{T}_{\leftarrow} \exp\Big[-\frac{i}{\hbar}\int_{t_0}^{t} dt'\, H(t')\Big], \tag{1.11}$$

where $\mathrm{T}_{\leftarrow}$ is the time-ordering operator, which orders time-dependent operators from right to left when expressed as a series. For isolated systems considered in this section, the Hamiltonian is time-independent and the evolution operator simply reads

$$U(t,t_0) = \exp\Big[-\frac{iH(t-t_0)}{\hbar}\Big]. \tag{1.12}$$

The evolution for a purely continuous spectrum is treated below. Here, for a purely discrete spectrum, we insert the identity into Eq. (1.10) to obtain

$$|\psi(t)\rangle = \sum_{i=1}^{N} c_i(t)|i\rangle \quad \text{with} \quad c_i(t) = c_i(t_0)\exp\Big[-\frac{ie_i(t-t_0)}{\hbar}\Big], \tag{1.13}$$

with the coefficients defined as $c_i(t_0) \equiv \langle i|\psi(t_0)\rangle$. Thus, the state vector evolves in time as a superposition of energy eigenstates with complex coefficients. The phase of the exponential describes a wave oscillating in time with angular frequency $e_i/\hbar$, according to Planck's relation. As usual, we interpret $|\langle j|\psi(t)\rangle|^2 = |c_j(t)|^2$ as the probability to find the state in the eigenstate $|j\rangle$ at time t after a given measurement. From the normalization of the state vector, it follows that $\sum_{j=1}^{N}|c_j(t)|^2 = 1$ so the probability of finding the system in any of its energy eigenstate is one.

Wave Packets

We now consider a particle moving freely in one dimension according to the Hamiltonian of kinetic energy $H_p = p^2/2m$, where m is the mass and the momentum operator p has a continuous spectrum with $\{|p\rangle\}$ being an improper eigenbasis of H such that $\langle p'|p\rangle = \delta(p-p')$. The position operator x is also continuous and obeys similar relations to p. These improper states can be used to expand proper state vectors, which belong to the Hilbert space of square-integrable functions in one dimension. Combining the resolution of identity in position with the inner product between two arbitrary states $|\psi_1\rangle$ and $|\psi_2\rangle$, we get $\langle\psi_2|\psi_1\rangle = \int_{-\infty}^{\infty}\psi_2(x)^*\psi_1(x)dx$, where $\psi(x) \equiv \langle x|\psi\rangle$ is a representation of the state vectors in position, or wave function in position. Inserting a resolution of identity in momentum in $\langle x|\psi\rangle$, we can related it to its wave function in momentum $\phi(p) \equiv \langle p|\psi\rangle$, which is just the Fourier transform

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\phi(p)\exp\Big(\frac{ipx}{\hbar}\Big)\,dp\,, \tag{1.14}$$

where we introduced the quantity

$$\langle x|p\rangle = (2\pi\hbar)^{-1/2}\exp\Big(\frac{ipx}{\hbar}\Big), \tag{1.15}$$

which are plane waves whose wave vector is $k = p/\hbar$ according to de Broglie's relation. The wave function at time t is thus directly obtained from Eq. (1.10)

$$\psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \phi(p) \exp\Big(\frac{ipx}{\hbar} - \frac{ip^2 t}{2m\hbar}\Big)\, dp\,, \tag{1.16}$$

where we set $t_0 = 0$ for simplicity. The last expression represents a wave packet, which is a superposition of plane waves whose weight is given by $\phi(p)$. The main results of this thesis are based on Gaussian wave packets, with wave function in momentum is given by

$$\phi(p) = (2\pi\sigma_p^2)^{-1/4} \exp\Big[-\frac{(p-p_0)^2}{4\sigma_p^2} - \frac{ipx_0}{\hbar}\Big], \tag{1.17}$$

where $p_0 \equiv \langle p(0)\rangle$ and $x_0 \equiv \langle x(0)\rangle$ are the initial expectation values of momentum and position and σ_p is the standard deviation, or width, in momentum. Substituting Eq. (1.17) into Eq. (1.16) and performing the integral, we obtain the solution

$$\psi(x,t) = [2\pi\sigma_x^2(t)]^{-1/4} \exp\Big[-\frac{(x-x_0-p_0 t/m)^2}{4\sigma_x^2(1+it/\tau_s)} + i\Theta(x,t)\Big], \tag{1.18}$$

where $\Theta(x,t)$ is a real function with the definition

$$\Theta(x,t) = \frac{p_0}{\hbar}\Big(x - x_0 - \frac{p_0 t}{2m}\Big) - \frac{1}{2}\arctan\Big(\frac{t}{\tau_s}\Big). \tag{1.19}$$

Expression (1.18) describes a Gaussian wave packet where $\sigma_x(t) \equiv \sigma_x\sqrt{1+(t/\tau_s)^2}$ is the width in position at time t and $\sigma_x = \hbar/2\sigma_p$. The spreading time $\tau_s \equiv 2m\sigma_x^2/\hbar$ describes how the packet spreads out of its center $x_0 + p_0 t/m$, the latter moving with constant velocity p_0/m called the group velocity. It leads to the uncertainty relation between position and momenta $\sigma_x(t)\sigma_p \geq \hbar/2$ where the equality holds at $t = 0$ for Gaussian states. The uncertainty relation implies that the particle cannot be simultaneously localized in space and momentum, in opposition to classical mechanics. It can be derived more generally for any two non-commuting observables [22, 24, 31, 32].[6] The phase $\Theta(x,t)$ describes a plane wave with wave vector $k_0 = p_0/\hbar$ and de Broglie wavelength $\lambda_0 = 2\pi/k_0$, modified by the spreading time. Finally, the square of the modulus of the wave function

$$|\psi(x,t)|^2 = \frac{1}{\sqrt{2\pi\sigma_x^2(t)}} \exp\Big[-\frac{(x-x_0-p_0 t/m)^2}{2\sigma_x^2(t)}\Big], \tag{1.20}$$

is interpreted as the probability per unit length. It is easily verified to be normalized over all space.

[6] The uncertainty in position is time-dependent while the uncertainty in momentum is not. This is best understood in the Heisenberg picture, where observables evolve in time. It is then clear that p is a constant of motion and so is any standard deviation or width computed from it.

1.2.3 The von Neumann Equation

The idea of an ensemble discussed in Subsec. 1.1.3 can be generalized for quantum systems. This is achieved by the introduction of a density operator ρ acting on $\mathscr{H}$, which is the quantum analog of the classical probability distribution. If we consider an ensemble of state vectors $\{|\psi_\alpha\rangle\}_{\alpha=1}^{M}$, each being assigned a probability $p_\alpha \geq 0$ where M is the dimension of the ensemble, then the density operator is written in terms of projection operators

$$\rho = \sum_{\alpha=1}^{M} p_\alpha |\psi_\alpha\rangle\langle\psi_\alpha| \,, \tag{1.21}$$

where $\sum_{\alpha=1}^{M} p_\alpha = 1$. We can also consider a continuous probability distribution for an ensemble instead of a discrete one (this issue is addressed in Sec. 2.1 when we treat a thermal gas of wave packets). The density operator is self-adjoint $\rho = \rho^\dagger$, positive $\langle\psi|\rho|\psi\rangle \geq 0$ for any $|\psi\rangle \in \mathscr{H}$ and has trace one $\mathrm{Tr}(\rho) = 1$. Another important property of this operator is $\mathrm{Tr}(\rho^2) \leq \mathrm{Tr}(\rho)$, where the equality holds if and only if $\rho = |\psi\rangle\langle\psi|$. If it holds, we know the state vector with certainty and we say that the quantum system is in a pure state; otherwise, it is in a mixed state [28].

Time Evolution

The density operator at time t is then obtained directly from the pure state solution of Schrödinger equation in Eq. (1.10). It reads

$$\rho(t) = U(t,t_0)\rho(t_0)U^\dagger(t,t_0) \,, \tag{1.22}$$

with $\rho(t_0) = \sum_{\alpha=1}^{M} p_\alpha |\psi_\alpha(t_0)\rangle\langle\psi_\alpha(t_0)|$ being the initial density operator. Differentiating with respect to time we obtain the von Neumann equation

$$\frac{d\rho(t)}{dt} = -\frac{i}{\hbar}[H(t),\rho(t)] \,, \tag{1.23}$$

which describes the time evolution of the ensemble and [,] is the commutator. For isolated systems, the Hamiltonian is time-independent. If it has a purely discrete spectrum, Eq. (1.22) reads in its eigenbasis

$$\rho(t) = \sum_{j,i=1}^{N} \rho_{ji}(t)\, |j\rangle\langle i| \quad \text{with} \quad \rho_{ji}(t) = \rho_{ji}(t_0)\, \exp[-i\omega_{ji}(t-t_0)] \,, \tag{1.24}$$

with the definition of the matrix element $\rho_{ji}(t_0) \equiv \langle j|\rho(t_0)|i\rangle$. The diagonal elements in the eigenbasis of the Hamiltonian are called populations $\rho_{jj}(t)$, representing the probability that the system is in a given state j and naturally $\mathrm{Tr}[\rho(t)] = \sum_{j=1}^{N} \rho_{jj}(t) = 1$ for all times t. The non-diagonal elements are called coherences $\rho_{ji}(t)$ for $j \neq i$, representing superpositions between different energy eigenstates. In opposition to the populations, they evolve in time according to the phase in the exponential, describing a wave with angular frequency $\omega_{ji} \equiv \Delta_{ji}/\hbar$ called the Bohr frequency, with $\Delta_{ji} \equiv e_j - e_i$. Its inverse $1/\omega_{ji}$ defines an intrinsic evolution time scale of the system (whenever $\omega_{ji} \neq 0$). Note that the phase is preserved throughout the evolution, therefore the evolution is called coherent.

von Neumann Entropy

The Shannon entropy in Eq. (1.6) also has a generalization for ensembles of quantum systems. It is called the von Neumann entropy, defined as

$$S(\rho) = -k_B \mathrm{Tr}\,(\rho \log \rho) \geq 0\,, \tag{1.25}$$

where the equality holds for pure states. It reduces to the Shannon entropy through the spectral decomposition of the density operator. Note that if ρ is already diagonal in the energy eigenbasis, then the von Neumann entropy is equal to the Shannon entropy in Eq. (1.6), where ρ_{jj} is the probability associated to a given energy state j. Importantly, the von Neumann entropy is invariant under unitary transformations of states $S(\rho) = S(U\rho U^\dagger)$ for any unitary operator U [28, 33]. In other words, the entropy of the system remains constant under unitary evolution, as expected from reversible dynamics.

The Interaction Picture

So far we considered eigenstates of the full Hamiltonian $H(t)$. Usually, this Hamiltonian is the sum of two parts $H(t) = H_0 + V(t)$, where H_0 is called the free Hamiltonian, assumed here to be time-independent, and $V(t)$ is the interaction operator which is in general time-dependent. In this case, it is useful to consider the unitary operator in the interaction picture

$$U_I(t, t_0) = U_0^\dagger(t, t_0) U(t, t_0)\,, \tag{1.26}$$

where $U_0(t, t_0)$ is the time evolution operator for H_0 and $U(t, t_0)$ is the equivalent for $H(t)$. Given some observable $A(t)$ in the usual Schrödinger picture, there is an observable $A_I(t)$ in the interaction picture defined by

$$\langle A(t)\rangle = \mathrm{Tr}[A(t)\rho(t)] = \mathrm{Tr}[A_I(t)\rho_I(t)]\,. \tag{1.27}$$

The last expression also defines how expectation values of observables are computed in the density operator formalism. The observable in the interaction picture is given by $A_I(t) \equiv U_0^\dagger(t, t_0) A(t) U_0^\dagger(t, t_0)$ and the density operator in this picture is

$$\rho_I(t) \equiv U_I(t, t_0)\rho(t_0)U_I^\dagger(t, t_0)\,. \tag{1.28}$$

Note that both picture coincide at initial times $\rho_I(t_0) = \rho(t_0)$. Expression (1.28) can be differentiated with respect to time to obtain

$$\frac{d\rho_I(t)}{dt} = -\frac{i}{\hbar}[V_I(t), \rho_I(t)]\,, \tag{1.29}$$

which is the von Neumann equation in the interaction picture. Since the density operator in the interaction picture evolves with the interaction $V_I(t)$, this expression form is often used as a starting point for derivations of quantum master equations based on perturbation theory.

1.3 Irreversibility in Quantum Systems

We review how irreversibility arises in quantum systems. At the center of the discussion is the theory of open quantum systems, describing how a quantum system evolves due to the interaction with its environment. The evolution of the open system is not unitary, but given instead by a completely positive and trace preserving map. This is enough to formulate the laws of thermodynamics for quantum systems interacting with a thermal reservoir. We discuss Markovian quantum master equations which obey detailed balance, ensuring thermalization of the open system.

1.3.1 Thermalization

The evolution of a closed or isolated system is reversible and thus its entropy remains constant over time. This is true for quantum systems, whose evolution in time is given by the von Neumann equation (1.25) or for classical systems governed by the Liouville equation [9, 10, 11]. This is in contrast with the empirical fact that natural processes are irreversible, as expressed by second law of thermodynamics in Eq. (1.3). Thus, statistical mechanics should not be restricted to thermal equilibrium (see Sec. 1.1.3), but should also describe how equilibrium is reached from initial non equilibrium conditions. This involves deriving irreversible dynamical equations starting from the microscopic reversible equations for classical or quantum systems.

Our discussion from now on focuses mainly on quantum systems, whose underlying equations of motion share many features with its classical counterpart. Nevertheless, we should point out the most crucial distinction between the quantum and classical cases: the presence of superposition or coherences for quantum systems, which have no classical analogue. This means that any equation describing thermalization of a quantum system should also describe how coherences are lost or suppressed – a phenomena called decoherence — and by consequence the emergence of a classical system described by a density operator diagonal in the relevant eigenbasis. In other words, for a discrete quantum system with Hamiltonian H we expect the quantum analog of Eq. (1.5) called the Gibbs state, or simply thermal state

$$\rho^{\mathrm{eq}} = Z^{-1} \exp(-\beta H) \quad \text{with} \quad Z = \mathrm{Tr}[\exp(-\beta H)] \,. \tag{1.30}$$

Below, we give a brief historical perspective on the problem of thermalization which serves as motivation for the theory of open quantum systems introduced in Subsec. 1.3.2.

Boltzmann's Approach

The problem of thermalization goes back to Boltzmann and his famous transport equation for a classical gas of particles, describing how the probability distribution changes in time due to particle collisions. Three main conditions lie at the heart of Boltzmann's approach. First, the gas is considered sufficiently

dilute so that only two-body collisions are relevant. Second, each collision is microscopically reversible, so that the scattering cross section or probability is invariant under time-reversal. Third, the momenta of the colliding particles are uncorrelated before and after the collision, an assumption known as molecular chaos or *Stosszahlansatz*. These conditions allowed Boltzmann to derive his famous H-theorem showing that, in the absence of external forces, the Maxwell-Boltzmann distribution in Eq. (1.7) is the equilibrium distribution corresponding to maximum entropy [7, 9, 11]. Boltzmann's approach was very successful in predicting transport coefficients for dilute gases. Nonetheless, the question of the validity of his approach remained unanswered, and there was considerable need for a theory describing transport processes in liquids (e.g. low-temperature helium), solids (e.g. heat conduction in crystals) and plasmas. This prompted the development of a general theory of irreversible processes, starting from the Liouville equation of classical mechanics or from the Schrödinger or von Neumann equation of quantum mechanics [14, 15, 16].

Pauli's Equation

The first microscopic derivation of a dynamical equation describing irreversible processes was achieved in 1928 by Wolfgang Pauli [34]. A rigorous study of this master equation, as it came to be known, was carried out by Léon van Hove almost 30 years later for quantum systems [35]. For a discrete system, the master equation reads in the Schrödinger picture

$$\frac{d\rho_{jj}(t)}{dt} = \sum_i \Big(T_{ji}\rho_{ii}(t) - T_{ij}\rho_{jj}(t) \Big). \tag{1.31}$$

It is a first-order, linear differential equation for the populations (probabilities) associated with each eigenstate of a quantum system. The quantities T_{ji} are time-independent rates expressing the transition probabilities (per unit time) for the system to jump from eigenstate i to j. Some comments on its original microscopic derivation and validity of Eq. (1.31) are now in order.

1. The starting point for its derivation is a many-body, time-independent Hamiltonian of the form $H = H_0 + \lambda V$, where H_0 is the free Hamiltonian, V is the interaction and λ is an adimensional coupling constant measuring its strength. It is assumed to be small $\lambda \ll 1$ so that perturbation theory can be applied to Eq. (1.23) or Eq. (1.29) up to second-order in λ. This is called the weak coupling limit.

2. It describes the dynamics only of the populations associated to the eigenstates of H_0. In this case, terms proportional to λ vanish and the rates become proportional to the square of the matrix element of the interaction $T_{ji} \propto \lambda^2 |\langle j|V|i\rangle|^2$.

3. The master equation is Markovian, so that the state of the system at time t does not depend on its past history, which follows immediately from the fact that the rates are time-independent. This property is essential in deriving quantum master equations as we discuss in Subsecs. 1.3.2 and Subsecs. 1.3.3. For Pauli's equation, it is enforced in the long time limit, so that the rates become $T_{ji} = (2\pi\lambda^2/\hbar)|\langle j|V|i\rangle|^2 \delta(\Delta_{ji})$, where $\pi\delta(\Delta_{ji}) = \lim_{t\to\infty} \sin(\Delta_{ji}t/\hbar)/\Delta_{ji}$. In other words, the time

scales considered in Eq. (1.31) are much larger than the intrinsic time scales of the system. Here, it implies that only transitions preserving energy are allowed. This is a discrete version of Fermi's golden rule: transitions between eigenstates due to a small perturbation occur at a constant rate within an energy shell. Note however that the δ-function presented above is not rigorously defined for H_0 with discrete spectrum but only for a continuous one. Indeed, the exact conditions under which Eq. (1.31) holds is called the van Hove limit, defined for an infinitely large system with continuous spectrum when $\lambda \to 0$, $t \to \infty$ with $\lambda^2 t$ being constant [35].

4. The symmetry of the rates $T_{ji} = T_{ij}$ implies that the thermal state in Eq. (1.30) with an infinite temperature ($\beta \to 0$ or $T \to \infty$) is a solution of Eq. (1.31). This symmetry is an expression of microscopic reversibility, or detailed balance, for an isolated system: transitions between any two eigenstates of the system are equally probable.

We do not pretend to be exhaustive in the derivation of Eq. (1.31), but only in providing and discussing its main ingredients. Detailed discussions can be found elsewhere [15, 35, 36]. This master equation is an important achievement, being the simplest equation describing irreversible processes that can be derived from the full unitary dynamics. It can also be interpreted as a stochastic (random) Markov process for the populations, where transitions are caused by a weak perturbation. Note that the classical analogue of Eq. (1.31) has also been derived in the weak coupling limit by Ilya Prigogine and others [14, 16]. In fact, the classical master equation has been extensively used in phenomenological approaches to dynamics and thermodynamics of stochastic processes [37, 38, 39, 40].

Thermalization in isolated systems is still an open issue and beyond the scope of this thesis [41, 42]. In Subsecs. 1.3.2 and 1.3.3, we show how Eq. (1.31) arises from quantum master equations in the framework of open quantum systems. There, the evolution of coherences is explicitly taken into account.

1.3.2 Open Quantum Systems

In practice, physical systems are never isolated. More precisely, the relevant degrees of freedom are only a subset of the total degrees of freedom at play. Henceforth, we call this relevant subset the open system or just system. The remaining degrees of freedom, called the exterior or environment, are usually too difficult to describe microscopically and not easily controllable. There is thus a practical necessity to describe the dynamics of the open system induced by interactions with its environment. To give some concrete examples, the quantum transport of electrons in conducting materials is coupled to the lattice vibrations called phonons, which act as an environment for the electrons and damp their motion [43]. In quantum optics, one builds a laser by stimulated emission of photons from excited atoms into a cavity. These photons are fed back into the excited atoms by reflecting mirrors in the cavity. A full description of the laser setup would involve not only the interaction of the atoms with light, but the pumping mechanisms for atomic excitation and the losses due to spontaneous emission and imperfect cavity [24, 43, 44, 45, 46]. By treating either the atom or the light as an open system, a more tenable description is obtained. In

quantum computation and information, a qubit (a two-level quantum system used to store or process information) experiences decoherence due to its environment, thus losing any computational advantage it has over classical systems [33]. Treating the qubit as an open quantum systems is there indispensable. Finally, a quantum system can be regarded as open with respect to some measurement apparatus [47, 48].

Below, we provide the mathematical framework to study open quantum systems relying on the notion of completely positive and trace preserving maps, which are generalizations of unitary evolution.

Time Evolution

We consider a Hilbert space $\mathscr{H}$ in a tensor product form $\mathscr{H} = \mathscr{H}_S \otimes \mathscr{H}_E$, where $\mathscr{H}_S$ is the Hilbert space of the system and $\mathscr{H}_E$ is the Hilbert space of the environment. The total Hamiltonian is of the form

$$H(t) = H_S \otimes \mathbb{I}_E + \mathbb{I}_S \otimes H_E + V(t)\,, \tag{1.32}$$

where the interaction can be time-dependent, $\mathbb{I}_S$ is the identity in $\mathscr{H}_S$ and an equivalent notation holds for the environment. The full dynamics in $\mathscr{H}$ is unitary and defined by Eq. (1.22). Our aim is to describe the dynamics in $\mathscr{H}_S$ with observables of the form $A \otimes \mathbb{I}_E$. This is achieved by taking the partial trace over the degrees of freedom of the environment $\rho_S = \mathrm{Tr}_E(\rho)$, where ρ_S is the reduced density operator representing the state of the system [49, 50, 51]. A reduced description for the environment can be obtained in a similar fashion. If the full state (system plus environment) is initially uncorrelated, we have the product state $\rho = \rho_S \otimes \rho_E$, where we set $t_0 = 0$ for simplicity and dropped the time-dependence of the initial states. The state of the system obtained from Eq. (1.22) reads

$$\rho_S(t) = \mathrm{Tr}_E\big[U(t)\big(\rho_S \otimes \rho_E\big)U^\dagger(t)\big] \equiv \mathscr{S}_t(\rho_S)\,, \tag{1.33}$$

where $U(t) \equiv U(t,0)$ and $\mathscr{S}_t \equiv \mathscr{S}_{t,0}$ is called a dynamical map, responsible for the evolution of the open system during time $t \geq 0$. Before we go any further, a dynamical map can be understood more generally in terms of quantum operations, without making reference to the dynamics as we show below.

The Kraus Decomposition

A quantum operation $\mathscr{S}$ is a map between density operators that can be written as

$$\mathscr{S}(\rho_S) = \sum_i K_i \rho_S K_i^\dagger \quad \text{with} \quad \sum_i K_i^\dagger K_i \leq \mathbb{I}_S\,, \tag{1.34}$$

where the sum is over some discrete index set and K_i are so-called Kraus operators. This decomposition of a quantum operation was proven in 1971 by K. Kraus [52]. We note that the subscript s (system) is here only kept for continuity with the notation introduced above, but Kraus' theorem is general. A quantum operation $\mathscr{S}$ admitting the above decomposition is characterized by three properties.

1. It obeys $0 \leq \mathrm{Tr}_S[\mathscr{S}(\rho_S)] \leq 1$ which follows directly from the property $\sum_i K_i^\dagger K_i \leq \mathbb{I}_S$.

2. It is convex-linear $\mathscr{S}(\sum_\alpha p_\alpha \rho_S^\alpha) = \sum_\alpha p_\alpha \mathscr{S}(\rho_S^\alpha)$, where α labels a density operator occurring in a mixture with probability p_α so that $\sum_\alpha p_\alpha = 1$.

3. It is completely positive, a technical requirement which we summarize as follows. If $(\mathscr{S} \otimes \mathbb{I}_E)$ is a combined operation on the full Hilbert space $\mathscr{H} = \mathscr{H}_S \otimes \mathscr{H}_E$, where $\mathscr{H}_E$ has an arbitrary dimensions and ω is a positive operator on $\mathscr{H}$, then $(\mathscr{S} \otimes \mathbb{I}_E)(\omega)$ is a positive operator [53, 54, 55, 56].

Equipped with the Kraus decomposition, we go back to Eq. (1.33), use the spectral decomposition of the environment (assumed here to be discrete) $\rho_E = \sum_i \gamma_i |i\rangle\langle i|$ and take the partial trace explicitly, obtaining

$$\rho_S(t) = \sum_{j,i} K_{ji}(t) \rho_S K_{ji}^\dagger(t) \quad \text{with} \quad K_{ji}(t) \equiv \sqrt{\gamma_i}\, \langle j|U(t)|i\rangle \ . \tag{1.35}$$

Since $U(t)$ is unitary, it follows immediately that $\sum_{j,i} K_{ji}^\dagger(t) K_{ji}(t) = \mathbb{I}_S$ and thus that $\mathrm{Tr}_S[\rho_S(t)] = 1$. The main conclusion is that the dynamical map $\mathscr{S}_t$ is a completely positive and trace preserving quantum operation. In fact, any map for the system obtained from an initially uncorrelated full state, followed by unitary evolution, is completely positive and trace preserving. The main results of this thesis presented throughout Chapter 2 are based on a such maps.

Relative Entropy and Irreversibility

In opposition to unitary evolution, the evolution of the system given by Eq. (1.33) is not reversible in time — in fact, the dynamical map $\mathscr{S}_t$ has an inverse if and only if it is unitary [51]. This is in keeping with the irreversibility of open quantum systems. The physical reason for this irreversibility can be understood as follows. During unitary evolution, correlations between system and reservoir are established and thus the full state cannot be generally represented as a product state $\rho(t) \neq \rho_S(t) \otimes \rho_E(t)$. Such a state $\rho(t)$ is said to be an entangled state. When we obtain the state of system by tracing out the degrees of freedom of the environment, we also discard the correlations established between them — from the point of view of the system, this information is then irreversibly lost. The same conclusion holds for the environment state $\rho_E(t) = \mathrm{Tr}_S[\rho(t)]$. We can make these statements more precise by referring to the sub-additivity property of the von Neumann entropy, which reads $S[\rho_S(t)] + S[\rho_E(t)] \geq S[\rho(t)]$ and the equality holds if the full system is uncorrelated [33, 50]. Physically, it means that we lose information about the correlations of system and environment when we trace over the degrees of freedom of either one. We can write the sub-additivity property as an equality in the following way

$$S[\rho_S(t)] + S[\rho_E(t)] = S[\rho(t)] + D[\rho(t)|\rho_S(t) \otimes \rho_E(t)] \tag{1.36}$$

where $D[\alpha|\omega]$ is the relative entropy between any two density operators α, ω in the relevant Hilbert space ($\mathscr{H}$ in the case of the last expression), defined by

$$D[\alpha|\omega] = k_B \mathrm{Tr}[\alpha(\log\alpha - \log\omega)] \geq 0 \,, \tag{1.37}$$

where we introduce the Boltzmann constant anticipating its thermodynamic interpretation. The fact that it is non-negative is known as Klein's inequality and it is zero only if and only if $\alpha = \omega$. Therefore, the quantity in Eq. (1.36) is identified as

$$I_{S:E}(t) \equiv D[\rho(t)|\rho_S(t)\otimes\rho_E(t)] \geq 0\,, \tag{1.38}$$

called the quantum mutual information, providing a measure of the correlations established between the open system and environment [33]. More generally, the relative entropy is invariant under unitary evolution $D[U\alpha U^\dagger|U\omega U^\dagger] = D[\alpha|\omega]$ for any unitary operator U. Moreover, if $\alpha_1 = \mathrm{Tr}_2(\alpha)$ and $\omega_1 = \mathrm{Tr}_2(\omega)$, where the traces are over a second sub-system, then $D[\alpha_1|\omega_1] \leq D[\alpha|\omega]$ and the equality holds for uncorrelated systems $D[\alpha_1|\omega_1] = D[\alpha_1\otimes\alpha_2|\omega_1\otimes\omega_2]$. Using these properties along with Eq. (1.33) applied to ρ and ω, it is easy to show that

$$D[\rho(t)|\omega(t)] \leq D[\rho|\omega]\,. \tag{1.39}$$

Therefore the relative entropy always decreases under the action of a dynamical map. This statement was proven in 1975 by G. Lindblad [57]. Denoting ρ_S^{ss} as the stationary state of the dynamical map, we have $\mathscr{I}_t(\rho_S^{\mathrm{ss}}) = \rho_S^{\mathrm{ss}}$, i.e. it is an eigenoperator of the map with eigenvalue one. Then $D[\rho_S(t)|\rho_S^{\mathrm{ss}}] \leq D[\rho_S|\rho_S^{\mathrm{ss}}]$ and thus we define

$$\Sigma(t) \equiv D[\rho_S|\rho_S^{\mathrm{ss}}] - D[\rho_S(t)|\rho_S^{\mathrm{ss}}] \geq 0\,. \tag{1.40}$$

In other words, the dynamical map decreases the relative entropy of the system with respect to the stationary state, being zero when this state is reached. This is a statement of irreversibility in open quantum systems and the last quantity can be interpreted phenomenologically as the entropy production (see Subsec. 1.1.2 and Eq. (1.3) in particular). We can use it to write an entropy balance. Simplifying the notation $S_S(t) \equiv S[\rho_S(t)]$ and $\Delta S_S(t) \equiv S_S(t) - S_S(0)$, we obtain [56]

$$\Delta S_S(t) = \Sigma(t) + k_B\,\mathrm{Tr}_S[(\rho_S(t) - \rho_S)\log\rho_S^{\mathrm{ss}}]\,. \tag{1.41}$$

The second term can be interpreted as the entropy exchanged with the environment. Indeed, if we assume that ρ_S^{ss} is the thermal state in Eq. (1.30) with Hamiltonian H_S, then we immediately obtain

$$\Delta S_S(t) = \Sigma(t) - \frac{\Delta E_S(t)}{T}\,, \tag{1.42}$$

where $\Delta E_S(t) \equiv \mathrm{Tr}_S[H_S(\rho_S(t) - \rho_S)]$ is the energy change in the system. Note, however, that we cannot directly interpret it as heat flowing out of the reservoir $\Delta E_S(t) \neq -Q(t)$, since this would require knowledge about the microscopic state of the environment and interaction. Instead, we interpret $\Delta E_S(t)$ more generally as the energy change in the system due to irreversible processes, here called dissipated energy. The last expression is then interpreted, phenomenologically, as the second law of thermodynamics for open systems.

Markovian Evolution

We have seen that for a fixed time interval $t \geq 0$ the evolution of the open system in Eq. (1.33) is given by a completely positive and trace preserving dynamical map. The full evolution of the system at any time is then given by a whole family of such maps $\{\mathscr{S}_t | t \geq 0\}$, which could be very involved to analyze. This difficulty arises because the system evolution is generally not Markovian. A dynamical map is Markovian if it satisfies the semigroup or Markov property

$$\mathscr{S}_{t_2} = \mathscr{S}_{t_2,t_1}\mathscr{S}_{t_1} \quad \text{with} \quad t_2 \geq t_1 \geq 0\,. \tag{1.43}$$

Generally, this is composition law is not satisfied by the dynamical map in Eq. (1.33), since as we discussed the system and environment are entangled after time t_1, so that the full state at that time is no longer a product state. However, under suitable physical conditions (discussed in Subsec. 1.3.3), the open system evolution can be considered Markovian. In this case, $\{\mathscr{S}_{t_2,t_1} | t_2 \geq t_1\}$ is a continuous family of dynamical maps called a quantum dynamical semigroup [49, 56]. This is in opposition to the group structure of unitary maps [51]. We restrict ourselves to one-parameter semigroups $\mathscr{S}_{t_2,t_1} = \mathscr{S}_{t_2-t_1}$ for simplicity, in which case the map $\mathscr{S}_t$ describes an evolution which is homogeneous in time

$$\rho_S(t) = \mathscr{S}_t(\rho_S) = \exp(\mathscr{L}t)\rho_S\,. \tag{1.44}$$

The time-independent linear map $\mathscr{L}$ is called the generator of semigroup and satisfies $\mathrm{Tr}_S[\mathscr{L}(\rho_S)] = 0$. Differentiating with respect to time we have

$$\frac{d\rho_S(t)}{dt} = \mathscr{L}[\rho_S(t)]\,, \tag{1.45}$$

which is referred to as the quantum master equation. The most general form of the generator $\mathscr{L}$ was derived in 1976 for an N-level quantum system by V. Gorini, A. Kossakowski, E. C. G. Sudarshan [54], and in the same year by G. Lindblad for a separable Hilbert space [55]. For a finite Hilbert space $\dim(\mathscr{H}_S) = N$, the map $\mathscr{S}_t$ can be represented in a Hilbert space of its own with an orthonormal basis $\{J_k\}_{k=1}^{N^2}$ and inner product $\mathrm{Tr}_S(J_k^\dagger J_j) = \delta_{jk}$. We choose one of these elements to be the identity operator, which means that the remaining N^2-1 are traceless operators. The generator $\mathscr{L}$ then has the form

$$\mathscr{L}[\rho_S(t)] = -\frac{i}{\hbar}[H_L, \rho_S(t)] + \sum_{j,k=1}^{N^2-1} \gamma_{jk}\Big[J_j\rho_S(t)J_k^\dagger - \frac{1}{2}\Big\{J_k^\dagger J_j, \rho_S(t)\Big\}\Big]\,, \tag{1.46}$$

where H_L is a self-adjoint operator having units of energy called the effective Hamiltonian; it does not necessarily correspond to the Hamiltonian of the system H_S. The commutator term on the right hand-side thus describes unitary evolution. The second term is usually called the dissipator, being responsible for the irreversible evolution of the open quantum system. The matrix (γ_{jk}) is positive (thus self-adjoint), has units of inverse time and $\{\,,\,\}$ denotes the anti-commutator. Physically, this matrix defines relaxation rates of the open system interacting with a given environment. Note that Eq. (1.46) can always expressed in diagonal form by a unitary transformation of the dissipator.

For the stationary state of the map, it follows from Eq. (1.44) and Eq. (1.45) that $\mathscr{L}(\rho_S^{\text{ss}}) = 0$, i.e. stationary states are eigenoperators of the generator with zero eigenvalue. Differentiating Eq. (1.40) with respect to time, we obtain

$$\dot{\Sigma}(t) \equiv -\frac{d}{dt} D[\rho_S(t)|\rho_S^{\text{ss}}] = -\text{Tr}_S[\mathscr{L}[\rho_S(t)]\,(\log\rho_S(t) - \log\rho_S^{\text{ss}})] \geq 0\,, \tag{1.47}$$

where $\dot{\Sigma}(t)$ is the rate of entropy production, which is always positive since the derivative of the relative entropy with respect to the stationary state is always negative. This last statement, derived in 1978 by Herbert Spohn [58], is a stronger statement than the positivity of the entropy production in Eq. (1.39). Assuming the stationary state is the Gibbs state, we can differentiate Eq. (1.42) to obtain

$$\frac{dS_S(t)}{dt} = \dot{\Sigma}(t) - \frac{J_S(t)}{T}\,, \tag{1.48}$$

where $J_S(t) \equiv \text{Tr}_S[H_S \mathscr{L}[\rho_S(t)]]$ is the rate of dissipated energy in the system. This is the differential version of Eq. (1.42), which we can interpret phenomenologically as the second law of thermodynamics for open quantum systems.

1.3.3 Quantum Master Equations

In the previous section, we laid out the general theory of open quantum systems and shown that, if the evolution of the system is Markovian, a description in terms of a quantum master equation is possible. In this section, we summarize how they can be obtained microscopically, starting from the full dynamics in Eq. (1.29) and the Hamiltonian in Eq. (1.32). This involves a treatment of the interaction V, environment Hamiltonian H_E and its state ρ_E. When the environment is in thermal equilibrium, these equations obey detailed balance, which ensures thermalization of the open system.

We should add that although the main results of this thesis, presented in Chapter 2, are not based on quantum master equations, we find this section necessary for several reasons. First, a formulation of our results in terms of quantum master equations is in preparation and should be available in the near future. Second, the property of detailed balance, necessary for thermalization, has been traditionally obtained for master equations. Finally, it is important to contrast how thermalization is achieved in the weak coupling and low density limits (both presented below) with how it is achieved at the single collision level between a system and a wave packet (see Sec. 2.3). We hope this section gives a broader understanding of our contribution to thermalization of open systems.

Several strategies can be employed to derive quantum master equations depending on the model under consideration. The most general procedure starts from Eq. (1.29) and applies so-called projection techniques, developed by S. Nakajima and R. Zwanzig [59, 60]. These techniques involve defining a projector $\mathscr{P}$ which acts on $\rho_I(t)$ and retrieves only those degrees of freedom which one wishes to describe. For instance $\mathscr{P}[\rho_I(t)]$ can represent the populations if one is interested in deriving Eq. (1.31) or it can be the product state $\text{Tr}_E[\rho_I(t)] \otimes \rho_E$ if one is interested in the open system dynamics, where ρ_E is a fixed state

of the environment. We focus here on the latter, which in any case allows the derivation of Eq. (1.31) for open systems. We assume an initial product state and also that $\mathrm{Tr}_E[V_I(t)\rho_E]=0$. The latter condition can always be adopted if the environment state is stationary $[\rho_E, H_E]=0$ [51]. We can write down an equation for the projected state

$$\frac{d\mathscr{P}[\rho_I(t)]}{dt}=\int_0^t \mathscr{K}(t,t')\mathscr{P}[\rho_I(t')]dt', \tag{1.49}$$

where $\mathscr{K}(t,t')$ is called the memory kernel. Due to the condition $\mathrm{Tr}_E[V_I(t)\rho_E]=0$, the kernel is at least second order in the interaction $V_I(t)$. It depends on the irrelevant degrees of freedom $\mathbb{I}-\mathscr{P}$ containing the correlations between system and environment, where $\mathbb{I}$ is identity. Thus, the memory kernel describes the non-Markovian evolution of the open system. The crucial point in deriving quantum master equations is to identify the physical conditions under which the kernel becomes Markovian.

Weak Coupling Limit

The weak coupling limit is essentially a generalization of van Hove's derivation of Eq. (1.31). In this case, it is possible to truncate the memory kernel to second-order in the interaction. Introducing the coupling parameter $V\to\lambda V$, taking the trace over the environment and performing a change of variables, Eq. (1.49) becomes

$$\frac{d\rho_S(t)}{dt}=-\frac{\lambda^2}{\hbar^2}\int_0^t \mathrm{Tr}_E[V_I(t),[V_I(t-u),\rho_S(t-u)\otimes\rho_E]]\,. \tag{1.50}$$

In order to achieve a Markovian kernel, one usually introduces a new time scale $\tau_R=\lambda^2 t$ describing the evolution of the system due to the interaction. In the weak coupling limit, the interaction only affects significantly the system over very long times. This corresponds to the limit $\lambda\to 0$, $t\to\infty$ with τ_R being constant. Moreover, if the interaction terms in the integrand vanish over a time $\tau_E\ll\tau_R$, we can substitute $\rho_S(t-u)\to\rho_S(t)$ and the integral can be taken to infinity. The Markovian equation thus obtained is called the Redfield equation, which was derived by A. G. Redfield to describe spin relaxation in the context of nuclear magnetic resonance [61]. Such an equation, however, cannot yet be described by a generator of the form in Eq. (1.46) and the associated map is not yet a semigroup. One then usually performs the so-called secular approximation, which is valid when $\tau_S\ll\tau_R$, where τ_S is a typical, intrinsic evolution time scale of the system. This approximation is similar in spirit to the rotating wave approximation used in quantum optics [24, 44, 45, 62]. Together, this set of approximations (weak coupling limit, Markovian approximation and secular approximation) is called the Born-Markov-Secular approximation [50, 56, 51]. Using these approximations and taking a general interaction of the form $V=\sum_\alpha A_\alpha\otimes B_\alpha$, where A_α and B_α are self-adjoint operators in the Hilbert space of the system and environment, respectively, we can write Eq. (1.50) as a generator in the interaction picture as

$$\mathscr{L}[\rho_S(t)]=-\frac{i}{\hbar}[H_{LS},\rho_S(t)]+\mathscr{D}(\rho_S(t) \tag{1.51}$$

In the last expression, H_{LS} is a self-adjoint operator called the Lamb-Shift Hamiltonian, which is proportional to λ^2 and commutes with the system Hamiltonian $[H_{LS}, H_S] = 0$. The explicit expression can be consulted elsewhere [50, 56, 51]. More important for us is the dissipator

$$\mathscr{D}(\rho_S(t) = \lambda^2 \sum_{\omega} \sum_{\alpha,\beta} \gamma_{\alpha\beta}(\omega) \left[A_\beta(\omega)\rho_S(t)A_\alpha^\dagger(\omega) - \frac{1}{2}\left\{ A_\alpha^\dagger(\omega)A_\beta(\omega), \rho_S(t) \right\} \right], \tag{1.52}$$

where ω denotes a particular Bohr frequencies of the system and the jump operators are given by

$$A_\alpha(\omega) = \sum_{j,i:e_j - e_i = \hbar\omega} \langle j|A_\alpha|i\rangle \, |j\rangle\langle i| \tag{1.53}$$

being eigenoperators of H_S obeying $[H_S, A_\alpha(\omega)] = \hbar\omega A_\alpha(\omega)$. As a consequence of the secular approximation, these operators describe transitions between eigenstates with the same Bohr frequency. The matrix element $\gamma_{\alpha\beta}(\omega)$ is given by

$$\gamma_{\alpha\beta}(\omega) = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} \mathrm{Tr}_E[B_\alpha^\dagger(t)B_\beta(0)\rho_E] \exp(i\omega t)\, dt\,, \tag{1.54}$$

where $B_\alpha(t)$ are the environment operators in the interaction picture. These quantities are Fourier transforms of two-point correlations functions of the environment, and represent the rates of dissipation of the open system. We should add that in order for these quantities to be well-defined, the environment correlations in the integrand have to decay in a finite time τ_E as we mentioned above. However, this can only happen if the reservoir has a continuous spectrum, which is the case if the environment is infinitely large [49, 50, 51]. The rates can then be shown to be positive and thus Eq. (1.51) is indeed the generator of a semigroup. We mention two important properties of this master equation.

1. If the Hamiltonian of the system is not degenerate, the populations and coherences decouple. This means that populations obey a closed master equation equivalent to Eq. (1.31) (either in Schrödinger or interaction picture) with rates $T_{ji} = \sum_{\alpha\beta} \gamma_{\alpha\beta}(e_i - e_j)\langle i|A_\alpha|j\rangle \langle j|A_\beta|i\rangle$. Thus we recover Pauli's equation for an open system. Fermi's golden rule now states that transitions happen between eigenstates with the same Bohr frequency.

2. If the environment state is a thermal reservoir given by Eq. (1.30) (with Hamiltonian H_E) then the rates obey the symmetry $\gamma_{\alpha\beta}(-\omega) = \exp(-\beta\omega)\gamma_{\beta\alpha}(\omega)$, which follows from the well-known Kubo-Martin-Schwinger relation for the correlation functions of the reservoir [63, 50, 56]. This symmetry suffices to prove that the thermal state in Eq. (1.30) (with Hamiltonian H_S) is a stationary state of the generator. Moreover, the aforementioned symmetry implies the detailed balance symmetry for the population rates $T_{ji} = \exp(-\beta\Delta_{ji})T_{ij}$.

The last two properties imply that the open quantum system undergoes decoherence and thermalizes. They are crucial to establish a microscopic theory of thermodynamics of weakly coupled quantum system [63, 64, 65]. Since the environment is a thermal reservoir and the Hamiltonian is time-independent, the

rate of entropy flow in Eq. (1.48) can be interpreted as heat flowing out of the reservoir and into the system. The same applies to the entropy flow in Eq. (1.42) obtained by integration over time. In other words, these equations can be interpreted as the second law of thermodynamics, derived microscopically in the weak coupling limit.

One can also derive quantum master equations in the so-called singular coupling limit, which is valid under strong coupling provided the environment correlations decay faster than any relevant time scale $\tau_E \to 0$. The derivation is similar to the weak coupling limit presented above, but the correlations do not obey detailed balance and are thus beyond the scope of this. Rigorous derivations can be found elsewhere [50, 56, 51].

Low Density Limit

A quantum master equation can be derived in the so-called low density limit, which is based on quantum scattering theory which we introduce in Sec. 2.2. A rigorous mathematical derivation of this equation was obtained in 1985 by R. Dümke [66] and finds applications in quantum optics, for instance in describing how emission and absorption spectra of atoms are modified as a result of collisions [67, 68, 24]. In this setup, the open quantum system considered is again discrete, while the environment is a thermal gas of N non-interacting particles in a volume V having uniform density $n = N/V$. Each one of the gas particles collides with the quantum system according to an interaction V, which is assumed to be such that scattering theory can be applied (see Sec. 2.2). The single-particle Hamiltonian is $H_E = \int (\vec{p}^2/2m)|\vec{p}\rangle\langle\vec{p}|d^3p$ where $\{|\vec{p}\rangle\}$ are improper momentum states in three dimensions and its state is

$$\rho_E = \frac{(2\pi\hbar)^3}{V} \int \mu_{\mathrm{MB}}(\vec{p})\, |\vec{p}\rangle\langle\vec{p}|\, d^3p\,, \tag{1.55}$$

where $\mu_{\mathrm{MB}}(\vec{p})$ is the Maxwell-Boltzmann distribution introduced in Eq. (1.7). In order to derive a quantum master equation starting from Eq. (1.49), the thermal gas should have a density low enough so that only two-body collisions are relevant, and moreover that the time between collisions τ_W is much larger than the duration of a collision τ_C. Indeed, if v is the typical velocity of a gas particle, then we require $\tau_W \sim n^{-1/3} v^{-1} \gg \tau_C$ which holds in the limit $n \to 0$. This limit is trivial since then the collision rate defined by $\gamma = \sigma n v$, where σ is the scattering cross section, goes strictly to zero. A constant collision rate is obtained only in the limit $n \to 0$ and $t \to \infty$ with nt being constant. After performing an average over these long time scales, in the same spirit as the secular approximation, the memory kernel in Eq. (1.49) becomes Markovian and is indeed the generator of a semigroup [66]. Before presenting the resulting equation, we define the jump operators

$$T_\omega(\vec{q},\vec{p}) = \sum_{j,i:e_j-e_i=\hbar\omega} \langle j,\vec{q}|T|i,\vec{p}\rangle\, |j\rangle\langle i| \tag{1.56}$$

which are eigenoperators of H_S. The operator T is called the transfer operator, being related to the scattering operator and capturing the effect of a single collision [69, 70, 71]. Using these operators we can write

a generator of the form in Eq. (1.51), with Lamb-Shift Hamiltonian

$$H_{LS} = (2\pi\hbar)^3 n \int \left(\frac{T_0(\vec{p},\vec{p}) + T_0^\dagger(\vec{p},\vec{p})}{2} \right) \mu_{\mathrm{MB}}(\vec{p}) d^3p \, . \tag{1.57}$$

Note that this Hamiltonian commutes with the system Hamiltonian $[H_S, H_{LS}] = 0$ and contributes only to transitions between degenerate levels. The dissipator reads

$$\mathscr{D}(\rho_S(t) = n \int\int \sum_\omega \gamma_\omega(\vec{q},\vec{p}) \Big[T_\omega(\vec{q},\vec{p}) \rho_S(t) T_\omega^\dagger(\vec{q},\vec{p}) - \frac{1}{2} \Big\{ T_\omega^\dagger(\vec{q},\vec{p}) T_\omega(\vec{q},\vec{p}), \rho_S(t) \Big\} \Big] d^3p\, d^3q \, , \tag{1.58}$$

where the quantity $\gamma_\omega(\vec{q},\vec{p})$ is positive and defined by

$$\gamma_\omega(\vec{q},\vec{p}) = (2\pi)^4 \hbar^2 \mu_{\mathrm{MB}}(\vec{p}) \, \delta\Big(\frac{\vec{q}^2}{2m} - \frac{\vec{p}^2}{2m} + \hbar\omega \Big) . \tag{1.59}$$

The most important properties of the aforementioned generator are similar to the weak coupling limit. Namely, if the spectrum of H_S is not degenerate, the populations and coherences decouple and we recover Pauli's equation for an open system. The main difference occurs at the level of detailed balance. The rates for the population read $T_{ji} = n \int\int \gamma_{e_j - e_i}(\vec{q},\vec{p}) \, |\langle j,\vec{q}|T|i,\vec{p}\rangle|^2 \, d^3p\, d^3q$ and can be shown to obey detailed balance if the property of micro-reversibility $\langle j,\vec{q}|T|i,\vec{p}\rangle = \langle i,-\vec{p}|T|j,-\vec{q}\rangle$ is obeyed [66]. This property was already mentioned in Subsec. 1.3.1 and is related to the fact that a single collision is reversible in time. Then the open system decoheres and thermalizes in the low density limit.

We finish by briefly comparing the low density limit with the approach taken in this thesis and laid out in Chapter 2. First, our approach focuses on the scattering map for a single collision in one dimension and not on quantum master equations. Second, our approach takes into account the spatial structure of the colliding particles as wave packets. This means that the notion of a thermal gas which is diagonal in the momentum according to Eq. (1.55) is no longer generally applicable, since as we covered in Subsec. 1.2.2 a wave packet is not localizable in momentum. Nevertheless, we show in Sec. 2.1 how the traditional notion of a thermal gas is recovered in terms of wave packets. Then in Sec. 2.3 we show how wave packets effusing from this thermal gas lead to thermalization of the system through collisions, where micro-reversibility is again an essential ingredient.

Other Equations Based on Scattering Theory

One can also derive quantum master equations describing decoherence and thermalization of the wave function of a quantum system as a result of collisions with a background gas, very much in the spirit of Boltzmann's approach [72, 73, 74, 75, 76]. These equations were successfully applied to predict decoherence rates of large molecules, like fullerenes, due to the their own emission of thermal radiation [77, 78]. They are related to the aforementioned low density limit, in the sense that a low density gas is always assumed for a consistent derivation of these equations. This is beyond the scope of our thesis, which deals mostly with irreversibility of internal degrees of freedom, but treatments of the background gas in terms of wave packets can be found in the these studies, which inspired our own treatment of thermal gas of wave packets in Sec. 2.1.

1.3.4 The Laws of Thermodynamics

We can now establish a general form of the first and second law of thermodynamics for quantum systems, starting from the full Hamiltonian in Eq. (1.32). We require the interaction to be time-dependent, allowing us to formulate the notion of work as the energy exchanged due to a time-dependent Hamiltonian. This is line with most approaches in thermodynamics of quantum systems [79, 80, 81, 82, 83, 84], where the time-dependence represents some external degrees of freedom over which we have full control and thus can be used to manipulate the system in a deterministic fashion. The environment is a thermal reservoir with state given by Eq. (1.30) and can be finite. As usual, the system and reservoir are initially uncorrelated $\rho = \rho_S \otimes \rho_E$. The full state evolves unitarily during a time t according to Eq. (1.22) and its von Neumann entropy does not change $\Delta S(t) := 0$. We thus define work as the energy exchanged in the full system

$$W(t) \equiv \mathrm{Tr}[H(t)\rho(t) - H(0)\rho]\,. \tag{1.60}$$

We can split work into two different contributions. First, the energy exchanged in the open system which is defined including the contribution of the interaction

$$\Delta E_S(t) \equiv \mathrm{Tr}_S[H_S(\rho_S(t) - \rho_S)] + \mathrm{Tr}[V(t)\rho(t) - V(0)\rho]\,. \tag{1.61}$$

The second contribution is due to the energy flowing out of the reservoir

$$Q(t) = -\mathrm{Tr}_E[H_E(\rho_E(t) - \rho_E)]\,. \tag{1.62}$$

Note that $\rho_S(t)$ and $\rho_E(t)$ are obtained from completely positive and trace preserving dynamical maps as discussed in Subsec. 1.3.2. Thus we write the first law of thermodynamics for quantum systems

$$\Delta E_S(t) = W(t) + Q(t)\,, \tag{1.63}$$

with the definitions above. An identification of $Q(t)$ as heat has to be justified through a formulation of a second law of thermodynamics. We follow Ref. [80] which starts from the invariance of the von Neumann entropy at the full system level $\Delta S(t) := 0$ to obtain the entropy change in the open system

$$\Delta S_S(t) = \Sigma(t) + \frac{Q(t)}{T}\,, \tag{1.64}$$

where the entropy production is written as a relative entropy

$$\Sigma(t) \equiv D[\rho(t)|\rho_S(t) \otimes \rho_E] \geq 0\,, \tag{1.65}$$

being an exact measure of the correlations established between system and a thermal reservoir of finite size. If we compare this relative entropy with the one formulated through the sub-additivity property of the entropy in Eq. (1.36) and Eq. (1.38), we get an exact relation $\Sigma(t) = I_{S:E}(t) + D[\rho_E(t)|\rho_E]$. The last term represents the information discarded from not knowing the state of the reservoir after the evolution.

Finally, we note that work vanishes for a time-independent Hamiltonian $W(t) := 0$. However, this is not enough to ensure thermalization of the open system even if the reservoir is infinite, since the interaction can still be strong and thus Markovianity is not guaranteed in the usual system-reservoir setup. However, in the weak coupling limit it is guaranteed and the aforementioned laws can be expressed solely in terms of system quantities. In this limit we can also obtain the differential version of these laws (see discussion of the weak coupling limit in Subsec. 1.3.3). However, we know of no attempt to connect the first and second laws stated above with the low density limit. In fact, this would require a treatment of energy and entropy changes using the scattering operator. The results of this thesis provide a first step in this direction.

1.4 Models of Repeated Interactions

We introduce a framework for open quantum systems based on repeated interactions, motivated by modern experiments in quantum optics. We formulate the first and second law of thermodynamics within this framework and discuss some problems associated with thermalization and the notion of work. These are the main motivations for the results of Chapter 2.

1.4.1 Motivation from Quantum Optics

We mentioned in Subsec. 1.3.2 that a laser is built by stimulated emission of photons from excited atoms into a cavity. This requires the populations of the excited level of the atom to be inverted with respect to a lower level. From a thermodynamic perspective, detailed balance is broken between the atomic transition which, via stimulated emission, generates the laser light: this means that lasers operate out of equilibrium. Since the photons emitted have ideally the same frequency and phase, the laser field constitutes a low entropy source which can be used to generate work — this is in contrast with thermal light, characterized by a broad range of frequencies and phases in thermal equilibrium. However, even at low temperatures where few thermal photons are present, there exist laser field losses due to spontaneous emission from the atoms and due to the imperfect cavity. The theory of open quantum systems and resulting master equations have been successfully applied to describe gains and losses in lasers [24, 44, 45].

Ideally, one could populate a lossless cavity with photons by sending an atom, modelled by a two-level system with a Bohr frequency resonant with the electromagnetic field. A theoretical model describing this situation was introduced in 1963 by E. T. Jaynes and F. W. Cummings [85]. Only later, with the advent of superconducting cavities and frequency-tunable lasers, did this model become experimentally feasible, thus leading to the development of the micromaser (single-atom maser) [86, 87] and more generally to the study of light-matter interaction in cavities — this field is called cavity quantum electrodynamics or cavity-QED for short [88, 89, 62]. A cavity-QED setup is shown in Fig. 1.1. Before entering the cavity, a conventional laser is used to excite a particular transition of an atom in the microwave regime. The long lifetime of the atom and the high quality of the cavities ensure that the rate at which losses of photons occur in the atom are low compared to the Rabi frequency, defined as the rate of oscillations induced by the atom-field coupling. Moreover, the flux of atoms is low enough that, at most, one atom is present in the cavity at a time. These features of cavity-QED allow the observation of unitary energy exchanges between the atoms and the field which are averaged out in conventional lasers and masers. It has also been a major tool to study quantum entanglement and light-matter interaction in the strong coupling regime [90, 62, 91]. Moreover, the micromaser has been used as a basis for a quantum heat engine, which exploits coherences in the atom to extract more work than classically allowed [92].

The relevant question is how to build a consistent theory of thermodynamics which includes strong non equilibrium contributions, such as those found in cavity-QED. This is addressed in the framework of repeated interactions, also known as collision models, introduced below.

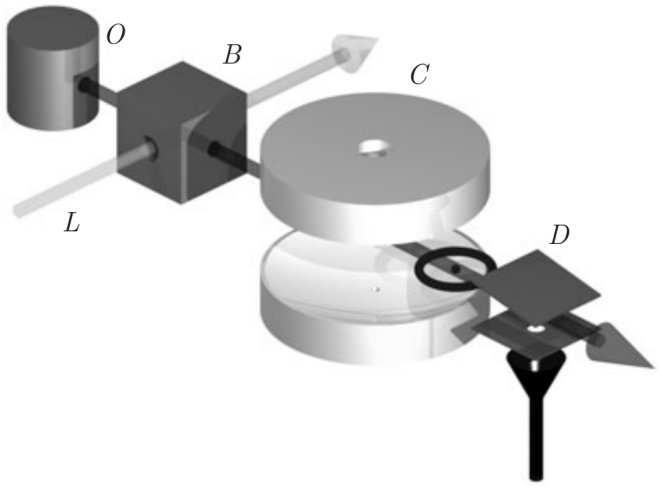

Figure 1.1: Cavity-QED experimental setup. Atoms effusing from an oven O enter into a box B, where they are prepared in very excited Rydberg states using a laser L. These states have a large dipole moment and interact very strongly with microwave photons in the superconducting cavity C. The atoms then leave the cavity and are detected by field-ionization detector D. The figure is taken from Ref. [62]. A velocity selector can also be included between O and C to fix the interaction time between atom and cavity field.

1.4.2 Repeated Interaction Models

Repeated interaction models are an alternative approach to quantum open systems [93, 94, 95], having proved useful in quantum information, thermodynamics and optics [96, 97, 98, 99, 100]. In these models, the environment is composed of an ensemble of sub-systems, which we call units, initially uncorrelated with each other and with the system. The system interacts sequentially with each unit during a given time, in a collision-like fashion. After each interaction, the unit is discarded and replaced by a new unit, the process being repeated several times and thus inducing a given dynamics in the system. We are interested in the case where the units are prepared all in the same state, but apart from this the state of system and units can be arbitrary. In this case, the evolution of the open system is described by a single (completely positive and trace preserving) dynamical map which is clearly Markovian since each unit is discarded after the interaction. These models are then quite different from the framework presented in Subsecs. 1.3.2 and 1.3.3, since Markovianity here holds *ab initio*, independently of the coupling strength between system and unit. This allows for simple derivations of quantum master equations which do not rely on weak coupling or low density limits [94, 95, 101, 102]. We also mention that these models can be extended to study non-Markovian evolution, for instance by correlating units with each other, but this is beyond the scope of our work [103, 104]. Below, we present the general formalism for repeated interactions, which we then use to establish an energy and entropy balance for a single interaction. We show how the laws of thermodynamics arise from this balance when the units are in thermal equilibrium.

Time Evolution

We start with the full Hilbert space $\mathscr{H} = \mathscr{H}_S \otimes \mathscr{H}_E$ where $\mathscr{H}_E = \bigotimes_n \mathscr{H}_U^n$ is the Hilbert space of the environment and $\mathscr{H}_U^n$ is the Hilbert space of the n^{th} unit. The number of units can potentially be infinite, thus we leave the limits of n implicit. The Hamiltonian of the full system is given by Eq. (1.32) where $H_E = \sum_n H_U^n$ and H_U^n is the Hamiltonian of the n^{th} unit, having discrete spectrum just like the system Hamiltonian H_S. We omit the identity operator in the sum for simplicity. The most important feature is the interaction, which in these models takes the form

$$V(t) = \sum_n V^n(t) = \sum_n \Theta(t - n\tau)\Theta(n\tau + \tau' - t) V_{SU}^n(t)\,. \tag{1.66}$$

In the last expression $\Theta(t)$ is the Heaviside theta function, having the value of unity if $t \geq 0$ and zero otherwise. The operator $V_{SU}^n(t)$ is an arbitrary time-dependent interaction between the system and the n^{th} unit. In other words, the interaction between system and n^{th} unit is switched on at a time $t = n\tau$ and switched off at a time $t = n\tau + \tau'$, where τ' is the interaction time and $\tau > \tau'$ is the waiting time. The full system then evolves freely until $t = (n+1)\tau$, where a new interaction with the $(n+1)^{\text{th}}$ unit occurs and the process is repeated. Finally, the initial state of the environment is given by $\rho_E = \bigotimes_n \rho_U^n$, being uncorrelated with the system. We let the first interaction start at $t = 0$ and wait until $t = \tau$, just before the second unit arrives. The state of the full system in the Schrödinger picture is then given by

$$\rho(\tau) = U_1(\tau)(\rho_S \otimes \rho_U^1)U_1^\dagger(\tau) \otimes \bigotimes_{n>1} \rho_U^n(\tau) \tag{1.67}$$

where $U_1(t)$ is the evolution operator associated with the Hamiltonian for the system and the first unit $H_{SU}^1(t) = H_S + H_U^1 + V^1(t)$ and $\rho_U^n(\tau)$ for $n > 1$ is the state of the n^{th} unit after evolving freely during time τ according to its own Hamiltonian H_U^n. From the last expression, we can obtain the state of the system by tracing out the first unit according to Eq. (1.33), and similar comments holds for the unit, both being described by a dynamical map which is completely positive and trace preserving. The initial state of the system and each unit can be arbitrary, making this setup quite versatile.

Nonetheless, we are here interested in not only repeated but identical interactions, with the goal of obtaining a map for the open system which is n independent. Thus we consider $V_{SU}^n(t)$, H_U^n and the initial state $\rho_U^n(0)$ to be of the same form for all units and thus independent of n. Since the units evolve freely when not interacting, a crucial assumption here is that the state of the units is the same when they reach the system, i.e. that $\rho_U^n(n\tau) = \rho_U^m(m\tau)$ for all $m, n \in \mathbb{N}$ [99]. In this case, we can drop the n dependence and focus on the dynamics of the first collision with Hamiltonian $H_{SU}(t) = H_S + H_U + V(t)$ where $V(t) = \Theta(t-\tau)\Theta(\tau + \tau' - t)V_{SU}(t)$ is the interaction. The full state after time τ now reads

$$\rho_{SU}(\tau) = U(\tau)(\rho_S \otimes \rho_U)U^\dagger(\tau) \tag{1.68}$$

where $U(t)$ is the evolution operator associated to $H_{SU}(t)$. The state of the system and unit are straightforwardly obtained through partial tracing.

Quantum Master Equations

It is now simple to derive quantum master equations for the system. There are two main strategies for this. In the first, one considers the waiting time τ to be Poisson-distributed and the interaction time τ' to be negligible. In this case, the system evolves freely most of the time, being interrupted by kicks corresponding to the interaction with the units [105, 99]. After averaging over many interactions, one recovers the desired equation. In the second strategy, the waiting time is negligible and the system evolves under a constant stream of units with $V_{SU}(t)$ being constant over τ'. One can then expand the unitary $U(\tau',0)$, rescale the interaction $V_{SU} \to V_{SU}/\sqrt{\tau'}$ and take the limit $\tau' \to 0$ to recover a quantum master equation [94, 95, 101, 102]. For our purposes in this thesis, we simply state that master equations derived in this way do not generally obey detailed balance [98, 106]. We discuss this issue in Subsec. 1.4.3.

Energy and Entropy Balance

At this point we can establish an energy and entropy balance for a single interaction. We use the same method as in Subsec. 1.3.4, except now the environment is a single unit which can be prepared in an arbitrary state. In order to capture correctly the boundary effect of the interaction, we consider an interval $(-\epsilon,\tau)$ and take the limit $\epsilon \to 0$ such that the interaction vanishes both at the start and end of the interval $V(-\epsilon) = V(\tau) = 0$. We remind that the interaction is not effective in the sub-interval (τ',τ), implying that the system and unit evolve isolated without exchanging energy or entropy. The work exchanged during the full interval follows from Eq. (1.60)

$$W(\tau) = \mathrm{Tr}[(H_S + H_U)(\rho_{SU}(\tau') - \rho_{SU})]\,. \tag{1.69}$$

The last expression is called switching work, corresponding to the work done by the time-dependent interaction on the system-unit composite. Since the energy change in the system now has the form $\Delta E_S(\tau) \equiv \mathrm{Tr}_S[H_S(\rho_S(\tau) - \rho_S)]$ and equivalently for the unit, we can write an energy balance from Eq. (1.63)

$$\Delta E_S(\tau) = W(\tau) - \Delta E_U(\tau)\,. \tag{1.70}$$

Since the unit is not necessarily thermal, the entropy balance for the system is written more generally using the sub-additivity property in Eq. (1.36)

$$\Delta S_S(\tau) = I_{S:U}(\tau) - \Delta S_U(\tau)\,. \tag{1.71}$$

The last two expressions are the energy and entropy balance, which lack any *a priori* thermodynamic interpretation. Of course, when the unit is in a thermal state we recover the first and second law of thermodynamics in Eqs. (1.63) and (1.64). We note that it is also possible to formulate the first and second law of thermodynamics in these models by coupling the system-unit composite to a thermal reservoir, while keeping the state of the unit arbitrary. It is then evident that the unit constitutes a non equilibrium resource for the system [99]. However, whether in the absence or presence of a thermal reservoir, the switching work of Eq. (1.69) represents a source of non equilibrium which is intrinsic to repeated interaction models. This is the focus of discussion in the next section.

1.4.3 Formulation of the Problem

The work in Eq. (1.69) is usually interpreted as the energy required by an external agent to switch on and off the system-unit interaction. This statement is however meaningless when one considers experiments where such models could be applied, such as those of cavity-QED, since there is no agent mediating the system-unit interaction. It is also meaningless if one remembers that these models are inspired by collisions, which happen in space through a time-independent potential and thus without external agency. Thus *a priori*, the switching work represents an extra energy source which lacks a physical interpretation in models of repeated interaction. However, its presence has important thermodynamic consequences. For instance, systems under repeated interactions with thermal units fail to thermalize and switching work is the energy that sustains the non equilibrium steady state [98, 107, 108]. This is line with the fact that the thermal state is not a stationary state of the dynamical map for the system even when the unit is thermal. As a consequence, quantum master equations derived from these models do not generally obey detailed balance [106]. In summary, repeated interaction models generally fail to describe thermalization. A potential solution for this problem comes from the field of quantum resource theories [109, 110, 111, 112]. Here, one is interested in the set of transformations that an agent can perform on a system with the goal of using it as a resource, e.g. for work extraction. The allowed transformations require no work and are in this sense free resources — they are called thermal maps. These are maps of the form in Eq. (1.33), where the environment is thermal and the unitary U is energy preserving $[U, H_S + H_E] = 0$. If we assume that the system-unit evolution is effected by energy preserving unitary, then clearly the switching work in Eq. (1.69) vanishes and this ensures thermalization [106]. To give a concrete example, if the system and unit are both spins with resonant energy gaps, then a unitary which swaps the states of the spins is clearly energy preserving and the system thermalizes over many interactions. This solves the problem of thermalization in these models, but at the cost of restricting the types of interactions that can occur between system and unit. Moreover, this solution does not shed any light on the physical origin of the switching work. A more satisfactory solution would describe thermalization without restricting the interaction and also explain the switching work from a microscopic point of view.

In the next chapter, we provide an alternative approach to these models by treating the system-unit interaction as a true collision happening in space. In other words, the unit is treated as a particle having some internal structure and travelling in space as a wave packet. The state of the full system before and after a single collision is obtained using the scattering operator, which is unitary and conserves total (internal and kinetic) energy. By tracing out all degrees of freedom of the particle, we obtain a dynamical map for the system whose properties depend strongly on the wave packet. We show how the kinetic energy exchanged during the collision can be either interpreted as heat, thus inducing thermalization of the system; or as switching work, thus acting as a source of non equilibrium energy.

Chapter 2

Thermodynamics of Quantum Collisions

2.1 Thermal Gas of Wave Packets

Before introducing quantum scattering theory, we show how to treat a thermal gas of wave packets in a box. To the author's knowledge, this treatment is rarely found in the literature except in Refs. [73, 113]. Since the wave packets have a finite width in position and momentum space, they are not diagonal in either representation. However, when the box is very large we recover the usual notion of a thermal bath without coherences in momentum given by Eq. (1.55). We compare our approach with the traditional approach based on plane waves, both matching in the limit of a large box. We comment on the state of the thermal gas of packets when it effuses the box to collide with a system of interest.

2.1.1 Wave Packet Approach

We consider an ensemble of massive particles without internal structure, each described by a Gaussian wave packets in a pure state having an average position x_0 and momentum p_0 according to Eq. (1.17). The particles are uniformly distributed in a one-dimensional box of length L and their average momenta is thermal according to the Maxwell-Boltzmann distribution in Eq. (1.7). The state of a single particle is then given by the mixture

$$\rho = \int_L \frac{d\,x_0}{L} \int d\,p_0\; \mu_{\rm MB}(p_0)\; |\phi_{x_0,p_0}\rangle\langle\phi_{x_0,p_0}|\;, \tag{2.1}$$

where we added the labels for the average positions and momenta of the pure states $|\phi_{x_0,p_0}\rangle\langle\phi_{x_0,p_0}|$. We can now insert two resolutions of identity in momentum p and p' at the left and right of the pure states in Eq. (2.1), respectively, and then use the definition Eq. (1.17) to get an explicit expression. We also perform a useful change of variables to the center of momenta $u=(p'+p)/2$ and relative momenta $v=(p'-p)/2$. After this, Eq. (2.1) reads as follows

$$\rho = \int \frac{d\,u}{Z_\beta} \int d\,p_0\; \exp\Big(-\frac{\beta(u-p_0)^2}{2\sigma_p^2}\Big)\exp\Big(-\frac{\beta\,p_0^2}{2m}\Big) \int \frac{d\,v}{(2\pi\sigma_p^2)^{1/2}}\delta^L(v)\exp\Big(-\frac{v^2}{2\sigma_p^2}\Big)|u-v\rangle\langle u+v|\;, \tag{2.2}$$

where $Z_\beta \equiv L/\lambda_\beta$ is the partition function at inverse temperature β and $\lambda_\beta = \hbar\sqrt{2\pi\beta/m}$ is the thermal wavelength. Importantly, the diffraction function

$$\delta^L(v) = \frac{L}{\pi\hbar}\;\mathrm{sinc}\Big(\frac{v\,L}{\hbar}\Big), \tag{2.3}$$

where $\mathrm{sinc}(x)=\sin(x)/x$, approaches a δ-function when the box is infinitely large. Before taking this limit, we perform the integral over p_0, the result being another Gaussian function

$$\rho = Z_{\beta_C}^{-1} \int d\,u\;\exp\Big(-\frac{\beta_C\,u^2}{2m}\Big) \int d\,v\;\delta^L(v)\exp\Big(-\frac{v^2}{2\sigma_p^2}\Big)\;|u-v\rangle\langle u+v|\;. \tag{2.4}$$

In the last expression, Z_{β_C} is a new partition function defined in terms of a modified thermal wavelength λ_{β_C} with $\beta_C = \beta/(1+\beta\sigma_p^2/m)$. This result is exact and equivalent to Eq. (2.1). It shows that the center of

momenta u are thermally distributed with a new inverse "temperature" β_C which depends on the width in momentum σ_p, while coherences v are generally present. To obtain a gas without coherences, we first estimate the width of $\delta^L(v)$, which can be approximated by twice the distance between the maximum at $v=0$ and the first zero at $v=\pi\hbar/L$, yielding the width $\Delta v \simeq 2\pi\hbar/L$. If the condition $\Delta v \ll \sigma_p$ holds, then we can approximate $\delta^L(v)$ as a δ-function and the integral over v simplifies. Using the relation between Gaussian wave packets $\sigma_x\sigma_p=\hbar/2$, the last condition can be written more simply as $L \gg \sigma_x$. We get

$$\rho = \frac{1}{Z_{\beta_C}} \int d\,u\ \exp\Big(-\frac{\beta_C\, u^2}{2m}\Big) = Z_{\beta_C}^{-1} \exp(-\beta_C H_p)\,, \tag{2.5}$$

where $H_p = p^2/2m$ is the Hamiltonian of kinetic energy. However, this is still not a thermal state with inverse temperature β, but instead depends on the width of the packets. However, if the condition $\beta\sigma_p^2/m \ll 1$ holds, or equivalently $\sigma_x \gg \lambda_\beta$, then we have $\beta_C \simeq \beta$ and therefore

$$\rho = Z_\beta^{-1}\exp(-\beta H_p) = \frac{2\pi\hbar}{L}\int dp\ \mu_{\rm MB}(p)|p\rangle\langle p|\,, \tag{2.6}$$

which is the one-dimensional version of the thermal gas presented in Eq. (1.55). The last expression is valid under the important condition $L \gg \sigma_x \gg \lambda_\beta$.

2.1.2 Plane Wave Approach

We start with a fully quantum description of a massive particle in a one-dimensional box of length L. The kinetic energy of the particle is discrete and specified by the Hamiltonian of kinetic energy H_p whose action on proper momentum eigenstates is $H_p|p_n\rangle = p_n^2/(2m)|p_n\rangle$ with $n\in\mathbb{N}$ and $p_n = 2\pi n\hbar/L$ is quantized according to periodic boundary conditions on the interval $x\in[-L/2, L/2]$. The resolution of identity in the box is given by $\mathbb{I}_L = \int_L |x\rangle\langle x|\,dx$ in position and $\mathbb{I}_p = \sum_n |p_n\rangle\langle p_n|$ in momentum. In fact, these last quantities are the same $\mathbb{I}_L = \mathbb{I}_p$ but this notation will prove useful when we take the large box limit below. The inner product between position and momentum states reads

$$\langle x|p_n\rangle = L^{-1/2}\exp(i\,p_n\,x/\hbar)\,, \tag{2.7}$$

which are plane waves with discrete momentum. With this in mind, we consider the state of the particle to be thermal with inverse temperature β and write it as follows

$$\rho = Z_\beta^{-1}\exp\Big(-\beta H_p/2\Big)\,\mathbb{I}_L\,\exp\Big(-\beta H_p/2\Big) \tag{2.8}$$

$$= Z_\beta^{-1}\sum_{n,n'}\exp\Big(-\frac{\beta p_n^2}{2m}\Big)|p_n\rangle\langle p_{n'}|\int_L\frac{dx}{L}\exp\Big[\frac{i(p_{n'}-p_n)x}{\hbar}\Big] \tag{2.9}$$

$$= Z_\beta^{-1}\sum_{n,n'}\exp\Big(-\frac{\beta p_n^2}{2m}\Big)|p_n\rangle\langle p_{n'}|\,\delta_{n'n} = Z_\beta^{-1}\exp\Big(-\beta H_p\Big)\,, \tag{2.10}$$

where $Z_\beta = \mathrm{Tr}[\exp(-\beta H_p)\,\mathbb{I}_L]$. The step from the second to the third line follows directly from the momentum boundary conditions and shows that the state is diagonal in momentum. We now show that this is not

generally the case when we take the continuous limit. For this, we note that the difference between any two momenta $\Delta p \equiv p_n - p_{n-1} = (2\pi\hbar/L)$ can be taken very small provided L is sufficiently large. Therefore, the continuous limit is formalized by the substitution of the identity in momentum

$$\mathbb{I}_p = \sum_n |p_n\rangle\langle p_n| \to \mathbb{I} = \int |p\rangle\langle p|\, dp\,, \tag{2.11}$$

so that the inner product between position and momentum states are now plane waves with continuous momentum given by Eq. (1.15). We can now obtain an explicit version for the partition function

$$Z_\beta = \mathrm{Tr}[\exp(-\beta H_p)\,\mathbb{I}_L] = \frac{1}{2\pi\hbar}\int_L dx \int dp\, \exp\Big(-\frac{\beta p^2}{2m}\Big) = \frac{L}{\lambda_\beta}\,. \tag{2.12}$$

We now repeat the calculation in Eq. (2.8) but in continuous momentum. We insert the resolution of identity in p and p' on the left and right of the first line and perform the change of variables $u = (p'+p)/2$ and relative momenta $v = (p'-p)/2$, obtaining

$$\rho = Z_\beta^{-1} \int du\, \exp\Big(-\frac{\beta u^2}{2m}\Big) \int dv\, \delta^L(v) \exp\Big(-\frac{\beta v^2}{2m}\Big)\, |u-v\rangle\langle u+v|\,. \tag{2.13}$$

This equation is very similar to Eq. (2.4) and we treat it in a similar fashion. Here, we obtain a state which is free from momentum coherences described by Eq. (2.6) if the condition holds $L \gg \lambda_\beta$. In summary, the wave packet and plane wave approaches in treating a thermal gas are equivalent when $L \gg \sigma_x \gg \lambda_\beta$.

2.1.3 Effusion of the Thermal Gas

Suppose we are interested in sending the thermal gas of particles described by Eq. (2.1) to collide with a system outside the box. We open a hole in the right side of the box at $t = 0$. All the particles that leave the box are known to eventually collide with the system. In order to compute the rate of collisions, we monitor the hole to know when the center of a particle x_0 has crossed it. When the first crossing happens at time $t > 0$, we know that its more probable that a fast particle with momentum $p_0 > 0$ crossed than a slow one, no matter the waiting time t. The momentum distribution of an effusing particle is then shifted towards higher momentum. It is given by

$$\mu_{\mathrm{eff}}(p_0) = \frac{\beta|p_0|}{m} \exp\Big(-\frac{\beta p_0^2}{2m}\Big), \tag{2.14}$$

called the effusion distribution, normalized here from $[0, +\infty)$. In Ref. [114], it was shown how this distribution arises from the Maxwell-Boltzmann distribution when particles hit a scattering center. We use it in Sec. 2.3 to study thermalization induced by a thermal gas of wave packets.

2.2 Quantum Scattering Theory

We motivate the use of quantum scattering theory in the study of thermodynamics of quantum system and review its mathematical formalism. We present the scattering map for the internal degrees of freedom of the colliding particles in Eq. (2.20) and perform an energy and entropy balance for a single collision. These are the essential ingredients of all results presented in Sec. 2.3.

2.2.1 Motivation

The discreteness of the internal energy of a particle is related to bound states, the typical example being the state of the electron bound to an atom by an attractive interaction. However, many interactions in nature can be described in terms of scattering states, which are travelling freely long before and after a given interaction. Such an interaction between quantum systems is called a collision and the mathematical framework that describes them is quantum scattering theory. Indeed, we have seen in Sec. 1.2 that particles travelling freely are described by wave packets and have a continuous energy spectrum. The wave packets are precisely the free states considered in quantum scattering theory, describing the motional state of the particles before and after a collision. In general, the particles also have internal structure which can change due to collisions and quantum scattering theory, in its multichannel formalism, takes this structure into account [69, 70, 71]. Let us further motivate the scattering approach used in this thesis.

First, we have seen in Subsec. 1.3.3 that microscopic approaches to thermalization require the environment to have continuous degrees of freedom — either in the form of an infinite thermal reservoir or a thermal gas of particles. In addition, we discussed in Sec. 1.4 how modern approaches to thermodynamics rely on collision-like events between the system and an environment having no continuous degrees of freedom, generally failing to induce thermalization. Since quantum scattering theory is a microscopic theory of collisions dealing with continuous spectra, it is a natural framework to study thermalization and, more generally, thermodynamics.

Second, from both a theoretical and experimental point of view, scattering has been ubiquitous in physics throughout its history [69, 70, 71]. We name a few examples without being exhaustive. In 1911, scattering experiments between α-particles and gold atoms allowed Rutherford to discover the atomic nucleus. We also briefly mentioned in Sec. 1.2 how scattering experiments confirmed many predictions of early quantum theory. In particle physics, quantum collisions are exhaustively used to create new particles and to test theoretical models. Furthermore, scattering is one of the mechanisms for decoherence [72, 77], it is at the basis of quantum transport [115, 116] and is indispensable in the field of ultra-cold atoms [117, 118]. Given its universality, it is not surprising that a rigorous quantum theory of scattering was developed in close connection with experiment, becoming a field of mathematical physics in its own right [119, 120].

2.2.2 Mathematical Formalism

The main goal of scattering theory is to obtain the scattering operator S which is a one-to-one map between free (incoming) states before the collision to free (outgoing) states after the collision. Whether or not such an operator exists depends on the dynamics during the collision through the interaction potential, which in general can support states which are either free or bound to the interaction region for very long times. However, its existence is guaranteed for a large class of potentials $V(x)$ which vanish at infinity. We then consider a quantum system with Hilbert space $\mathscr{H}$ and time-independent Hamiltonian

$$H = H_0 + V\,, \tag{2.15}$$

where H_0 is the free Hamiltonian having a continuous and possibly discrete spectrum. We take the interaction in position $V(x) = \langle x|V|x\rangle$ to belong to the aforementioned class of potentials.

The Scattering Operator

In this case, the Hilbert space $\mathscr{H}$ of the full system can be expressed as a direct sum of two mutually orthogonal subspaces $\mathscr{H} = \mathscr{S} \oplus \mathscr{B}$ where $\mathscr{S}$ and $\mathscr{B}$ are the subspaces of scattering and bound states [71, 70, 119, 120]. This allow us to define the so-called Møller wave operators, which are the central objects in the time-dependent formalism of scattering theory. Let $|\psi^{\pm}\rangle \in \mathscr{H}$ be any two states in the Hilbert space (labelled by $\pm$ for later convenience) at some time $t_0 = 0$. For the potentials under consideration, the following limit holds

$$\| \lim_{t\to\pm\infty} U(t)|\psi\rangle - \lim_{t\to\pm\infty} U_0(t)|\psi^{\pm}\rangle \| = 0 \iff \| |\psi\rangle - \lim_{t\to\pm\infty} U_I^{\dagger}(t)|\psi^{\pm}\rangle \| = 0\,, \tag{2.16}$$

where $|\psi\rangle \in \mathscr{S}$ is a scattering state at time $t_0 = 0$ and $\| |\psi\rangle \| = \sqrt{\langle\psi|\psi\rangle} \geq 0$ is the norm induced by the inner product. In words, there is a scattering state which evolves, in the past ($-$) or future ($+$), into a state that is indistinguishable from a freely evolving state. By indistinguishable, we mean in the sense of the norm in Eq. (2.16), since these states can still differ up to a global phase. In the right part of Eq. (2.16) we wrote the same statement in the interaction picture, which allow us to identify the Møller operators

$$\Omega_{\mp} \equiv \lim_{t\to\pm\infty} U_I^{\dagger}(t) = \lim_{t\to\pm\infty} U^{\dagger}(t)U_0(t)\,. \tag{2.17}$$

These operators are isometries of $\mathscr{H}$, i.e. they map state vectors onto the subset of scattering states $\Omega_{\pm} : \mathscr{H} \mapsto \mathscr{S}$ while preserving their norm. The isometric property reads $\Omega_{\pm}^{\dagger}\Omega_{\pm} = \mathbb{I}$. Note that a unitary operator is necessarily an isometry, but the reverse is not true. For instance, here the adjoint Møller operator $\Omega_{\pm}^{\dagger}$ acts only on scattering states $\Omega_{\pm}^{\dagger} : \mathscr{S} \mapsto \mathscr{H}$ and one has $\Omega_{\pm}\Omega_{\pm}^{\dagger} = \mathbb{I} - P_{\mathscr{B}}$, with $P_{\mathscr{B}}$ the projector onto the space $\mathscr{B}$ of bound states. Note that Ω_+ and Ω_- have the same range $\mathscr{S}$, a property called asymptotic completeness [71, 70, 119, 120]. Thus the scattering operator

$$S = \Omega_-^{\dagger}\Omega_+ = \lim_{t\to+\infty} U_I(t) \lim_{t'\to-\infty} U_I^{\dagger}(t') = U_I(+\infty, -\infty)\,, \tag{2.18}$$

exists and is a one-to-one map $S : \mathscr{H} \to \mathscr{H}$ in the full Hilbert space. It maps free states in the past to free states in the future $|\psi^+\rangle = S|\psi^-\rangle$ without formation of bound states. Since S is an isometry and one-to-one, it is unitary $S^\dagger S = SS^\dagger = \mathbb{I}$. Moreover, from the definition of the Møller operators it follows directly that $[S, H_0] = 0$ expressing total energy conservation in the collision. We prove this last property and many others in the Appendix of the manuscript in Sec. 2.3.2.

The Scattering Map for a Subsystem

We now consider the Hilbert space as a tensor product $\mathscr{H} = \mathscr{H}_\mathrm{I} \otimes \mathscr{H}_\mathrm{K}$, where $\mathscr{H}_\mathrm{I}$ and $\mathscr{H}_\mathrm{K}$ are the Hilbert spaces of internal and kinetic degrees of freedom of the full system. The free Hamiltonian now reads $H_0 = H_\mathrm{I} \otimes \mathbb{I}_\mathrm{K} + \mathbb{I}_\mathrm{I} \otimes H_\mathrm{K}$, where H_I has a discrete spectrum and H_K has a continuous spectrum. In the density matrix formalism, the scattering map for the full system reads

$$\rho' = S(\rho_\mathrm{I} \otimes \rho_\mathrm{K})S^\dagger \,, \tag{2.19}$$

where ρ' is the final state, being generally entangled while the initial internal and kinetic state are factorized. Note we are not assuming that $\mathscr{H}_\mathrm{I}$ and $\mathscr{H}_\mathrm{K}$ correspond to different particles. For instance, if we consider a fixed system colliding with an incoming particle, then $\mathscr{H}_\mathrm{I}$ might include the internal structure of both systems, but we keep the notation general for now. We can trace over the kinetic degrees of freedom in Eq. (2.19) to obtain

$$\rho'_\mathrm{I} \equiv \mathbb{S}(\rho_\mathrm{I}) = \mathrm{Tr}_\mathrm{K}[S(\rho_\mathrm{I} \otimes \rho_\mathrm{K})S^\dagger] \,. \tag{2.20}$$

Since the scattering operator is unitary and the initial state is factorized, the scattering map $\mathbb{S}$ is completely positive and trace preserving. The final state of the kinetic degrees of freedom ρ'_K is obtained by tracing over the internal degrees of freedom.

Energy and Entropy Balance

The unitary and energy preserving properties of the scattering operator allow us to perform an energy and entropy balance for a single collision. We follow Sec. 1.4 except we take the open system to be the internal degrees of freedom. Then the energy change in the internal structure is given by $\Delta E_\mathrm{I} \equiv \mathrm{Tr}_\mathrm{I}[H_\mathrm{I}(\rho'_\mathrm{I} - \rho_\mathrm{I})]$ and similarly for the kinetic degrees of freedom. Therefore Eq. (1.70) becomes

$$\Delta E_\mathrm{I} = -\Delta E_\mathrm{K} \,, \tag{2.21}$$

where there is no switching work since the scattering setup is time-independent. The entropy balance is the same as in Eq. (1.71)

$$\Delta S_\mathrm{I} = I_{\mathrm{I}:\mathrm{K}} - \Delta S_\mathrm{K} \,. \tag{2.22}$$

Again, the last expressions lack an *a priori* thermodynamic interpretation, but they are the most general balances we can perform at the single collision level.

2.3 Thermodynamics of Quantum Collisions

We present three manuscripts where we formulate the notions of heat and work in quantum scattering theory. Heat is the energy exchanged by thermally mixed wave packets which are narrow in energy with respect to the internal system. Work is the energy exchanged by pure and fast wave packets which are broad in energy with respect to the internal system. We discuss our results in connection to models of repeated interactions.

2.3.1 Discussion on Heat and Work

We have all the ingredients to tackle the main problem of this chapter: under what conditions can we interpret the change in internal energy, or kinetic energy, as heat or work? Once we establish an answer, then Eqs. (2.21) and (2.22) can be interpreted as the first and second laws of thermodynamics for a quantum collision. We discuss heat and thermalization in the first two manuscripts in Secs. 2.3.2 and 2.3.3, while work is discussed separately in the manuscript in Sec. 2.3.4. We provide below a preface to each of the manuscripts and put them in the context of this thesis. Figure 2.1 is a depiction of the main results.

First manuscript (Subsec. 2.3.2)

In Secs. II and III of the first manuscript, we establish the scattering setup that we use in all subsequent manuscripts, consisting of a fixed quantum system with internal structure colliding with a particle travelling as a wave packet. Our setup is general, so that the wave packet can be either pure (thus having a definite average momentum p_0 as we treated in Subsec. 1.2.2) or mixed (according to some momentum distribution as we treated in Sec. 2.1). The particle can also have an internal structure. The crucial point is that packets have a definite width in momentum or energy, which we show plays a crucial role in the internal dynamics governed by the scattering map $\mathbb{S}$.

Our first and general result is that wave packets can be divided into two categories: those with energy width smaller or larger than the internal energies, called narrow or broad wave packets, respectively. This distinction is made mathematically precise in Sec. IV. of the manuscript. There, we show that the scattering map $\mathbb{S}$ for narrow wave packets decouples populations and coherences in the energy eigenbasis of the internal system, when the latter is not degenerate. The dynamics of the populations is thus described by a Markov process in discrete time (Markov chain) and coherences decay. The notion of narrow wave packet is then the most important in this manuscript, since they are responsible for decoherence, whether in a pure or mixed state. As we explain in Sec. IV., this is because narrow wave packets are entangled with the internal system after the collision, thus carrying away information about internal transitions. However they do not, by themselves, lead to thermalization since the Markov chain does not generally obey detailed balance. In Sec. V. of the manuscript, we show that detailed balance is achieved when the narrow packet is mixed according to the effusion distribution and when the collisions are invariant under time-

reversal. In this case, the thermal state is a stationary state of the map $\mathbb{S}$. This allows us to identify heat as the kinetic energy lost by the thermal wave packet and transferred to the internal system due to a collision. Regarding entropy, we show in the same section only how the internal change in Shannon entropy (which takes into account only populations) can be decomposed into an entropy production and entropy flow terms. However, we can obtain an equivalent decomposition for the von Neumann in this thesis by appealing to Eq. (1.42), which has a microscopic interpretation in our scattering framework. This is due to two reasons: 1) The definition of entropy production used in Eq. (1.42) relies on the thermal state being the stationary state of the dynamical map, which we prove is the case in first manuscript. 2) Point 1) allow us to interpret the dissipated energy in Eq. (1.42) as (minus) heat. In summary, the results in Sec. V. of the first manuscript justify the interpretation of Eqs. (2.21) and (2.22) as the first and second law of thermodynamics in the absence of work sources. Remarkably, these laws can be expressed solely in terms of internal system quantities even when the collision is strong and they hold for a large class of interactions. Concerning thermalization, detailed balance implies that if the internal degrees of freedom of the particle are also thermal with the same temperature as the effusion distribution, then repeated collisions thermalize the fixed system (see Sec. VI. of the manuscript). This statement is true independently of the free evolution of the fixed system between each collision.

Regarding broad wave packets, the most general result of this manuscript is that they couple populations and coherences of the internal system during the collision, whether pure or mixed, leading to transfer of coherences to the internal system. They are studied in detail in the third manuscript, where we use them to establish the notion of work.

Second manuscript (Subsec. 2.3.3)

The results on thermalization derived in the first manuscript are general, but an exact analytical solution to the scattering problem is unavailable for most potentials. In this manuscript, we present two simple models of thermalization based on the first manuscript. The scattering setup is the same, except for two things. First, we study in more detail the scattering map for the fixed system, tracing out both kinetic and internal degrees of freedom of the particle after each collision. Second, we consider specifically a potential barrier (see Sec. II of the manuscript) allowing us to use transfer matrix methods to derive the scattering map at high energies, where transmission dominates over reflection. The models based on this map are rigorously presented in Secs. III-A. and III-B. of the manuscript, both of them inducing thermalization of the fixed system (given that the internal and kinetic degrees of freedom of the particle have the same temperature). Although they are very similar to each other, the second model, called random interaction time model, is important in connection with models of repeated interaction. This is because each wave packet interacts with the fixed system for a given time, where this time emerges in scattering theory in the

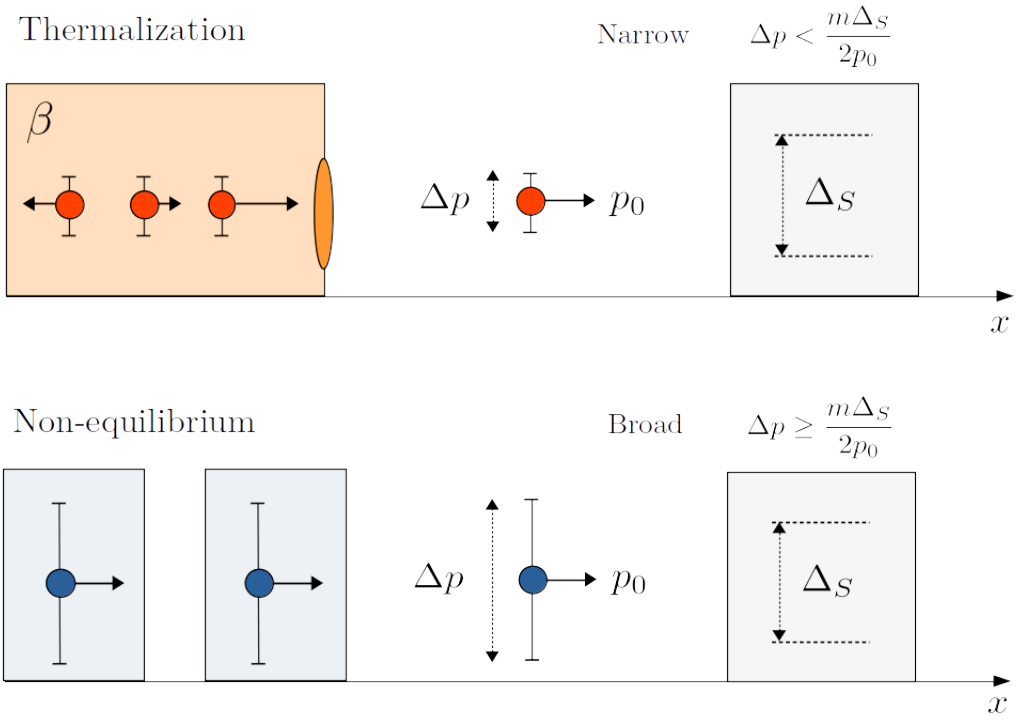

Figure 2.1: Upper panel: Thermalization of a fixed system with energy scale Δ_S is achieved after many collisions with particles described by narrow wave packets, effusing from a box with thermal momentum p_0. In general, we require that particles travel both to the right and left, but we show only the former case for simplicity. The internal structure is not depicted, but it is assumed to be thermal with the same temperature as the effusing packets. This corresponds to a heat source as we discuss in the manuscript in Sec. 2.3.2. Lower panel: When the wave packets are broad and prepared with a fixed momentum p_0, they act as a source of non-equilibrium by transferring coherences to the internal system as a whole (particle and fixed system). In the limit when the packets are very fast and broad, the internal evolution becomes unitary and energy is exchanged without entropy. This corresponds to a work source as we discuss in the manuscript in Sec. 2.3.4.

high energy kinetic regime.[1] However, in our model the time is random as a consequence of the effusion distribution, while in repeated interaction models it is fixed. As we discuss in Sec. V., the results suggest that the difference between heat and work arises from a specific randomization of interaction times.

[1]This interaction time is not equivalent to the time it takes for a packet with a given momentum to cross the potential region. Instead, it is a function that also depends on the internal energy of the system, which is a necessary requirement for thermalization. This subtle point is discussed in Sec. III-B. of the manuscript.

Third manuscript (Subsec. 2.3.4)

In this last manuscript, we deal only with pure, broad wave packets at the single collision level. We show that when the wave packet is very broad and its kinetic energy is much larger than all energy scales involved, the dynamics of the internal system (both particle and fixed system) becomes unitary.[2] The resulting scattering map $\mathbb{S}$ is shown in Eq. (6) of the manuscript and the accompanying text contains the precise conditions of its validity. In this regime, due its high kinetic energy and width, the effect of the internal system on the packet is negligible. As a consequence, the wave packet and internal system do not entangle, so that no information about the system can be retrieved from the outgoing packet. The internal dynamics is then unitary, with a phase proportional to the interaction time, i.e. the time it takes for a packet with a given momentum to cross the potential region. Since in this manuscript the wave packet is pure (not mixed according to the effusion momentum distribution), the interaction time is fixed just like in models of repeated interactions. Indeed, we show in the manuscript that the internal scattering dynamics is the same as the one of models of repeated interactions. This allow us to explain microscopically the switching work of Eq. (1.69) as the energy exchanged during a collision with a very fast and broad wave packet. Such a wave packet can then effectively mimick a time-dependent interaction, acting as an external source of energy for the internal system without incurring entropy changes.

In the light of these results, we argue that the fast and broad wave packet acts as a work source for the internal degrees of freedom. Of course, we recognize that the notion of work for quantum systems is highly debated [121, 122, 82], specially in autonomous systems which lack any explicit time-dependence [123]. However, since we have shown in the third manuscript that the packets can exchange energy without changing their own entropy, and also that they can also mimick a time-dependent interaction, we believe our interpretation to be justified [99, 123]. For this work source, all the terms in Eq. (2.22) vanish and Eq.(2.21) becomes an energy balance which can drive the internal system out of equilibrium.

[2] This regime of high energies is similar to the regime used in the second manuscript for a potential barrier. However, the derivation of the scattering map in the high energy regime is quite different in this third manuscript, allowing us to treat a potential of finite length but arbitrary shape. This is possible because the de Broglie wavelength of the packet is much shorter than the length over which the potential varies significantly. An arbitrary potential can then be effectively treated as a potential barrier, as we confirm numerically in the main text and prove analytically in the Appendix of the manuscript.

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Thermalization Induced by Quantum Scattering

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We use quantum scattering theory to study a fixed quantum system Y subject to collisions with massive particles X described by wave packets. We derive the scattering map for system Y and show that the induced evolution crucially depends on the width of the incident wave packets compared to the level spacing in Y. If Y is nondegenerate, sequential collisions with narrow wave packets cause Y to decohere. Moreover, an ensemble of narrow packets produced by thermal effusion causes Y to thermalize. On the other hand, broad wave packets can act as a source of coherences for Y, even in the case of an ensemble of incident wave packets given by the effusion distribution, preventing thermalization. We illustrate our findings on several simple examples and discuss the consequences of our results in realistic experimental situations.

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I. INTRODUCTION

Many phenomena in quantum physics can be described in terms of repeated collisions of moving particles X with a fixed target system Y. The effect of such collisions on Y is the subject of this paper. Such a framework is extremely rich, as the particles X can be prepared in an arbitrary state and used to control the dynamics of Y. Without loss of generality, we assume that these particles X have no internal structure. Indeed, we will see that the internal structure of X, if decorrelated from its center of mass motion, can be effectively incorporated into that of Y. This allows us to focus on how the motion of the center of mass of such particles—described by wave packets—affects the dynamics of Y. Besides a notable exception [1], it is surprising that such a simple question seems to have been little explored. For instance, one would expect that phenomena such as decoherence and thermalization of Y occur as a result of collisions with a thermal ensemble of wave packets X, but the conditions for this to happen have not been identified and the precise definition of the thermal ensemble is also lacking. Our approach contrasts with the theory of open quantum systems, in which a system is in permanent contact with equilibrium reservoirs [2,3] or subjected to continuous collisions with a quantum gas in thermal equilibrium [4–8], where such phenomena are well understood. One would also expect that a nonthermal ensemble, instead of causing decoherence and thermalization, can play the role of a thermodynamic resource for Y and bring it in a suitable coherent state. Related questions have been considered within the framework of repeated interaction models [9–11], where instead of treating a true scattering problem in real space, an interaction between X and Y is switched on for a given time.

Our results in this paper rely on three main concepts. The first is the scattering map, i.e., the quantum map for Y induced by a collision with a particle X in a generic (pure or mixed) state, defining the reduced dynamics of Y. The second is the distinction between pure wave packets whose energy width is smaller or larger than the smallest energy-level spacing in Y, which we call narrow or broad wave packets, respectively. These two concepts suffice to prove our first result: that collisions with narrow wave packets induce decoherence in a nondegenerate system Y,

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while collisions with broad packets can act as a source of coherences. The third is the notion of a statistical ensemble of effusing narrow packets, which we show not only decoheres but thermalizes Y, establishing our second and main result.

This framework offers a rich platform to analyze the interplays between various types of wave packets for X interacting with Y. A quantum thermodynamic perspective on the ensuing free energy transfers is left for future work.

The paper is organized as follows. The model and the scattering map for the fixed system Y subject to collisions with wave packets X are defined in Sec. II. The scattering map is then expressed in terms of the scattering matrix in Sec. III. Its properties when X is a pure wave packet are studied in Sec. IV, where we prove that decoherence occurs for collisions with narrow—but not with broad—wave packets. Mixtures, or statistical ensembles, of thermally effusing wave packets are considered in Sec. V. Narrow wave packets are shown to produce a detailed balance map, which leads not only to decoherence of Y but also to thermalization of its populations. Broad wave packets, on the other hand, can prevent the system from thermalizing by acting as a source of coherences. In Sec. VI, we comment on the extension of our framework to particles with an internal structure. In Sec. VII, we illustrate our findings in a simple model based on a Dirac-δ potential. Conclusions are drawn in Sec. VIII. Appendix A is used to recall some important results from scattering theory used in our calculations. The solution of the scattering problem used to illustrate the theory is detailed in Appendix B.

II. THE MODEL AND THE SCATTERING MAP

We consider a particle X with mass m, which travels freely before and after colliding with a fixed scatterer, which we call the system Y, having internal states in a Hilbert space $\mathcal{H}_Y$. For simplicity, we restrict ourselves to systems with finite dimension N and a one-dimensional space for the particle. If the latter has no internal structure, the Hilbert space of the global system is $\mathcal{H} = \mathcal{H}_X \otimes \mathcal{H}_Y$, where $\mathcal{H}_X$ is the Hilbert space of a one-dimensional particle, i.e., the set of normalized wave functions $\psi(x)$ with $x \in \mathbb{R}$ (as we argue in Sec. VI, one can also consider particles with internal structure, e.g., spin, by extending $\mathcal{H}_Y$).

The Hamiltonian for the global system is given by

$$H = H_0 + V = \frac{p^2}{2m} \otimes \mathbb{I}_Y + \mathbb{I}_X \otimes H_Y + V(x) \otimes \nu, \quad (1)$$

where x and p are the position and momentum operators of the particle X. The free Hamiltonian $H_0 \equiv p^2/2m \otimes \mathbb{I}_Y + \mathbb{I}_X \otimes H_Y$ is the sum of the kinetic energy of the particle X and the internal energy of the system Y, where $\mathbb{I}_Y$ is the identity in $\mathcal{H}_Y$ (equivalently for X) and the interaction is given by $V \equiv V(x) \otimes \nu$, with ν being an operator in $\mathcal{H}_Y$. Finally, we assume that the interaction potential $V(x)$ tends to zero sufficiently fast as $x \to \pm\infty$, as is usual in scattering theory [12].

For such a class of potentials, scattering theory guarantees the existence of a one-to-one map S between free (incoming) states before the collision to free (outgoing) states after the collision. More specifically, the total Hilbert space $\mathcal{H}$ can be decomposed into the direct sum of scattering and bound states. Only the asymptotic behavior of the former is that of free states, i.e., its evolution for $t \to \pm\infty$ is given by the unitary evolution operator $U_0(t) = \exp[-itH_0/\hbar]$ corresponding to the free Hamiltonian H_0, while the latter remain bound to the interaction region in the same limit. If $U(t) = \exp[-itH/\hbar]$ is the full evolution operator, one can define the isometric Møller operators [12]:

$$\Omega_\pm = \lim_{t \to \mp\infty} U(t)^\dagger U_0(t), \quad (2)$$

which, respectively, map incoming and outgoing states onto scattering states. The scattering operator defined as

$$S = \Omega_-^\dagger \Omega_+, \quad (3)$$

is then unitary $SS^\dagger = S^\dagger S = \mathbb{I}$ and maps incoming states onto outgoing states, providing all the information of how the full system changes in a collision. We add that one can prove mathematically, under mild conditions, that any state in the Hilbert space $\mathcal{H}$ can be interpreted as a free (incoming or outgoing) state. In other words, the domain of the Møller and the scattering operator is the whole Hilbert space $\mathcal{H}$ [12]. However, one is usually interested in incoming states where the incident particle is localized in space, far from the collision region and is approaching the scatterer in a state either from the left or from the right. These are the incoming states considered in this paper.

In our approach, the incoming and outgoing states are density operators associated to the Hilbert space $\mathcal{H}$. Namely, if the incoming state is factorized $\rho = \rho_X \otimes \rho_Y$, then the outgoing state of the full system is $\rho' = S(\rho_X \otimes \rho_Y)S^\dagger$, and the effect of the collision on the internal state of the system Y is given by

$$\rho_Y' = \mathrm{Tr}_X\left[S\big(\rho_X \otimes \rho_Y\big)S^\dagger\right] \equiv \mathbb{S}\rho_Y, \quad (4)$$

where Tr_X denotes the partial trace over X. Finally, the system Y can sequentially collide with a stream of particles in identical states ρ_X. Between collisions, the system Y evolves isolated. The dynamics is then obtained by the concatenation

$$\rho_Y^{(n)} = \mathcal{E}_{\tau_n} \circ \mathbb{S} \circ \cdots \circ \mathcal{E}_{\tau_2} \circ \mathbb{S} \circ \mathcal{E}_{\tau_1} \circ \mathbb{S}\, \rho_Y^{(0)}, \quad (5)$$

where τ_i is the time between collision i and $i+1$ and $\mathcal{E}_t(\cdot) = \exp[-itH_Y/\hbar](\cdot)\exp[itH_Y/\hbar]$ is the unitary map associated to the free evolution with Hamiltonian H_Y.

In the rest of the paper, we calculate and explore the main properties of the superoperator $\mathbb{S}$ defining the dynamics in Eqs. (4) and (5).

III. THE MAP IN TERMS OF THE SCATTERING MATRIX

The scattering operator commutes with the free Hamiltonian $[S, H_0] = 0$ (see Appendix A 1), implying that the energy is conserved in a collision. As a consequence, it is convenient to express S in terms of the eigenstates of H_0. We denote the eigenstates of H_Y by $|j\rangle \in \mathcal{H}_Y$:

$$H_Y |j\rangle = e_j |j\rangle , \tag{6}$$

where the eigenvalue e_j is the internal energy of the system and consider the eigenvalues of H_Y ordered as $e_1 \leq e_2 \leq \cdots \leq e_N$, denoting the Bohr frequencies by $\Delta_{jk}/\hbar$ with $\Delta_{jk} \equiv e_j - e_k$. Then the generalized eigenstates of H_0 are the tensor products $|p,j\rangle \equiv |p\rangle \otimes |j\rangle$, where $|p\rangle$ is a plane wave, i.e., an improper (non-normalizable) state of $\mathcal{H}_X$, whose position representation reads

$$\langle x|p\rangle = \frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}}, \tag{7}$$

and satisfies the generalized orthogonality condition $\langle p'|p\rangle = \delta(p'-p)$. The eigenvalue equation for H_0 reads

$$\begin{aligned} H_0 |p,j\rangle &= \left(\frac{p^2}{2m} \otimes \mathbb{I}_Y + \mathbb{I}_X \otimes H_Y\right) |p,j\rangle \\ &= (E_p + e_j) |p,j\rangle , \end{aligned} \tag{8}$$

$E_p \equiv p^2/2m$ being the kinetic energy of the plane wave $|p\rangle$.

Due to the conservation of energy, the elements of the scattering operator S in the eigenbasis of H_0, $\langle p',j'| S |p,j\rangle$, are proportional to $\delta(E_p - E_{p'} - \Delta_{j'j})$ (see Appendix A 1). We express these elements as

$$\langle p',j'| S |p,j\rangle = \frac{\sqrt{|pp'|}}{m} \delta(E_p - E_{p'} - \Delta_{j'j}) s^{(\alpha'\alpha)}_{j'j}(E_p + e_j), \tag{9}$$

where $s^{(\alpha'\alpha)}_{j'j}(E)$ is an element of the so-called scattering matrix with $\alpha = \text{sign}(p)$ and $\alpha' = \text{sign}(p')$ accounting for the initial and final direction of the momenta, which can be positive ($\alpha, \alpha' = +$) or negative ($\alpha, \alpha' = -$). These elements can be calculated by solving the stationary Schrödinger equation with appropriate asymptotic boundary conditions (see Appendices A 2 and A 3). Importantly, Eq. (9) defines $s^{(\alpha'\alpha)}_{j'j}(E)$ only for $E \geq \max\{e_j, e_{j'}\}$ because p^2 and p'^2 are non-negative. If j and j' fulfill this condition for a given value of E, we say that the transition $|j\rangle \to |j'\rangle$ is an open channel. Consequently, the dimension of the matrices $\mathbf{s}^{(\alpha'\alpha)}(E)$ is $N_{\text{open}}(E) \times N_{\text{open}}(E)$, where $N_{\text{open}}(E)$ is the number of open channels for an energy E. For example, if $e_1 < E < e_2$, there is only one open scattering channel ($j = j' = 1$) and, if $E > e_N$, all channels are open.

The scattering matrix is then ordered in four blocks

$$\mathbf{s}(E) = \begin{pmatrix} \hat{\mathbf{r}}^L(E) & \hat{\mathbf{t}}^R(E) \\ \hat{\mathbf{t}}^L(E) & \hat{\mathbf{r}}^R(E) \end{pmatrix}, \tag{10}$$

all of dimension $N_{\text{open}}(E) \times N_{\text{open}}(E)$. The entries of the transmission-from-the-left matrix $\hat{\mathbf{t}}^L(E)$ are $s^{(++)}_{j'j}(E)$, those of the transmission-from-the-right matrix $\hat{\mathbf{t}}^R(E)$ are $s^{(--)}_{j'j}(E)$, those of the reflection-from-the-left matrix $\hat{\mathbf{r}}^L(E)$ are $s^{(-+)}_{j'j}(E)$, and those of the reflection-from-the-right matrix $\hat{\mathbf{r}}^R(E)$ are $s^{(+-)}_{j'j}(E)$. They define the conditional probabilities

$$P^L_{j'j}(E) \equiv |\hat{t}^L_{j'j}(E)|^2 + |\hat{r}^L_{j'j}(E)|^2 = \sum_{\alpha=\pm} \left| s^{(\alpha+)}_{j'j}(E) \right|^2 \tag{11}$$

for a transition $|j\rangle \to |j'\rangle$ in the system Y given that the momentum of the plane wave is positive (coming from the left) and the total energy is E. We similarly define $P^R_{j'j}(E)$ for negative momentum (coming from the right). The normalization $\sum_{j'} P^L_{j'j} = \sum_{j'} P^R_{j'j} = 1$ follows from the unitary property of $\mathbf{s}(E)$, which corresponds to the diagonal elements of the relation $\mathbf{s}^\dagger(E)\mathbf{s}(E) = \mathbb{I}$ satisfied by the scattering matrix Eq. (10), as shown in Appendix A 4.

If we express the density matrix of the system in the eigenbasis of H_Y, i.e., $(\rho_Y)_{jk} \equiv \langle j|\rho_Y|k\rangle$ and $(\rho'_Y)_{jk} \equiv \langle j|\rho'_Y|k\rangle$, we write Eq. (4) as

$$(\rho'_Y)_{j'k'} = \sum_{j,k} \mathbb{S}^{jk}_{j'k'} (\rho_Y)_{jk} \tag{12}$$

with the scattering map

$$\mathbb{S}^{jk}_{j'k'} = \langle j'| \text{Tr}_X \left[S\big(\rho_X \otimes |j\rangle\langle k|\big) S^\dagger \right] |k'\rangle . \tag{13}$$

The superoperator $\mathbb{S}$ can be expressed in terms of the scattering matrix by introducing in Eq. (13) the decomposition $\rho_X = \int dp\, dp'' \rho_X(p,p'') |p\rangle\langle p''|$ in the eigenbasis of H_X:

$$\begin{aligned} \mathbb{S}^{jk}_{j'k'} = \int_{-\infty}^{\infty} dp' \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dp'' \rho_X(p,p'') \\ \langle p',j'| S |p,j\rangle \langle p'',k| S^\dagger |p',k'\rangle . \end{aligned} \tag{14}$$

Substituting Eq. (9) in Eq. (14) and using $dE_{p'} = |p'|dp'/m$ we obtain

$$\mathbb{S}^{jk}_{j'k'} = \sum_{\alpha'=\pm} \int dE_{p'}\, dp\, dp''\, \rho_X(p,p'') \frac{\sqrt{|pp''|}}{m} \delta(E_p - E_{p'} - \Delta_{j'j}) s^{(\alpha'\alpha)}_{j'j} (E_p + e_j) \delta(E_{p''} - E_{p'} - \Delta_{k'k}) \left[s^{(\alpha'\alpha'')}_{k'k}(E_{p''} + e_k) \right]^*, \tag{15}$$

where the integrals over the momenta p, p'' run along the entire real axis, whereas the integral over the energy $E_{p'}$ runs from 0 to infinity and the sum over α' accounts for the positive and negatives values of p'. We note that $s^{(\alpha'\alpha)}_{j'j}$ and $s^{(\alpha'\alpha'')}_{k'k}$ are well defined only if the channels $|j\rangle \to |j'\rangle$ and $|k\rangle \to |k'\rangle$ are open at the energies in their arguments, i.e., if $E_p + e_j \geq \max\{e_j, e_{j'}\}$ and $E_{p''} + e_k \geq \max\{e_k, e_{k'}\}$. These conditions are equivalent to $E_p \geq \Delta_{j'j}$ and $E_{p''} \geq \Delta_{k'k}$, respectively, and are enforced by the δ functions. Integration over the energy $E_{p'}$ yields

$$\mathbb{S}^{jk}_{j'k'} = \sum_{\alpha'=\pm} \int dp\, dp''\, \rho_X(p,p'') \frac{\sqrt{|pp''|}}{m} \times \delta(E_p - E_{p''} - \Delta_{j'j} + \Delta_{k'k}) s^{(\alpha'\alpha)}_{j'j}(E_p + e_j) \times \left[s^{(\alpha'\alpha'')}_{k'k}(E_{p''} + e_k) \right]^*, \tag{16}$$

where the integrals run over the region where $E_p \geq \Delta_{j'j}$ and $E_{p''} \geq \Delta_{k'k}$.

IV. WAVE PACKETS AND DECOHERENCE

In this section we study the properties of the scattering map, Eq. (12), when the incoming particle is in a pure state, i.e., $\rho_X = |\phi\rangle\langle\phi|$. We use the momentum representation $\phi(p) \equiv \langle p|\phi\rangle$ with $\int dp |\phi(p)|^2 = 1$. To simplify, we consider that all components of $|\phi\rangle$ travel to the right, i.e., $\phi(p) = 0$ if $p < 0$. For this pure state, $\rho_X(p,p'') = \phi(p)\phi^*(p'')$ and Eq. (16) reads

$$\mathbb{S}^{jk}_{j'k'} = \sum_{\alpha'=\pm} \int dp\, dp''\, \phi(p)\phi^*(p'') \frac{\sqrt{pp''}}{m} \times \delta(E_p - E_{p''} - \Delta_{j'j} + \Delta_{k'k}) s^{(\alpha'+)}_{j'j}(E_p + e_j) \times \left[s^{(\alpha'+)}_{k'k}(E_{p''} + e_k) \right]^*. \tag{17}$$

Recall that the integration domain in this expression is defined by the inequalities $E_p \geq \Delta_{j'j}$ and $E_{p''} \geq \Delta_{k'k}$. Since $dE_{p''} = |p''|dp''/m$, the integration of the δ function over p'' yields

$$\mathbb{S}^{jk}_{j'k'} = \sum_{\alpha'=\pm} \int_{p_{\rm inf}}^{\infty} dp\, \phi(p)\phi^*[\pi(p)] \sqrt{\frac{p}{\pi(p)}} s^{(\alpha'+)}_{j'j}(E_p + e_j) \times \left[s^{(\alpha'+)}_{k'k}(E_p - \Delta_{j'j} + e_{k'}) \right]^*, \tag{18}$$

with $\pi(p) = \sqrt{p^2 - 2m(\Delta_{j'j} - \Delta_{k'k})}$. The lower integration limit $p_{\rm inf}$ is obtained from $p^2_{\rm inf}/2m = \max\{0, \Delta_{j'j}, \Delta_{j'j} - \Delta_{k'k}\}$, which guarantees that the channels are open in the integration domain.

We now focus on wave packets centered at a momentum p_0 and with a width $2\Delta p$, that is, states where the function $\phi(p)$ is zero except for $p \in [p_0 - \Delta p, p_0 + \Delta p]$. The properties of the map, Eq. (18), depend crucially on the product

$$\phi(p)\phi^*[\pi(p)], \tag{19}$$

which is different from zero if and only if the arguments are within the support of ϕ, that is,

$$\begin{aligned} p_0 - \Delta p &< p < p_0 + \Delta p, \\ p_0 - \Delta p &< \pi(p) < p_0 + \Delta p. \end{aligned} \tag{20}$$

Squaring the two inequalities, we have

$$\begin{aligned} &(p_0 - \Delta p)^2 < p^2 < (p_0 + \Delta p)^2, \\ &(p_0 - \Delta p)^2 < p^2 - 2m(\Delta_{j'j} - \Delta_{k'k}) < (p_0 + \Delta p)^2 \end{aligned} \tag{21}$$

and, eliminating p, one gets the following necessary condition for the product (19) to be different from zero for some value of p:

$$(p_0 + \Delta p)^2 - (p_0 - \Delta p)^2 > 2m|\Delta_{j'j} - \Delta_{k'k}| \quad \Rightarrow \quad \Delta p > \frac{m|\Delta_{j'j} - \Delta_{k'k}|}{2p_0}. \tag{22}$$

This inequality defines an important distinction between two types of incoming wave packets: (a) Those where the function $\phi(p)$ is highly peaked around p_0 so that Δp verifies Eq. (22) only when $\Delta_{j'j} = \Delta_{k'k}$. Consequently, in Eq. (18) the term $\mathbb{S}^{jk}_{j'k'}$ vanishes except for transitions with equal energy change. From now on, we call them *narrow wave packets*. (b) Those where the function $\phi(p)$ is broad enough to verify Eq. (22) for at least a pair of transitions $|j\rangle \to |j'\rangle$ and $|k\rangle \to |k'\rangle$ with $\Delta_{j'j} \neq \Delta_{k'k}$. We call them *broad wave packets* and they allow for an overlap of the two factors in Eq. (19) for some value of p; hence the corresponding term $\mathbb{S}^{jk}_{j'k'}$ in Eq. (18) can be different from zero.

As we show below, narrow (wave) packets destroy most of the coherences or off-diagonal terms of the density matrix of the system, whereas they survive or are even created after repeated collisions with broad packets.

This is one of the main results of the paper. It is worth giving a physical interpretation of condition (22) and the distinction between narrow and broad wave packets. In order to do that, suppose that the initial state of the global system is the pure state $|\phi\rangle \otimes |j\rangle$. After the collision, the state can be written as

$$\begin{aligned} S\,|\phi\rangle \otimes |j\rangle &= \sum_{j'} \int dp'\, |p',j'\rangle\, \langle p',j'|\, S\, [|\phi\rangle \otimes |j\rangle], \\ &= \sum_{j'} \int dp'dp\, |p',j'\rangle\, \langle p',j'|\, S\, |p,j\rangle\, \phi(p). \end{aligned} \tag{23}$$

Using Eq. (9) and integrating the δ function, the outgoing state can be written as

$$S\,|\phi\rangle \otimes |j\rangle = \sum_{j'} \sum_{\alpha'=\pm} |\phi_{j'}^{\alpha'}\rangle \otimes |j'\rangle\,. \tag{24}$$

Here $|\phi_{j'}^{\alpha'}\rangle$ are non-normalized wave packets, whose momentum representation reads

$$\langle p\,|\phi_{j'}^{\alpha'}\rangle = \sqrt{\frac{|p\,|}{|\bar{\pi}\,(p)|}}\, s_{j'j}^{(\alpha'+)}(E_p + e_{j'})\phi[\bar{\pi}\,(p)]\Theta(\alpha' p), \tag{25}$$

with $\bar{\pi}\,(p) \equiv \sqrt{p^2 + 2m\Delta_{j'j}}$, and $\Theta(p)$ being the Heaviside step function. Hence, the state after the collision is a superposition of wave packets $|\phi_{j'}^{\alpha'}\rangle \otimes |j'\rangle$, corresponding to the different transitions $|j\rangle \to |j'\rangle$, that leave the scatterer with positive ($\alpha = +$, transmitted packets) or negative ($\alpha = -$, reflected packets) momentum. The support of this outgoing packet is given by the function ϕ and is determined by the inequalities

$$p_0 - \Delta p \,<\, \sqrt{p^2 + 2m\Delta_{j'j}} \,<\, p_0 + \Delta p, \tag{26}$$

with $p > 0$ for the transmitted packets and $p < 0$ for the reflected ones.

Consider now the initial states $|\phi\rangle \otimes |j\rangle$ and $|\phi\rangle \otimes |k\rangle$ and the corresponding transitions, $|j\rangle \to |j'\rangle$ and $|k\rangle \to |k'\rangle$. The transmitted wave packets overlap in the momentum representation if there is a positive p such that

$$\begin{aligned} p_0 - \Delta p \,&<\, \sqrt{p^2 + 2m\Delta_{j'j}} \,<\, p_0 + \Delta p, \\ p_0 - \Delta p \,&<\, \sqrt{p^2 + 2m\Delta_{k'k}} \,<\, p_0 + \Delta p. \end{aligned} \tag{27}$$

It is straightforward to prove that these two conditions are equivalent to Eq. (22). However, Eq. (27) provides an illuminating interpretation of the distinction between narrow and broad wave packets, which is sketched in Fig. 1. In the case of an incident narrow packet, condition (27) means that the outgoing wave packets resulting from channels $|j\rangle \to |j'\rangle$ and $|k\rangle \to |k'\rangle$ do not overlap unless they induce jumps in the system state with exactly the same energy, that is, $\Delta_{j'j} = \Delta_{k'k}$; in such a case, the outgoing packets are identical. On the other hand, for a broad packet obeying Eq. (27) for a pair of transitions with $\Delta_{j'j} \neq \Delta_{k'k}$, outgoing wave packets with different energy may overlap, as shown in the lower diagram of Fig. 1. If this occurs, then the collision preserves the coherences between states $|j\rangle$ and $|k\rangle$ and can even create new coherences when a single pure state $|j\rangle$ jumps to a superposition of $|j'\rangle$ and $|k'\rangle$ and the resulting wave packets overlap, as we show below in detail.

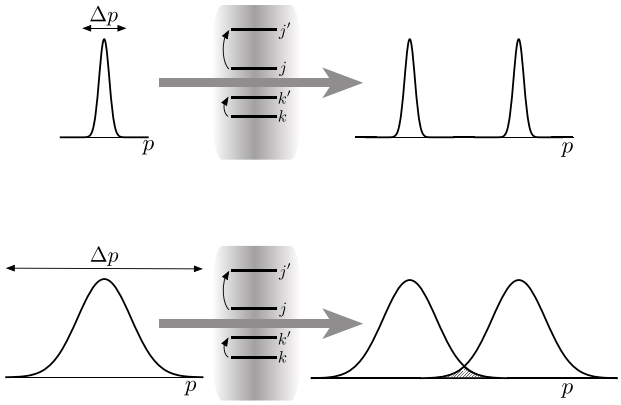

FIG. 1. Narrow (upper plate) and broad (lower plate) wave packets. The blurred gray zones represent the scatterer, which undergoes the transitions $|j\rangle \to |j'\rangle$ and $|k\rangle \to |k'\rangle$. The figure shows the two transmitted wave packets corresponding to these specific transitions (notice that the collision will generate, in general, much more outgoing packets than the two depicted). The crucial difference is that the overlap of the outgoing wave packets is zero in the narrow case, unless both have exactly the same energy: $\Delta_{j'j} = \Delta_{k'k}$. For broad packets, coherences between states do not vanish and can even be created due to the overlap (dark area) of the two outgoing packets depicted in the lower plate.

The same results apply to a wave packet where $\phi(p)$ decays and is almost zero far from its center at p_0. We consider, for instance, Gaussian wave packets $|\phi_{p_0,x_0}\rangle$ of the form:

$$\langle p\,|\phi_{p_0,x_0}\rangle = (2\pi\sigma^2)^{-1/4} \exp\Big[-\frac{(p-p_0)^2}{4\sigma^2} - i\frac{px_0}{\hbar}\Big], \tag{28}$$

where $p_0 = \langle\phi_{p_0,x_0}|\, p\, |\phi_{p_0,x_0}\rangle$ is the expectation value of the momentum, $\sigma > 0$ its standard deviation, and $x_0 = \langle\phi_{p_0,x_0}|\, x\, |\phi_{p_0,x_0}\rangle$ is the expectation value of the position operator. The condition $\phi_{p_0,x_0}(p) = 0$ for $p < 0$, which we

assume above, is practically satisfied if p_0 is positive and $p_0 \gg \sigma$. The previous discussion applies to Gaussian wave packets, for which the condition (22) for a narrow packet is

$$\sigma \ll \frac{m|\Delta_{j'j} - \Delta_{k'k}|}{2p_0} \tag{29}$$

for every quadruplet $\{j, k, j', k'\}$ with $\Delta_{k'k} \neq \Delta_{j'j}$.

A. Narrow wave packets

As discussed previously, a consequence of Eq. (22) is that, in a collision with an incident narrow packet, elements $(\rho_Y)_{jk}$ contribute to $(\rho'_Y)_{j'k'}$ only if $\Delta_{j'j} = \Delta_{k'k}$. In this case, $\pi(p) = p$ in Eq. (18). Moreover, since the packet is narrow, we can assume that the scattering matrix is approximately constant in the support of $\phi(p)$ and that $|\phi(p)|^2$ is approximately normalized in the integration domain $[p_{\inf}, \infty)$. Under these assumptions, Eq. (18) reduces to

$$\begin{aligned}\mathbb{S}^{jk}_{j'k'} &\simeq \sum_{\alpha'=\pm} s^{(\alpha'+)}_{j'j}(E_{p_0}+e_j)\left[s^{(\alpha'+)}_{k'k}(E_{p_0}+e_k)\right]^* \\ &= \hat{t}^L_{j'j}(E_{p_0}+e_j)\left[\hat{t}^L_{k'k}(E_{p_0}+e_k)\right]^* \\ &\quad + \hat{r}^L_{j'j}(E_{p_0}+e_j)\left[\hat{r}^L_{k'k}(E_{p_0}+e_k)\right]^*, \end{aligned} \tag{30}$$

if $\Delta_{j'j} = \Delta_{k'k}$ and zero otherwise. Let us apply this condition first to the diagonal terms of the density matrix $(\rho_Y)_{jj}$, which are the populations of the energy levels. The condition $\Delta_{j'j} = \Delta_{k'k}$ for $j' = k'$ implies $e_j = e_k$. If H_Y is nondegenerate, then $j = k$ and

$$\begin{aligned}\mathbb{S}^{jj}_{j'j'} &= \left[|\hat{t}^L_{j'j}(E_{p_0}+e_j)|^2 + |\hat{r}^L_{j'j}(E_{p_0}+e_j)|^2\right] \\ &= P^L_{j'j}(E_{p_0}+e_j), \end{aligned} \tag{31}$$

where the transition probability $P^L_{j'j}(E)$ is the one defined in Eq. (11). We see that the evolution of the populations or diagonal terms of the density matrix $(\rho_Y)_{jj}$ is independent of the off-diagonal terms or coherences. The diagonal terms obey the master equation

$$(\rho'_Y)_{j'j'} = \sum_j P^L_{j'j}(E_{p_0}+e_j)(\rho_Y)_{jj}, \tag{32}$$

which conserves the trace or total probability since $\sum_{j'} P^L_{j'j}(E) = 1$, due to the unitarity of the scattering matrix $\mathbf{s}(E)$ [see the discussion below Eq. (11)].

Let us discuss the evolution of the coherences or off-diagonal terms of the density matrix ρ_Y, and suppose first that H_Y is nondegenerate and the Bohr frequencies of the system are nondegenerate, i.e., the only solutions to $\Delta_{j'j} = \Delta_{k'k}$ are $j' = j$ and $k' = k$ or $j' = k'$ and $j = k$. The second case corresponds to the evolution of the populations that we discussed previously. The first case corresponds to $\mathbb{S}^{jk}_{jk}$ and yields the following evolution equation for the off-diagonal terms:

$$(\rho'_Y)_{jk} = \mathbb{S}^{jk}_{jk}(\rho_Y)_{jk} \quad \text{for } j \neq k. \tag{33}$$

Therefore, each coherence evolves independently and is simply changed by a multiplicative factor after a collision. Moreover, since $|t^L_{j'j}(E)|^2 + |r^L_{j'j}(E)|^2 \leq 1$ for any E, j, and j', a direct application of the Cauchy-Schwarz inequality yields

$$\begin{aligned}&\left|t^L_{j'j}(E)t^L_{k'k}(E')^* + r^L_{j'j}(E)r^L_{k'k}(E')^*\right|^2 \\ &\quad \leq \left[|t^L_{j'j}(E)|^2 + |r^L_{j'j}(E)|^2\right]\left[|t^L_{k'k}(E')|^2 + |r^L_{k'k}(E')|^2\right] \\ &\quad \leq 1 \end{aligned} \tag{34}$$

for all j, j', k, k', E, and E'. We conclude that all the entries of the scattering map, Eq. (30), are bound as $|\mathbb{S}^{jk}_{j'k'}| \leq 1$, and, according to Eq. (33), coherences either decay or remain finite only if $|\mathbb{S}^{jk}_{jk}| = 1$. The latter case happens only when the two equalities $|t^L_{aa}(E)|^2 + |r^L_{aa}(E)|^2 = 1$ for $a = j, E = E_{p_0} + e_j$, and $a = k, E = E_{p_0} + e_k$ are simultaneously satisfied. This is extremely unlikely in a multichannel scattering process. Therefore, generically one observes the strict inequality, which leads to decoherence in systems without degenerate Bohr frequencies. When the Bohr frequencies are degenerate, the scattering map now couples their coherences and is given by

$$(\rho'_Y)_{j'k'} = \sum_{\substack{jk: \\ \Delta_{j'k'}=\Delta_{jk}}} \mathbb{S}^{jk}_{j'k'}(\rho_Y)_{jk}. \tag{35}$$

If the incoming wave packet is narrow, repeated collisions will nonetheless decohere system Y. Indeed, using Eq. (30) and the Cauchy-Schwarz inequality, we find $|\mathbb{S}^{jk}_{j'k'}|^2 \leq P^L_{j'j}(E_{p_0}+e_j)P^L_{k'k}(E_{p_0}+e_k)$ and therefore

$$|(\rho'_Y)_{j'k'}| \leq \sum_{\substack{jk: \\ \Delta_{j'k'}=\Delta_{jk}}} |(\rho_Y)_{jk}|\sqrt{P^L_{j'j}(E_{p_0}+e_j)P^L_{k'k}(E_{p_0}+e_k)}, \tag{36}$$

with the sum over j and k restricted by the condition $\Delta_{j'k'} = \Delta_{jk}$. Since $\sqrt{P^L_{j'j}(E_{p_0}+e_j)P^L_{k'k}(E_{p_0}+e_k)} \leq 1$, the last expression shows that the amount of coherence between a pair of levels after the collision is generally smaller than the total amount of coherence present before the collision.

In summary, we find that decoherence is generic for systems with nondegenerate levels. Coupling between

eigenbasis coherences and populations is only possible if the energy spectrum displays degeneracies, in which case it occurs within the degenerate subspace. Since in that subspace the eigenenergy basis is arbitrary, the notion of decoherence becomes ill defined. These findings are reminiscent of those obtained using quantum master equations describing a system in weak contact with a thermal reservoir in theory of open quantum systems [3,13].

B. Broad wave packets

If the momentum width of the wave packet is large enough, the map $\mathbb{S}$ is more complex and can keep and create coherences. For example, suppose that condition (22) is satisfied for $k = j$ and some $j' \neq k'$, i.e.,

$$\Delta p > \frac{m|\Delta_{j'j} - \Delta_{k'j}|}{2p_0}. \tag{37}$$

In this case, the term $\mathbb{S}^{jj}_{j'k'}$ is different from zero. If the system is initially in the pure state $\rho_Y = |j\rangle\langle j|$ then, after the collision, we have

$$(\rho'_Y)_{j'k'} = \mathbb{S}^{jj}_{j'k'} \neq 0, \tag{38}$$

that is, a nonzero coherent or off-diagonal term.

Therefore, broad wave packets can induce coherences in a system initially diagonal in the energy basis, even for inelastic collisions. This is one of our main results, which may seem unexpected at first sight, since inelastic collisions are usually associated to thermalization or decoherence. In the case of broad packets, the origin of the coherence is that after the collision, the global state is of the form given by Eq. (24), where system Y is entangled with nonorthogonal states of system X, namely, the overlapping outgoing wave packets. Consequently, the partial trace over system X, which fully describes system Y, exhibits coherences that remain no matter the fate of those outgoing wave packets. In Sec. VII, we explore this crucial phenomenon and its contrast with the case of narrow packets in specific examples.

V. ENSEMBLES OF WAVE PACKETS AND THERMALIZATION

In this section we consider that the initial state of X is given by a statistical ensemble of wave packets and discuss sufficient conditions that lead to thermalization for system Y. Here, we assume that $[H_Y, \nu] \neq 0$ to ensure that $[S, \mathbb{I}_X \otimes \nu] \neq 0$, otherwise the scattering process induces transitions only between the (common) eigenstates of H_Y and ν with different eigenvalues, ruling out the possibility of thermalization of Y by repeated collisions.

The first condition for thermalization is that the ensemble consists of narrow wave packets. As we have just seen, narrow wave packets lead to decoherence while broad ones induce coherences even if the initial state of the system is diagonal in the energy basis. This remains true for an ensemble of packets described by a density matrix, as we illustrate in the examples of Sec. VII.

A. Microreversibility

The second condition is microscopic reversibility, that is, the invariance of the scattering operator under time reversal. In quantum mechanics, time reversal is implemented by an antiunitary operator T, which changes the sign of all momenta and other odd magnitudes under time reversal, like angular momentum, spin, and the magnetic field. It takes different forms, depending on the system. For instance, for a spinless point particle, T is the conjugation of the wave function in position representation: $\langle x|\mathsf{T}|\psi\rangle = \langle x|\psi\rangle^*$. In the momentum representation, on the other hand, the operator changes the sign of the momenta: $\langle p|\mathsf{T}|\psi\rangle = \langle -p|\psi\rangle$. If the free and the total Hamiltonian commute with $\mathsf{T} = \mathsf{T}_X \otimes \mathsf{T}_Y$, where T_X and T_Y are the time-reversal operators acting on the Hilbert space of X and Y, then the scattering operator also commutes with T and the collision is invariant under time reversal. For simplicity, we assume here that the eigenstates of H_Y are also invariant, that is, $\mathsf{T}_Y|j\rangle = |j\rangle$. In this case, the scattering matrix obeys the following symmetry relation:

$$s^{(\alpha'\,\alpha)}_{j'j}(E) = s^{(-\alpha\,-\alpha')}_{jj'}(E) \tag{39}$$

or equivalently $\hat{\mathbf{r}}^L = (\hat{\mathbf{r}}^L)^t$, $\hat{\mathbf{r}}^R = (\hat{\mathbf{r}}^R)^t$, and $\hat{\mathbf{t}}^L = (\hat{\mathbf{t}}^R)^t$, where $(\cdot)^t$ stands for transpose [12,14,15]. In other words, Eq. (10) is a symmetric matrix.

In our previous discussion, we considered only particles incident from the left. This setting is not time-reversal invariant. To satisfy microscopic reversibility, we have to consider particles coming from both left and right, as shown schematically in Fig. 2. That is, for every wave packet $|\phi_{p_0,x_0}\rangle$ in the ensemble, centered around the momentum $p_0 > 0$ and coming from the left ($x_0 < 0$), there must be a $|\phi_{-p_0,-x_0}\rangle$ centered around momentum $-p_0 < 0$ and coming from the right ($-x_0 > 0$). For narrow wave packets, the position x_0 becomes irrelevant and we omit it from the notation. With these ideas in mind, we consider a symmetric ensemble defined by the probability distribution $\mu(p_0)$, normalized in $[0, \infty)$:

$$\rho_X = \int_0^\infty dp_0 \frac{\mu(p_0)}{2}(|\phi_{p_0}\rangle\langle\phi_{p_0}| + |\phi_{-p_0}\rangle\langle\phi_{-p_0}|). \tag{40}$$

Inserting this incoming state into Eq. (16), and taking into account that all the packets are narrow, one obtains

$$\mathbb{S}^{jj}_{j'j'} = \int dp_0 \frac{\mu(p_0)}{2}\left[P^L_{j'j}(E_{p_0} + e_j) + P^R_{j'j}(E_{p_0} + e_j)\right], \tag{41}$$

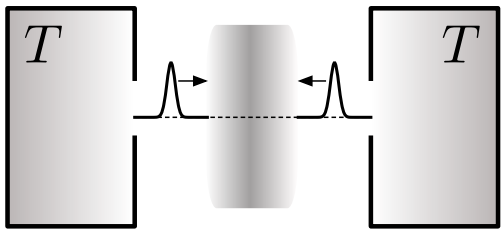

FIG. 2. Thermalization via collisions is achieved if the system (scatterer) is bombarded by narrow wave packets coming from equilibrium reservoirs at the two sides. If we remove one of the reservoirs, the setup is out of equilibrium. Notice however that, if the scatterer is symmetric, that is, if the interaction potential $V(x)$ is even, $V(x) = V(-x)$, then the second reservoir is not necessary.

where the integral over p_0 runs over all positive values satisfying $E_{p_0} \geq \Delta_{j'j}$. Recall that $P^L_{j'j}(E)$ is given by Eq. (11) and similarly for $P^R_{j'j}(E)$. To simplify the notation, we define

$$P_{j'j}(E) = \frac{P^L_{j'j}(E) + P^R_{j'j}(E)}{2} \tag{42}$$

and replace it in Eq. (41), which becomes

$$\mathbb{S}^{ij}_{j'j'} = \int dp_0\, \mu(p_0) P_{j'j}(E_{p_0} + e_j). \tag{43}$$

Let us recall that the energy in the argument of $P_{j'j}(E)$ is such that the scattering channel $|j\rangle \to |j'\rangle$ is open. Finally, from the definition of the transition probabilities in Eq. (11) and the microreversibility condition (39), we obtain

$$\begin{aligned} P^L_{j'j}(E) + P^R_{j'j}(E) &= P^L_{jj'}(E) + P^R_{jj'}(E) \\ \Rightarrow \quad P_{j'j}(E) &= P_{jj'}(E). \end{aligned} \tag{44}$$

B. Detailed balance and thermalization

A third condition for the thermalization of the system Y is that the statistics of the narrow wave packets X is thermal. We show below that, in this case, the map that evolves the populations obeys the detailed balance condition, ensuring thermalization.

According to the discussion in Ref. [16] we take $\mu(p_0) = \mu_{\rm eff}(p_0)$ with

$$\mu_{\rm eff}(p) = \beta \frac{p}{m} e^{-\beta p^2/2m} \tag{45}$$

the effusion distribution, in which case Eq. (43) satisfies the detailed balance relation

$$\mathbb{S}^{ij}_{j'j'} e^{-\beta e_j} = \mathbb{S}^{j'j'}_{jj} e^{-\beta e_{j'}}. \tag{46}$$

To prove it, let us compute the left-hand side using Eq. (43), Eq. (18), and the change of variable $E = E_{p_0} + e_j$:

$$\begin{aligned} \mathbb{S}^{ij}_{j'j'} e^{-\beta e_j} &= \int_{p_{\rm inf}}^{\infty} dp_0 \frac{\beta\, p_0}{m} e^{-\beta(E_{p_0}+e_j)} P_{j'j}(E_{p_0} + e_j) \\ &= \beta \int_{\max\{e_j, e_{j'}\}}^{\infty} dE\, e^{-\beta E} P_{j'j}(E), \end{aligned} \tag{47}$$

where $p_{\rm inf}$ is $\sqrt{2m\Delta_{j'j}}$ if $\Delta_{j'j} > 0$ and zero otherwise. Similarly, the right-hand side of Eq. (46) reads

$$\begin{aligned} \mathbb{S}^{j'j'}_{jj} e^{-\beta e_{j'}} &= \int_{p_{\rm inf}}^{\infty} dp_0 \frac{\beta\, p_0}{m} e^{-\beta(E_{p_0}+e_{j'})} P_{jj'}(E_{p_0} + e_{j'}) \\ &= \beta \int_{\max\{e_{j'}, e_j\}}^{\infty} dE\, e^{-\beta E} P_{jj'}(E), \end{aligned} \tag{48}$$

where now $p_{\rm inf}$ is $\sqrt{2m\Delta_{jj'}}$ if $\Delta_{jj'} > 0$ and zero otherwise. Both integrands are the same because time-reversal symmetry implies $P_{j'j}(E) = P_{jj'}(E)$. Hence, the detailed balance equality Eq. (46) is satisfied, which, in turn, guarantees the thermalization of system Y, that is, after a number of collisions the system reaches the thermal state $\rho_Y = \exp[-\beta H_Y]/Z_Y$ with $Z_Y = \mathrm{Tr}(\exp[-\beta H_Y])$.

Notice that if, on the other hand, we take the Maxwell-Boltzmann distribution $\mu(p_0) = \sqrt{\beta/(2m\pi)}\exp[-\beta p_0^2/(2m)]$ in Eq. (43), $(\mathbb{S}_Y)^{jj}_{j'j'}$ does not satisfy detailed balance and the map does not thermalize the system Y. The physical reason is that particles escaping from a small hole in a thermal box are distributed in momentum according to the effusion distribution, which is the Maxwell-Boltzmann distribution weighted with a flux factor. See Ref. [16] for a detailed discussion of this subtle issue.

We end this section with two remarks. First, if the potential $V(x)$ has the spatial symmetry $x \to -x$, then $\hat{\mathbf{r}}^L = \hat{\mathbf{r}}^R$ and $\hat{\mathbf{t}}^L = \hat{\mathbf{t}}^R$, and $P^L_{j'j}(E) = P^R_{j'j}(E)$. The spatial reflection symmetry $x \to -x$ plus time-reversal symmetry, Eq. (44), imply $P^L_{j'j}(E) = P^L_{jj'}(E)$. In this case, detailed balance (and therefore thermalization) is satisfied with just left (or right) incoming wave packets.

Second, we see that the narrow packets destroy coherences in the eigenbasis of H_Y. Consequently, once the diagonal state is reached, the unitary free evolution between collisions present in Eq. (5) does not change the density matrix ρ_Y. We conclude that narrow wave packets induce thermalization independently of the time intervals between collisions, which can be either random or deterministic.

C. Entropy production

The evolution of populations $p_j \equiv (\rho_Y)_{jj}$ in system Y is ruled by the discrete-time stochastic master equation

$$p'_j = \sum_k \mathbb{W}_{jk} p_k, \tag{49}$$

where $\mathbb{W}_{jk} \equiv \mathbb{S}^{kk}_{jj}$ satisfies $\sum_j \mathbb{W}_{jk} = 1$ and detailed balance $\mathbb{W}_{jk} e^{-\beta e_k} = \mathbb{W}_{kj} e^{-\beta e_j}$. This allows the identification of the average energy change of Y with heat, i.e., $\Delta S \geq \beta \Delta E$ where the entropy $S \equiv -\sum_j p_j \ln p_j$ is given by the Shannon entropy associated to system Y, and $E = \sum_j e_j p_j$ its average energy, as shown in Ref. [17] (see also Refs. [18,19]). The energy change is determined by

$$Q \equiv \Delta E = \sum_j e_j (p'_j - p_j) = \sum_{j,k} e_j (\mathbb{W}_{jk} - \delta_{jk}) p_k \tag{50}$$

that we denote Q, anticipating its interpretation as heat. We now consider the change in the Shannon entropy of the system Y

$$\Delta S = \sum_j (p_j \ln p_j - p'_j \ln p'_j) = \beta Q + \Sigma \tag{51}$$

that we split into two contributions. The first one is the entropy flow given by

$$\beta Q = -\sum_{j,k} \mathbb{W}_{jk} p_k \ln \frac{\mathbb{W}_{jk}}{\mathbb{W}_{kj}}, \tag{52}$$

where we used the detailed balance condition $\ln(\mathbb{W}_{jk}/\mathbb{W}_{kj}) = -\beta(e_j - e_k)$ for the identification with Eq. (50). The second one is the entropy production given by

$$\Sigma = \sum_{j,k} \mathbb{W}_{jk} p_k \ln \frac{\mathbb{W}_{jk} p_k}{\mathbb{W}_{kj} p'_j}. \tag{53}$$

This quantity is non-negative as can be shown using Jensen inequality. Indeed, since $-\ln x \geq x - 1$,

$$\Sigma \geq \sum_{j,k} \mathbb{W}_{jk} p_k \left(\frac{\mathbb{W}_{kj} p'_j}{\mathbb{W}_{jk} p_k} - 1 \right) = \sum_{j,k} \left(\mathbb{W}_{kj} p'_j - \mathbb{W}_{jk} p_k \right) = 0. \tag{54}$$

When the system reaches equilibrium, i.e., when $p_j = p'_j = \exp[-\beta e_j]/Z_Y$, we have $\Sigma = 0$.

VI. EXTENSION TO PARTICLES WITH INTERNAL STRUCTURE

We briefly comment on the statement from the introduction that if the incoming particle has an internal structure and its state is of the form $\rho_X \otimes \rho_\chi$ with ρ_X associated to the translation degree of freedom and ρ_χ to the internal structure, the effective system Y comprises χ and the fixed scatterer, here called Υ. The effective system Y before the collision has a state $\rho_Y = \rho_\chi \otimes \rho_\Upsilon$ and the effective Hamiltonian is $H_Y = H_\chi + H_\Upsilon$, with H_χ the Hamiltonian associated to the internal degrees of freedom of the traveling particle and H_Υ that of the fixed scatterer. Narrow wave packets (with respect to the smallest level spacing of Y) induce decoherence in Y, and thus also in χ and Υ. Thermalization of Υ after many collisions still holds if ρ_X is a thermal ensemble of wave packets and the internal structure of the particle is also thermal, i.e., $\rho_\chi \sim \exp[-\beta H_\chi]$. This follows from the detailed balance property of $\mathbb{S}^{jj}_{j'j'}$. The index j stands now for the pair (x, y) where x indexes the eigenvalues and eigenstates of H_χ and y those from H_Υ. Due to the product structure of the state of Y prior to the collision, the population of Y evolves with the equation $P_{\mathsf{x}'\mathsf{y}'} = \sum_{\mathsf{xy}} \mathbb{S}^{(\mathsf{xy})(\mathsf{xy})}_{(\mathsf{x}'\mathsf{y}')(\mathsf{x}'\mathsf{y}')} \exp[-\beta\epsilon_\mathsf{x}] P_\mathsf{y}$ and the reduced dynamics for the populations of Υ is given by $P_{\mathsf{y}'} = \sum_\mathsf{y} \mathbb{R}^\mathsf{y}_{\mathsf{y}'} P_\mathsf{y}$ with the reduced stochastic map $\mathbb{R}^\mathsf{y}_{\mathsf{y}'} = \sum_{\mathsf{xx}'} \mathbb{S}^{(\mathsf{xy})(\mathsf{xy})}_{(\mathsf{x}'\mathsf{y}')(\mathsf{x}'\mathsf{y}')} \exp[-\beta\epsilon_\mathsf{x}]$ also satisfying detailed balance and thus inducing thermalization of Υ.

VII. APPLICATIONS

In this section, we illustrate in simple models the results previously obtained. We consider a system Y with finite dimension N, i.e., $H_Y = \sum_{j=1}^N e_j |j\rangle\langle j|$ interacting with X via the coupling $V(x) \otimes \nu$ in Eq. (1) with $V(x) = g\delta(x)$ being a Dirac δ potential with strength parameter g. The scattering problem is solved in Appendix B. Since the potential is symmetric under the spatial inversion $x \to -x$, the transmission and reflection matrices from the left equal those from the right, i.e., $\hat{\mathbf{r}}^L(E) = \hat{\mathbf{r}}^R(E) \equiv \hat{\mathbf{r}}(E)$ and $\hat{\mathbf{t}}^L(E) = \hat{\mathbf{t}}^R(E) \equiv \hat{\mathbf{t}}(E)$. The resulting scattering matrix in Eq. (10) is given by

$$\hat{t}_{j'j} = \sqrt{\frac{p_{j'}}{p_j}} t_{j'j} \quad \text{and} \quad \hat{r}_{j'j} = \sqrt{\frac{p_{j'}}{p_j}} (\delta_{j'j} - t_{j'j}), \tag{55}$$

with $1 \leq j, j' \leq N_{\text{open}}(E)$, where $N_{\text{open}}(E) = \#\{e_{j'} \leq E\}$, the number of levels with energy smaller than E, $p_j = \sqrt{2m(E - e_j)}$ and $t_{j'j}$ are the elements of the $N \times N$ matrix

$$\mathbf{t} = \left[\mathbb{I} + \frac{img}{\hbar^2} \mathbb{D}^{-1} \mathbb{V} \right]^{-1}. \tag{56}$$

In Eq. (56), the matrix $\mathbb{D}$ is diagonal with $\mathbb{D}_{jj} = p_j/\hbar$ and $\mathbb{V}$ the matrix with elements $\mathbb{V}_{kj} = \langle k| \nu |j\rangle$. We take in the following numerical examples $\hbar = g = 1$.

A. Narrow and broad wave packets

We first illustrate the role of the width of the wave packet, i.e., the transition from narrow to broad wave packets. For this, the simplest is to investigate a two-level

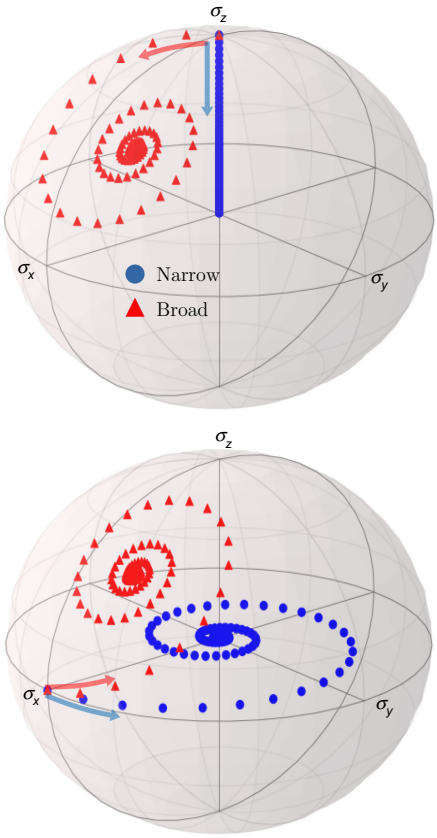

FIG. 3. Bloch sphere representation of the state $\rho_Y^{(n)}$ under repeated collisions ($n = 200$) with narrow and broad Gaussian wave packets (blue circles and red triangles, respectively). The colored arrows show the direction of the evolution of each state in the sphere starting from the initial states, which are pure (i.e., they lie on the surface of the sphere) and given by $(\rho_Y)_{11}^{(0)} = 1$ and $(\rho_Y)_{12}^{(0)} = 0$ (upper panel) and $(\rho_Y)_{11}^{(0)} = (\rho_Y)_{12}^{(0)} = 0.5$ (lower panel). All parameters are identical in the two panels, $\Delta_Y = m = 1, p_0 = 10$, except the widths, which are $\sigma/(m\Delta_Y/2p_0) = 0.2$ for narrow wave packets and $\sigma/(m\Delta_Y/2p_0) = 20$ for broad wave packets.

system Y. Let us remind that, according to Eq. (29), a Gaussian wave packet is considered to be narrow if $\sigma \ll m\Delta_Y/2p_0$ with $\Delta_Y = e_2 - e_1$. We take $\mathbb{V} = \sigma^x + \sigma^z$ (the Pauli matrices) in Eq. (56) and compute the map $\mathbb{S}$ according to Eq. (16). Between collisions, we simply take $\mathcal{E}_{\tau_n}$ as the identity for all n.

The results are shown in Fig. 3, where we plot the state in the Bloch sphere representation according to $\rho_Y = (\mathbb{I} + \vec{P}\cdot\vec{\sigma})/2$ and $\vec{P}$ is the polarization vector. We take two initially pure states (lying on the surface of the sphere), one being in an excited state and the other in a superposition of ground and excited states (Fig. 3, upper and lower panel, respectively).

Collisions with narrow wave packets lead to decoherence of Y for both initial states; see the blue dots converging to the invariant state in the z axis near the center of the sphere as the scattering map is iterated. The populations of the invariant state can be computed by evaluating the invariant state of Eq. (32). For the two-level system under consideration, the scattering matrix $\mathbf{s}(E)$ depends only weakly on E and therefore $P^L_{j'j}(E_{p_0} + e_j) \approx P^L_{j'j}(E_{p_0})$ for all $j'j$ in Eq. (32). Since $P^L_{j'j}(E)$ is a bistochastic matrix, the invariant state of Eq. (32) is very close to the maximally mixed state. In Fig. 3, upper panel, we see (blue dots) that a state, which is initially diagonal in the energy basis, remains diagonal throughout the evolution, i.e., its dynamics is confined to the z axis. In Fig. 3, lower panel, an initial superposition state with an equal amount of populations decoheres and changes its populations in an almost negligible way as it spirals towards the invariant state. Conversely, *collisions with broad wave packets* transfer coherences to an initially diagonal state (which leaves the z axis) and couple the populations and coherences of an initial superposition state (which quickly leaves the x-y plane). For such broad wave packets, the system evolves towards a steady state with coherences (red triangles in Fig. 3).

We finish this subsection by discussing the role played by adding a free system evolution of fixed time τ between the collisions with the wave packets. This time may correspond to integer or noninteger number of periods of the free evolution $T \equiv 2\pi\hbar/(\Delta_Y)$. From Eq. (5), the map $\mathcal{E}_{\tau_n}$ is the identity in the former case. Figure 4 shows the populations (left panel), modulus (middle panel), and phase of coherences (last panel), for $\tau = 0$ (no free evolution) and $\tau = 3T/4$, when considering both narrow and broad wave packets. For narrow wave packets, we observe that the free evolution does not affect the system populations. This is expected since populations do not evolve under free evolution and are decoupled from coherences during collisions. The free evolution also leaves the modulus of the coherences unchanged and only changes their phase, but eventually coherence will vanish due to the collisions. Turning to broad wave packets, we note that adding a free evolution between collisions modifies the evolution of populations and coherences in a significant way. Collisions in this case can induce coherences in the system and couple them to populations. With or without free evolution, the steady state displays coherences, although less in the former case. It is interesting to note that broad wave packets with free evolution display results quite close (but not identical) to narrow packets. To summarize, the results drawn in the previous sections for narrow and broad wave packets are still valid when free evolution is included. The effect of the free evolution on ensembles of broad wave packets is illustrated in Sec. VII C.

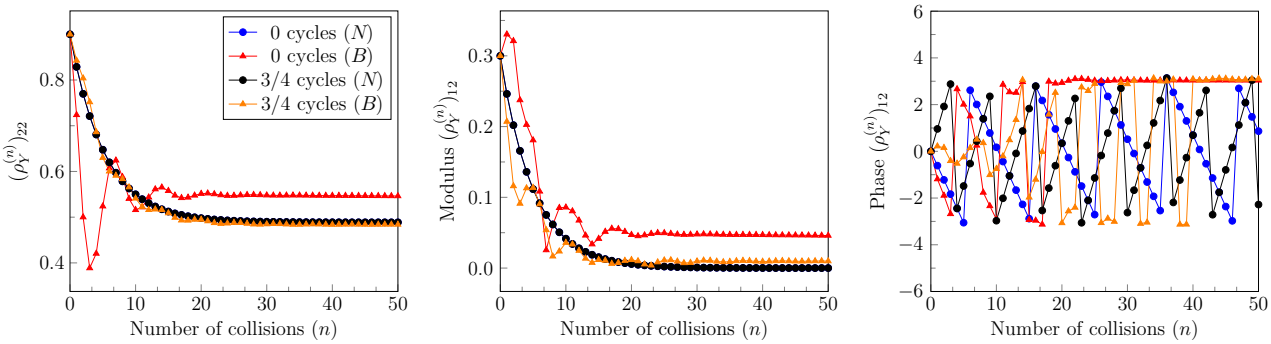

FIG. 4. Effect of free evolution between collisions on the populations (left panel), modulus and phase of coherences (middle and right panel, respectively) for a two-level system colliding with narrow (N) and broad (B) Gaussian wave packets. The system evolves freely for 0 or 3/4 cycles between each collision. The initial state is $(\rho_Y)^{(0)}_{22} = 0.9$ and $(\rho_Y)^{(0)}_{11} = 0.1$, $(\rho_Y)^{(0)}_{12} = 0.3$. The remaining parameters are $\Delta_Y = m = 1$, $p_0 = 6.3$, and $\sigma/(m\Delta_Y/2p_0) = 0.12$ for narrow wave packets and $\sigma/(m\Delta_Y/2p_0) = 12$ for broad wave packets.

B. Thermalization

In this section, we explore the dynamics of system Y under repeated collisions with narrow wave packets as described in Sec. V. In particular, we aim to illustrate the thermalization property observed with $\mathbb{S}^{ij}_{j'j'}$ in Eq. (43) when $\mu = \mu_{\text{eff}}$.

For that purpose, we take a system Y of dimension 5 and energy spectrum is $\{e_j = j^2\}_{j=1}^5$, which has nondegenerate Bohr frequencies. As coupling matrix $\mathbb{V}$, we take

$$\mathbb{V} = \begin{pmatrix} 0 & 1 & 0 & 1 & 0 \\ 1 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \\ 1 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \end{pmatrix}. \tag{57}$$

To check whether the collisions induce the thermalization of system Y, we evaluate the quantities

$$\mathsf{B}^{(n)}_{jk} \equiv -\frac{1}{e_j - e_k} \ln \frac{(\rho_Y^{(n)})_{jj}}{(\rho_Y^{(n)})_{kk}}, \tag{58}$$

where $\rho_Y^{(n)} = \mathbb{S}^n \rho_Y^{(0)}$ and $\rho_Y^{(0)}$ is the initial state. Since we are interested in the evolution of the populations, the free evolution of system Y between collisions does not play a role. If as n grows, the system Y approaches a thermal distribution $\exp[-\beta H_Y]/Z_Y$, then all $\mathsf{B}^{(n)}_{jk}$ converge to β. We see in Fig. 5 that, when the wave packets are weighted with the effusion distribution μ_{eff} in Eq. (45), the system Y thermalizes (upper panel). On the other hand, if they are weighted with the Maxwell-Boltzmann distribution $\mu \propto \exp[-\beta p^2/2m]$ (lower panel), the stationary state is not thermal. The evolution of coherences are also tracked (but not depicted) and observed to decay exponentially, as predicted.

C. Ensemble of broad wave packets

To complement our analysis, we consider here a mixture of broad wave packets, each being weighted according to the effusion distribution μ_{eff}. Despite the fact that incident particles have the same distribution of velocities as classical particles effusing from a gas at equilibrium, we see that the system Y does not thermalize. To illustrate this, we consider again a two-level system Y. The condition for a narrow packet for incident momentum p_0 is Eq. (29). Since the effusion distribution has its maximum at $p_{\max} = \sqrt{m/\beta}$, to satisfy the condition of broad wave packet for most of the incident particles we set the width of the packet as $\sigma > \Delta_Y\sqrt{m\beta}/2$.

In the upper panel of Fig. 6, we plot the iteration of $\mathbb{S}$ and observe that, despite the thermal distribution of the average velocities of the wave packets, the asymptotic state of Y is not thermal and in fact develops coherences that were absent in the initial state. In the lower panel of Fig. 6, we consider the iteration in Eq. (5) with the times τ_i drawn from a random distribution with Poissonian statistics. While this partially decoheres the system's state, the populations do not approach their thermal value (orange straight lines). Instead, they fluctuate near a value determined by the stationary state of the map for the populations, i.e., the master equation with $\mathbb{W}_{j'j} = \mathbb{S}^{jj}_{j'j'}$ where

$$\mathbb{S}^{jj}_{j'j'} = \int dp\, \rho_X(p,p) 2P_{j'j}(E_p + e_j). \tag{59}$$

Here $P_{j'j}(E)$ are the transition probabilities defined in Eq. (42) and $\rho_X(p,p)$ is the diagonal part of the density matrix of Gaussian wave packets Eq. (28) weighted with

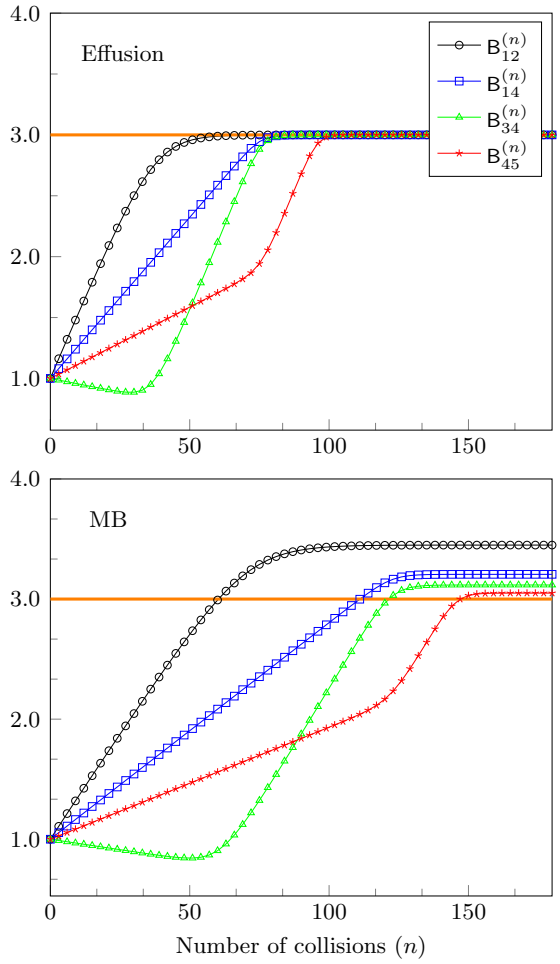

FIG. 5. Plot of $\mathsf{B}^{(n)}_{jk}$ defined in Eq. (58) computed for an ensemble of narrow Gaussian wave packets weighted by the effusion distribution in Eq. (45) and the Maxwell-Boltzmann (MB) distribution (upper and lower panel, respectively) with $\beta = 3$. In both cases, the initial state is the thermal state $e^{-\beta' H_Y}/Z_Y$ with $\beta' = 1$ and the mass of the wave packet is $m = 0.5$. The orange line corresponds to $\beta = 3$. For clarity, not all pairs of indices (j,k) are plotted.

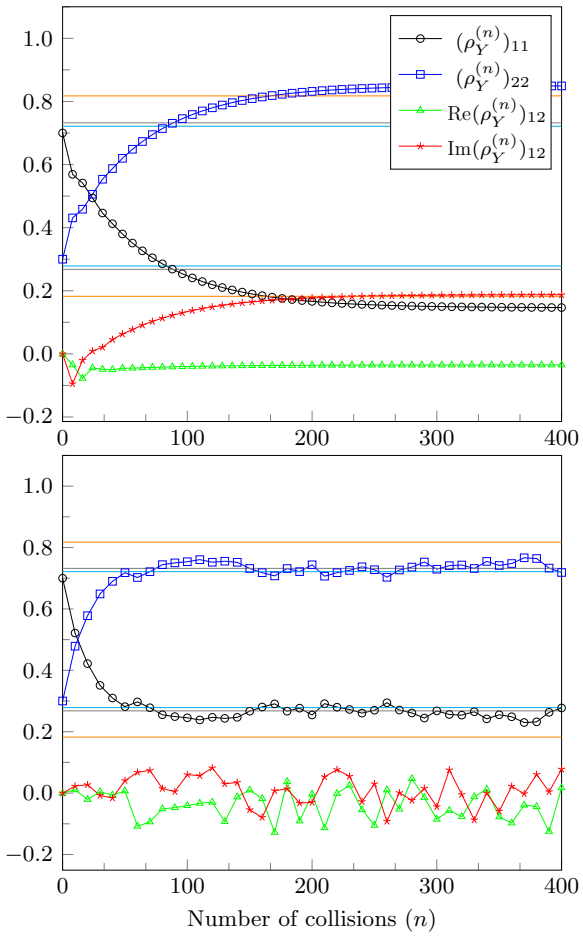

FIG. 6. Evolution of $\rho^{(n)}_Y$ when the state of X is a mixture of broad Gaussian wave packets weighted with the effusion distribution. Upper panel: The values $(\rho_Y)^{(n)}_{ij}$ are obtained by composing the map $\mathbb{S}_Y$. In black we depict $(\rho_Y)^{(n)}_{11}$ and $(\rho_Y)^{(n)}_{22}$ in blue, while the real and imaginary parts of $(\rho_Y)^{(n)}_{12}$ are depicted in green and red, respectively. Lower panel: The iterated map is given in Eq. (5) with random Poissonian times τ_i. In both panels: The orange lines indicates the thermal values $(\rho_Y)_{11}$ and $(\rho_Y)_{22}$ with inverse temperature β. The light blue lines indicate the thermal values $(\rho_Y)_{11}$ and $(\rho_Y)_{22}$ with inverse temperature β_C. The gray lines indicate the values $(\rho_Y)_{11}$ and $(\rho_Y)_{22}$ computed by considering the master equation for the populations ruled by $\mathbb{W}_{ik} = \mathbb{S}^{kk}_{ii}$ as given in Eq. (59). The initial state is $(\rho_Y)^{(0)}_{11} = 0.3$ and $(\rho_Y)^{(0)}_{12} = 0$. The remaining parameters are $\Delta_Y = m = 0.5$ with $e_2 = 2.5, e_1 = 2, \sigma = 0.31$ and $\beta = 3$.

the effusion distribution μ_{eff} Eq. (45). A cumbersome but straightforward calculation yields

$$\rho_X(p,p) = \frac{\beta_C}{m}\left[\frac{\sigma}{\sqrt{2\pi}} e^{-\frac{p^2}{2\sigma^2}} + \frac{p}{2\sqrt{r}}\,\mathrm{erf}\left(\frac{p}{\sqrt{2r}\sigma}\right) e^{-\beta_C \frac{p^2}{2m}}\right], \tag{60}$$

with

$$r = 1 + \frac{\beta\sigma^2}{m}, \quad \beta_C = \frac{\beta}{r}. \tag{61}$$

The map for the populations given by Eq. (59) does not satisfy detailed balance if σ is not negligible, implying that the system does not thermalize when bombarded by these broad packets. It is interesting to notice that the diagonal part, Eq. (60), behaves like an effusion distribution with a temperature β_C for $p \gg \sigma$. As shown in the lower panel of Fig. 6, for Poissonian collision times the system reaches an effective temperature close to β_C.

Notice, however, that the broad or narrow packet condition depends on Δ_Y, that is, on the energy spectrum of the system. Hence, the same ensemble of packets used for

Fig. 6 will thermalize the system to the temperature of the ensemble β if the level spacing Δ_Y is large enough. One can even induce a crossover from narrow to broad wave packets by decreasing Δ_Y.

VIII. CONCLUSIONS

We consider a quantum scattering process between a massive particle X described by a wave packet and a static system Y and study the resulting quantum map on Y. We find that the properties of the map strongly depend on the properties of the wave packet. For wave packets whose energy width is smaller than the smallest energy-level spacing (narrow wave packet), eigenstate populations and coherences decouple from each other if Y is nondegenerate and the latter decay. Instead, for broad wave packets, populations and coherences couple and influence each other. Our central finding is that thermal ensembles of wave packets, i.e., narrow wave packets distributed with the effusion probability distribution function, induce decoherence and thermalization in Y.

Our results strongly suggest that the distinction between narrow and broad packets could be observable in certain situations, like the interaction between single atoms and a single electromagnetic mode in cavity-QED experiments. Since the broadness of the packet depends on the level spacing Δ_Y, one could tune Δ_Y to measure the width of the packets and explore the wave-particle duality of atoms and molecules escaping by effusion from a gas in thermal equilibrium.

The scattering framework that we propose here is very rich and opens many interesting perspectives for the future. We are particularly interested in using it as a basis for a quantum thermodynamics formulation. Indeed, our present scattering approach avoids many difficulties encountered using other formulations as it is formally exact, autonomous, and the interaction energy is naturally vanishing before and after the collisions.

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APPENDIX A: SCATTERING THEORY

The main goal of scattering theory is to obtain the scattering operator S, which is a one-to-one map between free (incoming) states before the collision to free (outgoing) states after the collision. Whether or not such an operator exists depends on the dynamics during the collision through the interaction potential, which in general can support states that are either free or bound to the interaction region for very long times. However, its existence is guaranteed for a large class of potentials $V(x)$, which vanish fast enough at infinity. In this case, the Hilbert space $\mathcal{H}$ of the full system can be expressed as a direct sum of two mutually orthogonal subspaces $\mathcal{H} = \mathcal{S} \oplus \mathcal{B}$, where $\mathcal{S}$ and $\mathcal{B}$ are the subspaces of scattering and bound states [12,14,20,21].

According to their definition (2), the Møller operators are isometries of $\mathcal{H}$, i.e., they map state vectors onto the subset of scattering states $\Omega_\pm : \mathcal{H} \mapsto \mathcal{S}$ while preserving the norm $\langle\psi|\Omega_\pm^\dagger\Omega_\pm|\psi\rangle = \langle\psi|\psi\rangle\,, \forall\,|\psi\rangle \in \mathcal{H}$. The isometric property reads $\Omega_\pm^\dagger\Omega_\pm = \mathbb{I}$. Note that a unitary operator is necessarily an isometry, but the reverse is not true. For instance, here the "inverse" Møller operator $\Omega_\pm^\dagger$ acts only on scattering states $\Omega_\pm^\dagger : \mathcal{S} \mapsto \mathcal{H}$, and one has $\Omega_\pm\Omega_\pm^\dagger = \mathbb{I} - P_\mathcal{B}$, with $P_\mathcal{B}$ the projector onto the space $\mathcal{B}$ of bound states. The Møller operators define the scattering operator according to Eq. (3) in the main text. Its unitarity follows from the fact that $\Omega_\pm$ have the same range $\mathcal{S}$, a property called asymptotic completeness [12,14,20,21].

Some relevant properties of these operators are derived in the next sections.

1. Intertwinning relation

One of the main properties of the Møller operators $\Omega_\pm$ is the so-called intertwining relation:

$$H\Omega_\pm = \Omega_\pm H_0. \tag{A1}$$

The proof follows from the definition of the Møller operators in Eq. (2)

$$\begin{aligned} e^{iH\tau/\hbar}\,\Omega_\pm &= e^{iH\tau/\hbar}\left[\lim_{t\to\mp\infty} e^{iHt/\hbar}e^{-iH_0t/\hbar}\right] \\ &= \lim_{t\to\mp\infty} e^{iH(t+\tau)/\hbar}e^{-iH_0(t+\tau)/\hbar}e^{iH_0\tau/\hbar} \\ &= \Omega_\pm\, e^{iH_0\tau/\hbar}. \end{aligned} \tag{A2}$$

Differentiating with respect to τ at $\tau = 0$, we obtain the desired result, Eq. (A1). By writing Eq. (A1) as $\Omega_\pm^\dagger H\Omega_\pm = H_0$, it is clear that such a transformation of the Hamiltonian H is not unitary, since it relates the full Hamiltonian containing the interaction with the free Hamiltonian, which has a different energy spectrum.

From the intertwinning relation, we can straightforwardly derive the important commutation property of the scattering operator

$$\begin{aligned} SH_0 &= \Omega_-^\dagger \Omega_+ H_0 = \Omega_-^\dagger H \Omega_+ \\ &= H_0 \Omega_-^\dagger \Omega_+ = H_0 S \quad \Rightarrow \quad [S, H_0] = 0, \end{aligned} \tag{A3}$$

which implies the conservation of the total energy in the scattering event and that the elements of the scattering operator in the eigenbasis of H_0, i.e., $\langle p', j' | S | p, j \rangle$, are proportional to $\delta(E_p + e_j - E_{p'} - e_{j'}) = \delta(E_p - E_{p'} - \Delta_{j'j})$, allowing us to write these terms as in Eq. (9).

Another important consequence of the interwinning relation is that, if $|p, j\rangle$ is an improper eigenstate of H_0 with energy $E = E_p + e_j = p^2/(2m) + e_j$, then $\Omega_\pm |p, j\rangle$ is an eigenstate of the full Hamiltonian H with the same energy:

$$H \Omega_\pm |p, j\rangle = \Omega_\pm H_0 |p, j\rangle = E \, \Omega_\pm |p, j\rangle . \tag{A4}$$

2. The *T* operator

A crucial tool in scattering theory are the resolvents or Green's operators associated to the free and the full Hamiltonian:

$$G_0(z) \equiv (z - H_0)^{-1}, \quad G(z) \equiv (z - H)^{-1} \tag{A5}$$

defined for any complex number z, which does not belong to the spectrum of H_0 and H, respectively. It is not hard to prove that these operators verify

$$\begin{aligned} G(z) &= G_0(z) + G_0(z) V G(z) \\ &= G_0(z) + G(z) V G_0(z). \end{aligned} \tag{A6}$$

We also define the T operator as

$$T(z) \equiv V + V G(z) V. \tag{A7}$$

Applying $G_0(z)$ to this equation and making use of Eq. (A6), we get

$$G_0(z) T(z) = G(z) V, \tag{A8}$$

which relates the two resolvents through the T operator and the interaction potential.

To relate the scattering and the T operator, we rewrite the Møller operators (2) as

$$\begin{aligned} \Omega_\pm &= 1 + \int_0^{\mp\infty} dt \, \frac{d}{dt} (e^{iHt/\hbar} \, e^{-iH_0 t/\hbar}) \\ &= - \lim_{\epsilon \to 0^+} \left[e^{\pm \epsilon t/\hbar} e^{iHt/\hbar} \, e^{-iH_0 t/\hbar} \right]_0^{\mp\infty} \\ &\quad + \lim_{\epsilon \to 0^+} \int_0^{\mp\infty} dt \, e^{\pm \epsilon t/\hbar} \frac{d}{dt} (e^{iHt/\hbar} \, e^{-iH_0 t/\hbar}) \\ &= \lim_{\epsilon \to 0^+} \mp \frac{\epsilon}{\hbar} \int_0^{\mp\infty} dt \, e^{\pm \epsilon t/\hbar} e^{iHt/\hbar} \, e^{-iH_0 t/\hbar}, \end{aligned} \tag{A9}$$

where integration by parts is used from the second to the third equality. Its action on the improper eigenstates of H_0 gives

$$\begin{aligned} \Omega_\pm |p, j\rangle &= \lim_{\epsilon \to 0^+} \mp \frac{\epsilon}{\hbar} \int_0^{\mp\infty} dt \, e^{-i(E \pm i\epsilon)t/\hbar} \, e^{iHt/\hbar} \, |p, j\rangle \\ &= \lim_{\epsilon \to 0^+} \pm i \, \epsilon \, G(E \pm i\epsilon) \, |p, j\rangle \\ &= |p, j\rangle + G(E \pm i0) V |p, j\rangle , \end{aligned} \tag{A10}$$

where $E = E_p + e_j = p^2/(2m) + e_j$ is the energy of the state $|p, j\rangle$ and we introduce the notation $f(z + i0) \equiv \lim_{\epsilon \to 0^+} f(z + i\epsilon)$. The second equality follows from a direct calculation of the integral in Eq. (A9), while the third is obtained using Eq. (A6) and $G_0(z) |p, j\rangle = (z - E)^{-1} |p, j\rangle$. Multiplying Eq. (A10) by V we get the useful expression

$$V \Omega_\pm |p, j\rangle = T(E \pm i0) |p, j\rangle . \tag{A11}$$

Recalling the representation of the Dirac δ, $\pi \delta(x) = \lim_{\epsilon \to 0^+} \mathrm{Im}(x - i\epsilon)^{-1}$, one can prove that Eq. (A10) implies the identity

$$\begin{aligned} (\Omega_+ - \Omega_-) |p, j\rangle &= [G(E + i0) - G(E - i0)] V |p, j\rangle \\ &= -2\pi i \delta(E - H) V |p, j\rangle . \end{aligned} \tag{A12}$$

The action of the scattering operator on an eigenstate of H_0 can now be computed from its definition (3) and Eq. (A12):

$$\begin{aligned} S |p, j\rangle &= \Omega_-^\dagger \Omega_+ |p, j\rangle \\ &= (1 + \Omega_-^\dagger (\Omega_+ - \Omega_-)) |p, j\rangle \\ &= |p, j\rangle - 2\pi i \Omega_-^\dagger \delta(E - H) V |p, j\rangle . \end{aligned} \tag{A13}$$

Closing the last expression with $\langle p', j'|$ and taking into account that $\Omega_- |p', j'\rangle$ is an eigenstate of H with eigenvalue $E_{p'} + e_{j'}$, we get

$$\langle p',j'|\,S\,|p,j\rangle = \delta_{j'j}\delta(p'-p) - 2\pi i\delta(E_p - E_{p'} - \Delta_{j'j})\,\langle p',j'|\,\Omega_-^\dagger V\,|p,j\rangle\,. \tag{A14}$$

We can eliminate the Møller operator using Eq. (A11) and the property $T^\dagger(z) = T(z^*)$, yielding $\langle p',j'|\,\Omega_-^\dagger V\,|p,j\rangle = \langle p',j'|\,T(E+i0)\,|p,j\rangle$. Inserting this last expression into Eq. (A14), one finally gets

$$\begin{aligned}\langle p',j'|\,S\,|p,j\rangle &= \delta_{j'j}\delta(p'-p) - 2\pi i\delta(E_p - E_{p'} - \Delta_{j'j}) \times \langle p',j'|T(E+i0)|p,j\rangle \\ &= \delta(E_p - E_{p'} - \Delta_{j'j})\left[\delta_{j'j}\delta_{\alpha'\alpha}\frac{|p|}{m} - 2\pi i\,\langle p',j'|T(E+i0)|p,j\rangle\right].\end{aligned} \tag{A15}$$

Comparing this expression with Eq. (9) and taking into account that $j' = j$ implies $|p'| = |p|$, we get

$$s_{j'j}^{(\alpha'\alpha)}(E) = \delta_{j'j}\delta_{\alpha'\alpha} - \frac{2\pi i m}{\sqrt{|pp'|}}\,\langle p',j'|T(E+i0)|p,j\rangle\,. \tag{A16}$$

In this way, we relate the entries of the scattering matrix **s** to the T operator. In the next section of this appendix, we relate the elements of the T operator to the transmission and reflection coefficients, which, in turn, can be computed by solving the stationary Schrödinger equation.

3. Scattering states

The previous definitions and relationships can be used to compute the T operator and the scattering operator S in specific situations. For this purpose, let us introduce the so-called scattering states $|p,j\rangle_+$ defined as

$$\begin{aligned}|p,j\rangle_+ \equiv \Omega_+\,|p,j\rangle &= |p,j\rangle + G(E+i0)V|p,j\rangle \\ &= |p,j\rangle + G_0(E+i0)T(E+i0)\,|p,j\rangle\,.\end{aligned} \tag{A17}$$

Here, we use Eqs. (A10) and (A8). We also use the following identity derived from Eqs. (A11) and (A17):

$$|p,j\rangle_+ = |p,j\rangle + G_0(E+i0)V|p,j\rangle_+\,. \tag{A18}$$

The scattering state $|p,j\rangle_+$ is an eigenstate of H with energy $E = E_p + e_j$ as shown in Eq. (A4). Moreover, the asymptotic behavior of its wave function in real space $\langle x|p,j\rangle_+$ contains all the necessary information to calculate the operators T and S. To prove this, we start by expressing Eq. (A18) in the position representation, using the plane wave introduced in Eq. (7):

$$\begin{aligned}\langle x|p,j\rangle_+ &= \frac{e^{ikx}}{\sqrt{2\pi\hbar}}\,|j\rangle + \int_{-\infty}^{\infty}dx'\int_{-\infty}^{\infty}dx''\,\langle x|G_0(E+i0)|x'\rangle\,\langle x'|V|x''\rangle\,\langle x''|p,j\rangle_+ \\ &= \frac{e^{ikx}}{\sqrt{2\pi\hbar}}\,|j\rangle + \int_{-\infty}^{\infty}dx'\,V(x')\,\langle x|G_0(E+i0)|x'\rangle\,v\,\langle x'|p,j\rangle_+\,,\end{aligned} \tag{A19}$$

with $k = p/\hbar$. The resolvent in position representation $G_0^+(x,x') \equiv \langle x|G_0(E+i0)|x'\rangle$ is an operator in $\mathcal{H}_Y$ that obeys the equation

$$\left[E - H_Y + \frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right]G_0^+(x,x') = \delta(x-x')\otimes\mathbb{I}_Y. \tag{A20}$$

The solution is

$$G_0^+(x,x') = \sum_{j'}\frac{m}{ik_{j'}\hbar^2}e^{ik_{j'}|x-x'|}\,|j'\rangle\,\langle j'|\,, \tag{A21}$$

with $k_{j'} = \sqrt{2m(E-e_{j'})}/\hbar$, as one can check by direct substitution. Inserting this expression in Eq. (A19), we get

$$\langle x|p,j\rangle_+ = \frac{e^{ikx}}{\sqrt{2\pi\hbar}}\,|j\rangle + \sum_{j'}\frac{m}{ik_{j'}\hbar^2}\,|j'\rangle\int_{-\infty}^{\infty}dx'e^{ik_{j'}|x-x'|}V(x')\,\langle j'|\,v\,\langle x'|p,j\rangle_+\,. \tag{A22}$$

We are interested in the asymptotic behavior of $\langle x|p,j\rangle_+$ far from the collision region. Consider first the case $p>0$ and $x\to-\infty$. Due to the presence of $V(x')$, only the values of x' in the collision region contribute to the integral. Therefore, we can replace $|x-x'|$ by $x'-x$, yielding

$$\langle x|p,j\rangle_+ \underset{x\to-\infty}{=} \frac{1}{\sqrt{2\pi\hbar}}\left[e^{ikx}\,|j\rangle+\sum_{j'} r^L_{j'j}\,e^{-ik_{j'}x}\,|j'\rangle\right], \tag{A23}$$

where

$$r^L_{j'j}=\frac{m\,e^{-ik_{j'}x}}{ik_{j'}\hbar^2}\int_{-\infty}^{\infty}dx' e^{ik_{j'}x'}V(x')\,\langle j'|\,v\,\langle x'|p,j\rangle_+ . \tag{A24}$$

Hence, the scattering state $|p,j\rangle_+$ is a superposition of wave packets with certain amplitudes $r^L_{j'j}$, which we need to relate to T and the S operators. To achieve this, we express Eq. (A17) in position representation

$$\begin{aligned}\langle x|p,j\rangle_+ &= \frac{1}{\sqrt{2\pi\hbar}}\left[e^{ikx}\,|j\rangle+\int_{-\infty}^{\infty}dx'\int_{-\infty}^{\infty}dx'' e^{ikx''}G_0^+(x,x')\,\langle x'|T(E+i0)|x'',j\rangle\right]\\ &= \frac{1}{\sqrt{2\pi\hbar}}\left[e^{ikx}\,|j\rangle+\sum_{j'}\frac{m}{ik_{j'}\hbar^2}\,|j'\rangle\int_{-\infty}^{\infty}dx'\int_{-\infty}^{\infty}dx'' e^{ikx''}\,e^{ik_{j'}|x-x'|}\,\langle x',j'|T(E+i0)|x'',j\rangle\right].\end{aligned} \tag{A25}$$

To conform with the asymptotic behavior, Eq. (A23), the integrand must be localized in a finite region. We can then replace again $|x-x'|$ by $x'-x$ when $x\to-\infty$, obtaining

$$\langle x|p,j\rangle_+ \underset{x\to-\infty}{=} \frac{1}{\sqrt{2\pi\hbar}}\left[e^{ikx}\,|j\rangle+\sum_{j'}\frac{me^{-ik_{j'}x}}{ik_{j'}\hbar^2}\,|j'\rangle\int_{-\infty}^{\infty}dx'\int_{-\infty}^{\infty}dx'' e^{ikx''}\,e^{ik_{j'}x'}\,\langle x',j'|T(E+i0)|x'',j\rangle\right]. \tag{A26}$$

Comparing Eqs. (A23) and (A26), we get

$$r^L_{j'j}=\frac{m}{ik_{j'}\hbar^2}\int_{-\infty}^{\infty}dx'\int_{-\infty}^{\infty}dx'' e^{ikx''}\,e^{ik_{j'}x'}\,\langle x',j'|T(E+i0)|x'',j\rangle . \tag{A27}$$

If we go back to the momentum representation taking into account that $|p\rangle=(\sqrt{2\pi\hbar})^{-1}\int_{-\infty}^{\infty}dx\exp[ikx]\,|x\rangle$ then Eq. (A27) reduces to

$$r^L_{j'j}=-2\pi i\,\frac{m}{p_{j'}}\,\langle -p_{j'},j'|T(E+i0)|p,j\rangle , \tag{A28}$$

with $p_{j'}=\hbar k_{j'}=\sqrt{p^2-2m\Delta_{j'j}}$. Introducing the value of $\langle p',j'|T(E+i0)|p,j\rangle$ given by Eq. (A28) in Eq. (A16), we can express the entries of the scattering matrix in terms of the amplitudes $r^L_{j'j}$:

$$\hat{r}^L_{j'j}\equiv s^{(-+)}_{j'j}(E)=\sqrt{\frac{|p'|}{|p|}}\,r^L_{j'j} \tag{A29}$$

since the sign of the momentum of the incident wave $|p,j\rangle$ is $\alpha=+$ and the one of the reflected wave $|-p_{j'},j'\rangle$ is $\alpha=-$.

The asymptotic behavior of $|p,j\rangle_+$ for $x \to +\infty$ is analyzed in a similar way. First we proceed as above to get the analogous to Eq. (A23), which reads [notice that we can now include the first term in Eq. (A23) in the sum]:

$$\langle x|p,j\rangle_+ \underset{x\to+\infty}{=} \frac{1}{\sqrt{2\pi\hbar}} \sum_{j'} t^L_{j'j}\, e^{ik_{j'}x}\, |j'\rangle\,. \tag{A30}$$

The position representation of Eq. (A17) is still given by Eq. (A25), but now the absolute value in the exponential is $|x-x'| = x-x'$, yielding

$$\langle x|p,j\rangle_+ \underset{x\to\infty}{=} \frac{1}{\sqrt{2\pi\hbar}} \left[e^{ikx}\,|j\rangle + \sum_{j'} \frac{m e^{ik_{j'}x}}{ik_{j'}\hbar^2}\,|j'\rangle \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dx'' e^{ikx''} e^{-ik_{j'}x'}\, \langle x',j'|T(E+i0)|x'',j\rangle \right] \tag{A31}$$

and therefore

$$t^L_{j'j} = \delta_{j'j} - 2\pi i \frac{m}{p_{j'}}\, \langle p_{j'},j'|T(E+i0)|p,j\rangle\,. \tag{A32}$$

Finally, the corresponding entry in the scattering matrix reads

$$\hat{t}^L_{j'j} \equiv s^{(++)}_{j'j}(E) = \sqrt{\frac{|p'|}{|p|}}\, t^L_{j'j}. \tag{A33}$$

Summarizing, to obtain the entries of the scattering matrix with $\alpha = +$, one has to solve the stationary Schrödinger equation $H\,|\psi\rangle = E\,|\psi\rangle$ for an improper state $|\psi\rangle$ whose position representation $\langle x|\psi\rangle \in \mathcal{H}_Y$ has the following asymptotic behavior:

$$\langle x|\psi\rangle = \begin{cases} e^{ik_j x}\,|j\rangle + \sum_{j'} r^L_{j'j} e^{-ik_{j'}x}\,|j'\rangle & \text{for } x \to -\infty \\ \sum_{j'} t^L_{j'j} e^{ik_{j'}x}\,|j'\rangle & \text{for } x \to +\infty \end{cases}. \tag{A34}$$

The solution is unique and determines the amplitudes $t^L_{j'j}$ and $r^L_{j'j}$, which in turn determine the entries of the scattering matrix $\hat{t}^L_{j'j}$ and $\hat{r}^L_{j'j}$, as prescribed in Eqs. (A29) and (A33).

Repeating the whole analysis with $p < 0$, we get identical results. The solution of the Schrödinger equation now must obey the asymptotic conditions:

$$\langle x|\psi\rangle = \begin{cases} \sum_{j'} t^R_{j'j} e^{-ik_{j'}x}\,|j'\rangle & \text{for } x \to -\infty \\ e^{-ik_j x}\,|j\rangle + \sum_{j'} r^R_{j'j} e^{ik_{j'}x}\,|j'\rangle & \text{for } x \to +\infty \end{cases} \tag{A35}$$

and we finally obtain

$$\begin{aligned} \hat{t}^R_{j'j} &\equiv s^{(--)}_{j'j}(E) = \sqrt{\frac{|p'|}{|p|}}\, t^R_{j'j} \\ \hat{r}^R_{j'j} &\equiv s^{(+-)}_{j'j}(E) = \sqrt{\frac{|p'|}{|p|}}\, r^R_{j'j}, \end{aligned} \tag{A36}$$

for transmission and reflection from the right, respectively.

4. The scattering matrix

We order the channels such that the first N_{open} are right propagating and the last N_{open} are left propagating. In this way we write

$$\mathbf{s}(E) = \begin{pmatrix} \hat{\mathbf{r}}^L & \hat{\mathbf{t}}^R \\ \hat{\mathbf{t}}^L & \hat{\mathbf{r}}^R \end{pmatrix} = \begin{pmatrix} \mathbf{s}^{-+} & \mathbf{s}^{--} \\ \mathbf{s}^{++} & \mathbf{s}^{+-} \end{pmatrix}, \tag{A37}$$

which satisfies the identities

$$\mathbf{s}(E)\mathbf{s}^\dagger(E) = \begin{pmatrix} \hat{\mathbf{r}}^L\hat{\mathbf{r}}^{L\dagger} + \hat{\mathbf{t}}^R\hat{\mathbf{t}}^{R\dagger} & \hat{\mathbf{r}}^L\hat{\mathbf{t}}^{L\dagger} + \hat{\mathbf{t}}^R\hat{\mathbf{r}}^{R\dagger} \\ \hat{\mathbf{t}}^L\hat{\mathbf{r}}^{L\dagger} + \hat{\mathbf{r}}^R\hat{\mathbf{t}}^{R\dagger} & \hat{\mathbf{t}}^L\hat{\mathbf{t}}^{L\dagger} + \hat{\mathbf{r}}^R\hat{\mathbf{r}}^{R\dagger} \end{pmatrix} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix}, \tag{A38}$$

$$\mathbf{s}^\dagger(E)\mathbf{s}(E) = \begin{pmatrix} \hat{\mathbf{r}}^{L\dagger}\hat{\mathbf{r}}^L + \hat{\mathbf{t}}^{L\dagger}\hat{\mathbf{t}}^L & \hat{\mathbf{r}}^{L\dagger}\hat{\mathbf{t}}^R + \hat{\mathbf{t}}^{L\dagger}\hat{\mathbf{r}}^R \\ \hat{\mathbf{t}}^{R\dagger}\hat{\mathbf{r}}^L + \hat{\mathbf{r}}^{R\dagger}\hat{\mathbf{t}}^L & \hat{\mathbf{t}}^{R\dagger}\hat{\mathbf{t}}^R + \hat{\mathbf{r}}^{R\dagger}\hat{\mathbf{r}}^R \end{pmatrix} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix}, \tag{A39}$$

following from the unitarity of the scattering operator $S^\dagger S = \mathbb{I}$ and $SS^\dagger = \mathbb{I}$, respectively. We sketch the proof of Eq. (A38). Starting from

$$\langle p',j'|\, S^\dagger S\, |p,j\rangle = \delta(p'-p)\delta_{j'j}, \tag{A40}$$

inserting the resolution of identity and expressing the Dirac δ as a function of the kinetic energies, we get

$$\sum_k \int dp''\, \langle p',j'|\, S^\dagger\, |p'',k\rangle\, \langle p'',k|\, S\, |p,j\rangle = \frac{|p|}{m}\, \delta(E_{p'} - E_p)\delta_{j'j}\delta_{\alpha'\alpha}. \tag{A41}$$

We now write the matrix elements of the operator S in terms of the scattering matrix $s_{j'j}^{(\alpha'\alpha)}$ using Eq. (9) and perform the integral over p'' by recalling that $dE_{p''} = |p''|dp''/m$:

$$\delta(E_{p'} - E_p - \Delta_{j'j})\frac{\sqrt{|p\,p'|}}{m}\sum_k \sum_{\alpha''=\pm} [s_{kj'}^{(\alpha''\alpha')}(E_{p'} + e_{j'})]^* s_{kj}^{(\alpha''\alpha)}(E_p + e_j) = \frac{|p|}{m}\,\delta(E_p - E_{p'})\delta_{j'j}\delta_{\alpha'\alpha}. \tag{A42}$$

Taking into account that the δ function in the right-hand side of the equation implies $j = j' \Rightarrow |p| = |p'|$, one obtains

$$\sum_k \sum_{\alpha''=\pm} [s_{kj}^{(\alpha''\alpha')}(E)]^* s_{kj}^{(\alpha''\alpha)}(E) = \delta_{j'j}\delta_{\alpha'\alpha}, \tag{A43}$$

which is Eq. (A38) as a careful inspection shows. To prove Eq. (A39), one can follow similar steps starting from $\langle p',j'|\, SS^\dagger\, |p,j\rangle = \delta(p'-p)\delta_{j'j}$.

APPENDIX B: SCATTERING MATRIX FOR A δ POTENTIAL

Here we provide explicit computations of $\hat{\mathbf{t}} = \hat{\mathbf{t}}^L = \hat{\mathbf{t}}^R$ and $\hat{\mathbf{r}} = \hat{\mathbf{r}}^L = \hat{\mathbf{r}}^R$ for $V(x) = g\delta(x)$. According to Appendix A 3, we have to solve the stationary Schrödinger equation $H\,|\psi\rangle = E\,|\psi\rangle$ which, in position representation, can be written as

$$\left\{E - H_Y + \frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right\}\sum_k \psi_k(x)\,|k\rangle = V\sum_k \psi_k(x)\,|k\rangle\,, \tag{B1}$$

where $\langle x|\psi\rangle = \sum_k \psi_k(x)\,|k\rangle$. We look for solutions obeying the asymptotic boundary conditions Eq. (A34) or, equivalently, Eq. (A35). Since the support of the potential is a single point at $x = 0$, the asymptotic conditions are fulfilled for every $x \neq 0$:

$$\langle x|\psi\rangle = \begin{cases} e^{ik_j x}\,|j\rangle + \sum_{j'} r_{j'j} e^{-ik_{j'}x}\,|j'\rangle & \text{for } x < 0 \\ \sum_{j'} t_{j'j} e^{ik_{j'}x}\,|j'\rangle & \text{for } x > 0. \end{cases} \tag{B2}$$

Projecting the Schrödinger Eq. (B1) onto $\langle j'|$, we get

$$(E - e_{j'})\psi_{j'}(x) + \frac{\hbar^2}{2m}\psi''_{j'}(x) = g\delta(x)\sum_k \psi_k(x)\,\langle j'|\,\nu\,|k\rangle\,. \tag{B3}$$

The wave functions $\psi_{j'}(x)$ must be everywhere continuous, while their first derivative $\psi'_{j'}(x)$ has a jump discontinuity at $x = 0$. Imposing the continuity condition to the solution Eq. (B2), we get $\delta_{j'j} + r_{j'j} = t_{j'j}$ or, in matrix form

$$\mathbb{I} + \mathbf{r} = \mathbf{t}. \tag{B4}$$

To obtain the value of the jump discontinuity, we integrate both sides of Eq. (B3) in an interval $[-\epsilon, \epsilon]$ and then take $\epsilon \to 0^+$:

$$\frac{\hbar^2}{2m}[\psi'_{j'}(0^+) - \psi'_{j'}(0^-)] = g\sum_k \psi_k(0)\,\langle j'|\,\nu\,|k\rangle\,. \tag{B5}$$

According to Eq. (B2), the derivatives at $x = 0$ are $\psi'_{j'}(0^+) = ik_{j'}t_{j'j}$ and $\psi'_{j'}(0^-) = ik_{j'}(\delta_{j'j} - r_{j'j}) = ik_{j'}(2\delta_{j'j} - t_{j'j})$, where in the last equality we use Eq. (B4). From continuity we also have $\psi_k(0) = t_{kj}$. Collecting these results, Eq. (B5) yields

$$\frac{i\hbar^2}{m}k_{j'}[t_{j'j} - \delta_{j'j}] = g\sum_k t_{kj}\,\langle j'|\,\nu\,|k\rangle\,.$$

This relation can be expressed in matrix form by defining $\mathbb{D}$ as the diagonal matrix with elements $\mathbb{D}_{jj} = k_j$ and $\mathbb{V}$ the matrix with elements $\mathbb{V}_{jk} = \langle j|\,\nu\,|k\rangle$

$$\mathbb{D}[\mathbf{t} - \mathbb{I}] = \frac{mg}{\hbar^2 i}\mathbb{V}\,\mathbf{t},$$

hence

$$\mathbf{t} = \left[\mathbb{I} + \frac{img}{\hbar^2}\,\mathbb{D}^{-1}\mathbb{V}\right]^{-1}, \tag{B6}$$

which, together with Eq. (B4), determines the amplitudes $t_{j'j}$ and $r_{j'j}$ for the δ potential in space.

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Quantum collisional thermostats

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Collisional reservoirs are becoming a major tool for modelling open quantum systems. In their simplest implementation, an external agent switches on for a given time the interaction between the system and a specimen from the reservoir. Generically, in this operation the external agent performs work onto the system, preventing thermalization when the reservoir is at equilibrium. Thermalization only occurs if the global system is autonomous and this requires considering the kinetic degree of freedom of the reservoir particles colliding with the system. The corresponding scattering problem is rather involved. Here, we present a formal solution of the problem in one dimension and for flat interaction potentials. The solution is based on the transfer matrix formalism and allows us to explore the symmetries of the resulting scattering map. One of these symmetries is micro-reversibility, which is a condition for thermalization. We then introduce two approximations of the scattering map that preserve these symmetries and, consequently, thermalize the system. These relatively simple approximate solutions constitute models of quantum thermostats and are useful tools to study quantum systems in contact with thermal baths. We illustrate their accuracy in a specific example, showing that both are good approximations of the exact scattering problem even in situations far from equilibrium. Moreover, one of the models consists of the removal of certain coherences plus a very specific randomization of the interaction time. These two features allow one to identify as heat the energy transfer due to switching on and off the interaction. Our results prompt the fundamental question of how to distinguish between heat and work from the statistical properties of the exchange of energy between a system and its surroundings.

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I. INTRODUCTION

A proper understanding of the interaction between a system and a thermal reservoir is crucial for the development of thermodynamics. This interaction turns out to be more involved for quantum systems. The theory of quantum open systems was initiated more than fifty years ago and has provided robust and widely used tools, such as the Lindblad equation for autonomous systems weakly coupled to thermal baths [1–3]. However, there are a number of questions which are still open or even under some controversy. Examples are Lindblad equations for driven systems [4], local versus global Lindblad and master equations [5, 6], strong coupling [7, 8], and non-Markovian effects [9].

Some of these issues could be addressed and eventually clarified if we had simplified and analytically solvable models of the interaction between a quantum system and a thermal bath. Good candidates would be the so-called repeated-interaction or collisional reservoirs [10–13]. In these models, the system does not interact with the reservoir as a whole. The reservoir consists of a large ensemble of independent units in a given state (usually, the equilibrium Gibbs state). One unit is extracted and put in contact with the system during a certain time interval. The process is repeated with fresh units, i.e., in each interaction the initial state of the unit is always the same and given by the density matrix that characterizes the reservoir. The interaction induces a quantum map in the system, which is exact and usually simpler to analyze than a continuous-time Lindblad equation. Moreover, this type of interaction

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occurs in relevant experimental setups, as in cavity quantum electrodynamics [14]. Unfortunately, this approach has a drawback. The models explored up to now are not autonomous: an external agent is needed to switch on and off the interaction between the system and the unit. In general, this action involves an energy exchange, which is a work supply that prevents the system from thermalizing [10–13]. Consequently, repeated-interaction models cannot be used as thermostats.

In a series of papers [15, 16], we managed to overcome this drawback by considering a fully autonomous scenario, where the units escape from the reservoir with a random velocity given by the effusion distribution, move in space as quantum wave packets and collide with the system without the need of an external agent. In this case, the energy to switch on and off the interaction is provided by the spatial degree of freedom of the unit. It turns out that the width of the incident wave packets in momentum representation plays a crucial role in the thermodynamics of the whole setup [15]. For wave packets with a large momentum dispersion, the exchanged energy can be interpreted as work [17]. On the other hand, if one assumes that the velocity of the unit is in equilibrium and that the wave packets are narrow enough in momentum representation, then this energy exchange is no longer work but heat and the system thermalizes [15]. Consequently, this latter approach captures all the essential features of a real thermostat.

In this paper, we extend the analysis of our previous work [15] to include the internal degrees of freedom of the units. Then we apply the transfer matrix formalism [18] to obtain an exact solution of the scattering problem for a uniform interaction potential. This solution allows us to explore the symmetries of the scattering map. In particular, we analyze the role of micro-reversibility as a sufficient condition for the system to thermalize when it is bombarded by narrow wave packets with velocities distributed according to the effusion distribution [15, 16].

We then find approximations to the exact scattering map for large scatterers and high incident kinetic energy. The approximations preserve micro-reversibility and, consequently, induce thermalization when the particles come from a reservoir at equilibrium. The first approximation is based on wave-vector operators and can be further simplified for large kinetic energy. The final result is a scattering map that resembles the repeated-interaction scheme, where the interaction Hamiltonian acts during a given time. When the system is bombarded by effusion particles, this time is a random variable whose distribution depends on the total energy of the system and the unit. This very specific randomization of the interaction time, plus the decoupling of populations and coherences by narrow wave packets [15], allows one to interpret the energy exchanged in the switching of the interaction as heat. Recall that, in the standard non-autonomous repeated interaction schemes [11], the energy transfer between the system and the external agent that switches on and off the interaction is work. In contrast, in our models this energy is heat because it is exchanged with the kinetic degree of freedom of the unit, which is in thermal equilibrium. Our results show that the distinction between heat and work is reflected in the dynamics of the system. This raises the interesting question of whether the energy exchange between a generic open system (classical or quantum) and its surroundings can be characterized as work or heat just by analyzing the dynamics of this exchange.

The paper is organized as follows. Sec. II is essentially a review of the results of our previous paper [15]: we discuss the map induced on the system by a single collision with a unit consisting of a wave packet, as well as the sufficient conditions for this map to thermalize the system when the incident velocity is random. The relation between these conditions and the symmetries of the scattering matrix are discussed in detail in Appendix A. In Sec. III, we present two specific models of repeated-interaction thermostats fulfilling these conditions. These are based on an approximation that is carried out in the context of transfer matrix theory in Appendices A and B. Finally, we apply the results to a specific example in Sec. IV and present our main conclusions in Sec. V.

II. THERMALIZATION AND THE SCATTERING MAP

A. Collisional reservoirs

We consider units drawn from a reservoir and colliding, one by one, with the system [15]. Each unit U is a particle of mass m with internal states and moving in one dimension. Its corresponding Hilbert space is $\mathcal{H}_U = \mathcal{H}_{U,\mathrm{p}} \otimes \mathcal{H}_{U,\mathrm{int}}$, where $\mathcal{H}_{U,\mathrm{p}}$ refers to the spatial states and $\mathcal{H}_{U,\mathrm{int}}$ is the space of internal states. The units collide with the system S, which only has internal degrees of freedom and its states are vectors in the Hilbert space $\mathcal{H}_S$.

The system is a fixed scatterer located in an interval $[-L/2, L/2]$, as sketched in Fig. 1. The whole setup is described by the following Hamiltonian H_{tot}, which is an operator acting on $\mathcal{H}_U \otimes \mathcal{H}_S$:

$$H_{\mathrm{tot}} = \frac{\hat{p}^2}{2m} + \chi_L(\hat{x}) H_{US} + H_U + H_S \tag{1}$$

$\hat{p}$ and $\hat{x}$ being, respectively, the momentum and position operators in $\mathcal{H}_{U,\mathrm{p}}$. $\chi_L(x)$ is the index function of the scattering region $[-L/2, L/2]$: $\chi_L(x) = 1$ if $x \in [-L/2, L/2]$ and zero otherwise. Outside the scattering region, the free Hamiltonian $H_0 = H_U + H_S$ rules the evolution of the internal degrees of freedom and is the sum of the

Hamiltonian of the system H_S and of the internal degrees of freedom of the unit H_U. Within the scattering region, the Hamiltonian affecting the internal degrees of freedom is $H = H_{US} + H_0$, which we will call total internal Hamiltonian. The free and the total internal Hamiltonians, H_0 and H respectively, are operators in $\mathcal{H}_{U,\text{int}} \otimes \mathcal{H}_S$. We will assume that both have a discrete spectrum with eigenstates:

$$\begin{aligned} H_0 \left|s_J\right\rangle &= e_J \left|s_J\right\rangle \\ H \left|s'_J\right\rangle &= e'_J \left|s'_J\right\rangle . \end{aligned} \tag{2}$$

Notice that $\{|s_J\rangle\}$ and $\{|s'_J\rangle\}$ are orthonormal basis of the Hilbert space of the internal states of the unit and the system, $\mathcal{H}_{U,\text{int}} \otimes \mathcal{H}_S$. Moreover, the eigenvectors of H_0 can be written as $|s_J\rangle = |s_{j_U}\rangle_U \otimes |s_{j_S}\rangle_S \in \mathcal{H}_{U,\text{int}} \otimes \mathcal{H}_S$, with

$$\begin{aligned} H_U \left|s_{j_U}\right\rangle_U &= e^{(U)}_{j_U} \left|s_{j_U}\right\rangle_U \\ H_S \left|s_{j_S}\right\rangle_S &= e^{(S)}_{j_S} \left|s_{j_S}\right\rangle_S \end{aligned} \tag{3}$$

and total energy $e_J = e^{(U)}_{j_U} + e^{(S)}_{j_S}$. Here and in the rest of the paper, we use capital letters J for the quantum numbers labelling the eigenstates of H_0 and H and lower case letters, j_U, j_S, for the quantum numbers corresponding to H_U and H_S. In this notation, the quantum number J of an eigenstate of H_0 comprises the two quantum numbers $J = (j_S, j_U)$.

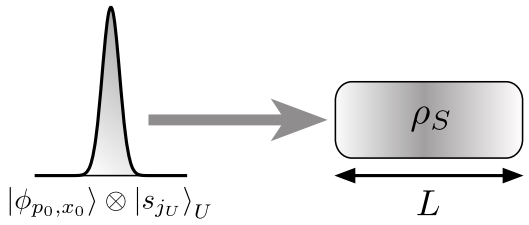

FIG. 1: A scheme of the setup analyzed in the text: a unit in state $|\phi_{p_0,x_0}\rangle \otimes |s_{j_U}\rangle_U$, which consists of a wave packet and an internal state with well defined energy $e^{(U)}_{j_U}$, collides with a system in state ρ_S. The length of the collision region is L.

In order to observe well-defined collisions, the spatial state of the units must be a wave packet $|\phi_{p_0,x_0}\rangle$ centered around position x_0 and momentum p_0, with momentum dispersion σ_p, as the one depicted in Fig. 1. An example is the Gaussian wave packet, whose wave function in momentum representation reads [15]

$$\langle p|\phi_{p_0,x_0}\rangle = (2\pi\sigma_p^2)^{-1/4} \exp\Big[-\frac{(p-p_0)^2}{4\sigma_p^2} - i\,\frac{p x_0}{\hbar}\Big] . \tag{4}$$

Here $|p\rangle$ denotes the non-normalizable plane wave with momentum p. The Hamiltonian (1) is invariant under spatial reflection $x \to -x$. Consequently, a collision with a unit coming from the left with positive velocity, $x_0 < 0$ and $p_0 > 0$, is equivalent to the mirror collision with a unit $|\phi_{-p_0,-x_0}\rangle$ coming from the right. Hence, we can limit our discussion to units with positive velocity, without loss of generality (the mathematical consequences of this spatial symmetry in the scattering problem are explained in detailed in Appendix A).

The internal state of the unit depends on the properties of the reservoir. For instance, if the reservoir is in thermal equilibrium at inverse temperature β, the internal state is the Gibbs state $\rho_{U,\text{eq}} = e^{-\beta H_U}/Z_U$, where Z_U is the corresponding partition function. We first analyze the case of a unit in a pure eigenstate of H_U, $|s_{j_U}\rangle_U$, and later on we consider thermal mixtures of these eigenstates.

B. The scattering map

The effect of the collision on the system is given by a CPTP map, which depends on the incident momentum p_0 and the internal state of the unit. However, it is convenient to consider first the effect of the collision on all the internal degrees of freedom, those of the system and of the internal state of the unit, following Ref. [15]. The scattering map $\mathbb{S}$ relates the internal state before the collision, ρ, and after, $\rho' = \mathbb{S}\rho$. Expressing the states in the eigenbasis of H_0, $\rho_{JK} = \langle s_J|\rho|s_K\rangle$ and $\rho'_{JK} = \langle s_J|\rho'|s_K\rangle$, the scattering map is given by a tensor $\mathbb{S}^{JK}_{J'K'}$ such that

$$\rho'_{J'K'} = \sum_{J,K} \mathbb{S}^{JK}_{J'K'} \rho_{JK} . \tag{5}$$

In Ref. [15], we have analyzed in detail this scattering map and found that the behavior of the state ρ crucially depends on the momentum dispersion of the packet, σ_p. If the dispersion is small enough, the outgoing wave packets corresponding to different transitions $|s_J\rangle \to |s_{J'}\rangle$ are either identical or do not overlap. The precise condition for these narrow wave packets in terms of the transition energies $\Delta_{JJ'} = e_J - e_{J'}$, reads

$$\sigma_p \ll \frac{m|\Delta_{JJ'} - \Delta_{KK'}|}{2p_0} \tag{6}$$

for every pair of transitions $|s_J\rangle \to |s_{J'}\rangle$ and $|s_K\rangle \to |s_{K'}\rangle$ with $\Delta_{J'J} \neq \Delta_{KK'}$. If the incident packet fulfills this condition, we call it narrow wave packet and the scattering map induced by the collision is given by [15]:

$$\begin{aligned}\mathbb{S}^{JK}_{J'K'} \simeq\ & t_{J'J}(E_{p_0} + e_J)\,[t_{K'K}(E_{p_0} + e_K)]^* \\ & + r_{J'J}(E_{p_0} + e_J)\,[r_{K'K}(E_{p_0} + e_K)]^* \ ,\end{aligned} \tag{7}$$

whenever

$$e_{J'} - e_J = e_{K'} - e_K \tag{8}$$

and $E_{p_0} + e_J \geq e_{J'}$, and zero otherwise. Here $t_{J'J}(E)$ and $r_{J'J}(E)$ are the transmission and reflection amplitudes that depend on the total energy, kinetic $E_{p_0} \equiv p_0^2/(2m)$ plus internal e_J. They are defined for all J and J' such that $E \geq e_J, e_{J'}$, which are the so-called open channels in the collision, and are usually arranged into two matrices $\mathbf{t}(E)$ and $\mathbf{r}(E)$ that form the scattering matrix

$$\tilde{\mathcal{S}}(E) = \begin{pmatrix} \mathbf{r}(E) & \mathbf{t}(E) \\ \mathbf{t}(E) & \mathbf{r}(E) \end{pmatrix} \ . \tag{9}$$

The two matrices $\mathbf{t}(E)$ and $\mathbf{r}(E)$ are defined on the subspace of open channels $\mathcal{H}_{\text{open}}$, spanned by the eigenvectors $|s_J\rangle$ of H_0 with $e_J \leq E$ (see Appendix A for a detailed discussion). One important property of the scattering matrix is that it is unitary on the subspace $\mathcal{H}_{\text{open}}$ for a given total energy E, that is, $\tilde{\mathcal{S}}^\dagger(E)\tilde{\mathcal{S}}(E) = \mathbb{I}$ for all E, implying

$$\begin{aligned}\mathbf{r}(E)\mathbf{r}^\dagger(E) + \mathbf{t}(E)\mathbf{t}^\dagger(E) &= \mathbb{I} \\ \mathbf{r}(E)\mathbf{t}^\dagger(E) + \mathbf{t}(E)\mathbf{r}^\dagger(E) &= 0 \ .\end{aligned} \tag{10}$$

In Appendix A, we present a detailed overview of the properties of the scattering matrix $\tilde{\mathcal{S}}(E)$ and its symmetries, and explain how it can be calculated by solving the time-independent Schrödinger equation for the so-called scattering states, which behave asymptotically as incoming and outgoing plane waves. The amplitudes of these plane waves are directly related to the reflection and transmission matrices and can be obtained using a transfer matrix technique. Moreover, in Appendix B, we derive an approximation valid for long scatterers (large L) and incident units with high momenta, which preserves the symmetries of $\tilde{\mathcal{S}}(E)$ and will be the basis to design consistent thermostats.

Let us first discuss the behavior of the diagonal terms of the density matrix ρ_{JJ}, which are the populations of the energy levels $e_J = e^{(U)}_{j_U} + e^{(S)}_{j_S}$. The evolution of the populations is determined by the coefficients $\mathbb{S}^{JK}_{J'J'}$ of the scattering map. Condition (8), particularized to $J' = K'$, indicates that these coefficients are different from zero only if $e_J = e_K$. Moreover, since the initial internal state of the unit is an eigenstate of H_U, $j_U = k_U$; hence, $e^{(S)}_{j_S} = e^{(S)}_{k_S}$. If the Hamiltonian of the system H_S is non degenerate, this implies $j_S = k_S$ and populations evolve independently of the off-diagonal terms of the density matrix

$$\rho'_{J'J'} = \sum_J P_{J'J}(p_0)\rho_{JJ} \tag{11}$$

with the following transition probabilities that depend on the momentum p_0 of the incident unit:

$$\begin{aligned}P_{J'J}(p_0) &\equiv \mathbb{S}^{JJ}_{J'J'} \\ &= |t_{J'J}(E_{p_0} + e_J)|^2 + |r_{J'J}(E_{p_0} + e_J)|^2\end{aligned} \tag{12}$$

if $p_0^2 \geq 2m\Delta_{J'J}$ and zero otherwise. The unitarity of the scattering matrix on the subspace $\mathcal{H}_{\text{open}}$ of open channels, Eq. (10), implies that the off-diagonal terms decay [15], since $|t_{J'J}|^2 + |r_{J'J}|^2 \leq 1$, and that the trace of the density matrix is preserved, $\sum_{J'} P_{J'J}(p_0) = 1$ for all p_0.

C. Conditions for thermalization

In this subsection we explore whether the system thermalizes if the units are in equilibrium at inverse temperature β. This implies that the units are in an internal state $|s_{j_U}\rangle_U$ with probability

$$p_{j_U} = \frac{e^{-\beta e^{(U)}_{j_U}}}{Z_U} \tag{13}$$

where Z_U is the internal partition function of the unit. The momentum of the units coming form a thermal bath is distributed as [15, 16]:

$$\mu(p) = \frac{\beta|p|}{m} e^{-\beta p^2/(2m)} \qquad p \in [0, \infty] \, . \tag{14}$$

This is the effusion distribution describing the momentum of particles in equilibrium that cross a given point or hit a fixed scatterer coming from the left (since our scatterer, as described by the total Hamiltonian (1), is symmetric, there is no need to explicitly consider the case of negative incident velocity). We have shown in Ref. [16] how this effusion distribution arises from the Maxwellian velocity distribution and a uniform density of classical particles, which characterize an ideal gas at equilibrium.

In this case, the populations $p(J) \equiv \rho_{JJ}$, obey the following master equation

$$p'(J') = \sum_J p(J) p(J \to J') \tag{15}$$

with

$$p(J \to J') = \int_0^\infty dp_0 \, \mu(p_0) P_{J'J}(p_0) \, . \tag{16}$$

The master equation for the state of the system

$$p(j_S) = \sum_{j_U} p(j_S, j_U) \, , \tag{17}$$

with $p(j_S, j_U) \equiv p(J)$, reads

$$p'(j'_S) = \sum_{j_S} p(j_S) p(j_S \to j'_S) \tag{18}$$

with

$$p(j_S \to j'_S) = \sum_{j_U, j'_U} \frac{e^{-\beta e^{(U)}_{j_U}}}{Z_U} p(J \to J') \tag{19}$$

where we recall that J denotes the pair of quantum numbers (j_S, j_U).

A sufficient condition for thermalization is micro-reversibility or invariance of the collision probabilities under time reversal [15]. In a quantum system, the states are transformed under time reversal by means of an anti-unitary operator T defined on the corresponding Hilbert space. Any anti-unitary operator can be written as $\mathsf{T} = CU$, where C is the conjugation of coordinates in a given basis and U is a unitary operator [19]. The time reversal operator depends on the physical nature of the system. Consider for instance a qubit with Hilbert space $\mathcal{H} = \mathbb{C}^2$. If the qubit is a 1/2 spin, then time-reversal must change the sign of all the components of the spin, i.e., $\mathsf{T}\sigma_\alpha\mathsf{T}^\dagger = -\sigma_\alpha$ for $\alpha = x, y, z$, where σ_α are the Pauli matrices. The anti-unitary operator that fulfills these transformations is $\mathsf{T} = C\sigma_y$, where C is the conjugation of the coordinates of the qubit in the canonical basis (the eigenbasis of σ_z) [19]. On the other hand, if the qubit is a two-level atom whose states are superpositions of real wave functions in the position representation, then the time reversal operator is just $\mathsf{T} = C$, since the time-reversal of spinless particles is the conjugation of the wave function in the position representation.

In our case, the total time-reversal operator acting on the Hilbert space $\mathcal{H}_{U,\mathrm{p}} \otimes \mathcal{H}_{U,\mathrm{int}} \otimes \mathcal{H}_S$ can be decomposed into three parts $\mathsf{T} = \mathsf{T}_{U,\mathrm{p}} \otimes \mathsf{T}_{U,\mathrm{int}} \otimes \mathsf{T}_S$. The operator $\mathsf{T}_{U,\mathrm{p}}$ is the conjugation of the spatial wave function of the unit in the position representation $\mathsf{T}_{U,\mathrm{p}}\psi(x) = \psi^*(x)$, whereas in momentum representation reads $\mathsf{T}_{U,\mathrm{p}}\phi(p) = \phi^*(-p)$

[19, 20]. The time-reversal operator for the internal degrees of freedom can in principle be any anti-unitary operator $\mathsf{T}_{\rm int} = \mathsf{T}_{U,\rm int} \otimes \mathsf{T}_S$.

Micro-reversibility occurs when the total Hamiltonian commutes with the time-reversal operator, $[H_{\rm tot}, \mathsf{T}] = 0$. Since the kinetic part is already invariant under time reversal, the commutation $[H, \mathsf{T}_{\rm int}] = 0$ is a sufficient condition for micro-reversibility. For simplicity, we further assume that $[H_0, \mathsf{T}_{\rm int}] = 0$ and that the eigenstates of H_0 are time-reversal invariant: $\mathsf{T}_{\rm int}\,|s_J\rangle = |s_J\rangle$ for all J. In Appendix A we show that, if these conditions are fulfilled, then the scattering matrix obeys $\tilde{\mathcal{S}}^*\tilde{\mathcal{S}} = \mathbb{I}$. Combining this expression with the unitarity of $\tilde{\mathcal{S}}$, we conclude that the matrices $\mathbf{t}$ and $\mathbf{r}$ are symmetric for a given energy E:

$$\begin{aligned} \langle s_{J'}|\mathbf{t}(E)|s_J\rangle &= \langle s_J|\mathbf{t}(E)|s_{J'}\rangle \\ \langle s_{J'}|\mathbf{r}(E)|s_J\rangle &= \langle s_J|\mathbf{r}(E)|s_{J'}\rangle \ . \end{aligned} \tag{20}$$

If we now apply this symmetry to the transition probabilities given by Eq. (12), we obtain

$$P_{J'J}(p_0) = P_{JJ'}\left(\sqrt{p_0^2 - 2m\Delta_{J'J}}\right) \tag{21}$$

for all p_0 satisfying $p_0^2 \geq 2m\Delta_{J'J}$.

Let us prove now that micro-reversibility, as expressed by Eq. (21) for the transition probabilities, is a sufficient condition for thermalization. We first focus on transitions of internal states including the unit, that is, from $|s_J\rangle$ to $|s_{J'}\rangle$. If $e_{J'} \geq e_J$, then $\Delta_{J'J} \geq 0$ and the transition probability reads

$$p(J \to J') = \int_{\sqrt{2m\Delta_{J'J}}}^{\infty} dp_0\, \frac{\beta p_0}{m} e^{-\beta p_0^2/(2m)} P_{J'J}(p_0) \ . \tag{22}$$

Here, the lower limit in the integral is due to the fact that $P_{J'J}(p_0)$ is zero for $p_0^2 \leq 2m\Delta_{J'J}$. If we change the integration variable to $p_0' = \sqrt{p_0^2 - 2m\Delta_{J'J}} \Rightarrow dp_0' = |p_0|dp_0/|p_0'|$, we obtain

$$p(J \to J') = \int_0^{\infty} dp_0'\, \frac{\beta p_0'}{m} e^{-\beta(p_0'^2/(2m) + \Delta_{J'J})}\, P_{J'J}\left(\sqrt{p_0'^2 + 2m\Delta_{J'J}}\right) . \tag{23}$$

Finally, applying the micro-reversibility condition (21),

$$\begin{aligned} p(J \to J') =& e^{-\beta\Delta_{J'J}} \int_0^{\infty} dp_0'\, \frac{\beta p_0'}{m} e^{-\beta p_0'^2/(2m)} P_{JJ'}(p_0') \\ =& e^{-\beta\Delta_{J'J}} p(J' \to J) \ . \end{aligned} \tag{24}$$

We can proceed in an analogous way for the case $e_{J'} \leq e_J$. The final result is the local detailed balance condition

$$\frac{p(J \to J')}{p(J' \to J)} = e^{-\beta(e_{J'} - e_J)} \qquad \text{for all } J, J' \ . \tag{25}$$

We now explicitly consider the internal states of the unit. Recall that the subindex J in the previous sections comprises two quantum numbers $J = (j_S, j_U)$. If the internal states of the unit are in thermal equilibrium at inverse temperature β, then the transition probabilities between the states of the system are given by (19). The detailed balance condition (25) can be written as

$$p(J \to J') = e^{-\beta\left[e^{(U)}_{j_U'} + e^{(S)}_{j_S'} - e^{(U)}_{j_U} - e^{(S)}_{j_S}\right]} p(J' \to J) \ . \tag{26}$$

Inserting (26) into (19), one gets

$$p(j_S \to j_S') = e^{-\beta\left[e^{(S)}_{j_S'} - e^{(S)}_{j_S}\right]} p(j_S' \to j_S) \tag{27}$$

which is the detailed balance condition for the populations of the states of the system and ensures thermalization.

III. COLLISIONAL THERMOSTATS

A. Wave-vector-operator model

In Appendix B, we solve the generic one dimensional scattering problem with internal states for large scatterers an high incident momentum p_0. In this limit, the reflecting waves vanish and the transition amplitudes $t_{J'J}(E)$ are given by ($\hbar = 1$)

$$t_{J'J}(E) \simeq e^{-iL(k_J+k_{J'})/2} \langle s_{J'}| e^{iL\mathbb{K}(E)} |s_J\rangle \tag{28}$$

where $k_J = \sqrt{2m(E-e_J)}$ and the wave-vector operator within the scattering region, defined as

$$\mathbb{K}(E) \equiv \sqrt{2m(E-H)}\,, \tag{29}$$

is a self-adjoint operator if E is larger than the maximum eigenvalue of H.

To complete the model, we need an expression for the transmission and reflection amplitudes at low velocities. To preserve micro-reversibility and the unitarity of the scattering matrix, we adopt the simplest assumption for low energies, namely, that the incident unit is reflected without affecting the state of the system. This is also justified by the fact that in a large scatterer the transmission amplitudes corresponding to tunneling vanish. However, from the point of view of the system, it does not matter whether the unit is reflected or transmitted, as long as it does not affect the system. Then, for simplicity, we define our model of a collisional thermostat as given by vanishing reflection amplitudes, $r_{J'J}(E) = 0$ for all E, and the following transmission amplitudes:

$$t_{J'J}(E) = \begin{cases} e^{-iL(k_J+k_{J'})/2} \langle s_{J'}| e^{iL\mathbb{K}(E)} |s_J\rangle & \text{if } E > e_{\max} \\ \delta_{J'J} & \text{if } E \le e_{\max} \end{cases} \tag{30}$$

where $E = p_0^2/(2m) + e_J$ and $e_{\max}$ is the maximum of the eigenvalues of H and H_0. With this choice

$$\sum_{J'} \left[|t_{J'J}(E)|^2 + |r_{J'J}(E)|^2\right] = 1 \tag{31}$$

for all J and E, ensuring the conservation of the trace of the density matrix $\mathrm{Tr}(\rho') = \mathrm{Tr}(\rho)$.

The transmission amplitudes defined by Eq. (30) obey condition (20), as shown in Appendix B. We conclude that our repeated-interaction model, based on the wave-vector operator $\mathbb{K}$, induces the thermalization of the system. Consequently, it constitutes a simple model of a thermostat. Furthermore, it is also a good approximation of a system colliding with units that escape from a thermal reservoir, specially for large scatterers. In section IV, we check the validity of this approximation in explicit examples.

B. Random-interaction-time model

We now present a second model that also induces thermalization and is more directly related to the repeated interaction schemes considered in the literature [11, 13], where the interaction H_{US} is switched on for a time interval. This can be done if the incident momentum is large and we can further expand the operator $\mathbb{K}(E) = \sqrt{2m(E-H)}$ as

$$\mathbb{K}(E) \simeq \sqrt{2mE} - \sqrt{\frac{m}{2E}}\, H\,. \tag{32}$$

An analogous expansion of the wave vectors outside the scattering region yields $k_J \simeq \sqrt{2mE} - e_J\sqrt{m/(2E)}$. Inserting these expressions in the transmission amplitudes given by Eq. (30), we get

$$t_{J'J}(E) \simeq e^{i\tau(E)[e_{J'}+e_J]/2}\ \langle s_{J'}| e^{-i\tau(E)H} |s_J\rangle\ . \tag{33}$$

Here, we have introduced the time

$$\tau(E) \equiv \frac{L}{v_E} = \frac{L}{\sqrt{2E/m}}\,, \tag{34}$$

which is the time a classical particle with velocity $v_E \equiv \sqrt{2E/m} = \sqrt{(p_0/m)^2 + 2e_J/m}$ takes to cross the scattering region of length L. Except for a phase, Eq. (33) is equivalent to the evolution of the state $|s_J\rangle$ under the total internal Hamiltonian $H = H_0 + H_{US}$ during a time $\tau(E)$, which is, approximately, the interaction time between the wave packet and the scatterer. We thus recover for the transmission amplitudes the usual picture that ignores the translational part of the unit and considers that the coupling is switched on for a given time $\tau(E)$ [11, 13]. Notice however that this velocity does not exactly coincide with the velocity of the wave packet $v_{\text{packet}} \equiv p_0/m$. In fact, the scattering matrix resulting from setting the interaction time equal to $\tau_{\text{packet}} \equiv L/v_{\text{packet}} = Lm/p_0$ does not obey micro-reversibility and does not thermalize the system, as we show in section IV for an specific example.

Two important remarks must be made. First, expression (33) can be evaluated for any pair of states, J and J', and any positive energy E. However, the transfer matrix is only defined for open channels, obeying $E \geq e_J, e_{J'}$. To preserve the unitarity of the scattering matrix we have to restrict the use of (33) to energies E larger than the eigenvalues of H_0. To be consistent with the wave-vector-operator model, we adopt here a more conservative strategy, restricting expression (33) to energies higher than $e_{\max}$, the maximum eigenvalue of both H_0 and H. We also assume that $e_{\max}$ is positive, to avoid a negative total energy E, which would yield an imaginary velocity v_E. Summarizing, our model consists of null reflection amplitudes, $r_{J'J}(E) = 0$ for all E, and transmission amplitudes given by

$$t_{J'J}(E) = \begin{cases} e^{i\tau(E)[e_{J'}+e_J]/2} \, \langle s_{J'}| \, e^{-i\tau(E)H} \, |s_J\rangle & \text{if } E > e_{\max} \\ \delta_{J'J} & \text{if } E \leq e_{\max}. \end{cases} \tag{35}$$

With this definition, our random-interaction-time model, like the wave-vector-operator model, preserves all the properties of the exact scattering matrix and consequently induces the thermalization of the system. As in the previous model, we have set to zero the reflection amplitudes for $E \leq e_{\max}$. Recall, however that for low energies the unit is most likely reflected and this is equivalent to taking a zero interaction time $\tau(E) = 0$ for $E \leq e_{\max}$.

The second remark is to notice that the interaction time $\tau(E)$ depends on the zero of the total energy, that is, if we add a constant E_0 to the total Hamiltonian H_{tot}, $\tau(E)$ changes. Then the transition amplitudes will depend as well on the zero of energy. The reason of this dependency is the Taylor expansion around $H = 0$ in Eq. (32). Shifting the internal energies an amount E_0 is equivalent to expanding the square root around $H = -E_0$ in Eq. (32). Hence, to minimize the error in the expansion we have to choose the zero of energy in such a way that H is small. There are several criteria to define the "smallness" of an operator, based on different matrix norms. For the example in section IV, we minimize the spectral norm of H, which is the square root of the largest eigenvalue of $H^\dagger H = H^2$. Notice however that all the models obtained by an energy shift with $e_{\max} > 0$ are effective thermostats when the scatterer is bombarded by equilibrium units, since Eq. (35) is unitary and fulfills micro-reversibility.

The model given by Eq. (35) and the corresponding scattering map in Eq. (7) are similar to the ones previously considered in the literature [11, 13], except for the randomization of the interaction time $\tau(E)$, which depends on the initial state $|s_J\rangle$, and for the removal of coherences due to tracing out the outgoing narrow packets [15].

C. Kraus representation

To further explore the differences and similarities between our thermostats and a repeated-interaction reservoir, it is convenient to use the Kraus representation of the scattering map given by Eq. (5), together with (7) and condition (8). If we neglect the reflecting amplitudes, a representation of this map is given by the following Kraus operators:

$$M_l = \sum_{J,J'} t_{J'J}(E_{p_0} + e_J) \, \delta_{\Delta_{J'J},\Delta_l} \, |s_{J'}\rangle \langle s_J| \tag{36}$$

where δ is a Kronecker delta and Δ_l runs over all possible Bohr frequencies of the free internal Hamiltonian H_0. Indeed, the map

$$\rho' = \sum_l M_l \rho M_l^\dagger \tag{37}$$

in the eigenbasis of H_0 is given by the tensor

$$\mathbb{S}^{JK}_{J'K'} = \sum_l \langle s_{J'}|M_l|s_J\rangle \, \langle s_K|M_l^\dagger|s_{K'}\rangle \, , \tag{38}$$

which coincides with the one given by Eqs. (5), (7), and (8), if the reflection amplitudes are neglected. If we now use the approximation (35), the Kraus operators in the eigenbasis of H_0 read

$$\langle s_{J'}|M_l|s_J\rangle = e^{-i\tau(E)(e_J+e_{J'})/2} \, \langle s_{J'}|e^{-i\tau(E)H}|s_J\rangle \, \delta_{\Delta_{J'J},\Delta_l} \tag{39}$$

with $E = p_0^2/(2m) + e_J$.

On the other hand, the Kraus representation of the unitary evolution in a repeated-interaction scheme consists of a unique unitary operator M given by

$$\langle s_{J'}|M|s_J\rangle = \langle s_{J'}|e^{-i\tau_{\rm int}H}|s_J\rangle \tag{40}$$

where $\tau_{\rm int}$ is the interaction time. Comparing (39) and (40), we see three main differences: First, the Kronecker delta kills all coherences between jumps with different Bohr frequencies. Recall that the map acting on a pure state can be seen as the application of a randomly chosen operator M_l [21]. The Kronecker delta only allows for superpositions with the same energy jump Δ_l. This is a consequence of using narrow packets, which is a necessary condition for thermalization, as proved in Ref. [15]. Remarkably, this condition has also been shown to be necessary to derive a fluctuation theorem for quantum maps (see Eq. (12) in Ref. [21]), and is equivalent to imposing that the energy exchange with the reservoir, i.e., the heat, is well defined for each possible transformation of a pure state given by the Kraus operators. This implies that heat is well defined for any quantum stochastic trajectory [21]. Second, the interaction time in the random-interaction-time model, $\tau(E)$, depends on the energy of the initial state e_J. Third, there is an extra phase that appears in the solution of the scattering problem, although it does not play a role in thermalization.

IV. AN EXAMPLE

In this section we analyze in detail an explicit example where the units and the system are single qubits. We consider the following free Hamiltonian and interaction term between the system and the internal state of the unit:

$$H_0 = \omega_U\, \sigma_z^U \otimes \mathbb{I} + \omega_S\, \mathbb{I} \otimes \sigma_z^S \tag{41}$$

$$H_{US} = J_x \sigma_x^U \otimes \sigma_x^S + J_y \sigma_y^U \otimes \sigma_y^S\ . \tag{42}$$

where $\sigma_i^{U,S}$ are the Pauli matrices in the Hilbert space of the unit and the system, respectively, $2\omega_{U,S}$ is the level spacing of each qubit, and $J_{x,y}$ are coupling constants. The eigenstates of the free Hamiltonian H_0 are $|00\rangle_{US}$, $|01\rangle_{US}$, $|10\rangle_{US}$, and $|11\rangle_{US}$ with energies $\omega_U + \omega_S$, $\omega_U - \omega_S$, $-\omega_U + \omega_S$, and $-\omega_U - \omega_S$, respectively. This system has been exhaustively studied in Ref. [13] in the context of the repeated-interaction coupling mediated by an external agent.

The system obeys the conditions for thermalization discussed in Sec. II C. First, $H_S = \omega_S \sigma_z^s$ has no degenerate levels and no Bohr degeneracies. Second, if we take as time-reversal operator $\mathsf{T}_{\rm int} = C$, where C the conjugation of coordinates in the canonical basis, then $\mathsf{T}_{\rm int}^\dagger \sigma_y^{U,S} \mathsf{T}_{\rm int} = -\sigma_y^{U,S}$, $\mathsf{T}_{\rm int}^\dagger \sigma_x^{U,S} \mathsf{T}_{\rm int} = \sigma_x^{U,S}$, and $\mathsf{T}_{\rm int}^\dagger \sigma_z^{U,S} \mathsf{T}_{\rm int} = \sigma_z^{U,S}$, hence $[H, \mathsf{T}_{\rm int}] = [H_0, \mathsf{T}_{\rm int}] = 0$ and micro-reversibility is fulfilled. Furthermore, the eigenstates of H_0 are invariant under time reversal, $\mathsf{T}_{\rm int}\,|e_J\rangle = |e_J\rangle$ for all J (notice that this is not the time reversal operator of a spin 1/2; it is however an admissible time reversal operator for a qubit, as discussed in section II C). Consequently, if the system is bombarded by narrow wave packets at equilibrium, the scattering map drives the system towards the equilibrium state, and this thermalization occurs for the exact scattering map as well as for any of the two effective models introduced in the previous section.

A. Transition probabilities

We first check whether the two models presented in the previous section are able to reproduce the transition probabilities $P_{J'J}(p_0)$. We calculate the transfer matrix given by Eq. (A27) and compare the exact transition probabilities in Eq. (12) for a given incident momentum p_0 with the ones obtained from the wave-vector operator model (WVO), Eq. (30), and the random interaction model (RIT), Eq. (35). The comparison is shown in Fig. 2 as a function of the kinetic energy $p_0/(2m)$, for the transition $|00\rangle_{US} \to |11\rangle_{US}$. As expected, the two models reproduce with good accuracy the exact transition probabilities for high kinetic energy. It is remarkable that the wave vector operator model is a very good approximation of the scattering problem even for low kinetic energy, as shown in the inset, whereas the random-interaction-time model fails in this regime.

B. Thermalization

We now bombard the qubit with narrow wave packets with random momentum, according to the effusion distribution at temperature T, and a random internal state, according to the Boltzmann distribution at the same temperature.

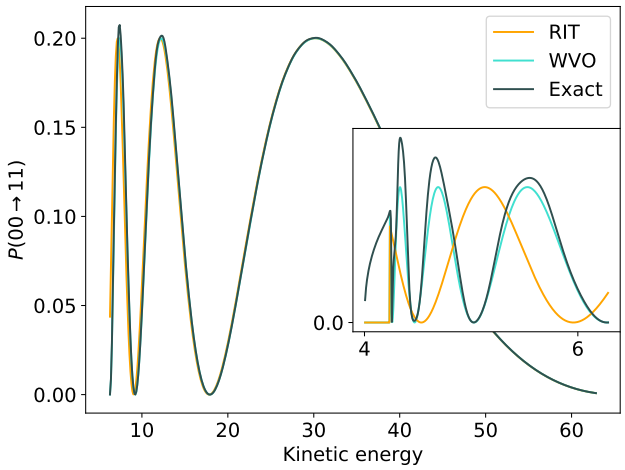

FIG. 2: Probability of the transition $|00\rangle_{US} \to |11\rangle_{US}$ for $J_x = 1$, $J_y = 0$, $\omega_S = \omega_U = 1$, $m = 0.1$, and $L = 50$. We show the exact result obtained from the transfer matrix Eq. (A27) (dark green), the wave-vector-operator model (WVO, light green) given by Eq. (30), the random-interaction-time model (RIT, orange) given by Eq. (35). The inset shows the behavior for low kinetic energy, where one can see that the WVO model still reproduces rather well the exact probabilities. Below $e_{\max} = 2.23$ the transition probability vanishes for the two models, WVO and RIT.

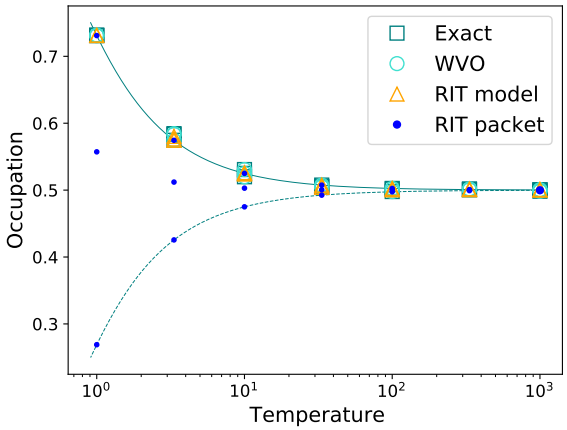

FIG. 3: Stationary population of the ground state of the qubit for $J_y = 1, 0, -1$, $J_x = 1$ and $\omega_S = \omega_U = 1$, $m = 0.1$, and $L = 50$. We depict the exact solution of the scattering problem using the transfer matrix (A27) (dark green squares) and the populations given by different models: the wave-vector-operator model given by Eq. (30) (green circles) and the random-interaction-time model given by Eq. (35) (orange triangles). The exact solution and the two models induce thermalization at the same temperature as the bath, as expected. We also show the population if the interaction time is chosen as $\tau_{\text{packet}} = Lm/p_0$ (dark blue dots, $J_y = 1, 0, -1$ from top to bottom), which clearly departs from the thermal state and even exhibits negative absolute temperatures or population inversion for $J_y = -J_x = -1$ (see Appendix C for an analytical proof of this result). The continuous and dashed light green curves depict the population of the fundamental level in the canonical ensemble with positive and negative temperature respectively.

As expected, the system thermalizes not only for the exact solution of the scattering problem, given by Eq. (A27), but also for the two models, Eq. (30) and Eq. (35). In the left panel of Fig. 3, we plot the stationary population of the ground state in the three cases and in the thermal state.

To stress the importance of micro-reversibility for thermalization, we also plot in the figure with dark blue circles the population when the interaction time is chosen as $\tau_{\text{packet}} = L/v_{\text{packet}}$, where $v_{\text{packet}} = p_0/m$ is the velocity of the incoming wave packet. In this case, the system does not reach the temperature of the reservoir and can even exhibit

population inversion (see Appendix C for a detailed discussion of the model and Ref. [22] for a general discussion of the phenomenon within the repeated interaction framework). From the point of view of the dynamics of the system, it is striking that the replacement of $v_E = \sqrt{2E/m}$ by $v_{\text{packet}} = p_0/m$ in the calculation of the interaction time has such significant consequences. Notice however that the interaction time in the RIT model with time given by Eq. (34) depends both on the energy of the system $e_{j_S}^{(S)}$ and of the internal state of the unit $e_{j_U}^{(U)}$.

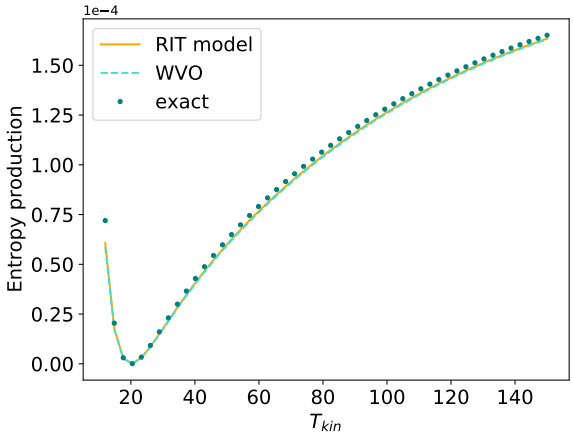

FIG. 4: Entropy production per collision as a function of the temperature of the kinetic degrees of freedom, T_{kin}, for $J_x = 1$, $J_y = 0$, $\omega_U = \omega_S = 1$, $m = 1$, $L = 50$ and a temperature $T_{\text{int}} = 20$ of the internal degrees of freedom of the units. We compare the exact (numerical) solution of the scattering problem using the transfer matrix (A27), the wave-vector-operator (WVO) model and the random-interaction-time (RIT) model.

C. Non-equilibrium

Finally, we check the models in a non-equilibrium scenario where the internal states of the unit are in equilibrium at temperature T_{int}, different from the temperature T_{kin} of the effusion distribution. In this situation, the system is exchanging heat with two different thermal baths and reaches a non-equilibrium steady state where heat Q is transferred from the hot to the cold bath in each collision. This irreversible heat transfer induces an entropy production per collision $\Delta S = Q|1/T_{\text{int}} - 1/T_{\text{kin}}|$, which is shown in Fig. 4 for the two different models and for the exact solution of the scattering matrix. We see in the figure that, for this range of temperatures, the two thermostats are accurate approximations of the exact solution of the scattering problem, even far from equilibrium.

V. CONCLUSIONS

We have presented two heuristic models of collisional thermostats that induce thermalization. Our models are relatively simple to implement numerically and analytically, and overcome the main drawback of previous repeated-interaction schemes, namely that they do not induce thermalization due to the energy introduced when switching on and off the interaction [10, 11, 13]. Moreover, the two thermostats are good approximations to the scattering problem even in situations far from equilibrium, as shown in section IV.

Besides the practical interest of our models as tools to simulate or study analytically the behavior of quantum systems in contact with one or several thermal baths, they are also related to a fundamental issue in thermodynamics: the nature of heat and work.

The random-interaction-time model is similar to the repeated-interaction reservoirs considered in the literature [11, 13]. We have explored the differences between both schemes in section III B. The main ones are the removal of coherences resulting from jumps with different energy and that the interaction time is random. Both differences make the energy transferred from the reservoir to the system to be heat instead of work. Notice also that populations thermalize for a very specific distribution of interaction times —the one resulting from the effusion distribution and fulfilling the micro-reversibility condition. This result raises the question of which are the conditions or signatures for an energy transfer to be considered as heat. Heat is defined as an energy transfer between a system and its

surroundings inducing a change of entropy in the latter. The definition is precise and unambiguous if the environment is at equilibrium. The distinction between heat and work is also determinant for the performance of thermal machines: work "can do more" than heat. Since a transfer of heat Q from a thermal bath at temperature T is accompanied by a decrease of entropy $\Delta S_{\rm bath} = -Q/T$ in the bath, the second law implies that either Q is negative or there must be an increase of entropy in the system or a dissipation of heat into another bath to compensate $\Delta S_{\rm bath}$. In other words, not all the extracted heat can be transformed into useful work.

Hence, we can identify an energy transfer as heat by analyzing either where this energy comes from or what it can do. In most situations, the first option is the easiest to follow: by knowing where the energy comes from we can infer what it can do. This is one of the main achievements of classical thermodynamics.

However, if we do not have information about the physical nature or the state of the environment and know only the statistical properties of the energy transfer, how can we split it into heat and work? Our models shed some light into this problem. First, heat destroys certain coherences. Second, the random interaction times must follow a very specific distribution. If one uses a distribution different from effusion [16] or if, for instance, the interaction time is calculated using the incident velocity p_0/m instead of the one given by Eq. (34), thermalization fails. This implies that part of the energy exchanged can be considered as work, since, if the system does not thermalize, it would be possible to create a thermal machine able to extract energy from a single thermal bath, even with classical systems [16].

To summarize, we have presented two simple models of collisional thermostats given by Eqs. (30) and (33), which are novel tools to analyze open quantum systems. The models involve the removal of coherences resulting from jumps with different energy transfers between the system and the reservoir, allowing to interpret the energy exchange as heat. These results help to address the problem of how to split a given random transfer of energy into heat and work, a fundamental open question with practical implications. Its solution could be useful even for classical, meso- and macro-scopic systems, since it will help to establish benchmarks for energy harvesting from fluctuations.

Acknowledgments

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Appendix A: Properties of the scattering matrix

1. Scattering states

To obtain the scattering amplitudes we have to find the scattering states, which are solutions of the time-independent Schrödinger equation

$$H_{\rm tot}\,|\psi\rangle = \left[\frac{\hat{p}^2}{2m} + H_0 + \chi_L(\hat{x})H_{US}\right]|\psi\rangle = E\,|\psi\rangle \tag{A1}$$

and behave asymptotically as plane waves. The scattering states can be written in terms of the eigenstates $|s_J\rangle$ of the free Hamiltonian H_0 and the eigenstates $|s'_J\rangle$ of the total internal Hamiltonian $H = H_0 + H_{US}$:

$$H_0\,|s_J\rangle = e_J\,|s_J\rangle \tag{A2}$$

$$H\,|s'_J\rangle = e'_J\,|s'_J\rangle\ . \tag{A3}$$

Using these internal states, the most general solution of the time-independent Schrödinger equation reads

$$|\psi\rangle = \begin{cases} \sum_J \left(\alpha_J e^{ik_J x} + \beta_J e^{-ik_J x}\right)|s_J\rangle & \text{for } x < -L/2 \\ \sum_J \left(\alpha'_J e^{ik'_J x} + \beta'_J e^{-ik'_J x}\right)|s'_J\rangle & \text{for } -L/2 < x < L/2 \\ \sum_J \left(\alpha''_J e^{ik_J x} + \beta''_J e^{-ik_J x}\right)|s_J\rangle & \text{for } L/2 < x \quad . \end{cases} \tag{A4}$$

Applying the total Hamiltonian $H_{\rm tot}$ to state $|\psi\rangle$, we get ($\hbar = 1$):

$$H_{\rm tot}|\psi\rangle = \begin{cases} \sum_J \left(\frac{k_J^2}{2m} + e_J\right)\left(\alpha_J e^{ik_J x} + \beta_J e^{-ik_J x}\right)|s_J\rangle & \text{for } x < -L/2 \\ \sum_J \left(\frac{k_J'^2}{2m} + e'_J\right)\left(\alpha'_J e^{ik'_J x} + \beta'_J e^{-ik'_J x}\right)|s'_J\rangle & \text{for } -L/2 < x < L/2 \\ \sum_J \left(\frac{k_J^2}{2m} + e_J\right)\left(\alpha''_J e^{ik_J x} + \beta''_J e^{-ik_J x}\right)|s_J\rangle & \text{for } L/2 < x \quad . \end{cases} \tag{A5}$$

Therefore, for $|\psi\rangle$ to be a scattering eigenstate of the total Hamiltonian with energy E, the following energy conservation condition must be fulfilled:

$$\frac{k_J^2}{2m} + e_J = \frac{k_J'^2}{2m} + e'_J = E \quad \text{for all } J \quad . \tag{A6}$$

The transmission and reflection amplitudes $t_{J'J}(E)$ and $r_{J'J}(E)$, which define the scattering map via Eq. (7) and the scattering matrix (9), can be obtained from the amplitudes of the scattering state $|\psi\rangle$ by setting $\alpha_K = \delta_{KJ}$, $\beta''_K = 0$ for all K and solving for $\alpha''_{J'}$ and $\beta_{J'}$. These solutions are related with the transmission and reflection amplitudes as [15, 20]:

$$t_{J'J}(E) = \frac{k_{J'}}{k_J}\alpha''_{J'} \qquad r_{J'J}(E) = \frac{k_{J'}}{k_J}\beta_{J'} \ , \tag{A7}$$

and are defined for J and J' such that k_J and $k_{J'}$ are real, which correspond to the so-called open channels.

We now turn to an important property of the scattering states. If we write the global state as

$$|\psi\rangle = \sum_J \psi_J(x)\,|s_J\rangle \tag{A8}$$

and introduce this expression in the Schödinger equation (A1), we get

$$-\frac{1}{2m}\frac{\partial^2\psi_J(x)}{\partial x^2} + (e_J - E)\psi_J(x) + \chi_L(x)\sum_K \psi_K(x)\,\langle s_J|H_{US}|s_K\rangle = 0 \ . \tag{A9}$$

The generalization of the Wronskian

$$W(x) \equiv \sum_J \left[\frac{\partial\psi_J(x)}{\partial x}\psi_J^*(x) - \psi_J(x)\frac{\partial\psi_J^*(x)}{\partial x}\right] \tag{A10}$$

can be interpreted as a total current of particles and is independent of x. To prove it, we use the Schrödinger equation to compute the derivative

$$\begin{aligned} \frac{dW(x)}{dx} &= \sum_J \left[\frac{\partial^2\psi_J(x)}{\partial x^2}\psi_J^*(x) - \psi_J(x)\frac{\partial^2\psi_J^*(x)}{\partial x^2}\right] \\ &= 2m\ \chi_L(x)\sum_{J,K}\left[\psi_K(x)\psi_J^*(x)\,\langle s_J|H_{US}|s_K\rangle - \psi_J(x)\psi_K^*(x)\,\langle s_J|H_{US}|s_K\rangle^*\right] = 0 \ . \end{aligned} \tag{A11}$$

To prove the last equality, we have taken into account that H_{US} is self-adjoint and, consequently, the two terms in the sum are equal under a permutation of the indexes.

For a given total energy E, the solution (A4) at $x \to -\infty$ corresponds to $\psi_J(x) = \alpha_J e^{ik_J x} + \beta_J e^{-ik_J x}$ if k_J is real ($e_J \leq E$) and $\psi_J(x) \simeq 0$ if k_J is imaginary ($e_J \geq E$). Then, the Wronskian reads

$$W(x) \simeq \sum_{J:e_J \leq E} 2ik_J \left[|\alpha_J|^2 - |\beta_J|^2\right] . \tag{A12}$$

Similarly, for $x \to \infty$:

$$W(x) \simeq \sum_{J:e_J \leq E} 2ik_J \left[|\alpha''_J|^2 - |\beta''_J|^2\right] . \tag{A13}$$

Therefore

$$\sum_{J:e_J \leq E} k_J \left[|\alpha_J|^2 - |\beta_J|^2\right] = \sum_{J:e_J \leq E} k_J \left[|\alpha''_J|^2 - |\beta''_J|^2\right] . \tag{A14}$$

Notice that the sums in the previous expressions run only over the states $|s_J\rangle$ with k_J real, i.e., the incoming and outgoing plane waves. In particular, since the transmission and reflection amplitudes are given by Eq. (A7) with the coefficients of $|\psi\rangle$ calculated by setting $\alpha_K = \delta_{KJ}$ and $\beta''_K = 0$ for all K, and $E \geq e_J$, one has:

$$\sum_{J':e'_J \geq E} \frac{k_{J'}}{k_J} \left[|\beta_{J'}|^2 + |\alpha''_{J'}|^2\right] = \sum_{J':e'_J \geq E} \left[|r_{J'J}(E)|^2 + |t_{J'J}(E)|^2\right] = 1 . \tag{A15}$$

We further explore this important property in the subsection A 3.

2. Transfer and scattering matrices

The coefficients α_J, β_J, etc. in (A4) are determined by imposing the continuity of the wave function and its first derivative at $x = -L/2$ and $x = L/2$. At $x = -L/2$:

$$\sum_J \left(\alpha_J e^{-ik_J L/2} + \beta_J e^{ik_J L/2}\right) |s_J\rangle = \sum_J \left(\alpha'_J e^{-ik'_J L/2} + \beta'_J e^{ik'_J L/2}\right) |s'_J\rangle \tag{A16}$$

$$\sum_J k_J \left(\alpha_J e^{-ik_J L/2} - \beta_J e^{ik_J L/2}\right) |s_J\rangle = \sum_J k'_J \left(\alpha'_J e^{-ik'_J L/2} - \beta'_J e^{ik'_J L/2}\right) |s'_J\rangle . \tag{A17}$$

and, at $x = L/2$:

$$\sum_J \left(\alpha''_J e^{ik_J L/2} + \beta''_J e^{-ik_J L/2}\right) |s_J\rangle = \sum_J \left(\alpha'_J e^{ik'_J L/2} + \beta'_J e^{-ik'_J L/2}\right) |s'_J\rangle \tag{A18}$$

$$\sum_J k_J \left(\alpha''_J e^{ik_J L/2} - \beta''_J e^{-ik_J L/2}\right) |s_J\rangle = \sum_J k'_J \left(\alpha'_J e^{ik'_J L/2} - \beta'_J e^{-ik'_J L/2}\right) |s'_J\rangle . \tag{A19}$$

These equations can be written in a more compact form using the operators:

$$\begin{aligned} \mathbb{K}_0(E) &\equiv \sqrt{2m(E - H_0)} \\ \mathbb{K}(E) &\equiv \sqrt{2m(E - H)} \end{aligned} \tag{A20}$$

and the vectors in $\mathcal{H}_{U,\text{int}} \otimes \mathcal{H}_S$:

$$\begin{aligned} |a\rangle &= \sum_J \alpha_J |s_J\rangle ; \quad |b\rangle = \sum_J \beta_J |s_J\rangle \\ |a'\rangle &= \sum_J \alpha'_J |s'_J\rangle ; \quad |b'\rangle = \sum_J \beta'_J |s'_J\rangle \\ |a''\rangle &= \sum_J \alpha''_J |s_J\rangle ; \quad |b''\rangle = \sum_J \beta''_J |s_J\rangle . \end{aligned} \tag{A21}$$

We define the following matrix acting on the Hilbert space $[\mathcal{H}_{U,\mathrm{int}} \otimes \mathcal{H}_S] \oplus [\mathcal{H}_{U,\mathrm{int}} \otimes \mathcal{H}_S]$ and depending on a position x and an operator $\mathbb{K}$:

$$\mathbb{M}(x,\mathbb{K}) = \begin{pmatrix} e^{i\mathbb{K}x} & e^{-i\mathbb{K}x} \\ \mathbb{K}e^{i\mathbb{K}x} & -\mathbb{K}e^{-i\mathbb{K}x} \end{pmatrix} . \tag{A22}$$

Its inverse reads:

$$\mathbb{M}^{-1}(x,\mathbb{K}) = \frac{1}{2}\begin{pmatrix} e^{-i\mathbb{K}x} & \mathbb{K}^{-1}e^{-i\mathbb{K}x} \\ e^{i\mathbb{K}x} & -\mathbb{K}^{-1}e^{i\mathbb{K}x} \end{pmatrix} = \frac{1}{2}\mathbb{M}^{\dagger}(-x,\mathbb{K}^{-1}) . \tag{A23}$$

With these matrices the boundary conditions can be written as

$$\mathbb{M}(-L/2,\mathbb{K}_0)\begin{pmatrix} |a\rangle \\ |b\rangle \end{pmatrix} = \mathbb{M}(-L/2,\mathbb{K})\begin{pmatrix} |a'\rangle \\ |b'\rangle \end{pmatrix} \tag{A24}$$

$$\mathbb{M}(L/2,\mathbb{K}_0)\begin{pmatrix} |a''\rangle \\ |b''\rangle \end{pmatrix} = \mathbb{M}(L/2,\mathbb{K})\begin{pmatrix} |a'\rangle \\ |b'\rangle \end{pmatrix} . \tag{A25}$$

The transfer matrix $\mathcal{M}$ is defined as the one that connects the amplitudes of the plane waves at the right and at the left sides of the scatterer (see Fig. 5):

$$\begin{pmatrix} |a''\rangle \\ |b''\rangle \end{pmatrix} = \mathcal{M}\begin{pmatrix} |a\rangle \\ |b\rangle \end{pmatrix} . \tag{A26}$$

From the boundary conditions (A24) and (A25) one immediately gets

$$\mathcal{M} = \mathbb{M}^{-1}(L/2,\mathbb{K}_0)\mathbb{M}(L/2,\mathbb{K})\mathbb{M}^{-1}(-L/2,\mathbb{K})\mathbb{M}(-L/2,\mathbb{K}_0) . \tag{A27}$$

We also define the matrix $\mathcal{S}$ as the one relating the incoming and outgoing amplitudes (see Fig. 5):

$$\begin{pmatrix} |b\rangle \\ |a''\rangle \end{pmatrix} = \mathcal{S}\begin{pmatrix} |a\rangle \\ |b''\rangle \end{pmatrix} = \begin{pmatrix} \mathcal{S}_{11}|a\rangle + \mathcal{S}_{12}|b''\rangle \\ \mathcal{S}_{21}|a\rangle + \mathcal{S}_{22}|b''\rangle \end{pmatrix} . \tag{A28}$$

A direct comparison between (A26) and (A28) yields [18]:

$$\begin{aligned} \mathcal{S}_{11} &= -\mathcal{M}_{22}^{-1}\mathcal{M}_{21} & \mathcal{S}_{12} &= \mathcal{M}_{22}^{-1} \\ \mathcal{S}_{21} &= \mathcal{M}_{11} - \mathcal{M}_{12}\mathcal{M}_{22}^{-1}\mathcal{M}_{21} & \mathcal{S}_{22} &= \mathcal{M}_{12}\mathcal{M}_{22}^{-1} . \end{aligned} \tag{A29}$$

The matrix $\mathcal{S}$ is not exactly the scattering matrix $\tilde{\mathcal{S}}$ for two reasons. First, $\mathcal{S}$ acts on the whole Hilbert space $[\mathcal{H}_{U,\mathrm{int}} \otimes \mathcal{H}_S] \oplus [\mathcal{H}_{U,\mathrm{int}} \otimes \mathcal{H}_S]$, whereas the scattering matrix $\tilde{\mathcal{S}}$ introduced in Eq. (9) is restricted to the open channels that correspond to solutions with real wave vectors k_J. Second, the entries of $\tilde{\mathcal{S}}$ are the transmission and reflection amplitudes, which are given respectively by the amplitudes of the transmitted and reflected waves multiplied by the ratio of outgoing to incoming momenta, as given by Eq. (A7).

To define the scattering matrix, we have to introduce the subspace of open channels:

$$\mathcal{H}_{\mathrm{open}} = \mathrm{lin}\{|s_J\rangle : e_J \leq E\}. \tag{A30}$$

According to Eqs. (9) and (A7), the scattering matrix can be written as the following operator acting on $\mathcal{H}_{\mathrm{open}} \oplus \mathcal{H}_{\mathrm{open}}$:

$$\tilde{\mathcal{S}} \equiv \begin{pmatrix} \mathbb{K}_0^{1/2} & 0 \\ 0 & \mathbb{K}_0^{1/2} \end{pmatrix} \mathcal{S} \begin{pmatrix} \mathbb{K}_0^{-1/2} & 0 \\ 0 & \mathbb{K}_0^{-1/2} \end{pmatrix} = \mathbb{K}_0^{1/2}\mathcal{S}\mathbb{K}_0^{-1/2} \tag{A31}$$

where all the operators $\mathbb{K}_0$ and $\mathcal{S}_{ij}$ are restricted to $\mathcal{H}_{\mathrm{open}}$.

3. Symmetries

a. Conservation of probability current

The conservation of the total probability current (A14) imposes some constraints on the matrices $\mathcal{M}$ and $\mathcal{S}$. Let $\mathbb{P}_{\mathrm{open}}$ be the projector onto $\mathcal{H}_{\mathrm{open}}$, i.e., onto the eigenstates $|s_J\rangle$ with k_J real:

$$\mathbb{P}_{\mathrm{open}} = \sum_{J:e_J \leq E} |s_J\rangle\langle s_J| \tag{A32}$$

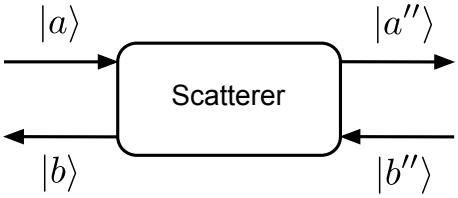

FIG. 5: Incoming and outgoing vectors in the scattering problem.

and let us define the operator acting on $[\mathcal{H}_{U,\text{int}} \otimes \mathcal{H}_S] \oplus [\mathcal{H}_{U,\text{int}} \otimes \mathcal{H}_S]$

$$\mathcal{P} = \begin{pmatrix} \mathbb{P}_{\text{open}} & 0 \\ 0 & \mathbb{P}_{\text{open}} \end{pmatrix} , \tag{A33}$$

which verifies $\mathcal{P}^2 = \mathcal{P}$. Condition (A14) can be written as

$$(\langle a| \ \langle b|) \begin{pmatrix} \mathbb{K}_0\mathbb{P}_{\text{open}} & 0 \\ 0 & -\mathbb{K}_0\mathbb{P}_{\text{open}} \end{pmatrix} \begin{pmatrix} |a\rangle \\ |b\rangle \end{pmatrix} = (\langle a''| \ \langle b''|) \begin{pmatrix} \mathbb{K}_0\mathbb{P}_{\text{open}} & 0 \\ 0 & -\mathbb{K}_0\mathbb{P}_{\text{open}} \end{pmatrix} \begin{pmatrix} |a''\rangle \\ |b''\rangle \end{pmatrix} . \tag{A34}$$

Applying the relationship (A26) between the amplitudes of the waves at the right and left sides of the scatterer via the transfer matrix, we obtain

$$\begin{pmatrix} \mathbb{K}_0 & 0 \\ 0 & -\mathbb{K}_0 \end{pmatrix} \mathcal{P} = \mathcal{M}^\dagger \begin{pmatrix} \mathbb{K}_0 & 0 \\ 0 & -\mathbb{K}_0 \end{pmatrix} \mathcal{P}\mathcal{M} \tag{A35}$$

and, multiplying by $\mathcal{P}$ from right, we get

$$\mathcal{M}^\dagger \begin{pmatrix} \mathbb{K}_0 & 0 \\ 0 & -\mathbb{K}_0 \end{pmatrix} \mathcal{P}\mathcal{M} = \mathcal{M}^\dagger \begin{pmatrix} \mathbb{K}_0 & 0 \\ 0 & -\mathbb{K}_0 \end{pmatrix} \mathcal{P}\mathcal{M}\mathcal{P} . \tag{A36}$$

Since $\mathcal{M}^\dagger$ and $\mathbb{K}_0$ are both invertible in their respective Hilbert spaces (we assume that $k_J \neq 0$ for all J), we conclude that $\mathcal{P}\mathcal{M}\mathcal{P} = \mathcal{P}\mathcal{M}$ or $\mathcal{P}\mathcal{M}(\mathbb{I} - \mathcal{P}) = 0$. This relationship indicates that the amplitudes of the real exponentials (k_J imaginary) do not affect the amplitudes of the plane waves (k_J real) and that we can restrict ourselves to $\mathcal{H}_{\text{open}}$, the subspace of eigenstates of H_0 with k_J real, which correspond to the open channels in a collision with total energy E [15, 20]. Notice however that $\mathcal{P}$ and $\mathcal{M}$ do not necessarily commute, i.e., $\mathcal{H}_{\text{open}}$ is not in general invariant under the transfer matrix $\mathcal{M}$. However, the action of $\mathcal{M}$ on vectors in $\mathcal{H}_{\text{open}}$ is entirely determined by its restriction to this subspace $\mathcal{P}\mathcal{M}\mathcal{P}$. In particular any power n of $\mathcal{M}$ verifies $\mathcal{P}\mathcal{M}^n\mathcal{P}{=}(\mathcal{P}\mathcal{M}\mathcal{P})^n$ and the inverse of $\mathcal{M}$ in $\mathcal{H}_{\text{open}}$ is $\mathcal{P}\mathcal{M}^{-1}\mathcal{P}$, that is $[\mathcal{P}\mathcal{M}\mathcal{P}][\mathcal{P}\mathcal{M}^{-1}\mathcal{P}] = [\mathcal{P}\mathcal{M}^{-1}\mathcal{P}][\mathcal{P}\mathcal{M}\mathcal{P}] = \mathcal{P}$. The same arguments apply to the matrix $\mathcal{S}$, which obeys $\mathcal{P}\mathcal{S}(\mathbb{I} - \mathcal{P}) = 0$. Hence, from now on, we can neglect the eigenstates $|s_J\rangle$ with imaginary k_J and explore the properties of the matrices $\mathcal{M}$ and $\mathcal{S}$ restricted to $\mathcal{H}_{\text{open}}$. Nevertheless, we will keep the same notation, for simplicity. Notice also that k'_J, the wave vectors within the scattering region $[-L/2, L/2]$, can be imaginary, indicating that the corresponding channel is associated with tunneling.

A second important consequence of the conservation of probability current is the unitarity of the scattering matrix. Condition (A14) can be written as

$$(\langle a| \ \langle b''|)\, \mathbb{K}_0 \begin{pmatrix} |a\rangle \\ |b''\rangle \end{pmatrix} = (\langle b| \ \langle a''|)\, \mathbb{K}_0 \begin{pmatrix} |b\rangle \\ |a''\rangle \end{pmatrix} = (\langle a| \ \langle b''|)\, \mathcal{S}^\dagger\mathbb{K}_0\mathcal{S} \begin{pmatrix} |a\rangle \\ |b''\rangle \end{pmatrix} \tag{A37}$$

where all vectors and operators are restricted to $\mathcal{H}_{\text{open}}$. Hence, $\mathbb{K}_0 = \mathcal{S}^\dagger\mathbb{K}_0\mathcal{S}$ in this subspace and we finally obtain

$$\tilde{\mathcal{S}}^\dagger\tilde{\mathcal{S}} = \mathbb{K}_0^{-1/2}\mathcal{S}^\dagger\mathbb{K}_0^{1/2}\mathbb{K}_0^{1/2}\mathcal{S}\,\mathbb{K}_0^{-1/2} = \mathbb{I} \tag{A38}$$

that is, the scattering matrix $\tilde{\mathcal{S}}$ is unitary.

b. Spatial symmetry

The collision problem that we consider in this paper is invariant under spatial inversion $x \to -x$, which is equivalent to the following transformation of vectors:

$$|a\rangle \leftrightarrow |b''\rangle \qquad |b\rangle \leftrightarrow |a''\rangle \tag{A39}$$

This transformation converts (A28) into

$$\begin{pmatrix} |a''\rangle \\ |b\rangle \end{pmatrix} = \mathcal{S} \begin{pmatrix} |b''\rangle \\ |a\rangle \end{pmatrix} \tag{A40}$$

and comparing this expression with (A40), we get

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \mathcal{S} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \mathcal{S} \tag{A41}$$

which yields $\mathcal{S}_{11} = \mathcal{S}_{22}$ and $\mathcal{S}_{12} = \mathcal{S}_{21}$. The same symmetry applies to the scattering matrix $\tilde{\mathcal{S}}$. The entries of this matrix are denoted as [15]

$$\tilde{\mathcal{S}} = \begin{pmatrix} \mathbf{r} & \mathbf{t} \\ \mathbf{t} & \mathbf{r} \end{pmatrix} \tag{A42}$$

where $\mathbf{r}$ and $\mathbf{t}$ are matrices whose elements are the reflection and transmission amplitudes, respectively. The unitarity of $\tilde{\mathcal{S}}$ derived in Eq. (A38), can be written now as

$$\begin{aligned} \mathbf{r}\mathbf{r}^\dagger + \mathbf{t}\mathbf{t}^\dagger &= \mathbb{I} \\ \mathbf{r}\mathbf{t}^\dagger + \mathbf{t}\mathbf{r}^\dagger &= 0 \, . \end{aligned} \tag{A43}$$

c. Time-reversal symmetry

The symmetry under time reversal implies that there is an anti-unitary operator $\mathsf{T}_{\rm int}$ in the Hilbert space of internal states that commutes with H_0 and H_{US}. As discussed in the main text, the total time-reversal operator is $\mathsf{T} = \mathsf{T}_{U,\rm p} \otimes \mathsf{T}_{\rm int}$ where $\mathsf{T}_{U,\rm p}$ is the conjugation of the wave function in the position representation. Hence, if $|\psi\rangle$ is given by (A8), then

$$\mathsf{T}\,|\psi\rangle = \sum_J \psi_J^*(x) \mathsf{T}_{\rm int}\,|s_J\rangle \ . \tag{A44}$$

For simplicity, we assume that the eigenstates of H_0 are invariant under time reversal, i.e., $\mathsf{T}_{\rm int}\,|s_J\rangle = |s_J\rangle$. In this case, $[H_{US}, \mathsf{T}_{\rm int}] = 0$ implies that $\langle s_J|H_{US}|s_K\rangle$ is real, that is, the matrix of the interaction Hamiltonian H_{US} in the eigenbasis of H_0 is real and symmetric. To prove this property, take into account that an anti-unitary operator verifies $(\mathsf{T}\,|a\rangle\,, \mathsf{T}\,|b\rangle) = (|a\rangle\,, |b\rangle)^*$, where $(\cdot,\cdot)$ is the scalar product in the Hilbert space. Hence, we can take the complex conjugate of the Schrödinger equation (A9) and obtain the following transformation under time reversal for the vectors restricted to $\mathcal{H}_{\rm open}$:

$$|a\rangle \leftrightarrow |b^*\rangle \qquad |a''\rangle \leftrightarrow |b''^*\rangle \tag{A45}$$

where $|b^*\rangle = \mathsf{T}|b\rangle = \sum_j \beta_j^*\,|s_j\rangle$. This symmetry implies

$$\begin{pmatrix} |a^*\rangle \\ |b''^*\rangle \end{pmatrix} = \mathcal{S} \begin{pmatrix} |b^*\rangle \\ |a''^*\rangle \end{pmatrix} . \tag{A46}$$

Using (A28), we obtain $\mathcal{S}^*\mathcal{S} = \mathbb{K}_0^{-1/2} \tilde{\mathcal{S}}^* \tilde{\mathcal{S}}\, \mathbb{K}_0^{1/2} = \mathbb{I}$, implying $\tilde{\mathcal{S}}^*\tilde{\mathcal{S}} = \mathbb{I}$, and

$$\begin{aligned} \mathbf{r}\mathbf{r}^* + \mathbf{t}\mathbf{t}^* &= \mathbb{I} \\ \mathbf{r}\mathbf{t}^* + \mathbf{t}\mathbf{r}^* &= 0 \, . \end{aligned} \tag{A47}$$

Combining this symmetry with the unitarity of the scattering matrix, Eq. (A43), we conclude that the matrices $\mathbf{t}$ and $\mathbf{r}$ are symmetric.

Appendix B: The high energy and large scatterer limit

The matrix $\mathcal{M}$ can be calculated exactly from Eq. (A27). Here we introduce an approximation that preserves the symmetries and the unitarity of the scattering matrix and therefore provides a simple implementation of a thermal reservoir. The approximation is valid for incident particles with a large kinetic energy and a long scatterer, that is E and L large. In this case, we can approximate $\mathbb{K}^{-1}\mathbb{K}_0 \simeq \mathbb{I}$ and

$$\begin{aligned}\mathbb{M}^{-1}(L/2,\mathbb{K}_0)\mathbb{M}(L/2,\mathbb{K}) &= \frac{1}{2}\begin{pmatrix} e^{-i\mathbb{K}_0 L/2} & \mathbb{K}_0^{-1}e^{-i\mathbb{K}_0 L/2} \\ e^{i\mathbb{K}_0 L/2} & -\mathbb{K}_0^{-1}e^{i\mathbb{K}_0 L/2}\end{pmatrix}\begin{pmatrix} e^{i\mathbb{K}L/2} & e^{-i\mathbb{K}L/2} \\ \mathbb{K}e^{i\mathbb{K}L/2} & -\mathbb{K}e^{-i\mathbb{K}L/2}\end{pmatrix} \\ &\simeq \begin{pmatrix} e^{-i\mathbb{K}_0 L/2}e^{i\mathbb{K}L/2} & 0 \\ 0 & e^{i\mathbb{K}_0 L/2}e^{-i\mathbb{K}L/2}\end{pmatrix} \end{aligned} \tag{B1}$$

and

$$\begin{aligned}\mathbb{M}^{-1}(-L/2,\mathbb{K})\mathbb{M}(-L/2,\mathbb{K}_0) &= \frac{1}{2}\begin{pmatrix} e^{i\mathbb{K}L/2} & \mathbb{K}^{-1}e^{i\mathbb{K}L/2} \\ e^{-i\mathbb{K}L/2} & -\mathbb{K}^{-1}e^{-i\mathbb{K}L/2}\end{pmatrix}\begin{pmatrix} e^{-i\mathbb{K}_0 L/2} & e^{i\mathbb{K}_0 L/2} \\ \mathbb{K}_0 e^{-i\mathbb{K}_0 L/2} & -\mathbb{K}_0 e^{i\mathbb{K}_0 L/2}\end{pmatrix} \\ &\simeq \begin{pmatrix} e^{i\mathbb{K}L/2}e^{-i\mathbb{K}_0 L/2} & 0 \\ 0 & e^{-i\mathbb{K}L/2}e^{i\mathbb{K}_0 L/2}\end{pmatrix} \end{aligned} \tag{B2}$$

yielding

$$\mathcal{M} \simeq \begin{pmatrix} e^{-i\mathbb{K}_0 L/2}e^{i\mathbb{K}L}e^{-i\mathbb{K}_0 L/2} & 0 \\ 0 & e^{i\mathbb{K}_0 L/2}e^{-i\mathbb{K}L}e^{i\mathbb{K}_0 L/2}\end{pmatrix}. \tag{B3}$$

Using Eqs. (A29) and the definition of the scattering matrix (A31), we find that the scattering matrix $\tilde{\mathcal{S}}$ and the matrix $\mathcal{S}$ in this approximation read

$$\tilde{\mathcal{S}} \simeq \mathcal{S} \simeq \begin{pmatrix} 0 & e^{-i\mathbb{K}_0 L/2}e^{i\mathbb{K}L}e^{-i\mathbb{K}_0 L/2} \\ e^{-i\mathbb{K}_0 L/2}e^{i\mathbb{K}L}e^{-i\mathbb{K}_0 L/2} & 0\end{pmatrix}. \tag{B4}$$

We see that, in this approximation, the reflection amplitudes vanish and the transition amplitudes read

$$\langle s_{J'}|\mathbf{t}|s_J\rangle \simeq e^{-i(k_J+k_{J'})L/2}\,\langle s_{J'}|e^{i\mathbb{K}L}|s_J\rangle\ . \tag{B5}$$

This matrix is unitary and symmetric for a given energy $E = k_J^2/(2m) + e_J = k_{J'}^2/(2m) + e_{J'}$ if $\mathbb{K}$ is self-adjoint, that is, if all k'_J are real. Therefore, this approximation, which is the basis for the wave-vector-operator model described in section III A, fulfills all the symmetries of the original collision problem. To see that the matrix is symmetric under the assumptions made in the main text, notice that $[H, \mathsf{T}_{\rm int}] = 0$ implies $e^{i\mathbb{K}L}\mathsf{T}_{\rm int} = \mathsf{T}_{\rm int}e^{-i\mathbb{K}L}$ in the subspace where $\mathbb{K}$ is self-adjoint. Therefore, for energies $E \geq e_{\max}$, we have

$$\begin{aligned}\langle s_{J'}|e^{i\mathbb{K}L}|s_J\rangle &= (\mathsf{T}_{\rm int}\,|s_{J'}\rangle\,, e^{i\mathbb{K}L}\mathsf{T}_{\rm int}\,|s_J\rangle) \\ &= (\mathsf{T}_{\rm int}\,|s_{J'}\rangle\,, \mathsf{T}_{\rm int}e^{-i\mathbb{K}L}\,|s_J\rangle) \\ &= (|s_{J'}\rangle\,, e^{-i\mathbb{K}L}\,|s_J\rangle)^* \\ &= \langle s_{J'}|e^{-i\mathbb{K}L}|s_J\rangle^* \\ &= \langle s_J|e^{i\mathbb{K}L}|s_{J'}\rangle \end{aligned} \tag{B6}$$

where we have used the time-reversal invariance of the eigenstates of H_0, $\mathsf{T}_{\rm int}\,|s_J\rangle = |s_J\rangle$ for all J. The same symmetry holds if we replace $\mathbb{K}L$ by $H\tau$, as in the random-interaction-time model, or by any real function of H.

Appendix C: The random-interaction-time model for the two-qubit example

Here we explicitly derive some properties of the example studied in Sec. IV. The total internal Hamiltonian H in the eigenbasis of the free Hamiltonian (42), ordered as $\{|00\rangle_{US}\,, |01\rangle_{US}\,, |10\rangle_{US}\,, |11\rangle_{US}\}$, reads

$$H = H_0 + H_{US} = \begin{pmatrix} \Omega & 0 & 0 & \xi \\ 0 & \Delta\omega & \Xi & 0 \\ 0 & \Xi & -\Delta\omega & 0 \\ \xi & 0 & 0 & -\Omega\end{pmatrix} \tag{C1}$$

where $\Omega = \omega_S + \omega_U$, $\Delta\omega = \omega_U - \omega_S$, $\Xi = J_x + J_y$, and $\xi = J_x - J_y$. The block structure of this matrix allows only for transitions $|11\rangle_{US} \leftrightarrow |00\rangle_{US}$ and $|10\rangle_{US} \leftrightarrow |01\rangle_{US}$. The eigenvalues of H are $\pm\sqrt{\Omega^2 + \xi^2}$ and $\pm\sqrt{\Delta\omega^2 + \Xi^2}$.

If $J_x = J_y$, then $\xi = 0$ and the only permitted transitions are the swaps $|10\rangle_{US} \leftrightarrow |01\rangle_{US}$ and the probability that the system jumps from 0 to 1 in the random-interaction-time model with $\tau_{\text{packet}}(p_0) \equiv Lm/p_0$ reads:

$$p(j_S = 0 \to j'_S = 1) = \frac{e^{-\beta\omega_U}}{Z_U} \int_{\sqrt{2me_{\max}}}^{\infty} dp_0\, \mu(p_0) \left\langle 0\,1 \right| e^{-i\tau_{\text{packet}}(p_0)H} \left| 1\,0 \right\rangle \tag{C2}$$

whereas

$$p(j_S = 1 \to j'_S = 0) = \frac{1}{Z_U} \int_{\sqrt{2me_{\max}}}^{\infty} dp_0\, \mu(p_0) \left\langle 1\,0 \right| e^{-i\tau_{\text{packet}}(p_0)H} \left| 0\,1 \right\rangle . \tag{C3}$$

Then, the ratio verifies

$$\frac{p(j_S = 0 \to j'_S = 1)}{p(j_S = 1 \to j'_S = 0)} = e^{-\beta\omega_U} \tag{C4}$$

and the system thermalizes in the resonant case, $\omega_U = \omega_S$, where heat is identically zero.

On the other hand, if $J_x = -J_y$, then $\Xi = 0$ and the only permitted transitions are $|00\rangle_{US} \leftrightarrow |11\rangle_{US}$. Hence

$$p(j_S = 1 \to j'_S = 0) = \frac{e^{-\beta\omega_U}}{Z_U} \int_{\sqrt{2me_{\max}}}^{\infty} dp_0\, \mu(p_0) \left\langle 0\,0 \right| e^{-i\tau_{\text{packet}}(p_0)H} \left| 1\,1 \right\rangle \tag{C5}$$

whereas

$$p(j_S = 0 \to j'_S = 1) = \frac{1}{Z_U} \int_{\sqrt{2me_{\max}}}^{\infty} dp_0\, \mu(p_0) \left\langle 1\,1 \right| e^{-i\tau_{\text{packet}}(p_0)H} \left| 0\,0 \right\rangle . \tag{C6}$$

Now the ratio verifies

$$\frac{p(j_S = 0 \to j'_S = 1)}{p(j_S = 1 \to j'_S = 0)} = e^{\beta\omega_U} \tag{C7}$$

which indicates that the steady state exhibit a population inversion with negative absolute temperature, as shown in Fig. 3.

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Quantum scattering as a work source

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We show that the state of two quantum systems A and B after a short time-dependent interaction equals the state after a collision between A and B provided that the wave packet associated to their relative motion is fast and broad compared to the energies of A and B. The entropy change in the joint system A and B vanishes and the change in kinetic energy due to their collision is equivalent to (minus) the work generated by the time-dependent interaction.

Time-dependent Hamiltonians are commonly used to describe the interaction of quantum systems with external degrees of freedom. The most prominent example is the semi-classical treatment of light-matter interaction, where one introduces a time-dependent function to describe the effect of the electromagnetic field upon the atom [1–4].

Another example more relevant to our work is the description of a collision between two particles. In a semi-classical approximation, one can replace the relative motion between the particles with a time-dependent interaction [5]. But while the energy change resulting from a time-dependent Hamiltonian is identified as work in quantum thermodynamics [6–12], we have shown in Ref. [13] that the energy exchanged in the collision may correspond to heat, even at high kinetic energy when one expects the semi-classical limit to be valid.

In this letter, we investigate this problem and derive the conditions for the equivalence between the autonomous collision dynamics of two particles with internal structure and the corresponding time-dependent model. We do so by monitoring thermodynamic quantities like energy and entropy change. In this way, we identify an ideal autonomous work source for an open system subjected to collision events, which is relevant for quantum thermodynamics in general [8, 9] and for developing autonomous work extraction devises [14] in particular.

We start by considering time-dependent models (TDM) describing two interacting quantum systems A and B for a time τ with Hamiltonian $\hat{H}(t) = \hat{H}_Y + \hat{V}(t)$. Here, $\hat{H}_Y = \hat{H}_A \otimes \hat{\mathbb{I}}_B + \hat{\mathbb{I}}_A \otimes \hat{H}_B$ is the Hamiltonian of the joint system Y and $\hat{\mathbb{I}}_A$ denotes the identity operator on the Hilbert space of A (equivalently for B). The time-dependent interaction is given by $\hat{V}(t) = \tilde{V}(t)\hat{\nu}$, where $\tilde{V}(t)$ is a non-vanishing function only in the interval $t \in (-\tau/2, \tau/2)$ and $\hat{\nu}$ is a time-independent operator. In the interaction picture, the density operator describing the state Y after the interaction is given by

$$\hat{\rho}_\tau = \hat{U}_I(\tau)(\hat{\rho}_A \otimes \hat{\rho}_B)\hat{U}_I^\dagger(\tau) \,, \tag{1}$$

where the initial state is assumed factorized. The unitary operator in the interaction picture is the solution to the von Neumann equation

$$d_t \hat{U}_I(t) = -\frac{i}{\hbar}\hat{V}_I(t)\hat{U}_I(t) \tag{2}$$

where d_t is the total time derivative and $\hat{V}_I(t) = e^{i\hat{H}_Y t/\hbar}\hat{V}(t)e^{-i\hat{H}_Y t/\hbar}$ is the interaction in the interaction picture. The unitary evolution of Y implies the invariance of its von Neumann entropy $\Delta S_\tau \equiv S(\hat{\rho}_\tau) - S(\hat{\rho}_A \otimes \hat{\rho}_B) = 0$ with $S(\hat{\rho}) = -k_B \mathrm{Tr}[\hat{\rho}\log\hat{\rho}] \geq 0$. The energy change during the interaction is interpreted as work and given by [6, 7, 10]

$$W = \mathrm{Tr}[\hat{H}_Y(\hat{\rho}_\tau - \hat{\rho}_A \otimes \hat{\rho}_B)] \,, \tag{3}$$

and vanishes if $\hat{H}_Y$ and $\hat{V}(t)$ commute for all times.

We now compare these models with one dimensional scattering models (SCM) in which a moving particle of mass m with internal and kinetic degrees of freedom, respectively denoted by B and X, collides with a fixed system A. In general, both particles can move but our choice simplifies the treatment without loss of generality. The Hamiltonian of the full system reads $\hat{H} = \hat{H}_0 + \hat{V}(\hat{x})$, where $\hat{H}_0 = \hat{H}_Y \otimes \hat{\mathbb{I}}_X + \hat{\mathbb{I}}_Y \otimes \hat{p}^2/2m$ and $\hat{H}_Y$ is the same as for TDM. The kinetic energy operator accounts for the motion of the particle, obeying the eigenvalue equation $(\hat{p}^2/2m)\,|p\rangle = E_p\,|p\rangle$. Here, $\{|p\rangle\}$ are improper (non-normalizable) eigenstates whose position representation are plane waves $\langle x|p\rangle = \exp(\mathrm{i}px/\hbar)/\sqrt{2\pi\hbar}$ and $E_p = p^2/2m \geq 0$ is the kinetic energy. The interaction between the particles is described by the operator $\hat{V}(\hat{x}) = V(\hat{x}) \otimes \hat{\nu}$, where $V(x)$ is a non-vanishing function only inside the interval $x \in (-a/2, a/2)$ defined by $V(\hat{x})\,|x\rangle \equiv V(x)\,|x\rangle$. We take the full system to be initially in a factorized state $\hat{\rho}_A \otimes \hat{\rho}_B \otimes \hat{\rho}_X$ with $\hat{\rho}_X = |\phi\rangle\langle\phi|$,

where $\phi(p) \equiv \langle p|\phi\rangle = (2\pi\sigma^2)^{-1/4}\exp[-(p-p_0)^2/4\sigma^2 - ipx_0/\hbar]$ is a Gaussian wave packet with average momentum $p_0 = \langle\phi|\,\hat{p}\,|\phi\rangle$ and position $x_0 = \langle\phi|\,\hat{x}\,|\phi\rangle$, normalized according to $\int dp\,\langle p|\hat{\rho}_X|p\rangle = \int dp|\phi(p)|^2 = 1$. We consider that $p_0 \gg \sigma > 0$, so that the particle is incident from the left with positive momenta: $\phi(p) \simeq 0$ for $p < 0$. Scattering theory allow us to compute the final state of Y after the collision

$$\hat{\rho}' = \mathrm{Tr}_X\left[\hat{S}\left(\hat{\rho}_A \otimes \hat{\rho}_B \otimes \hat{\rho}_X\right)\hat{S}^\dagger\right] , \tag{4}$$

where Tr_X denotes the partial trace over X, $\hat{S}$ is the unitary scattering operator satisfying $\hat{S}\hat{S}^\dagger = \hat{S}^\dagger\hat{S} = \hat{\mathbb{I}}$ and $\hat{\mathbb{I}}$ is the identity in the Hilbert space of the full system. In general, the dynamics for the system Y described by Eq. (4) is not unitary and thus the associated entropy change for a collision $\Delta S = S(\hat{\rho}') - S(\hat{\rho}_A \otimes \hat{\rho}_B)$ is nonzero. The energy change in Y is given by

$$\Delta E = \mathrm{Tr}_Y\left[\hat{H}_Y(\hat{\rho}' - \hat{\rho}_A \otimes \hat{\rho}_B)\right] = -\Delta E_p , \tag{5}$$

where $\Delta E_p = \mathrm{Tr}_X[(\hat{p}^2/2m)(\hat{\rho}'_X - \hat{\rho}_X)]$ is the change in kinetic energy and $\hat{\rho}'_X$ is the final state of the wave packet, obtained by tracing over Y instead of X in Eq. (4). The second equality in Eq. (5) follows from energy conservation in a collision as expressed by the commutation relation $[\hat{S}, \hat{H}_0] = 0$.

For the TDM and SCM respectively, we introduce the effective interaction potentials $\langle\tilde{V}\rangle \equiv \tau^{-1}\int_{-\tau/2}^{\tau/2}\tilde{V}(t)dt$ and $\langle V\rangle \equiv a^{-1}\int_{-a/2}^{a/2}V(x)dx = \tau_{p_0}^{-1}\int_{-\tau_{p_0}/2}^{\tau_{p_0}/2}V(p_0 t/m)dt$, where the respective interaction times are τ and $\tau_p \equiv ma/p$ (the time needed for the center of the wave packet with incoming momentum p to travel the distance a).

Provided the equivalence $\tau = \tau_{p_0}$ and $\langle\tilde{V}\rangle = \langle V\rangle$ our first main result is that the dynamics given by Eq. (1) and Eq. (4) are equivalent when: 1) The interaction time is much smaller than the time associated with the free evolution of the internal system $\tau \ll \hbar/\Delta_Y$. 2) The wave packet is fast and broad with respect to the system $p_0 \gg \sigma \gg m\Delta_Y/p_0$. 3) The wave packet travels semiclassically over the potential $E_{p_0} \gg V(x)$ and $p_0 a_{\min} \gg \hbar$. Here, $a_{\min}$ is the minimal length scale over which $V(x)$ varies and Δ_Y is a characteristic energy scale of the internal system Y. Specifically, considering $\{|i\rangle\}_{i=1}^N$ the eigenbasis of $\hat{H}_Y$ and $\hat{H}_Y\,|i\rangle = e_i\,|i\rangle$, where e_i increase with i, we define $\Delta_{j'j} \equiv e_{j'} - e_j$ and $\Delta_Y \equiv \Delta_{N1}$.

Under these conditions, the dynamics in either model is given by the unitary transformation

$$\hat{\rho}' = e^{-i\tau\hat{V}/\hbar}\,\left(\hat{\rho}_A \otimes \hat{\rho}_B\right)\,e^{i\tau\hat{V}/\hbar} , \tag{6}$$

where $\hat{V} \equiv \langle V\rangle\hat{\nu}$. This immediately implies a vanishing entropy change in both models. Our second result follows directly from the last expression applied to Eqs. (3) and (5), showing that work in the TDM is given by minus the change in kinetic energy of the wave packet.

Time dependent model: We first discuss how to derive the aforementioned results for TDM starting from Eq. (2). The solution to this equation can be generally written as $\hat{U}_I(\tau) = \exp\hat{\Omega}(\tau)$, where $\hat{\Omega}(\tau) = \sum_{k=1}^{\infty}\hat{\Omega}_k(\tau)$ is the Magnus expansion [26, 28], whose first two terms read

$$\hat{\Omega}_1(\tau) = -\frac{i}{\hbar}\int_{-\tau/2}^{\tau/2}\hat{V}_I(t)dt , \tag{7}$$

$$\hat{\Omega}_2(\tau) = -\frac{1}{2\hbar^2}\int_{-\tau/2}^{\tau/2}dt\int_{-\tau/2}^{t}dt'[\hat{V}_I(t), \hat{V}_I(t')] . \tag{8}$$

The higher-order terms consist of linear combinations of nested commutators of $[\hat{V}_I(t), \hat{V}_I(t')]$. To simplify this expansion, we take the interaction time to be very short compared to the internal dynamics (condition 1) which immediately implies that $\hat{V}_I(t) \simeq \hat{V}(t)$. In this case, we have $[\hat{V}(t), \hat{V}(t')] \simeq \tilde{V}(t)\tilde{V}(t')[\hat{\nu}, \hat{\nu}] = 0$, due to the factorized form of the interaction, and we are left with the first order term of the expansion. Using the definition given above for $\langle\tilde{V}\rangle$, and the equality $\langle\tilde{V}\rangle = \langle V\rangle$, we immediately get $\hat{U}_I(\tau) = \exp(-i\tau\hat{V}/\hbar)$, which is also the evolution operator in the Schrödinger picture due to condition 1. We thus conclude that Eq. (1) reduces to Eq. (6) under condition 1.

Scattering model: We now discuss how to derive our main results from SCM starting from Eq. (4). We recall that, due to the conservation of energy, the scattering operator in the eigenbasis of $\hat{H}_0$, denoted by $|p, j\rangle \equiv |p\rangle \otimes |j\rangle$, is given by [13, 18, 19]

$$\langle p', j'|\,\hat{S}\,|p, j\rangle = \frac{\sqrt{|pp'|}}{m}\delta(E_p - E_{p'} - \Delta_{j'j})s_{j'j}^{(\alpha'\alpha)}(E) , \tag{9}$$

where $s_{j'j}^{(\alpha'\alpha)}(E)$ is the scattering matrix at total energy $E = E_p + e_j$ and $\alpha = \mathrm{sign}(p)$ and $\alpha' = \mathrm{sign}(p')$ accounts for the initial and final direction of the momenta, which can be positive ($\alpha, \alpha' = +$) or negative ($\alpha, \alpha' = -$). Using expression (9) and taking the partial trace over momentum, we write Eq. (4) in the eigenbasis of $\hat{H}_Y$ as [13]

$$\rho'_{j'k'} = \sum_{jk}\mathbb{S}_{j'k'}^{jk}(\hat{\rho}_A \otimes \hat{\rho}_B)_{jk} , \tag{10}$$

where $\rho'_{j'k'} \equiv \langle j'|\hat{\rho}'|k'\rangle$ and the scattering map for a pure, incoming state X is given by

$$\mathbb{S}_{j'k'}^{jk} = \sum_{\alpha'=\pm}\int_{p_{\inf}}^{\infty}dp\,\phi(p)\phi^*\left(\pi(p)\right)\sqrt{\frac{p}{\pi(p)}} \times s_{j'j}^{(\alpha'+)}(E_p + e_j)\left[s_{k'k}^{(\alpha'+)}(E_p - \Delta_{j'j} + e_{k'})\right]^* . \tag{11}$$

In the last expression, $\pi(p) = \sqrt{p^2 - 2m(\Delta_{j'j} - \Delta_{k'k})}$, and the lower integration limit $p_{\inf}$ is obtained from $p_{\inf}^2/2m = \max\{0, \Delta_{j'j}, \Delta_{j'j} - \Delta_{k'k}\}$, which guarantees that the channels are open in the integration domain.

First, we consider that the wave packet travels at very high kinetic energies compared to the energies of the internal system $E_p \gg \Delta_Y$ for all p, and that the packet is very broad with respect to the system $\sigma \gg m\Delta_Y/p_0$. We show in the Supplementary Material [28] that under these conditions $\phi(p)\phi(\pi(p))^* \simeq |\phi(p)|^2$, meaning that the outgoing wave packets associated with different transitions in the internal system Y fully overlap, and the populations and coherences in Eq. (11) are coupled in the collision [13]. Moreover, under the conditions mentioned above, summarized by condition 2, the lower integration limit in Eq. (11) can be extended to minus infinity.

Secondly, the dependence on the shape of the potential $V(x)$ of the scattering matrix simplifies in the semi classical regime (condition 3) [29, 30]. Indeed, reflection is negligible and the effect of the collision is a shift in $(m/\hbar p)\int_{-a/2}^{a/2} V(x)\hat{\nu}\ dx = \tau_p\langle V\rangle\hat{\nu}/\hbar$ on the phase of Y. As we show in the Supplementary Material [28], the scattering matrix simplifies to

$$s_{j'j}^{(\alpha'+)}(E_p) = \delta_{\alpha'+}\ \langle j'|e^{-i\tau_p\hat{V}/\hbar}|j\rangle\ . \tag{12}$$

In other words, we are justified in treating the potential $V(x)$ as an effective barrier of length a and height $\langle V\rangle$. The last expression has been obtained for a potential barrier via transfer matrix methods in the semi classical regime [27].

After these considerations, the scattering map in Eq. (11) is greatly simplified and Eq. (10) can be written in a basis-independent fashion as

$$\hat{\rho}' = \int_{-\infty}^{\infty} dp|\phi(p)|^2\ e^{-i\tau_p\hat{V}/\hbar}\ (\hat{\rho}_A\otimes\hat{\rho}_B)\ e^{i\tau_p\hat{V}/\hbar}\ . \tag{13}$$

The last step involves performing a saddle point around p_0 to perform the integral, which is possible since $p_0 \gg \sigma$ is fulfilled (see Supplementary Material [28]). After this we obtain our main result in Eq. (6) with $\tau = ma/p_0$, showing the equivalence between the dynamics of TDM and SCM. It follows that work in the former can be interpreted as change in kinetic energy in the latter.

Application: To illustrate our results, we consider a numerical model where A and B are both spins 1/2 with Hamiltonians $\hat{H}_A = \Delta_A\hat{\sigma}_A^z$ where $2\Delta_A$ is the energy gap of A and $\hat{\sigma}_A^i$ are Pauli matrices $i = x, y, z$ in the Hilbert space of A (equivalently for B). The internal interaction between the spins is given by $\hat{\nu} = \hat{\sigma}_A^x\otimes\hat{\sigma}_B^x$. Regarding the potential $\tilde{V}(t)$ in TDM we choose a triangular barrier $\tilde{V}(t) = (4/\tau)V_0(\tau/2 - |t|)$ for $|t| < \tau/2$ and zero otherwise with $V_0 > 0$. The exact dynamics is computed by solving Eqs. (2) and (1). For SCM, we take a sinusoidal potential vanishing at the boundaries $V(x) = (\pi/2)V_0\cos(\pi x/a)$ for $|x| < a/2$ and zero otherwise. The minimal scale characterizing this potential is $a_{\min} \sim a$. The exact scattering matrix is solved by using the non-linear equations of multi-channel scattering theory [16] summarized in the Supplementary Material [28]. These are plugged in Eq. (11) which in turn is used in the scattering map Eq. (10). As required by our theory, $\langle\tilde{V}\rangle = \langle V\rangle = V_0$.

The model in Eq. (6) can be solved analytically (see [28]). The unitary operator $\exp(-i\lambda\hat{\sigma}_A^x\otimes\hat{\sigma}_B^x)$ generates an oscillatory dynamics with period π in terms of the coupling parameter $\lambda \equiv V_0\tau/\hbar$ with two independent sectors, $\{|\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$ and $\{|\downarrow\uparrow\rangle, |\uparrow\downarrow\rangle\}$. For degenerate spins $\Delta_A = \Delta_B$, as in Fig. 1, the dynamics in $\{|\downarrow\uparrow\rangle, |\uparrow\downarrow\rangle\}$ does not involve energy changes. Therefore we focus our attention to the sector $\{|\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$.

In Fig. 1 we display the joint state of the two spins (populations $\langle\uparrow\uparrow|\,\hat{\rho}'\,|\uparrow\uparrow\rangle$ in panel A and coherences $\langle\downarrow\downarrow|\,\hat{\rho}'\,|\uparrow\uparrow\rangle$ in panel B), as well as the energy and entropy changes after one interaction (panels C and D), as a function of the coupling parameter $\lambda \equiv V_0\tau/\hbar$ which we increase by increasing V_0 while keeping τ fixed. Since we require $\tau = \tau_p$, we take in SCM $p_0 = ma/\tau$. We display the results for $\tau = 2.5\times10^{-3}$ and $\tau = 2.5\times10^{-1}$, with condition 1 holding in the former case but not in the latter. Condition 2 and $p_0 a_{\min} \gg \hbar$ are here always fulfilled. For $\tau = 2.5\times10^{-3}$ (high E_{p_0}), we observe a very good matching between TDM, SCM and our model, even when the coupling is strong. Indeed, when $\lambda = 10$ we still have $E_{p_0}/V_0 \gg 1$ and thus all conditions of our model are fulfilled. The wave packet therefore excites both spins without changing their entropy with Rabi-like oscillations [4, 31, 32] of period π with λ as predicted by the model. For $\tau = 2.5\times10^{-1}$ (low E_{p_0}), we see that our model departs from those in SCM and TDM at the level of coherences and entropy change. Remarkably, our model still replicates the populations and energy changes of TDM and SCM provided the coupling is not too large (i.e., $E_{p_0}/V_0 \gg 1$ still holds), but they mismatch for larger couplings (i.e., $E_{p_0}/V_0 \sim 1$ and reflection is no longer negligible).

We tested many other potentials $\tilde{V}(t)$ and $V(x)$ with $\langle\tilde{V}\rangle = \langle V\rangle$ and numerically confirmed in this two-spin system that they induce the same dynamics in Y provided the conditions for our theory hold.

Conclusions: We have considered the effect of a collision between a particle at rest and an incoming fast particle described by a broad wave packet and showed that the map describing the effect of the collision on the internal states of the particles becomes unitary. Since the energy transfers within the internal system occur without entropy change, such collisions can be used to model the effect of a work source on the particle at rest.

This finding nicely complements the results of Refs. [13, 27] where we showed that collisions with effusing mixtures of incoming narrow packets can model heat sources. The width of the packet is crucial to discriminate between these two cases. In the narrow case, the outgoing packets associated with each transition in the scattering map are distinguishable because they do not overlap. Therefore, the environment can collect informa-

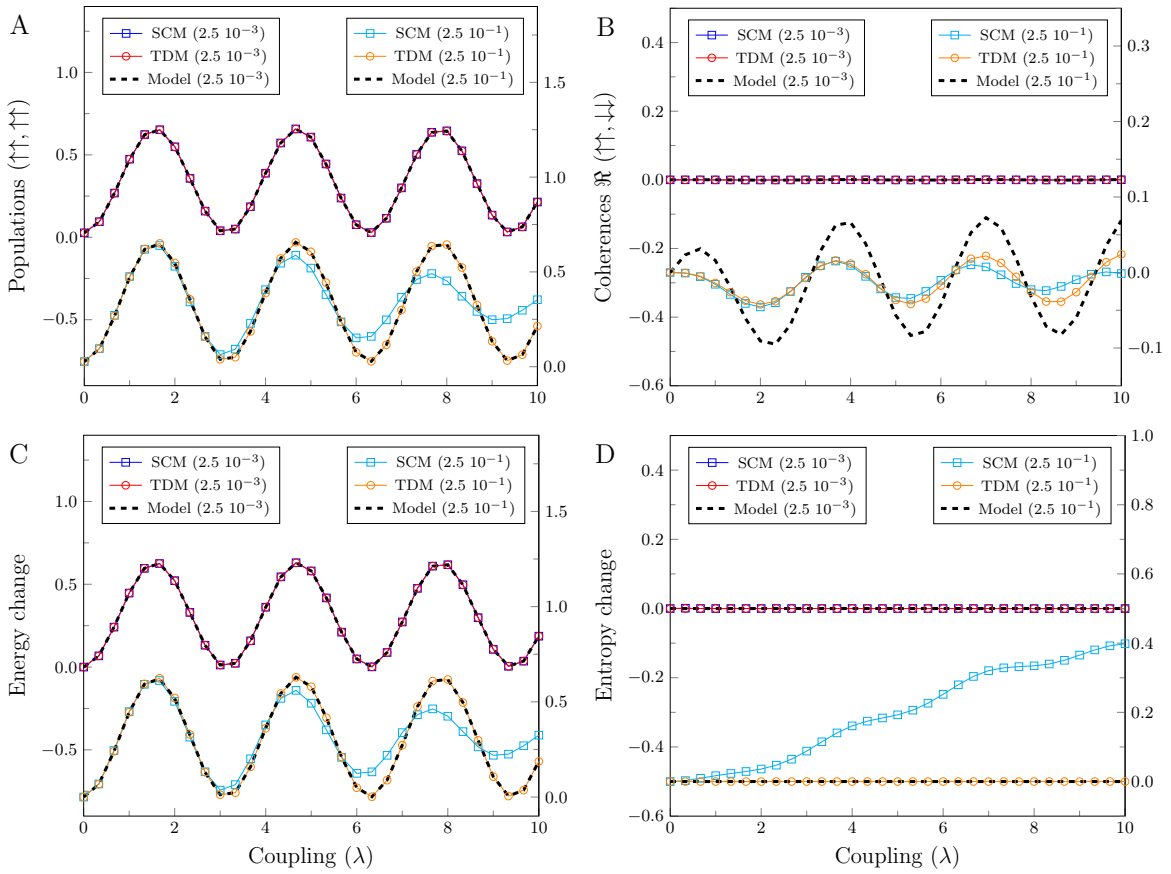

FIG. 1: Upper panels: Populations (panel A) and real part of coherences (panel B) of a two spin 1/2 system after one collision according to the exact SCM in Eq. (4) (squares), TDM in Eq. (1) (circles) and our model Eq. (6) (black dashed lines) as a function of coupling parameter $\lambda \equiv V_0\tau/\hbar$. We vary λ by varying V_0 while keeping τ fixed at $\tau = 2.5 \times 10^{-3}$ (plots with dark color markers, read on the left axis) or $\tau = 2.5 \times 10^{-1}$ (plots with light markers, read on the right axis). Lower panel: Equivalent of upper panels for energy (panel C) and entropy changes (panel D), respectively. The state of the spins is initially diagonal in the eigenbasis of $\hat{H}_Y$, with $(\hat{\rho}_A)_{\uparrow\uparrow} = 0.1$, $(\hat{\rho}_A)_{\downarrow\downarrow} = 0.9$ and $(\hat{\rho}_A)_{\uparrow\downarrow} = (\hat{\rho}_A)_{\downarrow\uparrow} = 0$ while the state of B is thermal $\hat{\rho}_B = \exp(-\beta\hat{H}_B)/\mathrm{Tr}[\exp(-\beta\hat{H}_B)]$ with inverse temperature $\beta = \Delta_B^{-1}$. The model parameters are $2\Delta_A = 2\Delta_B = 1$ (degenerate spins), $\hbar = m = 1$, $a = 3.5$, $\tau_p = \tau \Rightarrow p_0 = ma/\tau$ and $\sigma \gg 20 \times (m\Delta_Y/p_0)$ for SCM.

tion about the transitions in the internal system, acting as a measurement apparatus. Instead, in the broad case, the outgoing packets strongly overlap. As a result they do not reveal information about the internal system transitions, and coherences are preserved.

Since quantum scattering is ubiquitous throughout physics [15–19] and plays an essential role in many other aspects of open quantum systems [20–25], our results should be of wide relevance in the exploration of the quantum properties of matter and energy and could open the way for scattering-based realistic implementations of quantum thermodynamic operations.

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Quantum scattering as a work source: supplementary material

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TIME-DEPENDENT MODEL

In this section, we summarize the Magnus expansion as a solution to the time-dependent model introduced in the main text. We remind that the full Hamiltonian of the time-dependent model (TDM) is given by $\hat{H}(t) = \hat{H}_Y + \hat{V}(t)$, with $\hat{H}_Y = \hat{H}_A \otimes \hat{\mathbb{I}}_B + \hat{\mathbb{I}}_A \otimes \hat{H}_B$ being the Hamiltonian of the internal degrees of freedom. The interaction operator is $\hat{V}(t) = \tilde{V}(t)\hat{\nu}$, where $\tilde{V}(t)$ is a non-vanishing function in the interval $(-\tau/2, \tau/2) \in \mathbb{R}$ and zero everywhere else. In the interaction picture, the state of Y after the interaction is given by

$$\hat{\rho}_\tau = \hat{U}_I(\tau)(\hat{\rho}_A \otimes \hat{\rho}_B)\hat{U}_I^\dagger(\tau) \,, \tag{S1}$$

where the initial state is assumed factorized. The unitary operator in the interaction picture is the solution to the von Neumann equation

$$d_t\hat{U}_I(t) = -\frac{i}{\hbar}\hat{V}_I(t)\hat{U}_I(t) \tag{S2}$$

where d_t is the total time derivative, $\hat{V}_I(t) = \exp(i\hat{H}_Y t/\hbar)\hat{V}(t)\exp(-i\hat{H}_Y t/\hbar)$ is the interaction in the interaction picture and $\hat{U}_I(\tau/2) = \hat{U}_I(-\tau/2) = \hat{1}_Y$. Due to the time-dependence of $\hat{V}_I(t)$, the last equation does not generally have a closed form. Usually, one expands $\hat{U}_I(t)$ as an infinite series of time-ordered integrals of $\hat{V}_I(t)$ — the so-called Dyson series — which is specially useful for perturbative calculations. However, an alternative solution is to write the unitary operator as an exponential of an infinite series

$$\hat{U}_I(t) = \exp\left(\hat{\Omega}(t)\right) = \exp\Big(\sum_{n=1}^{\infty}\hat{\Omega}_n(t)\Big) \,, \tag{S3}$$

where the series is called the Magnus expansion (see Ref. [1] for a precise relationship between this approach and the Dyson series). The first three terms are as follows:

$$\hat{\Omega}_1(t) = -\frac{i}{\hbar}\int_{-\tau/2}^{t}\hat{V}_I(t')dt' \,, \tag{S4}$$

$$\hat{\Omega}_2(t) = -\frac{1}{2\hbar^2}\int_{-\tau/2}^{t}dt'\int_{-\tau/2}^{t'}dt''[\hat{V}_I(t'),\hat{V}_I(t'')] \,, \tag{S5}$$

$$\hat{\Omega}_3(t) = \frac{i}{6\hbar^3}\int_{-\tau/2}^{t}dt'\int_{-\tau/2}^{t'}dt''\int_{-\tau/2}^{t''}dt'''\big([\hat{V}_I(t'),[\hat{V}_I(t''),\hat{V}_I(t''')]] + [\hat{V}_I(t'''),[\hat{V}_I(t''),\hat{V}_I(t')]]\big) \,. \tag{S6}$$

If we take $\hat{V}_I(t)$ to be an element of a Lie algebra, i.e. an element of linear space of operators with commutation as a binary operation, then all higher order terms can be obtained by linear combinations of nested commutators of $\hat{V}_I(t)$. Thus, if we show that these commutators vanish under some conditions, we reduce the Magnus expansion to the first term. The matrix element of $\hat{V}_I(t)$ in the eigenbasis of $\hat{H}_Y$ reads

$$\langle j|\hat{V}_I(t)|i\rangle = \langle j|\hat{V}(t)|i\rangle\, e^{i\Delta_{ji}t/\hbar} = \tilde{V}(t)\,\langle j|\hat{\nu}|i\rangle\, e^{i\Delta_{ji}t/\hbar} \,, \tag{S7}$$

where $\Delta_{ji} \equiv e_j - e_i$ is the energy difference between eigenstates $|j\rangle$ and $|i\rangle$, as in the main text. Thus, if the free evolution is negligible $\Delta_Y \tau/\hbar \ll 1$ (condition 1), we simply get $[\hat{V}_I(t), \hat{V}_I(t')] \simeq \tilde{V}(t)\tilde{V}(t')[\hat{\nu}, \hat{\nu}] = 0$. The unitary operator in Eq. (S3) evaluated at $t = \tau/2$ then reads

$$\hat{U}_I(\tau) = \exp\Big[-\frac{i}{\hbar} \int_{-\tau/2}^{\tau/2} \hat{V}(t) dt \Big] . \tag{S8}$$

The last step involves simplifying the integral using the mean-value theorem $\langle \tilde{V} \rangle \tau \equiv \int_{-\tau/2}^{\tau/2} \tilde{V}(t) dt$. As discussed in the main text, the identification with SCM involves setting $\langle \tilde{V} \rangle = \langle V \rangle$, where $\langle V \rangle \equiv a^{-1} \int_{-a/2}^{a/2} V(x) dx$ is the average potential in SCM. We immediately get $\hat{U}_I(\tau) = \exp(-i\tau \hat{V}/\hbar)$ with the definition $\hat{V} \equiv \langle V \rangle \hat{\nu}$.

SCATTERING MODEL

In this section we study the reduced scattering dynamics for the internal degrees of freedom Y and the conditions under which it matches those of TDM. Consider the scattering model (SCM) with full Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{V}(\hat{x}) = \hat{H}_Y \otimes \hat{\mathbb{I}}_X + \hat{\mathbb{I}}_Y \otimes \hat{p}^2/2m + \hat{V}(\hat{x}) \tag{S9}$$

where $\hat{H}_0$ is the free Hamiltonian. The kinetic energy operator accounts for the motion of the particle B and is unbounded, obeying the eigenvalue equation $(\hat{p}^2/2m)\,|p\rangle = E_p\,|p\rangle$, where $\{|p\rangle\}$ are improper eigenstates representing plane waves with kinetic energy $E_p \equiv p^2/2m \geq 0$. The interaction between the particles is described by the operator $\hat{V}(\hat{x}) = V(\hat{x}) \otimes \hat{\nu}$, where $V(x)$ is a non-vanishing function only inside the interval $x \in (-a/2, a/2)$ and $V(\hat{x})\,|x\rangle \equiv V(x)\,|x\rangle$.

The goal of scattering theory is to obtain the scattering operator $\hat{S}$ which is a one-to-one map between free (incoming) states before the collision to free (outgoing) states after the collision. Whether or not such an operator exists depends on the dynamics during the collision through the interaction potential $V(x)$. However, its existence is guaranteed for a large class of potentials which vanish fast enough at infinity, and the one introduced above belongs to this class [2, 3]. Thus $\hat{S}$ exists with the usual properties $\hat{S}\hat{S}^\dagger = \hat{S}^\dagger\hat{S} = \hat{\mathbb{I}}$ and $[\hat{S}, \hat{H}_0] = 0$ expressing unitarity and total energy conservation for the full system, respectively. Due to the latter, the scattering operator in the eigenbasis of $\hat{H}_0$, denoted by $|p, j\rangle \equiv |p\rangle \otimes |j\rangle$, is given by

$$\langle p', j'|\,\hat{S}\,|p, j\rangle = \frac{\sqrt{|pp'|}}{m} \delta(E_p - E_{p'} - \Delta_{j'j}) s_{j'j}^{(\alpha'\alpha)}(E) \tag{S10}$$

where $s_{j'j}^{(\alpha'\alpha)}(E)$ is the scattering matrix at total energy $E = E_p + e_j$ and $\alpha = \mathrm{sign}(p)$ and $\alpha' = \mathrm{sign}(p')$ accounts for the initial and final direction of the momenta, which can be positive ($\alpha, \alpha' = +$) or negative ($\alpha, \alpha' = -$). The absolute value squared of the scattering matrix determines the transitions probabilities at a given total energy E.

The scattering map

We take the full system to be initially in a factorized state $\hat{\rho}_A \otimes \hat{\rho}_B \otimes \hat{\rho}_X$ with $\hat{\rho}_X = |\phi\rangle\langle\phi|$ being a pure state, normalized according to $\int dp\,\langle p|\hat{\rho}_X|p\rangle = \int dp |\phi(p)|^2 = 1$. The state of the full system after the collision is given by $\hat{S}(\hat{\rho}_A \otimes \hat{\rho}_B \otimes \hat{\rho}_X)\hat{S}^\dagger$. Taking the partial trace over momentum, we can write the map in the eigenbasis of $\hat{H}_Y$ as [4]

$$\rho'_{j'k'} = \sum_{jk} \mathbb{S}^{jk}_{j'k'} (\hat{\rho}_A \otimes \hat{\rho}_B)_{jk} \tag{S11}$$

where $\rho'_{j'k'} \equiv \langle j'|\hat{\rho}'|k'\rangle$ and the scattering map is given by,

$$\mathbb{S}^{jk}_{j'k'} = \sum_{\alpha'=\pm} \int_{p_{\mathrm{inf}}}^{\infty} dp\, \phi(p)\phi^*(\pi(p)) \sqrt{\frac{p}{\pi(p)}}\, s_{j'j}^{(\alpha'+)}(E_p + e_j) \Big[s_{k'k}^{(\alpha'+)}(E_p - \Delta_{j'j} + e_{k'}) \Big]^* \tag{S12}$$

with $\pi(p) = \sqrt{p^2 - 2m(\Delta_{j'j} - \Delta_{k'k})}$. The lower integration limit p_{inf} is obtained from $p^2_{\mathrm{inf}}/2m = \max\{0, \Delta_{j'j}, \Delta_{j'j} - \Delta_{k'k}\}$, which guarantees that the channels are open in the integration domain. As discussed in Ref. [4], the scattering map is completely positive and trace-preserving and does not generally lead to unitary dynamics. In the next sections, we derive in detail the conditions - already presented in the main text - under which it does.

Broad wave packet approximation

The map in Eq. (S12) depends crucially on the product $\phi(p)\phi^*(\pi(p))$ which measures the overlap between wave packets at different momenta. In this section, we prove that if such packets are sufficiently broad with respect to the energy scale of Y, we can replace $\phi(p)\phi^*(\pi(p))$ by $|\phi(p)|^2$ in Eq. (S12).

Consider for simplicity that the support of the packet $\phi(p)$ is $[p_0-\sigma, p_0+\sigma]$ and that of $\phi(\pi(p))$ is $[p_0+\delta-\sigma, p_0+\delta+\sigma]$ shifted by $\delta = \pi(p_0) - p_0$. The support of the product $\phi(p)\phi^*(\pi(p))$ is the intersection of these intervals, i.e., $[p_0+\delta-\sigma, p_0+\sigma]$ for $\delta > 0$ and $[p_0-\sigma, p_0-|\delta|+\sigma]$ for $\delta < 0$. Thus, we see that if $|\delta| \approx 2\sigma$ the support of $\phi(p)\phi^*(\pi(p))$ is narrow and very different from the support of $\phi(p)$. Therefore a necessary condition for the approximate equality

$$\int dp\phi(p)\phi^*(\pi(p))f(p) \approx \int dp|\phi(p)|^2 f(p) \tag{S13}$$

with a smooth function $f(p)$ is $|\delta| \ll 2\sigma$. Since $\pi(p) = \sqrt{p^2 - 2m(\Delta_{j'j} - \Delta_{k'k})}$, the difference $\pi(p) - p$ decays with increasing p. Therefore for large p_0 we have $\delta \approx -m(\Delta_{j'j} - \Delta_{k'k})/p_0$. Considering that Δ_Y is the maximal value for the energy differences $\Delta_{j'j}$, we arrive at the condition $m\Delta_Y/p_0 \ll \sigma$, which is the broad wave packet condition 2 presented in the main text.

The validity of the approximation Eq. (S13) is also due the fact that the difference

$$|\phi(\pi(p)) - \phi(p)| \approx \frac{d\phi(p)}{dp}\frac{2m\Delta_Y}{p}$$

decreases as p increases because the value for the slopes $d\phi(p)/dp$ depends on the shape of the packet and not in it location in the p axis. For instance, consider a smooth wave packet centered around p_0. The maximum values of the derivatives $d\phi/dp$ are located at some $p^* = p_0 + C(\sigma, x_0)$ where $C(\sigma, x_0)$ is some function of the parameters of the packet. For example, for a Gaussian wave packet $C(\sigma, x_0) = ix_0\sigma^2 \pm \sqrt{\sigma^2 - x_0^2\sigma^4}$. Therefore $\frac{d\phi(p)}{dp}|_{p^*}$ is independent of p_0. Thus, the difference $\phi(\pi(p)) - \phi(p)$ decreases with increasing p as

$$|\phi(\pi(p)) - \phi(p)| \approx \mathrm{M} \times \frac{2m\Delta_Y}{p} \approx \mathrm{M}\ \times \frac{2m\Delta_Y}{p_0},$$

where $\mathrm{M} = \frac{d\phi(p)}{dp}|_{p^*}$, justifying the use of Eq. (S13) in Eq. (S12) for $p_0 \gg \mathrm{M}\,(2m\Delta_Y)$ and $\sigma \gg m\Delta_Y/p_0$. Interestingly, for a Gaussian packet $\mathrm{M} \sim 1/\sigma$ and both conditions are equivalent. Further conditions on the value of p_0 are imposed by the interaction energy as we see below.

Semi-classical regime

Introduction

Consider the time-independent Schrödinger equation in the absence of internal degrees of freedom, with the potential $V(x)$ being effective over the region $x \in (-a/2, a/2)$. If we take a position very far away to the left of this region, then $\psi(x) \sim \exp(\mathrm{i}px/\hbar)$ is a solution to the equation, representing a plane wave of some wave packet which travels free from the potential. In general, inside the region of the potential $V(x)$ the solutions are not plane waves. However, it is well known that if the wave packet is fast $E_p \gg V(x)$ and if its de Broglie wave length is much shorter than the scales over which the potential varies significantly $pa_{min} \gg \hbar$, where a_{min} is this scale, then the effect of the potential on the wave can be simplified. The plane wave at position x inside the potential is then multiplied by a phase proportional to the integral of the interaction [5, 6]. More precisely, we have

$$\psi(x) \sim \exp\Big(\frac{\mathrm{i}px}{\hbar}\Big)\exp\Big(-\frac{\mathrm{i}m}{\hbar p}\int_{-\infty}^{x} V(x)dx\Big)\,. \tag{S14}$$

By taking $x \to +\infty$ the the total phase shift due scattering with the potential, which is proportional to the scattering amplitude is recovered [5]. Since the potential is supported on the interval $x \in (-a/2, a/2)$, we have $\int_{-a/2}^{a/2} V(x)dx = \langle V\rangle a$. In other words, the potential can be effectively treated as a barrier of length a and height $\langle V\rangle$. The purpose of this section is to show that the same is true in the presence of internal degrees of freedom, which then allows us to simplify the scattering matrix appearing in Eq. (S12).

Derivation

Let $|\psi\rangle$ be a solution to the time-independent Schrödinger equation $\hat{H}\,|\psi\rangle = E\,|\psi\rangle$ with some energy E and $|\psi_0\rangle$ the corresponding free solution with the same energy, valid very far away from the potential. Projecting the former equation onto the position eigenbasis $\langle x|\hat{H}|\psi\rangle = E\,\langle x|\psi\rangle$ and using Eq. (S9), we obtain an operator equation for $|\psi(x)\rangle \equiv \langle x|\psi\rangle$ in the Hilbert space of Y

$$(\hbar^2 d_x^2 + \hat{P}_0^2)\,|\psi(x)\rangle = 2m\hat{V}(x)\,|\psi(x)\rangle \ , \tag{S15}$$

where d_x is a total derivative and the interaction is $\hat{V}(x) \equiv V(x)\hat{\nu}$. The momentum operator is defined as

$$\hat{P}_0 \equiv \sqrt{2m(E - \hat{H}_Y)} \tag{S16}$$

and we assume that E is larger than the maximum eigenvalue of $\hat{H}_Y$, in which case $\hat{P}_0$ is a positive operator and thus self-adjoint. To make progress in solving Eq. (S15), we look for solutions of the form

$$|\psi(x)\rangle = e^{i\hat{P}_0 x/\hbar}\,|\hat{\psi}(x)\rangle \ , \tag{S17}$$

where the exponential operator is unitary. Substituting in Eq. (S15) and noting that $[\exp(i\hat{P}_0 x/\hbar), \hat{P}_0] = 0$ we obtain that $|\hat{\psi}(x)\rangle$ satisfies

$$(\hbar^2 d_x^2 + 2i\hbar\hat{P}_0 d_x)\,|\hat{\psi}(x)\rangle = 2m(e^{-i\hat{P}_0 x/\hbar}\hat{V}(x)e^{i\hat{P}_0 x/\hbar})\,|\hat{\psi}(x)\rangle \ , \tag{S18}$$

The last expression is completely equivalent to Eq. (S15). Since we are interested in taking the semi-classical limit where $\hbar$ is very small compared to some action, we ignore the second derivative in the equation above. After we obtain the solution, we derive exactly the conditions under which this is valid. We thus get the equation

$$i\hbar d_x\,|\hat{\psi}(x)\rangle = (e^{-i\hat{P}_0 x/\hbar} m\hat{P}_0^{-1}\hat{V}(x)e^{i\hat{P}_0 x/\hbar})\,|\hat{\psi}(x)\rangle \ , \tag{S19}$$

which formally has the same form of a Schrödinger equation in the interaction picture where x plays the role of time, $m\hat{P}_0^{-1}\hat{V}(x)$ is the interaction and $-\hat{P}_0$ the free Hamiltonian [8]. This Schrödinger equation is integrated with an "initial" position x_0 and an "initial" state with the same energy E appearing in Eq. (S16). We take the asymptotic state $|\psi_0\rangle$ introduced above, and through Eq.(S17), the corresponding $|\hat{\psi}_0\rangle$ to pick the "initial" condition. The evolution operator associated with this equation can be written in terms of a Magnus series as we did in section . In analogy to Eq. (S4), we have the first order term of the expansion

$$\hat{\Omega}_1(x) = -\frac{i}{\hbar}\int_{x_0}^{x} \hat{V}_{\hat{P}_0}(x')\,dx' \ , \tag{S20}$$

where $\hat{V}_{\hat{P}_0}(x') \equiv e^{-i\hat{P}_0 x'/\hbar} m\hat{P}_0^{-1}\hat{V}(x')e^{i\hat{P}_0 x'/\hbar}$ has units of momentum. The higher order terms $\hat{\Omega}_n(x)$ contain nested commutators of $[\hat{V}_{\hat{P}_0}(x), \hat{V}_{\hat{P}_0}(x')]$ similarly to Eqs. (S5) and (S6). Now we show that one can neglect the higher order terms in the Magnus expansion when the kinetic energy is sufficiently large. For large E we have

$$\hat{P}_0 = \sqrt{2m(E - \hat{H}_Y)} = \sqrt{2mE} - \sqrt{\frac{m}{2E}}\hat{H}_Y\Big[1 - \mathcal{O}\Big(\frac{\hat{H}_Y}{E}\Big)^2\Big] \ , \tag{S21}$$

allowing the replacement

$$\hat{V}_{\hat{P}_0}(x') \approx e^{i\sqrt{\frac{m}{2E}}\hat{H}_Y x'/\hbar}\frac{m}{\sqrt{2mE}}\left[1 + \frac{\hat{H}_Y}{E}\right]\hat{V}(x')e^{-i\sqrt{\frac{m}{2E}}\hat{H}_Y x'/\hbar} \approx \sqrt{\frac{m}{2E}}\hat{V}(x')$$

where in the last approximation we used that $|x'| < a/2$ and considered $\sqrt{2E/m} \gg a\Delta_Y/\hbar$, eliminating the exponentials of the expression at the left. In this limit we have $[\hat{V}_{\hat{P}_0}(x), \hat{V}_{\hat{P}_0}(x')] = m(V(x)V(x')/2E)[\hat{\nu}, \hat{\nu}] = 0$ and all higher orders can be neglected. The above inequality, $\sqrt{2E/m} \gg a\Delta_Y/\hbar$ allows us to consider $E \approx E_p$ which is equivalent to $\tau_p\Delta_Y/\hbar \ll 1$ (condition 1 of the main text). Thus, the Magnus series is

$$\hat{\Omega}(x) = -\frac{i}{\hbar}\sqrt{\frac{m}{2E}}\int_{x_0}^{x}\hat{V}(x')\,dx' = -\frac{im}{\hbar p}\int_{x_0}^{x}\hat{V}(x')\,dx' \tag{S22}$$

meaning that

$$|\hat{\psi}(x)\rangle = \exp\Big(-\frac{im}{\hbar p}\int_{x_0}^{x} V(x)\hat{\nu}\Big)\,|\hat{\psi}_0(x_0)\rangle\ . \tag{S23}$$

The last expression applied to Eq. (S17) is the generalization of Eq. (S14) in the presence of internal degrees of freedom. Now that we have a closed expression, we can verify the conditions under which $\hbar^2 d_x^2\,|\hat{\psi}(x)\rangle$ is negligible in Eq. (S18). Differentiating Eq. (S23) twice with respect to x and multiplying by $\hbar^2/p^2$ to get an adimensional quantity, we obtain

$$\left(\frac{1}{p^2}\right)\hbar^2 d_x^2\hat{\psi}(x) = -\left(\frac{1}{p^2}\right)\Big[\frac{im\hbar V'(x)}{p} + \frac{m^2V(x)^2}{p^2}\Big]\hat{\nu}\hat{\psi}(x)\ . \tag{S24}$$

Therefore, for high momentum, the term $\hbar^2 d_x^2\hat{\psi}(x)$ is negligible in comparison to the rest of the terms in Eq. (S18) if the potential varies very slowly $p^3/(2m\hbar) \gg V'(x)$, a condition well known from semi-classical approximations in quantum mechanics [5]. We simplify this condition by integrating over a minimum scale a_{min} where the potential varies significantly by an amplitude ΔV obtaining $(E_p/\Delta V)pa_{min}/\hbar \gg 1$. Since we are interested in high kinetic energies, in the worst case scenario we have $E_p/\Delta V \sim 1$ and thus $pa_{min}/\hbar \gg 1$ is a sufficient condition.

The scattering matrix

Eq.(S23) in terms of the original wave function is

$$|\psi(x)\rangle = e^{i\hat{P}_0 x/\hbar}\exp\Big(-\frac{im}{\hbar p}\int_{x_0}^{x} V(x)\hat{\nu}\Big)e^{-i\hat{P}_0 x_0/\hbar}\,|\psi_0(x_0)\rangle\ . \tag{S25}$$

From this expression we can deduce the transmission coefficient. Taking $x > a/2$ and $x_0 < -a/2$, considering $(m/p)\int_{x_0}^{x} V(x) = \tau_p\langle V\rangle$, recalling the definition $\hat{V} \equiv \langle V\rangle\hat{\nu}$ and projecting Eq. (S25) on the left with $\langle j'|$ we have

$$\langle j'|\psi(x)\rangle = \langle j'|e^{i\hat{P}_0 x/\hbar}e^{-i\tau_p\hat{V}/\hbar}e^{-i\hat{P}_0 x_0/\hbar}|\psi_0(x_0)\rangle \tag{S26}$$

Taking $|\psi_0(x_0)\rangle = e^{ip_j x_0}\,|j\rangle$ with $p_j = \sqrt{2m(E-e_j)}$ in Eq. (S26) we obtain

$$\langle j'|\psi(x)\rangle = e^{ip_{j'}x/\hbar}\,\langle j'|e^{-\frac{i\tau_p}{\hbar}\hat{V}}|j\rangle\,e^{-ip_j x_0}e^{ip_j x_0} = t_{j'j}e^{ip_{j'}x/\hbar} \tag{S27}$$

with $p_{j'} = \sqrt{2m(E-e_{j'})}$, from where we read that the elements of the transmission matrix $\mathbf{t}$ are $t_{j'j} = \langle j'|e^{-\frac{i\tau_p}{\hbar}\hat{V}}|j\rangle$. Since $\mathbf{t}$ is unitary, the reflection coefficients vanish in this limit. Thus, the scattering matrix under the conditions stated above is

$$s^{(\alpha'+)}_{j'j}(E_p) = \delta_{\alpha'+}\ \langle j'|e^{-i\tau_p\hat{V}/\hbar}|j\rangle\ , \tag{S28}$$

as presented in the main text. It is valid when $\tau_p\Delta_Y/\hbar \ll 1$ (condition 1), $E_p \gg V(x)$ and $pa_{min} \gg \hbar$ (condition 3) and $E_p \gg \Delta_Y$ (inequality present in condition 2 of the main text).

Averaging the interaction

After performing the broad wave packet approximation and inserting the scattering matrix Eq. (S28) into Eq. (S11), we get a simplified expression for the scattering map. Using the representation of the density matrix $(\hat{\rho}_A\otimes\hat{\rho}_B) = \sum_{ji}(\hat{\rho}_A\otimes\hat{\rho}_B)_{ji}\,|j\rangle\,\langle i|$ we get a basis-independent result

$$\hat{\rho}' = \int_{-\infty}^{\infty} dp|\phi(p)|^2\ e^{-i\tau_p\hat{V}/\hbar}\ (\hat{\rho}_A\otimes\hat{\rho}_B)\ e^{i\tau_p\hat{V}/\hbar}\ , \tag{S29}$$

where we extended the lower integration limit to minus infinity since $|\phi(p)|^2 = (2\pi\sigma^2)^{-1/4}\exp[-(p-p_0)^2/2\sigma^2]$ is supported at very high kinetic energies. Using the spectral decomposition $\hat{V} = \sum_\alpha V_\alpha\,|\alpha\rangle\,\langle\alpha|$, we can simplify the integral by studying the function in the exponent

$$F_{\alpha\beta}(p) \equiv -\frac{(p-p_0)^2}{2\sigma^2} - \frac{ima(V_\alpha - V_\beta)}{\hbar}\ , \tag{S30}$$

and performing a saddle point approximation assuming $p_0 \gg \sigma$, a condition already fulfilled for the wave packets considered in this study. We can do this by finding the extrema $F'_{\alpha\beta}(p) = 0$

$$\Big(\frac{p}{p_0} - 1\Big)\frac{p^2}{p_{\alpha\beta}\sigma} = \frac{i\sigma}{p_0}\,, \tag{S31}$$

where $p_{\alpha\beta} \equiv ma(V_\alpha - V_\beta)/\hbar$ has units of momentum. Thus, if $p_0 \gg \sigma$ then $p = p_0$ is an approximate solution corresponding to a maximum (as can be confirmed by computing the second derivative). We expand $F_{\alpha\beta}(p)$ to second-order around p_0 and perform the integral, obtaining our final result with $\tau = ma/p_0$

$$\hat{\rho}' = e^{-i\tau\hat{V}/\hbar}\,(\hat{\rho}_A \otimes \hat{\rho}_B)\,e^{i\tau\hat{V}/\hbar}\,. \tag{S32}$$

Multi-channel scattering equations

In this section we present the multi-channel equations of scattering theory which allow us to compute numerically the exact scattering matrix presented in the main text. For a wave packet coming from the left, we have the following relations

$$s^{(-+)}_{j'j}(E) = \sqrt{\frac{|p'|}{|p|}}r_{j'j}(E) \quad \text{and} \quad s^{(++)}_{j'j}(E) = \sqrt{\frac{|p'|}{|p|}}t_{j'j}(E) \tag{S33}$$

where p' and p the final and initial momentum before and after the transition, while $r_{j'j}(E)$ and $t_{j'j}(E)$ are the reflection and transmission coefficients. The latter can be found by solving the coupled multi-channel scattering equations

$$\begin{aligned}
\frac{dr_{j'j}(x)}{dx} &= \sum_{n,m}\frac{imV(x)}{\hbar p_n}\big[\delta_{j'n}e^{ip_nx/\hbar} + r_{j'n}(x)e^{-ip_nx/\hbar}\big]\nu_{nm}\big[\delta_{mj}e^{ip_mx/\hbar} + r_{mj}(x)e^{-ip_mx/\hbar}\big]\,, \\
\frac{dt_{j'j}(x)}{dx} &= \sum_{n,m}\frac{imV(x)}{\hbar p_n}\big[t_{j'n}(x)e^{-ip_nx/\hbar}\big]\nu_{nm}\big[\delta_{mj}e^{ip_mx/\hbar} + e^{-ip_mx/\hbar}r_{mj}(x)\big]\,,
\end{aligned} \tag{S34}$$

where we omitted the dependence on energy E and $p_j = \sqrt{2m(E-e_j)}$ in the last expression. These are a set of non-linear, coupled differential equations for the transmission and transmission coefficients in space. They were derived by Razavy in the context of quantum tunneling [7]. By using the boundary conditions $r_{ji}(\infty) = 0$, $t_{ji}(\infty) = \delta_{ji}$, $r_{ji}(-\infty) = r_{ji}$ and $t_{ji}(-\infty) = t_{ji}$ we recover the reflection and transmission coefficients defined which then completely determine scattering matrix.

ANALYTICAL SOLUTION FOR THE TWO-SPINS MODEL

In this example we have $\langle\tilde{V}\rangle = \langle V\rangle = V_0$ and $\hat{\nu} = J_1\hat{\sigma}^x_A \otimes \hat{\sigma}^x_B + J_2\hat{\sigma}^y_A \otimes \hat{\sigma}^y_B$. Defining $\lambda \equiv V_0\tau/\hbar$, the unitary transformation of our analytical model (Eq. 6 in the main text or Eq. (S32) in this document) in the eigenbasis of $\hat{H}_Y$ is the 4×4 matrix

$$e^{-i\lambda\hat{\nu}} = \begin{pmatrix}
\cos[\lambda(J_1-J_2)] & 0 & 0 & -i\sin[\lambda(J_1-J_2)] \\
0 & \cos[\lambda(J_1+J_2)] & -i\sin[\lambda(J_1+J_2)] & 0 \\
0 & -i\sin[\lambda(J_1+J_2)] & \cos[\lambda(J_1+J_2)] & 0 \\
-i\sin[\lambda(J_1-J_2)] & 0 & 0 & \cos[\lambda(J_1-J_2)]
\end{pmatrix}$$

which can be reordered and written as

$$e^{-i\lambda\hat{\nu}} = e^{-i\lambda(J_1+J_2)\hat{\sigma}^x_1} \oplus e^{-i\lambda(J_1-J_2)\hat{\sigma}^x_2}$$

a direct sum on two two-dimensional subspaces $\{|+\rangle_1 \equiv |\uparrow\downarrow\rangle, |-\rangle_1 \equiv |\downarrow\uparrow\rangle\}$ and $\{|+\rangle_2 \equiv |\uparrow\uparrow\rangle, |-\rangle_2 \equiv |\downarrow\downarrow\rangle\}$. Similarly, with the same order for the basis, the Hamiltonian

$$H_Y = \{(\Delta_A - \Delta_B)\hat{\sigma}^z_1\} \oplus \{(\Delta_A + \Delta_B)\hat{\sigma}^z_2\}$$

is a direct sum. Here $\hat{\sigma}_1^i$ are the Pauli matrix in the basis $\{|+\rangle_1, |-\rangle_1\}$ and similarly for $\hat{\sigma}_2^i$. Thus, for this example, the dynamics given by Eq. (S32) is equivalent to the oscillatory dynamics of two independent qubits. One of them having the period $\pi/(J_1 - J_2)$ and the other $\pi/(J_1 + J_2)$. For Fig. 1 in the main text we take $J_1 = 1, J_2 = 0$ and $\Delta_A = \Delta_B$, thus only qubit $\{|+\rangle_2 \equiv |\uparrow\uparrow\rangle, |-\rangle_2 \equiv |\downarrow\downarrow\rangle\}$ changes its energy, peaking when the coupling is an odd multiple of $\pi/2$.

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[8] Note that it is also possible to define in $\hat{P}_0$ with a negative sign in Eq.(S16), and therefore one has two Schrödinger equations, one for the "forward" time x and another for the "backward". For our purposes we need only the former.

Chapter 3

Conclusions and Perspectives

3.1 Conclusions

In this thesis, we presented a novel approach to thermodynamics based on quantum scattering theory. Here, the traditional picture of an environment in permanent interaction with the open system is no longer applicable. Instead, one must picture the environment as being composed of particles, whose internal and kinetic degrees of freedom are described quantum mechanically and which collide sequentially and repeatedly with a fixed system. Our framework is particularly suited for modern experiments with light and matter, where single interactions between two quantum systems can be quite strong and far from thermal equilibrium. Moreover, it overcomes the difficulties of models of repeated interactions by explaining microscopically the origin of heat and work as exchanges in the kinetic energy of the travelling particles.

The distinction between heat and work in our approach can only be understood by appealing to the quantum nature of the particle motion, i.e. to the fact that particles travel as wave packets before and after they collide with the system. In opposition to plane waves, these packets are not localized in momentum or energy, but instead have a quantum uncertainty which plays a crucial role in the internal scattering dynamics and ensuing energy and entropy changes. If this uncertainty is smaller than the internal transition energies, the narrow packet entangles with the internal system during the collision and carries away information about the internal state, thus inducing decoherence. This is necessary but not sufficient for thermalization. Only when the momentum of the packets is thermal according to the effusion distribution do they induce thermalization — provided, of course, that the internal structure of the travelling particle has the same temperature as the effusing packets. By exchanging heat with the particles, the fixed system thermalizes over many collisions, even if each of the collisions is strong. If the uncertainty is larger than the internal transition energies, the broad wave packet can instead transfer coherences to the internal system as a whole. In the limit of high kinetic energy and uncertainty, these wave packets drive the internal system unitarily, exchanging energy without exchanging entropy. This is because they do not entangle with the internal system and therefore do not carry away any information about it. They can thus act a work source which keeps the internal degrees of freedom from thermalizing.

Another crucial distinction between the picture of work and that of thermalization is that, in the former, the average momentum of the packet must be known before the collision. This is the reason why we can assign an deterministic interaction time to the fast, broad packet and effectively mimic a time-dependent interaction, thus explaining microscopically the dynamics and switching work of repeated interaction models. In this sense, repeated interactions models can be looked at as a semi-classical limit of our scattering framework.

3.2 Perspectives

We conclude this thesis by first addressing limitations of our approach and then discuss possible extensions as well as future research directions.

Regarding limitations, we recognize that our approach focuses on the internal dynamics of a fixed system without taking into account its center of mass. This is reasonable if we are thinking of applying scattering to cavity-QED, where the internal system is the number of photons in the cavity [124]. It is also warranted if one is interested in modifications to the emission and absorption spectra of atoms as a result of collisions, much in the spirit of the low density limit presented in Subsec. 1.3.3. Nevertheless, if the system to be described is an atom whose mass is not much larger than the mass of incoming particles, a complete description would have to account for the atom's center of mass, treating it as a wave packet in its own right. Even if initially at rest, the atom would move as a result of collisions with travelling particles while the total momentum would, of course, be conserved. Indeed, we mentioned briefly in Subsec. 1.3.3 some dynamical equations based on scattering theory which describe the center of mass, so we could use this framework to extend our own. Let us also recognize that our scattering approach is implemented in one dimension. Again, this is adequate for comparisons with repeated interaction models and applications in cavity-QED [124], while simplifying the less tractable scattering problem in three dimensions [125, 126]. Since the dimensionality of the problem does not compromise any of the results on the narrow and broad wave packets, our one-dimensional approach is more pedagogical. It also covers many relevant setups in quantum transport, for instance that of a particle travelling in a waveguide (where the transverse modes of propagation are discrete while the longitudinal ones are continuous and one dimensional), as well as tunneling of molecules through potential barriers [127, 115, 128, 116]. Nonetheless, if one is interested in differential cross sections, then this would certainly require a three-dimensional treatment.

There are several research topics which we did not explore thoroughly in this thesis. The first is the transition between narrow and broad packets. Since the narrow-broad distinction is relative to the internal energy scales, we could change the internal energies to cross from the narrow to the broad regimes. By using thermal wave packets, we could then study how detailed balance and heat are modified across these different regimes. In addition, it is also not clear the role that reflection plays (if any) in the internal dynamics and thermodynamics. For instance, Ref. [124] points out that slow atoms can be reflected from a micromaser field even when no photons are present; this takes place in light-matter coupling strengths which are much higher than in the typical regime of Rabi oscillations. Our framework could be potentially used to study the dynamics and thermodynamics in this regime. Finally, we did not formulate the first and second law of thermodynamics in the presence of both heat and work sources. We are currently writing a manuscript where we do so, which also includes a study of the continuous time limit and resulting quantum master equations.

Chapter 4

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