Violation of Detailed Balance in Quantum Open Systems

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(Received 27 November 2022; revised 4 May 2023; accepted 5 July 2023; published 26 July 2023)

We consider the dynamics of a quantum system immersed in a dilute gas at thermodynamic equilibrium using a quantum Markovian master equation derived by applying the low-density limit technique. It is shown that the Gibbs state at the bath temperature is always stationary while the detailed balance condition at this state can be violated beyond the Born approximation. This violation is generically related to the absence of time-reversal symmetry for the scattering T matrix, which produces a thermalization mechanism that allows the presence of persistent probability and heat currents at thermal equilibrium. This phenomenon is illustrated by a model of an electron hopping between three quantum dots in an external magnetic field.

DOI: [10.1103/PhysRevLett.131.040401](https://doi.org/10.1103/PhysRevLett.131.040401)

Introduction.—Detailed balance at equilibrium (DBE) [\[1](#page-4-3)–[3](#page-4-4)] is a core principle of today's thermodynamics. It ensures the lack of persistent currents at equilibrium [\[4](#page-4-5)] and plays a key role in a wide range of fields, including the Onsager relations [[5,](#page-4-6)[6\]](#page-4-7) and reaction kinetics [\[7\]](#page-4-8) in chemistry, fluctuation theorems [[8](#page-4-9)–[12\]](#page-5-0) in statistical mechanics, open quantum systems [\[13](#page-5-1)[,14\]](#page-5-2) in quantum mechanics, and Kirchhoff's law [[15](#page-5-3)] in electromagnetism. Detailed balance has been so closely identified with thermal equilibrium [\[16\]](#page-5-4) that its violation has been used as an indicator of lack of equilibrium [[17](#page-5-5),[18](#page-5-6)] and has also been suggested as a measure of distance from equilibrium [\[19\]](#page-5-7).

The assumption of DBE is prevalent across several fields. But interestingly, it is not actually required by any fundamental law [\[20\]](#page-5-8). This was long ago recognized by Onsager [[5](#page-4-6)] himself who brought up the Hall effect as an example where this principle does not hold. Other examples of systems that violate detailed balance include the Michaelis-Menten kinetics for enzyme kinetics [\[21,](#page-5-9)[22](#page-5-10)], totally asymmetric simple exclusion process for onedimensional transport [\[23](#page-5-11)[,24\]](#page-5-12), directed percolation for fluid dynamics [[25](#page-5-13)], and nonreciprocal systems [\[26](#page-5-14)–[28](#page-5-15)]. Many unexpected effects in nonreciprocal materials have been theoretically predicted in the last years: persistent heat currents in thermal equilibrium [\[29\]](#page-5-16), violations of the Kirchhoff law [[28](#page-5-15)], potential violations of Earnshaw's theorem [\[30\]](#page-5-17), deviations from the Green-Kubo relations [\[31\]](#page-5-18), photon thermal Hall effect [[32](#page-5-19)], giant magnetoresistance for the heat flux [\[33\]](#page-5-20), and the creation of a Casimir heat engine [[34](#page-5-21)].

Unfortunately, currently used tools are insufficient for developing the microscopic models needed to study the dynamics and thermodynamics of systems that violate DBE. Here, we use the following definition of DBE:

$$
a_{k\ell}e^{-\beta \mathcal{E}_{\ell}} = a_{\ell k}e^{-\beta \mathcal{E}_{k}}, \qquad (1)
$$

where $a_{k\ell}$ are transition rates between microstates of the system with energies \mathcal{E}_k , \mathcal{E}_ℓ and β is the inverse temperature of the bath. The Gorini, Kossakowski, Lindblad, and Sudarshan (GKLS) [[35](#page-5-22)[,36\]](#page-5-23) equation derived at the weak coupling limit [\[37\]](#page-5-24) cannot be used because it automatically complies with DBE (see Ref. [\[38\]](#page-5-25) and Sec. III). The lack of microscopic models has resulted in contradicting statements in the literature regarding basic thermodynamic properties, such as the possibility of reaching thermal equilibrium [\[27](#page-5-26)[,39](#page-5-27)–[42](#page-5-28)] and the divergence of entropy production [\[43](#page-5-29)–[47](#page-5-30)].

To clarify the thermodynamic properties of systems that violate DBE, we use a GKLS master equation in the low density limit (LDL) [\[48\]](#page-5-31) which can lead into the violation of DBE. We note that the notion of DBE is not restricted to this limit, and it will be interesting to study its violation beyond this regime. We prove that despite the violation of DBE, fundamental thermodynamic behavior still holds: the reduced system reaches thermal equilibrium, at which the entropy production is zero. Nevertheless, DBE violation produces a different thermalization mechanism that allows persistent probability and heat currents at thermal equilibrium. To exemplify these effects we study a toy model for a single electron tunneling between three quantum dots in the presence of a magnetic field.

Quantum master equations at low density limit.—We consider a quantum system S with a discrete spectrum physical Hamiltonian, $H_S = \sum_k \mathcal{E}_k |k\rangle\langle k|$, immersed in an ideal bosonic or fermionic gas of free (quasi-) particles at a thermal equilibrium state given by the inverse temperature β and particle density ν . The derivation of the dynamics for the reduced density matrix is performed under the assumption that the density of gas particles is low. As shown in Ref. [[48](#page-5-31)] this assumption implies that the form of the master equation does not depend on particle statistics and is fully determined by the scattering of a single particle by the system S. Therefore, it is sufficient to determine the Hamiltonian H_{tot} of the system composed of S and a single particle, $H_{\text{tot}} = H_s + H_p + H_{\text{int}}$. We assume for simplicity that the gas particle is spinless and is described by its Hamiltonian H_P in momentum representation,

$$
H_P = \int d\mathbf{p} E_{\mathbf{p}} |\mathbf{p}\rangle\langle\mathbf{p}|, \qquad \langle \mathbf{p} | \mathbf{p}'\rangle = \delta(\mathbf{p} - \mathbf{p}'). \quad (2)
$$

The state of the gas is described by the single-particle probability distribution in momentum space $G(\mathbf{p})$.

The single-particle scattering Møller wave operator is defined as [\[49\]](#page-5-32)

$$
\Omega_{+} = \lim_{t \to \infty} e^{-iH_{\text{tot}}t} e^{i(H_{S} + H_{P})t}, \tag{3}
$$

and its superoperator version is $\Gamma_+ = \Omega_+ \cdot \Omega_+^{\dagger}$. The T
operator is the main mathematical object describing the operator is the main mathematical object describing the scattering process and is defined as

$$
T = H_{\rm int} \Omega_+.
$$
 (4)

It produces a family of transition operators acting on the Hilbert space of S and labeled by the Bohr frequencies of H_S denoted by $\{\omega\}$ and pairs of the particle's momenta,

$$
T_{\omega}(\mathbf{p}', \mathbf{p}) = \sum_{\mathcal{E}_k - \mathcal{E}_\ell = \omega} \langle k, \mathbf{p}' | T | \mathbf{p}, \mathcal{E} \rangle | k \rangle \langle \mathcal{E} |.
$$
 (5)

We further assume that the dilute ideal gas is at a stationary state fully characterized by the probability distribution in momentum space $G(\mathbf{p})$ and the particle density ν . As proven in Ref. [\[48\]](#page-5-31) the reduced dynamics of S is governed by the following quantum master equation (QME)

$$
\frac{d}{dt}\rho_S = -i[H_S, \rho_S] + \mathcal{L}\rho_S,\tag{6}
$$

where the dissipative generator is

$$
\mathcal{L}\rho_S = \nu \pi \sum_{\omega} \int d\mathbf{p} \int d\mathbf{p}' G(\mathbf{p}) \delta(E_{\mathbf{p}'} - E_{\mathbf{p}} + \omega)
$$

$$
\times \{ [T_{\omega}(\mathbf{p}', \mathbf{p}) \rho_S, T_{\omega}^{\dagger}(\mathbf{p}', \mathbf{p})] + [T_{\omega}(\mathbf{p}', \mathbf{p}), \rho_S T_{\omega}^{\dagger}(\mathbf{p}', \mathbf{p})] \}.
$$
 (7)

 $\mathcal L$ can be expressed in the form of an ergodic average

$$
\mathcal{L} = \lim_{a \to \infty} \frac{1}{a} \int_0^a dt e^{it[H_s, \cdot]} \mathcal{L}_0 e^{-it[H_s, \cdot]}, \tag{8}
$$

where \mathcal{L}_0 is given by

$$
\mathcal{L}_0 \rho_S = -i \int d\mathbf{p} \langle \mathbf{p} | [H_{\text{int}}, \Gamma_+ (\rho_S \otimes \rho_P)] | \mathbf{p} \rangle. \qquad (9)
$$

 ρ_P is the formal density matrix for the gas particle. This averaging [Eq. [\(8\)\]](#page-1-0) is usually associated with the secular approximation which is a necessary step to assure positivity preserving of the derived QME.

The basic properties of the QME given by Eqs. [\(6\)](#page-1-1) and [\(7\)](#page-1-2) are the following. (1) The dissipative generator $\mathcal L$ commutes with the Hamiltonian part $-i[H_S, \cdot],$

$$
\mathcal{L}[H_S, \cdot] = [H_S, \cdot] \mathcal{L}.
$$
 (10)

This implies that populations of H_S eigenstates evolve independently of their coherences. (2) If the gas is at thermal equilibrium at the inverse temperature β the probability distribution of the particle's momenta is given by

$$
G(\mathbf{p}) = Z^{-1} e^{-\beta E_{\mathbf{p}}},\tag{11}
$$

and the stationary state of the system is the Gibbs state,

$$
\rho_S^{\beta} = Z_S^{-1} e^{-\beta H_S}.
$$
\n(12)

(3) Under the additional ergodicity condition, any initial state of the system relaxes to the Gibbs state ρ_S^{β} .

Proofs.—Property (1) is a direct consequence of the averaging procedure [Eq. [\(8\)](#page-1-0)]. Namely, using the following identity, valid for any fixed τ ,

$$
\mathcal{L} = \lim_{a \to \infty} \frac{1}{a} \int_0^a dt e^{i(t+\tau)[H_S, \cdot]} \mathcal{L}_0 e^{-i(t+\tau)[H_S, \cdot]}
$$

= $e^{i\tau[H_S, \cdot]} \mathcal{L} e^{-i\tau[H_S, \cdot]},$ (13)

and differentiating both sides of Eq. [\(13\)](#page-1-3) at $\tau = 0$ one obtains Eq. [\(10\).](#page-1-4)

Property (2) is a new result, as in Ref. [[48](#page-5-31)] it is assumed that the system complies with microreversibility. This implies DBE. Here, we use only the intertwining property of the wave operator Ω_{+} ,

$$
\Omega_{+}(H_{S} + H_{P})\Omega_{+}^{\dagger} = H_{S} + H_{P} + H_{\text{int}} = H_{\text{tot}},\qquad(14)
$$

or equivalently,

$$
\Omega_{+}e^{-\beta(H_{S}+H_{P})}\Omega_{+}^{\dagger}=e^{-\beta H_{\text{tot}}}.
$$
 (15)

 $\mathcal{L}\rho_S^{\beta} = 0$ is obtained by assuming the gas particle is in a thermal state $\rho_S = 7^{-1} e^{-\beta H_P}$ and using Eqs. (8) (15) and thermal state, $\rho_P = Z^{-1}e^{-\beta H_P}$ and using Eqs. [\(8\),](#page-1-0) [\(15\),](#page-1-5) and [\(9\)](#page-1-6) (below C is an irrelevant constant). $\mathcal{L}\rho_S^{\beta}$ is equal to

$$
C \lim_{a \to \infty} \frac{1}{a} \int_0^a dt \, e^{iH_S t} \text{Tr}_P[H_{\text{int}}, \Omega_+ e^{-\beta(H_S + H_P)} \Omega_+^{\dagger}] e^{-iH_S t}.
$$
\n(16)

Using Eq. [\(15\)](#page-1-5), $H_{int} = H_{tot} - H_s - H_p$, and the fact that $[H_{\text{tot}}, e^{-\beta H_{\text{tot}}}] = 0$ we get

$$
C \lim_{a \to \infty} \frac{-1}{a} \int_0^a dt \, e^{iH_S t} \text{Tr}_P[H_S + H_P, e^{-\beta H_{\text{tot}}}] e^{-iH_S t}
$$
\n
$$
= C \lim_{a \to \infty} \frac{-1}{a} \int_0^a dt [H_S, e^{iH_S t} \text{Tr}_P(e^{-\beta H_{\text{tot}}}) e^{-iH_S t}]. \tag{17}
$$

In the last equality we have used that the trace of a commutator is zero. Equation [\(17\)](#page-2-0) can be rewritten as

$$
C \lim_{a \to \infty} \frac{-1}{a} \int_0^a dt \frac{d}{dt} \left(e^{iH_S t} \text{Tr}_P(e^{-\beta H_{\text{tot}}}) e^{-iH_S t} \right)
$$

=
$$
C \lim_{a \to \infty} \frac{-1}{a} \left\{ e^{iH_S a} \text{Tr}_P(e^{-\beta H_{\text{tot}}}) e^{-iH_S a} - \text{Tr}_P e^{-\beta H_{\text{tot}}} \right\} = 0,
$$
(18)

where we use the fact that the numerator has finite norm.

Property (3) is a consequence of the results obtained in Ref. [\[50\]](#page-5-33).

Properties (1) – (3) show that the Gibbs state is the steady state of the QME obtained in LDL for thermal equilibrium environments (ideal gas) without any additional assumptions such as DBE or microreversibility.

Detailed balance condition for LDL dynamics.—In this section we discuss the sufficient generic conditions leading to the detailed balance condition [Eq. [\(1\)\]](#page-0-0) for QME of the LDL type [Eqs. [\(6\)](#page-1-1) and [\(7\)\]](#page-1-2). The analysis is much simpler for the case of an H_S with nondegenerated spectrum.

For an H_S with a nondegenerated spectrum the diagonal elements of the density matrix, $p_k \equiv \langle k | \rho_S | k \rangle$, evolve independently from the off diagonal ones and satisfy the Pauli master equation of the form

$$
\frac{d}{dt}p_k = \sum_{\ell} (a_{k\ell}p_{\ell} - a_{\ell k}p_k) \tag{19}
$$

with

$$
a_{k\ell} = \nu \pi \int d\mathbf{p} \int d\mathbf{p}' G(\mathbf{p}) \delta \{ (E_{\mathbf{p}'} + \mathcal{E}_k) - (E_{\mathbf{p}} + \mathcal{E}_\ell) \} \times |\langle k, \mathbf{p}' | T | \mathbf{p}, \ell \rangle|^2.
$$
\n(20)

Using Eq. [\(20\)](#page-2-1) with $G(\mathbf{p}) = Z^{-1}e^{-\beta E_{\mathbf{p}}}$ one derives the following identity:

$$
a_{k\ell}e^{-\beta \mathcal{E}_{\ell}} = a_{\ell k}e^{-\beta \mathcal{E}_{k}}I(k,\ell), \qquad (21)
$$

where

$$
I(k,\ell) = \frac{\int d\mathbf{p} \int d\mathbf{p}' e^{-\beta E_{\mathbf{p}}} \delta\{E_{\mathbf{p}'} + \omega_{kl} - E_{\mathbf{p}}\} |\langle k, \mathbf{p}' | T | \mathbf{p}, \ell \rangle|^2}{\int d\mathbf{p} \int d\mathbf{p}' e^{-\beta E_{\mathbf{p}}} \delta\{E_{\mathbf{p}'} + \omega_{kl} - E_{\mathbf{p}}\} |\langle \ell, \mathbf{p} | T | \mathbf{p}', k \rangle|^2}.
$$
\n(22)

Here $\omega_{kl} = \mathcal{E}_k - \mathcal{E}_\ell$. The DBE condition is satisfied if and only if $I(k, \ell) = 1$ for those pairs (k, ℓ) for which transition probabilities are nonzero. It may happen incidentally for a particular choice of the parameters, but we discuss only the generic situations which are related to symmetries of the system.

The first sufficient symmetry condition is *Hermicity* of the T matrix $(T = T^{\dagger})$, that is $\langle k, \mathbf{p}'|T|\mathbf{p}, \ell \rangle = \overline{\langle \ell, \mathbf{p}|T|\mathbf{p}',k \rangle}$.
This is always satisfied for the Born approximation where This is always satisfied for the Born approximation where $T \simeq H_{\text{int}}$. This approximation is valid at the weak coupling limit where DBE always holds. Physically, at the dilute limit, a Hermitian T matrix represents a lossless system [[26](#page-5-14)].

The second sufficient condition is assuming that the T matrix is a symmetric matrix, $\langle k, \mathbf{p'}|T|\mathbf{p}, \ell \rangle = \langle \bar{\ell}, \mathbf{p}|T|\mathbf{p'}, k \rangle$,
which implies that the system is reciprocal [26,27] which implies that the system is reciprocal $[26,27]$ $[26,27]$ $[26,27]$.

The third case corresponds to *time-reversal symmetry* or microreversibility. It means that the states $|k\rangle$ are invariant with respect to time reversal, $E_p = E_{-p}$, and the probability of the scattering event $|\ell, \mathbf{p}\rangle \mapsto |k, \mathbf{p}'\rangle$ is equal to the probability of a time-reversed event $|k - \mathbf{n}'\rangle \mapsto |\ell - \mathbf{n}\rangle$ probability of a time-reversed event $\ket{k, -\mathbf{p}'} \mapsto \ket{\ell, -\mathbf{p}}$.
This condition means This condition means

$$
|\langle k, \mathbf{p}'|T|\mathbf{p}, \mathscr{E}\rangle|^2 = |\langle \mathscr{E}, -\mathbf{p}|T| - \mathbf{p}', k\rangle|^2, \qquad (23)
$$

which leads to $I(k, \ell) = 1$.

The fourth condition combines time reversal with parity transformation (space inversion) which leads to the condition

$$
|\langle k, \mathbf{p'}|T|\mathbf{p}, \mathscr{E}\rangle|^2 = |\langle \mathscr{E}, \mathbf{p}|T|\mathbf{p'}, k\rangle|^2. \tag{24}
$$

We note here that only on shell processes have to be considered. This is a consequence of the delta function in Eq. [\(20\),](#page-2-1) which ensures energy conservation. For particular systems it may happen that certain geometric symmetry can restore detailed balance (see a toy model in Sec. V and the Supplemental Material [[51](#page-6-0)]).

The above conditions were derived for the T matrix. Some of them can also be obtained for Green's operator [see discussion below Eq (S9) in the Supplemental Material [\[51](#page-6-0)]].

Fulfilling at least one of the mentioned conditions will be enough to ensure DBE. In Sec. V we show a toy model that does not comply with any of the above conditions, resulting in DBE violation (see Sec. S.2.a in the Supplemental Material [\[51](#page-6-0)]).

Thermodynamic laws and entropy production.—DBE violation provides additional freedom to the reduced dynamics. Nevertheless, the time invariance of the Gibbs state still allows for preserving the fundamental principles of thermodynamics: the impossibility of steady work extraction from a single thermal bath or cooling of a cold bath without an external driving. Mathematically, the LDL master equation [Eq. [\(6\)\]](#page-1-1) satisfies (i) the zeroth law of thermodynamics [see Eq. (11)], (ii) the first law of thermodynamics (implied by the Hamiltonian model of open system), and (iii) the second law of thermodynamics (implied by the Spohn inequality [\[3](#page-4-4)]).

For diagonal density matrices the entropy production defined as

$$
\sigma = \sum_{k} \frac{dp_k}{dt} [\ln p_k^{eq} - \ln p_k]; \qquad p_k^{eq} \equiv Z^{-1} e^{-\beta \mathcal{E}_k} \qquad (25)
$$

can be written in terms of the DBE violation as

$$
\sigma = \sum_{k>j} \left[K_{jk} \ln \left(\frac{p_k \, a_{jk}}{p_j \, a_{kj}} \right) + K_{jk} \ln I(k, j) \right] \tag{26}
$$

where $K_{jk} = a_{jk}p_k - a_{kj}p_j$ is the probability current from the microstate $\{k\}$ to the microstate $\{j\}$. The first term in Eq. [\(26\)](#page-3-0) corresponds to the Schnakenberg formulation of entropy production [[52](#page-6-1)] and the second to deviations due to the lack of DBE. Equation [\(26\)](#page-3-0) is valid for any temporal state as long as the steady state of the dynamics is a Gibbs state [see Eq. (12)] as is the case for Eq. (6) .

Furthermore, at thermal equilibrium the second term can be rewritten as

$$
\sum_{k > j} a_{jk} p_k^{eq} [1 - I(k, j)] \ln I(k, j), \tag{27}
$$

which is always negative. At thermal equilibrium the first and second laws force the entropy production to be zero. Therefore, to compensate for the negativity of Eq. [\(27\)](#page-3-1), the Schnakenberg entropy production should be positive and increases with the DBE violation: $|(1 - I(k, j))|$.

Three-level open system without time-reversal symmetry.—As a toy model we consider a single (spinless) electron that can occupy three dots (1,2,3) in an equilateral triangle arrangement in the presence of a magnetic field. The positions of the quantum dots (QD) are given by ${q_i; i = 1, 2, 3}$. This system (3QD) is governed by the single particle Hubbard Hamiltonian. This Hamiltonian type has been used to study more complex systems, such as Benzene molecules [[53](#page-6-2)] and could be used to extend our results to more realistic scenarios. In the single electron localized basis $(|1\rangle, |2\rangle, |3\rangle)$, the Hamiltonian is given by

$$
H_{\rm el} = \tau \begin{pmatrix} 0 & e^{-i2\pi\phi/3} & e^{i2\pi\phi/3} \\ e^{i2\pi\phi/3} & 0 & e^{-i2\pi\phi/3} \\ e^{-i2\pi\phi/3} & e^{i2\pi\phi/3} & 0 \end{pmatrix}, \quad (28)
$$

where τ is the tunneling parameter and ϕ is the magnetic flux [[54](#page-6-3)]. The diagonal form of this Hamiltonian is $H_{el} = \sum_{j \in \{\pm, 0\}} = \mathcal{E}_j|j\rangle\langle j|$ where $\mathcal{E}_j = -2|\tau|\cos[2\pi(\phi + j*1)/3]$. For most values of the magnetic flux the Hamiltonian is nondegenerated.

The 3QD interacts with a low-density gas of free particles of mass m that is at a thermal state with inverse temperature β . We assume a simple form of the interaction potential given by

$$
H_{\text{int}}(\mathbf{q}) = \sum_{\iota \in \{1,2,3\}} V_{\iota}(\mathbf{q} - \mathbf{q}_{\iota}) | \iota \rangle \langle \iota |, \tag{29}
$$

where $V_i(\mathbf{q} - \mathbf{q}_i)$ is a short range repulsive potential between the electron and the particle. In order to simplify numerical calculations we assume that the distance between dots is small in comparison with the typical wavelength of a quantum scatterer. This allows one to treat all dots as sitting at the same point, while keeping the structure of the internal electron Hamiltonian [Eq. [\(28\)\]](#page-3-2). Then we can replace smooth potentials in Eq. [\(29\)](#page-3-3) by 1D Dirac deltas $V_i\delta(q)$ and at the same time use as a heat bath a one-dimensional particle gas. Figure [1](#page-3-4) shows the results of numerical calculations for this simplified model showing a substantial violation of DBE while the stationary state remains a Gibbs one. Notice that in the presented example all coupling constants V , are different. It is shown in the Supplemental Material [[51](#page-6-0)] that if at least two constants are equal DBE is preserved. This is an example of a system-specific

FIG. 1. $I(k, l)$ as function of the normalized inverse temperature $\beta \Delta E$. DBE only holds if all the $I(k, l) = 1$. For large $\beta \Delta E$, $I(0,-)$ tends to 1. Nevertheless, $I(+,-)$ and $I(0,+)$ are still different from 1 indicating the lack of DBE. Inset: lhs (continuous line) and rhs (dotted line) of the thermalization conditions, Eqs. [\(30a\)](#page-4-10) and [\(30b\)](#page-4-11). The compliance with these conditions $(lhs = rhs)$ verifies our numeric calculation. The y axis of the inset has been multiplied by a factor of 10^4 . Parameters: $\mathcal{V}_1 = 1, \mathcal{V}_2 = 0.7, \ \mathcal{V}_3 = 1.5, \ \mathcal{E}_+ = 0.5, \ \mathcal{E}_0 = 0.0, \ \mathcal{E}_- = -0.5,$ and $\Delta E = \mathcal{E}_0 - \mathcal{E}_-$. For more details see the SupplementalMaterial [\[51\]](#page-6-0).

symmetry that restores DBE. Namely, here time reversal exchanges the eigenstates $| \pm \rangle$ that can be undone by the permutation of two states from the set $\{|i\rangle\}$ with equal couplings to the bath.

DBE establishes a relation between transition rates involving the same Bohr frequencies (i.e., a_{kl} and a_{lk}) allowing independent transition rates among different Bohr frequencies [[16](#page-5-4)]. This relation, together with the Kubo-Martin-Schwinger condition (KMS), forces the reduced system to thermalize. In contrast, systems violating DBE use a different thermalization mechanism. While they have some extra degree of freedom due to the DBE violation, thermalization imposes a complex dependence among rates for different Bohr frequencies that we term thermalization conditions. For example, in the case of the 3QD model they read as

$$
a_{+0}[1 - I(0, +)] = a_{-0}[I(0, -) - 1]; \qquad (30a)
$$

$$
a_{0+}[1 - 1/I(0, +)] = a_{-+}[I(+, -) - 1].
$$
 (30b)

Probability and heat currents: The different thermalization mechanisms could be better understood by analyzing the probability currents, K_{ik} [see discussion below Eq. [\(26\)](#page-3-0) and Ref. [[4\]](#page-4-5)]. Systems complying with DBE thermalize by reducing each individual probability's currents, until all of them become zero at thermal equilibrium. In contrast, systems violating DBE thermalize by reducing $\sum_i K_{ik}$ which becomes zero at thermal equilibrium, while at least some of the individual currents,

$$
K_{jk} = a_{kj} p_k^{eq} [I(j,k) - 1], \tag{31}
$$

remain nonzero even at equilibrium forming closed loops. These persistent currents are different from those found on aromatic [[55](#page-6-4)–[57\]](#page-6-5) or mesoscopic rings [[58](#page-6-6),[59](#page-6-7)]. The currents found in these works are also present in isolated systems. They are produced by breaking the time-reversal symmetry of the system eigenfunctions [[60](#page-6-8)]. In contrast, the current described by Eq. [\(31\)](#page-4-12) requires a nonisolated system and the breakdown of other symmetries (see Sec. III).

It has been claimed that violation of DBE produces persistent heat currents in nonreciprocal systems [\[29\]](#page-5-16). The existence of these currents does not violate any fundamental thermodynamic law. Using the Spohn inequality it is possible to define thermodynamically consistent heat currents [[61\]](#page-6-9) between individual pairs of the system energy levels and the thermal bath. At the equilibrium state they are defined as $J_{ml} = -\beta^{-1} a_{lm} p_m^{\text{eq}} [I(m, l) - 1] \ln (p_m^{\text{eq}} / p_l^{\text{eq}})$. In particular for the toy model we get $(i, i - 0 + 0)$. particular for the toy model we get $(i, j = 0, +, -)$

$$
J_{ij} = N[I(+, -) - 1](\mathcal{E}_i - \mathcal{E}_j),
$$
 (32)

where $N = a_{-+}e^{-\beta(\mathcal{E}_- - \mathcal{E}_0)} \left[1 + e^{-\beta(\mathcal{E}_- - \mathcal{E}_0)} + e^{-\beta(\mathcal{E}_+ - \mathcal{E}_0)}\right]$
Even though there are heat currents to and from individent Even though there are heat currents to and from individual $]^{-1}.$ pairs of the system energy levels, the total heat exchange between the bath and the system is zero, as expected from the first law of thermodynamics. It is important to notice that both probabilities and heat currents are related to transitions between delocalized energy levels and do not necessarily imply the existence of heat currents in space. In particular, for our 3QD model all energy eigenstates yield equal occupation probabilities for all dots.

In summary, here we develop an open quantum system framework to study systems that violate DBE. This extra degree of freedom changes the system dynamics and could be beneficial for many applications, such as speeding up thermalization, increasing the sensitivity of measuring devices, and improving the operation of heat machines. One should stress that DBE is not easy to break. The effect appears in the higher-order expansion with respect to the system-bath coupling constant and could vanish in the presence of certain spatial symmetries (see the Supplemental Material [[51](#page-6-0)]).

We thank Natan Granit, Thales Pinto Silva, U. Peskin, and N. Moiseyev for useful discussions. R. A. is supported by the Foundation for Polish Science's International Research Agendas, with structural funds from the European Union (EU) for the ICTQT and at the Technion by a fellowship from the Lady Davis Foundation. M. Š. gratefully acknowledges financial support of the Helen Diller Quantum Center of the Technion (March 1–May 31, 2023). D. G. K. is supported by the ISRAEL SCIENCE FOUNDATION (Grant No. 2247/22) and by the Council for Higher Education Support Program for Hiring Outstanding Faculty Members in Quantum Science and Technology in Research Universities.

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