Time-energy and time-entropy uncertainty relations in dissipative quantum dynamics

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We derive exact relations and general inequalities that extend the usual time-energy uncertainty relations from the domain of unitary Hamiltonian dynamics to that of dissipative dynamics as described by a broad class of linear and nonlinear evolution equations for the density operator. We restrict our attention to intrinsic characteristic times of dynamical variables associated with the linear functionals $\text{Tr}(\rho F)$ of the density operator, as well as with the nonlinear entropy functional $-k_B\text{Tr}(\rho \ln \rho)$. For non-dissipative dynamics, by using the Schrödinger inequality instead of the Heisenberg-Robertson inequality, we obtain a general exact time-energy uncertainty relation which is sharper than the usual Mandelstam-Tamm-Messiah relation $\tau_F \Delta_H \geq \hbar/2$. For simultaneous unitary/dissipative dynamics, the usual time-energy uncertainty relation is replaced by a less restrictive relation that depends on the characteristic time of dissipation, $\tau$, and the uncertainty associated with the generalized nonequilibrium Massieu-function operator which defines the structure of the dissipative part of the assumed class of evolution equations. Within the steepest-entropy-ascent dissipative quantum dynamics of an isolated system introduced earlier by this author, we obtain the interesting time-energy and time-entropy uncertainty relation $(2\tau_F \Delta_H/h)^2 + (\tau_F \Delta_S/k_B) \geq 1$. We illustrate this result and various other inequalities by means of numerical simulations.

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I. INTRODUCTION

The time-energy uncertainty relation has remained an open and at times controversial issue throughout the history of quantum theory. Several reviews are available on the pioneering discussions and the more recent developments 1]. We are motivated by the recent revival of foundational questions and the development of dynamical theories that seek to build into the laws of quantum mechanics those of equilibrium and non-equilibrium thermodynamics. Such revival is currently paralleled by the steady advancement of experimental techniques dealing with single ion traps 2], qubits 3], neutron interferometry 4], and a growing number of other developments all pointing at microscopic few-particle setups that nevertheless exhibit non-unitary dissipative dynamical behaviour and call for the investigation of the role of general thermodynamic principles at the microscopic quantum level. Here we address the question of how the usual time-energy uncertainty relation, as interpreted according to the Mandelstam-Tamm-Messiah intrinsic-time approach 5] based on unitary Hamiltonian dynamics, is modified by the presence of dissipation in the dynamical law or model.

Let $\mathcal{H}$ (dim$\mathcal{H} \leq \infty$) be the Hilbert space and $H$ the Hamiltonian operator associated with a system in standard Quantum Mechanics. We assume that the quantum states are one-to-one with the linear hermitian operators $\rho$ on $\mathcal{H}$ with $\text{Tr}(\rho) = 1$ and $\rho \geq \rho^2$, and we assume a dynamical equation of the form

$$\frac{d\rho}{dt} = \rho E(\rho) + E^\dagger(\rho) \rho,$$

where $E(\rho)$ is an operator-valued function of $\rho$ that we may call the “evolution” operator and in general is non-hermitian. Without loss of generality, we write $E = E_+ + iE_-$ where $E_+ = (E + E^\dagger)/2$ and $E_- = (E - E^\dagger)/2i$ are hermitian operators that, for convenience, we rename as $\Delta M(\rho)/2k_B\tau(\rho)$ and $H/\hbar$, respectively, so that Eq. (1) takes the form

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] + \frac{1}{2k_B\tau(\rho)}(\Delta M(\rho), \rho),$$

where $[\cdot, \cdot]$ and $\{\cdot, \cdot\}$ are the usual commutator and anticommutator, $H$ (assumed independent of $\rho$, but not necessarily independent of time $t$) is identified with the Hamiltonian operator, $\hbar$ the reduced Planck constant, $k_B$ the Boltzmann constant; moreover, $\Delta M(\rho)$ is a hermitian operator-valued, possibly nonlinear function of $\rho$ which, together with the positive definite, possibly nonlinear functional $\tau(\rho)$ of $\rho$, describes the dissipative dynamics of the system, and is such that $\text{Tr}[\rho \Delta M(\rho)] = 0$ as required to preserve $\rho$ unit trace.

The reason for considering a dynamical law of the form 6] is that the explicit expression of $\Delta M(\rho)$ that generates steepest-entropy-ascent (maximal entropy generation) conservative dynamics of an isolated system compatible with all thermodynamics requirements 6] is known 6]. We use it in Sections VII and VIII as an illustration of our general results, within a model for irreversible relaxation in a Boltzmann gas of $N$-level atoms. The extension to structured composite systems, which is nontrivial in view of the assumed nonlinearity of the dynamical law with respect to $\rho$, will be discussed else-
where. Additional discussion about the form of equation (2) is given in the Appendix.

The steepest-entropy-ascent form of the operator function \( \Delta M(\rho) \) is discussed in Section VII after introducing the necessary notation, in terms of the operator

\[
M(\rho) = S(\rho) - \frac{H}{\theta(\rho)} + \frac{\mu(\rho) \cdot N}{\theta(\rho)},
\]

(3)

where \( S(\rho) \) is the entropy operator [the precise definition is given in Section III Eq. (3)], and the functionals \( \theta(\rho) \) and \( \mu(\rho) \) are defined in Section VI Eqs. (63)- (65). We call operator \( M(\rho) \) the generalized nonequilibrium Massieu-function operator, because at thermodynamic equilibrium its mean value belongs to the family of entropic characteristic functions introduced by Massieu [3], i.e.,

\[
\langle M \rangle_e = \langle S \rangle_e - \frac{\langle H \rangle_e}{T} + \frac{\mu \cdot \langle N \rangle_e}{T},
\]

(4)

where \( \langle S \rangle_e, \langle H \rangle_e, \langle N \rangle_e, T \) and \( \mu \) are the equilibrium entropy, energy, amounts of constituents, temperature and chemical potentials, respectively.

The specific physical interpretations of the uncertainty relations that we derive from dynamical law [2] depend on the theoretical or modeling context in which it is assumed. In this article we limit the discussion to generalities in Sections III-VI and to illustrative considerations and numerical results valid within the simplest framework of steepest-entropy-ascent conservative dynamics in Sections VII and VIII.

II. GENERAL UNCERTAINTY RELATIONS

We consider the space \( \mathcal{L}(\mathcal{H}) \) of linear operators on \( \mathcal{H} \) equipped with the real scalar product

\[
(F|G) = \text{Tr}(F^\dagger G + G^\dagger F)/2 = (G|F),
\]

(5)

and the real antisymmetric bilinear form

\[
(F\not G) = i\text{Tr}(F^\dagger G - G^\dagger F)/2 = -(G\not F) = (F|G),
\]

(6)

so that for any (time-independent) hermitian \( F \) in \( \mathcal{L}(\mathcal{H}) \) the corresponding mean-value state functional can be written as

\[
\langle F \rangle = \text{Tr}(\sqrt{\rho} F \sqrt{\rho}) = (\sqrt{\rho}|F\sqrt{\rho}),
\]

and can therefore be viewed as a functional of \( \sqrt{\rho} \), the square-root density operator, obtained from the spectral expansion of \( \rho \) by substituting its eigenvalues with their positive square roots. When \( \rho \) evolves according to Eq. (1), the rate of change of \( \text{Tr}(\rho F) \) can be written as

\[
d\text{Tr}(\rho F)/dt = \text{Tr}(F d\rho/dt) = 2 (\sqrt{\rho} F | \sqrt{\rho} E(\rho)) .
\]

(7)

In particular, for the evolution equation (1) to be well defined, the functional \( \text{Tr}(\rho I) \) where \( I \) is the identity on \( \mathcal{H} \) must remain equal to unity at all times; therefore, \( d\text{Tr}(\rho I)/dt = 2 (\sqrt{\rho} I | \sqrt{\rho} E(\rho)) = 0 \), in view of Eq. (2) implies the condition

\[
(\sqrt{\rho} | \sqrt{\rho} \Delta M(\rho)) = 0 .
\]

(8)

For \( F \) and \( G \) hermitian in \( \mathcal{L}(\mathcal{H}) \), we introduce the following shorthand notation

\[
\Delta F = F - \text{Tr}(\rho F) I ,
\]

\[
\sigma_{FG} = (\Delta F \Delta G) = (\sqrt{\rho} \Delta F | \sqrt{\rho} \Delta G) = \frac{1}{2} \text{Tr}(\rho (\Delta F \Delta G)) = \sigma_{GF} ,
\]

\[
\Delta F = \sqrt{\sigma_{FF}} = (\sqrt{\rho} \Delta F | \sqrt{\rho} \Delta G) = \frac{1}{2} \text{Tr}(\rho (\Delta F G)) = \eta_{FG} ,
\]

\[
\Delta F = \sqrt{\sigma_{GG}} = (\sqrt{\rho} \Delta F | \sqrt{\rho} \Delta G) = \frac{1}{2} \text{Tr}(\rho (F G)) = \eta_{GF} = -\eta_{FG} ,
\]

(9)-(12)

For example, we may write the rate of change of the mean value of a time-independent observable \( F \) as

\[
\frac{d\text{Tr}(\rho F)}{dt} = \frac{(F, H)/2i}{\hbar/2} + \frac{(\Delta F \Delta M)}{\kappa_\tau} = \eta_{FH} + \frac{\sigma_{FM}}{\kappa_\tau} ,
\]

(13)

from which we see that not all operators \( F \) that commute with \( H \) correspond to constants of the motion, but only those for which \( (\Delta F \Delta M) = 0 \), i.e., such that \( \sqrt{\rho} \Delta F \) is orthogonal to both \( \sqrt{\rho} \Delta H \) and \( \sqrt{\rho} \Delta M \), in the sense of scalar product. For an isolated system, conservation of the mean energy functional \( \text{Tr}(\rho H) \) requires an operator function \( \Delta M(\rho) \) that maintains \( \sqrt{\rho} \Delta M \) always orthogonal to \( \sqrt{\rho} \Delta H \), so that \( (\Delta H \Delta M) = 0 \) for every \( \rho \).

From Schwarz inequality, we readily verify [3] the following generalized Schrödinger uncertainty relation [11]

\[
(\Delta F \Delta G)(\Delta G \Delta F) \geq (\Delta F \Delta G)^2 + (\langle F, G \rangle/2i)^2 ,
\]

(14)

usually written in the form \( \sqrt{\sigma_{FF} \sigma_{GG}} - \sigma_{FG}^2 \geq |\eta_{FG}| \). Relation (14) obviously entails the less precise and less symmetric Heisenberg-Robertson uncertainty relation

\[
(\Delta F \Delta F)(\Delta G \Delta G) \geq (\langle F, G \rangle/2i)^2 ,
\]

(15)

usually written in the form \( \Delta F \Delta G \geq |\eta_{FG}| \).

For further compactness, we introduce the notation

\[
r_{FG} = \sigma_{FG}/\sqrt{\sigma_{FF} \sigma_{GG}} ,
\]

\[
c_{FG} = \eta_{FG}/\sqrt{\sigma_{FF} \sigma_{GG}} ,
\]

(16)

where clearly, \( r_{FG} \) represents the cosine of the angle between the ‘vectors’ \( \sqrt{\rho} \Delta F \) and \( \sqrt{\rho} \Delta G \) in \( \mathcal{L}(\mathcal{H}) \), and \( r_{FG}^2 \leq 1 \). Inequality (14) may thus be rewritten as

\[
r_{FG}^2 + c_{FG}^2 \leq 1 \quad (17)
\]

and clearly implies

\[
c_{FG}^2 \leq \frac{1}{1 + (r_{FG}^2/c_{FG}^2)} \leq 1 - r_{FG}^2 \leq 1 .
\]

(18)
Next, for any hermitian $F$ we define the characteristic
time of change of the corresponding property defined by
the mean value of the linear functional $\langle F \rangle = \text{Tr}(\rho F)$ as follows
\[
\tau_F = \frac{\Delta F}{|d\langle F \rangle/dt|}.
\] (19)
As is well known $^1$, $^3$, $^5$, $^6$, $^13$, $^14$, $^15$, $\tau_F$ represents the time required for
the statistical distribution of measurements of observable $F$ to be appreciably modified, i.e., for the mean value $\langle F \rangle$
to change by an amount equal to the width $\Delta_F$ of the distribution.

Now, defining the nonnegative, dimensionless functional
\[
a_r = \frac{\hbar \Delta_M}{2k_n \tau \Delta_H},
\] (20)
we rewrite $^13$, $^14$, $^15$ in the form
\[
d\langle F \rangle/dt = 2\Delta_F \Delta_H (c_FH + a_r r_{FM})/\hbar
\] (21)
and, substituting into $^13$, $^14$, $^15$, we obtain the general exact
uncertainty relation
\[
\frac{\hbar}{\tau_F \Delta_H} = |c_FH + a_r r_{FM}|.
\] (22)
For non-dissipative dynamics, $a_r = 0$, Eq. (22) yields the
time-energy uncertainty relations
\[
\frac{\hbar^2/4}{\tau_F^2 \sigma_{HH}} = c_F^2 \leq \frac{1}{1 + (r_F^2/c_F^2)} \leq 1 - \frac{\hbar^2}{4 \tau_F^2} \leq 1,
\] (23)
which entail but are more precise than the usual
time-energy uncertainty relation, in the same sense as
Schrödinger’s relation $^11$, $^13$, $^14$, $^15$, $^16$ entails but is more precise
than Heisenberg’s relation $^11$, $^13$, $^14$, $^15$, $^16$. According to $^14$, $^15$, the
last inequality in (23) implies that property $\langle F \rangle$ cannot
change at rates faster than $2\Delta_F \Delta_H/\hbar$.

For dissipative dynamics let us first consider an observable $A$
that commutes with $H$, so that $\langle [A, H]/2i \rangle = 0$
while $\langle A \Delta H \rangle \neq 0$; in other words, an observable
conserved by the Hamiltonian term in the dynamical law
(2), but not conserved by the dissipative term. Then Eq. (22)
yields the equivalent time-energy uncertainty relations
\[
\frac{\hbar}{\tau_A \Delta_H} = a_r |r_{AM}| \leq a_r,
\] (24)
\[
\frac{k_n \tau(\rho)}{\tau_A \Delta_M} = |r_{AM}| \leq 1.
\] (25)
We note that while $r_{AM}^2 / \Delta_M \leq 1$, the value of $a_r$
depends on how $\tau(\rho)$ is defined and, a priori, could well be
larger than unity, in which case there could be some observables
$A$ for which $\tau_A \Delta_H \leq \hbar/2$. If instead we impose that the
functional $\tau(\rho)$ be defined in such a way that $a_r \leq 1$, i.e.,
\[
\tau(\rho) \geq \hbar \Delta_M/2k_n \Delta_H,
\] (26)
then we obtain that even in dissipative dynamics the usual
time-energy uncertainty relations are never violated by observables $A$ commuting with $H$.

However, in general, if the dynamics is dissipative ($\tau \neq \infty$) there are density operators for which $|c_{FH} + a_r r_{FM}| > 1$
so that $\tau_F \Delta_H$ takes a value less than $\hbar/2$ and thus the
usual time-energy uncertainty relation is violated. The sharpest
general time-energy uncertainty relation always satisfied
when both Hamiltonian and dissipative dynamics are active (proof in Section IV)
\[
\frac{\hbar^2}{4 \tau_F^2 \sigma_{HH}} \leq 1 + a_r^2 + 2a_r c_{MH},
\] (27)
which may also take the equivalent form
\[
\frac{\hbar^2}{4 \tau_F^2 \sigma_{HH}} + \frac{\tau_F^2 \sigma_{MM}}{k_n^2 \tau^2(\rho)} + \frac{\tau_F^2 \Delta_M \Delta_{H MH}}{k_n \tau(\rho) \hbar/4} \geq 1.
\] (28)
The upper bound in the rate of change of property $\langle F \rangle$
becomes
\[
\Delta_F \sqrt{\frac{\sigma_{HH}/(\hbar^2/4) + \sigma_{MM}/(k_n^2 \tau^2(\rho)) + \Delta_M \Delta_{H MH}/(k_n \tau(\rho) \hbar/4)}{}}.
\] (29)
As anticipated, because the dissipative term in Eq. (4)
implies an additional dynamical mechanism, this bound (29),
valid for the particular nonunitary dynamics we are considering,
is higher than the standard bound valid in unitary
Hamiltonian dynamics, given by $2\Delta_F \Delta_H/\hbar$. For
observables commuting with $H$, however, (29) provides
the sharper general bound $\Delta_F \Delta_M/k_n \tau$, solely due to
dissipative dynamics, which is lower than (29).

Because in general $|c_{MH}| < 1$, (28) obviously implies the
less precise relation
\[
\frac{\hbar^2}{4 \tau_F^2 \sigma_{HH}} \leq (1 + a_r)^2.
\] (30)
However, as for the dynamics we discuss in Section IV if
the Massieu operator function $\Delta M(\rho)$ is a linear combination
(with coefficients that may depend nonlinearly on $\rho$)
of operators that commute with either $\rho$ or $H$, then it is
easy to show that $c_{HH} = 0$. Therefore, in such important
case, (28) becomes
\[
\frac{\hbar^2}{4 \tau_F^2 \sigma_{HH}} \leq 1 + a_r^2.
\] (31)

**III. RATE OF ENTROPY CHANGE CHARACTERISTIC TIME**

We now consider the entropy functional $\langle S \rangle = \text{Tr}(\rho S) = -k_n \text{Tr}(\rho \ln \rho) = -k_n \sqrt{\rho} \sqrt{\rho \ln(\sqrt{\rho})^2}$ and its
rate of change, which using Eqs. 2 and 3 may be written as
\[ \frac{d \text{Tr}(\rho S)}{dt} = 2 (\sqrt{\rho S}) |\sqrt{\rho E(\rho)}| = (\Delta S \Delta M)/k_B \tau \]
\[ = \Delta S \Delta M r_{SM}/k_B \tau \]
where, for convenience, we define the entropy operator
\[ S = -k_B P_{\rho > 0} \ln \rho \, , \]
where \( P_{\rho > 0} \) is the projection operator onto the range of \( \rho \).

Interestingly, the rate of entropy change, being proportional to the correlation coefficient between entropy measurements and \( M \) measurements, under the assumptions made so far, may be positive or negative, depending on how \( M \) is defined, i.e., depending on the specifics of the physical model in which Eq. 4 is adopted.

The characteristic time of change of the entropy functional, defined as
\[ \tau_S(\rho) = \Delta S/|d\langle S \rangle/dt| \, , \]
gives rise to the following equivalent exact time-energy uncertainty relations
\[ \frac{\hbar/2}{\tau_S \Delta_H} = a_\tau |r_{SM}| \leq a_\tau \, , \]
\[ \frac{k_B \tau(\rho)}{\tau_S \Delta_M} = |r_{SM}| \leq 1 \, , \]
where \( r_{SM} \) is defined as in 10 using operators \( \Delta M(\rho) \) and \( \Delta S = S - \langle S \rangle \). The physical interpretation of 33, as immediately obvious also from 32.

We notice from 36 that if the dissipation time functional \( \tau(\rho) \) satisfies condition 26 then \( a_\tau \leq 1 \) and, therefore, the entropy change characteristic time \( \tau_S \) satisfies the usual uncertainty relation \( \tau_S \Delta_H \geq \hbar/2 \) and the rate of entropy change cannot exceed \( 2\Delta S \Delta_H/\hbar \).

We conclude this Section by noting that, in general, the equality in 35 may be used to rewrite Relation 27 in the form
\[ \frac{a_\tau}{1 + a_\tau} |r_{SM}| \tau_S \leq \tau_F \sqrt{1 + a_\tau^2 + 2a_\tau r_{CMH}}/1 + a_\tau \leq \tau_F \, , \]
where the last inequality follows from \( |r_{CMH}| \leq 1 \). This relation shows, on one hand, that the entropy change characteristic time \( \tau_S \) is not necessarily the shortest among the characteristic times \( \tau_F \) associated with observables of the type \( \langle F \rangle = \text{Tr}(\rho F) \) according to the Mandelstam-Tamm definition 15. On the other hand, it also shows that the left-hand side defines a characteristic-time functional
\[ \tau_{UD} = \frac{a_\tau}{1 + a_\tau} |r_{SM}| \tau_S \leq \tau_F \, , \]
which constitutes a general lower bound for all \( \tau_F \)’s, and may therefore be considered the shortest characteristic time of simultaneous unitary/dissipative dynamics as described by Equation 2. This observation prompts the discussion in the next Section.

IV. SHORTEST CHARACTERISTIC TIMES FOR PURELY-UNITARY AND PURELY-DISSIPATIVE DYNAMICS

The Mandelstam-Tamm definition 15 of characteristic times has been criticized for various reasons (see for example Refs. 24, 27, 28) mainly related to the fact that depending on which observable \( F \) is investigated, as seen by inspecting 29, the bound \( \tau_F \geq \hbar/2\Delta_H \) may be very poor whenever \( \Delta_H \) is much smaller than \( \hbar \).

Therefore, different attempts have been made to define characteristic times that (1) refer to the quantum system as a whole rather than to some particular observable, and (2) bound all the particular \( \tau_F \)’s from below. Notable examples are the characteristic times \( \tau_{ES} \) and \( \tau_{LK} \), respectively defined by Eberly and Singh 24 and Leubner and Kiener 27 as follows.

The following definitions are based on the observation that \( \tau_F \) may be interpreted as the norm of \( \sqrt{\Delta F} \) (viewed as a vector in \( L(\mathcal{H}) \)) in the sense that it equals \( \sqrt{\langle \sqrt{\Delta F} \rangle} \sqrt{\langle \Delta F \rangle} \), therefore, we may use it to define the (generally non hermitian) unit norm vector in \( L(\mathcal{H}) \)
\[ \tilde{F}_\rho = \sqrt{\rho F}/\Delta_F \, . \]
As a result, Eq. 13 may be rewritten in the form
\[ \frac{1}{\Delta_F} \frac{d\langle F \rangle}{dt} = \frac{\Delta_H}{\hbar/2} (\tilde{F}_\rho \parallel \hat{H}_\rho) + \frac{\Delta_M}{k_B \tau} (\tilde{F}_\rho \parallel \hat{M}_\rho) = (\tilde{F}_\rho | C \rangle \, , \]
where for shorthand we define the operator
\[ C = i \frac{\Delta_H \hat{H}_\rho}{\hbar/2} + \frac{\Delta_M \hat{M}_\rho}{k_B \tau} = 2 \sqrt{\rho E(\rho)} \, , \]
directly related [see Eq. 4] with the evolution operator function \( E(\rho) \) defined in the Introduction, which determines the rates of change of all linear functionals of the state operator \( \rho \), i.e., all observables of the linear type \( \text{Tr}(\rho F) \), by its projection onto the respective directions \( \tilde{F}_\rho \).

Each characteristic time \( \tau_F \) can now be written as
\[ \tau_F = \frac{\Delta_F/|d\langle F \rangle/dt|}{1/(\tilde{F}_\rho | C \rangle) \, . \]
Because \( \tilde{F}_\rho \) is unit norm, \( |(\tilde{F}_\rho | C \rangle) \) is bounded by the value attained for an operator \( \tilde{F}_\rho \) that has the same ‘direction’ in \( L(\mathcal{H}) \) as operator \( C \), i.e., for
\[ \tilde{F}_\rho = \pm C/\sqrt{(C | C \rangle) \, , \]
in which case \( |(\tilde{F}_\rho | C \rangle) = \sqrt{(C | C \rangle) = \sqrt{\text{Tr}(C^\dagger C)} \). Thus we conclude that, for any \( F \),
\[ 1/\sqrt{(C | C \rangle) \leq \tau_F \, , \]
and, therefore, we introduce the shortest characteristic time for the combined unitary-dissipative dynamics described by Eq. 2.

\[ \tau_{UD} = 1/\sqrt{(C | C \rangle) \, , \]
which bounds from below all $\tau_F$’s. From (11) and (14), and the identities $(i\hat{H}_\rho|i\hat{H}_\rho) = (M_\rho|\hat{M}_\rho) = 1$ and $(i\hat{H}_\rho|\hat{M}_\rho) = (\hat{M}_\rho|i\hat{H}_\rho) = \epsilon_{\text{MH}}$ we obtain

$$\frac{1}{\tau_F} \leq \frac{1}{\tau_{UD}} = \frac{\langle C|C \rangle}{\hbar^2/4} = \frac{\sigma_F}{\hbar^2/4} (1 + a_\tau^2 + 2a_\tau\epsilon_{\text{MH}}),$$

(46)

which proves Relations (27) and (28).

For nondissipative (purely Hamiltonian, unitary) dynamics the same reasoning (or substitution of $\tau = \infty$, $a_\tau = 0$ in the above relations) leads to the definition of the shortest characteristic time

$$\tau_U = \hbar/2\Delta_H,$$

(47)

with which the usual time-energy relation reduces to

$$\tau_F \geq \tau_U.$$  

(48)

Its physical meaning is that when the energy dispersion (or uncertainty or spread) $\Delta_H$ is small, $\tau_U$ is large and $\tau_F$ must be larger for all observables $F$, therefore, the mean values of all properties change slowly [27], i.e., the state $\rho$ has a long lifetime. Conversely, states with a small energy spread cannot change rapidly with time. States that change rapidly due to unitary dynamics, necessarily have a large energy spread.

Another interesting extreme case obtains from Eq. (2) when $\Delta M(\rho)$ is such that the condition $[\rho, H] = 0$ implies $[\Delta M(\rho), H] = 0$ for any $\rho$, as for the steepest-entropy-ascent dynamics discussed in Sections VI and VII. In this case, it is easy to see that if the state operator $\rho$ commutes with $H$ at one instant of time then it commutes with $H$ at all times and, therefore, the entire time evolution is purely dissipative. Then, the reasoning above leads to the definition of the shortest characteristic time

$$\tau_D = k_\alpha \tau/\Delta_M.$$  

(49)

It is noteworthy that $\tau_D$ can be viewed as the characteristic time associated not with the (generally nonlinear) Massieu functional $\langle M \rangle = \text{Tr}(\rho M(\rho))$ but with the linear functional $\langle A \rangle = \text{Tr}(\rho A)$ corresponding to the time-independent operator $A$ which at time $t$ happens to coincide with $M(\rho(t))$.

For purely dissipative dynamics, the bound $\tau_F \geq \tau_D = k_\alpha \tau/\Delta_M$ implies that when $\Delta_M/k_\alpha \tau$, i.e., the ratio between the spread in our generalized nonequilibrium Massieu function and the dissipation time functional, is small, then $\tau_D$ is large and $\tau_F$ must be larger for all observables $F$, therefore, the state $\rho$ has a long lifetime. Conversely, if some observable changes rapidly, $\tau_F$ is small and since $\tau_D$ must be smaller, we conclude that the spread $\Delta_M$ [more precisely, the ratio $\Delta_M(\rho)/k_\alpha \tau(\rho)$] must be large.

In terms of $\tau_U$ and $\tau_D$ we can rewrite (20), (36) and (46) as

$$a_\tau = \frac{\tau_U}{\tau_D},$$

(50)

and

$$\frac{1}{\tau_U} = \frac{|r_{\text{FSM}}|}{\tau_D} \leq \frac{1}{\tau_D},$$

(51)

$$\frac{1}{\tau_F} \leq \frac{1}{\tau_{UD}} = \left(\frac{c_{\text{FH}} + \tau_{FSM}}{\tau_U} \right)^2 \leq \left( \frac{1}{\tau_U} + \frac{1}{\tau_D} \right)^2 \leq \left( \frac{1}{\tau_U} + \frac{1}{\tau_D} \right)^2.$$

(52)

Eq. (51) implies that the entropy cannot change rapidly with time if the ratio $\Delta_M(\rho)/k_\alpha \tau(\rho)$ is not large. The first equality in (52) follows from (20), (36) and (51), the second from (22) follows from (56) and (57) which also imply that Eq. (10) may take the form

$$\frac{d\langle F \rangle}{dt} = \Delta_F \left( \frac{c_{\text{FH}}}{\tau_U} + \frac{r_{\text{FSM}}}{\tau_D} \right),$$

(53)

and operator $C$ defined in (11) takes the forms

$$C = C_F = \frac{\hat{H}_\rho}{\tau_U} + \frac{\hat{\tilde{M}}_\rho}{\tau_D} = i\sqrt{\tau_D} \frac{\Delta_H}{\Delta_M \tau_U} + \sqrt{\tau_U} \frac{\Delta M}{\Delta_M \tau_D},$$

(54)

and its norm is $\sqrt{\tau_U^2 + 1/\tau_D^2 + 2c_{\text{MH}}/\tau_U \tau_D}$. Similarly, the rate of entropy change (32) takes the form

$$\frac{d\langle S \rangle}{dt} = \Delta_S \left( \frac{5}{\tau_D} \langle \tilde{S}_\rho | \hat{M}_\rho \rangle = \frac{\Delta S_{\text{FSM}}}{\tau_D} \right),$$

(55)

which, because $|r_{\text{FSM}}| \leq 1$, implies the bounds [equivalent to (50) and (51)],

$$-\Delta_S \frac{1}{\tau_D} \leq \frac{d\langle S \rangle}{dt} \leq \Delta_S \frac{1}{\tau_D}. $$

(56)

V. OCCUPATION PROBABILITIES

An important class of observables for a quantum system are those associated with the projection operators. For example, for pure states evolving unitarily [27], the mean value $\langle P \rangle = \text{Tr}(\rho(t)P)$ where $P = |\phi_0 \rangle \langle \phi_0 | = \rho(0)$ represents the survival probability of the initial state, and is related to several notions of lifetimes [27].

We do not restrict our attention to pure states, and we discuss first results that hold for any projector $P$ associated with a yes/no type of measurement. Let $P = P_1 = P_2$ be an orthogonal projector onto the $g$-dimensional subspace $PH$ of $H$. Clearly, $g = \text{Tr}(P)$, the
variance $\langle \Delta P \Delta P \rangle = p(1-p)$ where $p = \langle P \rangle = \text{Tr}(\rho P)$ denotes the mean value and represents the probability in state $\rho$ of obtaining a ‘yes’ result upon measuring the associated observable, and the characteristic time of the rate of change of this occupation probability is defined according to [4] by

$$\frac{1}{\tau_p} = \frac{|d\rho/dt|}{\sqrt{\rho(1-\rho)}} = 2 \left| \frac{d}{dt} \arccos(\sqrt{\rho}) \right| = 2 \left| \frac{d}{dt} \arcsin(\sqrt{\rho}) \right| \leq \frac{1}{\tau_{UD}},$$

where the inequality follows from [40]. Therefore,

$$\frac{1}{2\tau_{UD}} \leq \frac{d}{dt} \arccos(\sqrt{\rho}) \leq \frac{1}{2\tau_{UD}}, \quad (57)$$

or, over any finite time interval of any time history $p(t)$,

$$\left| \arcsin(\sqrt{p(t_2)}) - \arcsin(\sqrt{p(t_1)}) \right| \leq \left| \int_{t_1}^{t_2} \frac{dt'}{2\tau_{UD}(t')} \right|. \quad (59)$$

This result generalizes the results on lifetimes obtained in [26] where the focus is restricted to full quantum decay $|p(\infty) \approx 0|$ of an initially fully populated state $|p(0) \approx 1|$ and $\tau_U$ (here $\tau_{UD}$) is assumed constant during the time interval. It is also directly related to some of the results in [27], where a number of additional inequalities and bounds on lifetimes are obtained for unitary dynamics, and may be straightforwardly generalized to the class of simultaneous unitary/dissipative dynamics described by our Eq. 2.

Because $p(1-p)$ attains its maximum value when $p = 1/2$, we also have the inequality

$$\left| \frac{dp}{dt} \right| \leq \frac{1}{2\tau_{UD}} \quad (60)$$

which, analogously to what noted in [26], implies that no full decay or full population can occur within a time $2\tau_{UD}$, so that this time may be interpreted as a limit to the degree of instability of a quantum state.

Next, we focus on the projectors onto the eigenspaces of the Hamiltonian operator $H$, assumed time-independent. Let us write its spectral expansion as $H = \sum_n e_n P_n$ where $e_n$ is the $n$-th eigenvalue and $P_n$ the projector onto the corresponding eigenspace. Clearly, $H P_n = e_n P_n$, $P_n P_m = \delta_{nm} P_n, g_n = \text{Tr}(P_n)$ is the degeneracy of eigenvalue $e_n$, $p_n = \langle P_n \rangle = \text{Tr}(\rho P_n)$ the occupation probability of energy level $e_n$, $\langle \Delta P_n \Delta P_n \rangle = p_n (\delta_{nm} - p_m)$ the covariance of pairs of occupations, and $\langle \Delta P_n \Delta P_n \rangle = p_n (1 - p_n)$ the variance or fluctuation of the $n$-th occupation. Because $[P_m, H] = 0$, $e_n H = 0$, by [48] we have

$$\frac{dp_n}{dt} = \Delta p_n \frac{r_{PM}}{\tau_D}, \quad (61)$$

and the corresponding characteristic time is

$$\frac{1}{\tau_{p_n}} = \frac{|r_{PM}|}{\tau_D} \leq \frac{1}{\tau_D}. \quad (62)$$

Energy level occupation probabilities $p_n$ are used in Section [41] for numerical illustration/validation of inequalities [42] within the steepest entropy ascent dynamical model outlined in the next Section.

### VI. EXAMPLE.

#### STEEPEST-ENTROPY-ASCENT, CONSERVATIVE DISSIPATIVE DYNAMICS

So far we have not assumed an explicit form of $\Delta M(\rho)$ except for condition [5] that maintains $\rho$ unit trace. In this section, we illustrate the above results by further assuming steepest-entropy-ascent, conservative dissipative dynamics as obtained by assuming for our generalized nonequilibrium Massieu operator function the expression

$$\Delta M(\rho) = \Delta S - \Delta H'(\rho)/\theta(\rho), \quad (63)$$

where $S$ is the entropy operator defined in [43].

$$\Delta H'(\rho) = \Delta H - \mu(\rho) \cdot \Delta N, \quad (64)$$

$H$ is the Hamiltonian, $N = \{N_1, \ldots, N_r\}$ a (possibly empty) set of operators commuting with $H$, that we call non-Hamiltonian generators of the motion (for example, the number-of-particles operators or a subset of them, or the momentum component operators for a free particle), such that operators $\sqrt{\theta(\Delta H)}$ and $\sqrt{\theta(\Delta N)}$ are linearly independent, $\theta(\rho)$ and $\mu(\rho) = \{\mu_1(\rho), \ldots, \mu_r(\rho)\}$ a set of real functionals defined for each $\rho$ by the solution of the following system of linear equations

$$\langle \Delta S \Delta H \rangle \theta + \sum_{i=1}^{r} \langle \Delta N_i \Delta H \rangle \mu_i = \langle \Delta H \Delta H \rangle, \quad (65)$$

$$\langle \Delta S \Delta N_j \rangle \theta + \sum_{i=1}^{r} \langle \Delta N_i \Delta N_j \rangle \mu_i = \langle \Delta H \Delta N_j \rangle, \quad (66)$$

which warrant the conditions that $\langle \Delta H \Delta M \rangle = 0$ and $\langle \Delta N_i \Delta M \rangle = 0$, and hence that the mean values $\text{Tr}(\rho H)$ and $\text{Tr}(\rho N)$ are maintained time invariant by the dissipative term of the equation of the motion.

Operators $\sqrt{\theta(\Delta H)}$ and $\sqrt{\theta(\Delta N)}$ are always orthogonal, in the sense that $\langle \Delta M \Delta H' \rangle = 0$ for every $\rho$. It follows that, in general, $\langle \Delta S \Delta H' \rangle = \langle \Delta H' \Delta H' \rangle/\theta$, 

$$\langle \Delta S \Delta M \rangle = \langle \Delta M \Delta M \rangle = \langle \Delta S \Delta S \rangle - \frac{\langle \Delta H' \Delta H' \rangle}{\theta^2(\rho)} \geq 0 \quad (67)$$

and hence the rate of entropy generation [92] is always strictly positive except for $\langle \Delta M \Delta M \rangle = 0$ (which occurs iff $\sqrt{\theta(\Delta M)} = 0$), i.e., for $\rho_{nd} = \rho_{nd} \text{Tr}(\rho)\Delta S_{nd} = (\sqrt{\rho_{nd} \Delta H - \mu_{nd} \cdot \sqrt{\rho_{nd} \Delta N}})/\theta_{nd}$, for some real scalars $\theta_{nd}$ and $\mu_{nd}$, that is, for density operators (that we call non-dissipative) of the form

$$\rho_{nd} = B \exp[-(H - \mu_{nd} \cdot N)/k_B \theta_{nd}] B \quad \text{Tr}B \exp[-(H - \mu_{nd} \cdot N)/k_B \theta_{nd}], \quad (68)$$
where $B$ is any projection operator on $\mathcal{H} \ (B^2 = B)$.

The nonlinear functional
\[
\theta(\rho) = \frac{\sigma_{HH'} - \Delta_H}{\sigma_{SH'}} = \frac{\Delta_{H'}}{\Delta_S \tau_{SH'}}
\] (69)

may be interpreted in this framework as a natural generalization to nonequilibrium of the temperature, at least insofar as for $t \to +\infty$, while the state operator $\rho(t)$ approaches a non-dissipative operator of form $\rho_{eq}$, $\theta(t)$ approaches smoothly the corresponding thermodynamic equilibrium (or partial equilibrium) temperature $\theta_{eq}$.

Because here $H$ always commutes with $M$, $\sigma_{MH} = 0$ and $(M|H) = 0$, which means that $\sqrt{\rho} \Delta M(\rho)$ is always orthogonal to $i \sqrt{\rho} \Delta H$. This reflects the fact that on the entropy surface the direction of steepest entropy ascent is orthogonal to the (constant entropy) orbits that characterize purely Hamiltonian (unitary) motion (in which the entropy is maintained constant by keeping invariant each eigenvalue of $\rho$).

Inequality (67), which follows from $r_{SM}^2 \leq 1$, implies that $\sigma_{SM} \leq \sigma_{SS}$ and $0 \leq r_{SM} = \Delta_M / \Delta_S \leq 1$ or, equivalently,
\[
\tau_K = k_B \tau / \Delta_S \leq \tau_D ,
\] (70)

where for convenience we define the characteristic time $\tau_K$, which is simply related to the entropy spread, but cannot be attained by any rate of change, being shorter than $\tau_D$. In addition, we have the identities
\[
r_{SM}^2 \sigma_{MM} / \sigma_{SS} = \frac{r_M^2}{r_D} = \frac{\tau_K}{\tau_D} \leq 1 - \frac{\sigma_{HH'}}{\theta^2 \sigma_{SS}} = 1 - r_{SM}^2 ,
\] (71)

and, from $r_{SH'}^2 \leq 1$, the bounds
\[
|\theta| \geq \frac{\Delta_{H'}}{\Delta_S} \quad \text{or} \quad -\frac{\Delta_S}{\Delta_{H'}} \leq \frac{1}{\theta} \leq \frac{\Delta_S}{\Delta_{H'}} ,
\] (72)

where the equality $|\theta| = \Delta_{H'}/\Delta_S$ holds when and only when the state is non-dissipative [Eq. (68)]. Additional bounds on our generalized nonequilibrium temperature $\theta$ obtain by combining (71) with the inequality $4r_{SM}^2 (1 - r_{SH'}^2) \leq 1$ (which clearly holds because $r_{SM}^2 \leq 1$), to obtain $4r_{SM}^2 r_{SH'}^2 \leq 1$ and, therefore,
\[
\frac{2 \Delta_M \Delta_{H'}}{|\theta | \sigma_{SS}} \leq 1 \quad \text{or} \quad -\frac{\sigma_{SS}}{2 \Delta_M \Delta_{H'}} \leq \frac{1}{\theta} \leq \frac{\sigma_{SS}}{2 \Delta_M \Delta_{H'}} .
\] (73)

At equilibrium, $\Delta_M = 0$ and (73) implies no actual bound on $\theta$, but in nonequilibrium states bounds (73) may be tighter than (72) as illustrated by the numerical example in Section 11.

Notice that whereas in steepest entropy ascent dynamics $\tau_K$ is always shorter than $\tau_D$ and obeys the identity
\[
\tau_S \tau_K = \tau_D^2 ,
\] (74)

in general it is not necessarily shorter than $\tau_D$ and obeys the identity
\[
\frac{\Delta_M}{\Delta_S} \frac{\tau_D^2}{\tau_S \tau_K} = |r_{SM}| ,
\] (75)

In summary, we conclude that within steepest-entropy-ascent, conservative dissipative quantum dynamics, the general uncertainty relations (67), (68), and (69) that constitute the main results of this paper, yield the time-energy/time-Massieu uncertainty relation
\[
\left( \frac{\tau_F \Delta_H}{\hbar / 2} \right)^2 + \left( \frac{\tau_F \Delta_M}{k_B \tau}(\rho) \right)^2 \geq 1 \quad \text{or} \quad \frac{\tau_F^2}{\tau_U} + \frac{\tau_F^2}{\tau_D} \geq 1 ,
\] (76)

which implies the interesting time-energy/time-entropy uncertainty relation
\[
\left( \frac{\tau_F \Delta_H}{\hbar / 2} \right)^2 + \left( \frac{\tau_F \Delta_S}{k_B \tau}(\rho) \right)^2 \geq 1 \quad \text{or} \quad \frac{\tau_F^2}{\tau_U} + \frac{\tau_F^2}{\tau_K} \geq 1 ,
\] (77)

and the time-entropy uncertainty relation
\[
\frac{\tau_K}{\tau_S} \frac{k_B \tau}{\tau_S \Delta_S} = \frac{r_{SM}}{r_{SM}} \leq r_{SM} \leq 1 ,
\] (78)

which implies that the rate of entropy generation never exceeds $\sigma_{SS}/k_B \tau$, i.e.,
\[
\frac{d(S)}{dt} = -k_B \frac{d}{dt} \operatorname{Tr}(\rho \ln \rho) = \frac{\sigma_{MM}}{k_B \tau} \leq \frac{\Delta_S \Delta_M}{k_B \tau} \leq \frac{\sigma_{SS}}{k_B \tau} .
\] (79)

If in addition the dynamics is purely dissipative, such as along a trajectory $\rho(t)$ that commutes with $H$ for every $t$, then (77) may be replaced by the time-entropy uncertainty relation
\[
\frac{\tau_K}{\tau_F} = \frac{k_B \tau}{\tau_F \Delta_S} \leq 1 .
\] (80)

As shown in Refs. [7], the dissipative dynamics generated by Eq. (2) with $\Delta M(\rho)$ as just defined and a time-independent Hamiltonian $H$: (i) maintains $\rho(t) \geq \rho^2(t)$ at all times, both forward and backward in time for any initial density operator $\rho(0)$ (see also [12]); (ii) maintains the cardinality of $\rho(t)$ invariant; (iii) entails that the entropy functional is an $S$-function in the sense defined in [12] and therefore that maximal entropy density operators obtained from (68) with $B = 1$ are the only equilibrium states of the dynamics that are stable with respect to perturbations that do not alter the mean values of the energy and the other time invariants (if any): this theorem of the dynamics coincides with a well-known general statement of the second law of thermodynamics [14]; (iv) entails Onsager reciprocity in the sense defined in [15]; (v) can be derived from a variational principle [12], equivalent to our steepest entropy ascent geometrical construction [16], by maximizing the entropy generation rate subject to the $\operatorname{Tr}(\rho)$, $\operatorname{Tr}(\rho H)$, and $\operatorname{Tr}(\rho N)$ conservation constraints and the additional constraint $(\sqrt{\rho E}, \sqrt{\rho E}) = c(\rho)$ [16].

We finally note that assuming in Eq. (2), in addition to $\Delta M(\rho)$ given by (68), the nonlinear relaxation time $\tau(\rho)$ given by (20) with strict equality, we obtain the most dissipative (maximal entropy generation rate [17]) dynamics
in which the entropic characteristic time \( \tau_S \) [Eq. (B6)] is always compatible with the time-energy uncertainty relation \( \tau \Delta H \geq \hbar /2 \) and the rate of entropy generation is always given by \( 2\Delta M \Delta H /\hbar \).

The physical meaning of relations \( 22 \), \( 23 \), \( 24 \), \( 25 \), \( 75 \), \( 77 \) are worth further investigations and experimental validation in specific contexts in which the dissipative behavior is correctly modeled by a dynamical law of form \( 4 \), possibly with \( \Delta M(\rho) \) of form \( 63 \). One such context may be the currently debated so-called “fluctuation theorems” \( 18 \) whereby fluctuations and, hence, uncertainties are measured on a microscopic system (optically trapped colloidal particle \( 10 \), electrical resistor \( 20 \)) driven at steady state (off thermodynamic equilibrium) by means of a work interaction, while a heat interaction (with a bath) removes the entropy being generated by irreversibility. Another such context may be that of pion-nucleon scattering, where available experimental data have recently allowed partial validation \( 21 \) of “entropic” uncertainty relations \( 22 \). Yet another is within the model we propose in Ref. \( 23 \) for the description of the irreversible time evolution of a perturbed, isolated, physical system during relaxation toward thermodynamic equilibrium by spontaneous internal rearrangement of the occupation probabilities. We pursue this example in the next section.

VII. NUMERICAL RESULTS FOR RELAXATION WITHIN A DILUTE BOLTZMANN GAS OF \( N \)-LEVEL PARTICLES

To illustrate the time dependence of the uncertainty relations derived in this paper, we consider an isolated, closed system composed of noninteracting identical particles with single-particle eigenstates with energies \( e_i \) for \( i = 1, 2, \ldots, N \), where \( N \) is assumed finite for simplicity and the \( e_i \)'s are repeated in case of degeneracy, and we restrict our attention to the class of dilute-Boltzmann-gas states in which the particles are independently distributed among the \( N \) (possibly degenerate) one-particle energy eigenstates. This model is introduced in Ref. \( 24 \), where we assume an equation of form \( 2 \) with \( \Delta M(\rho) \) given by \( 63 \) with the further simplification that \( \Delta H'(\rho) = \Delta H \) so that our generalized nonequilibrium Massieu-function operator is

\[
M(\rho) = S - H/\theta(\rho) ,
\]

and, therefore,

\[
\Delta M(\rho) = \Delta S - \Delta H/\theta(\rho) .
\]

For simplicity and illustrative purposes, we focus on purely dissipative dynamics by considering a particular trajectory \( \rho(t) \) that commutes with \( H \) at all times \( t \), assuming that \( H \) is time independent and has a nondegenerate spectrum. As a result, the energy-level occupation probabilities \( p_n \) coincide with the eigenvalues of \( \rho \), and the dynamical equation reduces to the simple form \( 23 \)

\[
\frac{dp_n}{dt} = -\frac{1}{\tau} \left[ p_n \ln p_n + p_n \left( S \right)_{k_B} + p_n \frac{\sigma_{n\sigma} - \langle H \rangle}{k_B \theta} \right] , \quad (83)
\]

where

\[
\left( S \right) = -k_B \sum_n p_n \ln p_n , \quad (84)
\]

\[
\left( H \right) = \sum_n p_n \epsilon_n , \quad (85)
\]

\[
\sigma_{HH} = \sum_n p_n \epsilon_n^2 - \left( H \right)^2 , \quad (87)
\]

\[
\sigma_{HS} = -k_B \sum_n p_n \epsilon_n \ln p_n - \left( H \right) \left( S \right) . \quad (88)
\]

To obtain the plots in Figures 1-4, that illustrate the main inequalities derived in this paper for a sample trajectory, we consider an initial state with cardinality equal to 4, with nonzero occupation probabilities only for the four energy levels \( e_1 = 0, e_2 = u/3, e_3 = u/3, \) and \( e_4 = u \), and with mean energy \( \langle H \rangle = 2u/5 \) (\( u \) is arbitrary, with units of energy). Moreover, as done in \( 22 \), we select an initial state \( \rho(0) \) at time \( t = 0 \) such that the resulting trajectory \( \rho(t) \) passes in the neighborhood of the partially canonical nondissipative state \( \rho_{nd}^\theta \) that has nonzero occupation probabilities only for the four energy levels \( e_1, e_2, \) and \( e_4, \) and mean energy \( \langle H \rangle = 2u/5 \) (\( \rho_{nd1}^\theta = 0.3725, \rho_{nd2}^\theta = 0.3412, \rho_{nd3}^\theta = 0, \rho_{nd4}^\theta = 0.2863, \theta_{nd}^\theta = 3.796 \)) as shown in Figure 1, during the first part of the trajectory, this nondissipative state appears as an attractor, an approximate or ‘false target’ equilibrium state; when the trajectory gets close to this state, the evolution slows down, the entropy generation drops almost to zero and the value of \( \theta \) gets very close \( 3.767 \) to that of \( \theta_{nd}^\theta \); however eventually the small, but nonzero initial occupation of level \( e_3 \) builds up and a new rapid rearrangement of the occupation probabilities takes place, and finally drives the system toward the maximal entropy state \( \rho_{nd}^\theta \) with energy \( \langle H \rangle = 2u/5 \) and all four active levels occupied, with partially canonical distribution \( p_{nd}^{\sigma e} \) characterized according to \( 63 \) by the (partial equilibrium) temperature \( \theta_{nd}^{\sigma e} = 1.366 \) (\( k_B \)).

The trajectory is computed by integrating Eq. \( 68 \) numerically, both forward and backward in time, starting from the chosen initial state \( \rho(0) \), and assuming for Figures 1 and 2 that the dissipation time \( \tau \) is a constant, and for Figures 3 and 4 that it is given by \( 20 \) with strict equality (\( \alpha_{r} = 1, \tau_{p} = \tau_{n} \)), i.e., assuming

\[
\tau = \frac{\hbar/2}{k_B \Delta H} = \frac{\hbar/2}{k_B} \sqrt{\frac{\sigma_{SS}}{\sigma_{HH}}} - \frac{1}{\theta^2} , \quad (89)
\]

\[
\sigma_{SS} = k_B^2 \sum_n p_n (\ln p_n)^2 - \left( S \right)^2 . \quad (90)
\]

The system of ordinary differential equations \( 83 \) is highly nonlinear, especially when \( \tau \) is assumed according to \( 88 \), nevertheless it is sufficiently well behaved to
allow simple integration by means of a standard Runge-Kutta numerical scheme. Of course, we check that at all times \(-\infty < t < \infty\) each \(p_n\) remains nonnegative, \(\sum_n p_n\) remains equal to unity, \(\sum_n p_n c_n\) remains constant at the value \(2n/5\) fixed by the selected initial state, and the rate of change of \(\langle S \rangle\) is always nonnegative.

In each Figure, the top subfigure shows for ease of comparison the plots of the four nonzero occupation probabilities as functions of dimensionless time: \(t/\tau\), in Figures 1 and 2; \(u/t, h\), in Figures 3 and 4. The dots on the right represent the maximal entropy distribution, \(p_n(+\infty) = \rho^{\text{nd}}_n\); the dots at the left represent the lowest-entropy or ‘primordial’ distribution, \(p_n(-\infty) = \rho^{\text{ls}}_n\), which for the particular trajectory selected here, corresponds to a nondissipative state \(\rho^{\text{nd}}_n\) that has only two occupied energy levels, \(e_1\) and \(e_4\), with probabilities \(\rho^{\text{ls}}_{\text{nd}1} = 0.6\) and \(\rho^{\text{ls}}_{\text{nd}4} = 0.4\) (and temperature \(\rho^{\text{ls}}_3 = 2.466u/k_b\); in fact the system has no lower entropy states \(\rho\) that commute with \(H\), have energy \(2u/5\), and have zero occupation probabilities \(p_n\) for every \(n > 4\) [22]. The dots in the middle represent the nondissipative state \(\rho^{\text{nd}}_n\) which appears as the false target state during the first part of the trajectory, plotted at the instant in time when the entropy of the time-varying trajectory is equal to the entropy of this distribution.

It is interesting to observe from Figures 1 (bottom subfigure), and Figure 2 (second subfigure) that during the early part of the trajectory, \(\tau_D\) almost exactly coincides with \(\tau_E\), while in the later part it almost exactly coincides with \(\tau_F\), and the switch occurs when the trajectory slows down in the neighborhood of the ‘false target’ nondissipative state.

In Figure 1, the second subfigure shows the time dependence of the dimensionless entropy \(\langle S \rangle/k_b\); the third subfigure shows its rate of change (proportional to \(\sigma_{\text{IM}}\)) and compares it with \(\sigma_{\text{SS}}\) and \(\sigma_{\text{HFI}}/\theta^2\), to illustrate relation (67); the fourth shows the time dependence of our generalized ‘nonequilibrium temperature’ \(\theta\) (properly nondimensionalized) and compares it with \(\Delta H/\Delta S\) and \(2\Delta_M\Delta\mu/\sigma_{\text{SS}}\) to illustrate relations (72) and (73); the fifth subfigure shows the time dependence of \(1/\tau_D\) (which here is proportional to the square root of the rate of entropy generation, third subfigure) and compares it with \(1/\tau_K\) and \(1/\tau_S\) to illustrate relations (70) and (71); the sixth subfigure shows \(1/\tau_p\) for each of the four occupation probabilities and compares them with \(1/\tau_D\) to illustrate relation (62), which for this particular trajectory has the feature we just discussed.

In Figure 2, the second subfigure illustrates again relation (62) for each of the four observables \(p_n = \langle P_n \rangle\); the third subfigure illustrates the time-entropy uncertainty relation (64) for the same observables; the fourth illustrates inequality (66); the fifth illustrates relations (61) and (65).

Similar remarks hold for Figures 3 and 4, where it is noteworthy that most qualitative features remain the same, except for the almost singular behavior near canonically distributed nondissipative states, where \(\Delta_M\) approaches zero and so does the dissipative time \(\tau\) assumed in this case according to (39). The approach to (partial) equilibrium in this case is not exponential in time as for \(\tau = \text{const}\). This puzzling behavior suggests that assumption (39) may hardly be physically sensible. However, as already noted after (24), it represents an extreme behavior, i.e., the minimum dissipative time functional \(\tau(\rho)\) by which observables which commute with \(H\), like the occupations \(P_n\), never violate the usual time-energy uncertainty relations \(\tau(\rho)\Delta H \geq \hbar/2\), even though their time dependence is not determined here by unitary dynamics but by purely dissipative dynamics. These usual time-energy uncertainty relations, \(\tau(\rho) \geq \tau_U\), are illustrated by the second subfigure of Fig. 4, because in this case \(\tau_U = \tau_D\).

VIII. CONCLUSIONS

The Mandelstam-Tamm-Messiah time-energy uncertainty relation \(\tau_F\Delta H \geq \hbar/2\) provides a general lower bound to the characteristic times of change of all observables of a quantum system that can be expressed as linear functionals of the density operator \(\rho\). This has been used to obtain estimates of rates of change and lifetimes of unstable states, without solving explicitly the time dependent evolution equation of the system. It may also be used as a general consistency check in measurements of time dependent phenomena. In this respect, the exact relation and inequalities [23] (that we derive for standard unitary dynamics based on the generalized Schrödinger inequality [13]) provide a more general and sharper chain of consistency checks than the usual time-energy uncertainty relation.

The growing interest during the last several decades in quantum dynamical models of systems undergoing irreversible processes has been motivated by impressive technological advances in the manipulation of smaller and smaller systems, from the micrometer scale to the nanometer scale, and down to the single atom scale. The laws of thermodynamics, that fifty years ago were invariably understood as pertaining only to macroscopic phenomena, have gradually earned more attention and a central role in studies of mesoscopic phenomena first, and of microscopic phenomena more recently. In this paper we do not address the controversial issues currently under discussion about interpretational matters, nor do we attempt a reconstruction and review of the different views, detailed models and pioneering contributions that propelled this fascinating advance of thermodynamics towards the realm of few particle and single particle systems.

However, motivated by this context and background, we derive extensions of the usual time-energy uncertainty relations that extend their usefulness to studies of dissipative phenomena. We do this by focusing on a special but broad class of model evolution equations, that has been designed for the description of dissipative quantum
phenomena and for satisfying a set of compatibility conditions with general thermodynamic principles, and we derive in this framework various forms of time-energy and time-entropy uncertainty relations, and other interesting general inequalities, that should turn out to be useful as additional consistency check in measurements of time-dependent dissipative phenomena. Finally, we illustrate and discuss some of these relations with numerical results obtained by integration of the nonlinear evolution equation introduced by this author for the description of steepest entropy ascent dynamics of an isolated system far from thermodynamic equilibrium.

APPENDIX A: REASONS FOR NOT ASSUMING A KOSSAKOWSKI-LINDBLAD FORM OF THE EVOLUTION EQUATION

With various motivations, fundamental or phenomenological, a number of different generalizations of quantum dynamics have been proposed in which the evolution equation for the density operator \( \rho \) does not conserve the functional \(- \text{Tr} (\rho \ln \rho)\). In particular, in theories of systems in contact with a heat bath, or subsystems of composite systems which as a whole evolve unitarily, a variety of successful model evolution equations for the reduced density operator have the Kossakowski-Lindblad [28] form

\[
\frac{d\rho}{dt} = - i [H, \rho] + \frac{1}{2} \sum_j \left( 2V_j^\dagger \rho V_j - \{ V_j^\dagger V_j, \rho \} \right), \tag{A1}
\]

where the \( V_j \)'s are operators on \( \mathcal{H} \) (each term within the summation, often written in the alternative form \( \{ V_j, \rho V_j^\dagger \} + [V_j \rho, V_j^\dagger] \), is obviously traceless). Evolution equations of this form are linear in the density operator \( \rho \) and preserve its hermiticity, nonnegativity and trace [25].

For example, in a number of successful models of dissipative quantum dynamics of open subsystems, operators \( V_j \) are in general interpreted as creation and annihilation, or transition operators. For example, by choosing \( V_j = c_{rs} | r \rangle \langle s | \), where \( c_{rs} \) are complex scalars and \( | s \rangle \) eigenvectors of the Hamiltonian operator \( H \), and defining the transition probabilities \( w_{rs} = c_{rs}^* c_{tr} \), equation (A1) becomes

\[
\frac{d\rho}{dt} = - i [H, \rho] + \sum_{rs} w_{rs} \left( | r \rangle \langle s | \rho \rangle \langle s | - \frac{1}{2} | s \rangle \langle s | r \rangle \langle r | \rho \langle s | \langle s | \rho \rangle \right), \tag{A2}
\]

or, equivalently, for the \( nm \)-th matrix element of \( \rho \) in the \( H \) representation,

\[
\frac{d\rho_{nm}}{dt} = - i \frac{\hbar}{\rho_{nm} (E_n - E_m)} + \delta_{nm} \sum_r w_{nr} \rho_{rr} - \rho_{nm} \frac{1}{2} \sum_r (w_{rn} + w_{rm}) \tag{A3}
\]

which, for the occupation probabilities \( p_n = \rho_{nn} \), is the Pauli master equation

\[
\frac{dp_n}{dt} = \sum_r w_{nr} p_r - p_n \sum_r w_{rn}. \tag{A4}
\]

In this paper, we consider a class of model evolution equations applicable not only to open systems but also to closed isolated systems, capable of describing, simultaneously with the usual Hamiltonian unitary evolution, the natural tendency of any initial nonequilibrium state to relax towards canonical or partially-canonical thermodynamic equilibrium, i.e., capable of describing the irreversible tendency to evolve towards the highest entropy state compatible with the instantaneous mean values of the energy, the other constants of the motion, and possibly other constraints. To avoid the severe restrictions imposed by the linearity of the evolution equation, we open our attention to evolution equations nonlinear in the density operator \( \rho \). Therefore, it may at first appear natural to maintain the Kossakowski-Lindblad form (A1) and simply assume that operators \( V_j \) are functions of \( \rho \). This is true only in part for the evolution equation [2] that we assume. Indeed, our hermitian operator \( \Delta M(\rho)/k_B \tau(\rho) \) can always be written as \(- \sum V_j^\dagger \rho V_j \rho \) and therefore our anticommutator term may be viewed as a generalization of the corresponding term in (A1).

However, in our equations (1) and (2) we suppress the term corresponding to \( \sum_j V_j^\dagger \rho V_j \) in (A1). The reason for this suppression is the following. Due to the terms \( V_j^\dagger \rho V_j \), whenever the state operator \( \rho \) is singular, i.e., it has one or more zero eigenvalues, Eq. (A1) implies that these zero eigenvalues may change at a finite rate. This can be seen clearly from (A1) by which \( dp_n/dt \) is finite whenever there is a nonzero transition probability \( w_{nr} \) from some other populated level \( \rho_r \neq 0 \), regardless of whether \( p_n \) is zero or not. When this occurs, for one instant in time the rate of entropy change is infinite, as seen clearly from the expression of the rate of entropy change [4].

\[
\frac{d(S)}{dt} = k_B \sum_j \text{Tr}(V_j^\dagger V_j \rho \ln \rho - V_j^\dagger V_j \ln \rho)
\]

\[
= k_B \sum_{j \neq n} (V_j^\dagger V_j)_{nr} \rho_r - \rho_n \ln \rho_r, \tag{A5}
\]

where \( \rho_r \) denotes the \( r \)-th eigenvalue of \( \rho \) and \( (V_j^\dagger V_j)_{nr} \) the matrix elements of \( V_j \) in the \( \rho \) representation.

We may argue that an infinite rate of entropy change can be tolerated, because it would last only for one instant in time. But the fact that zero eigenvalues of \( \rho \) in general could not survive, i.e., would not remain zero (or close to zero) for longer than one instant in time, is an unphysical feature, at least because it is in contrast with a wealth of successful models of physical systems in which great simplification is achieved by limiting our attention to a restricted subset of relevant eigenstates (forming a subspace of \( \mathcal{H} \) that we call the effective Hilbert
space of the system \( \rho \). Such common practice models yield extremely good results, that being reproducible, ought to be relatively robust with respect to including in the model other less relevant eigenstates. In fact, such added eigenstates, when initially unpopulated, are irrelevant if they remain unpopulated (or very little populated) for long times, so that neglecting their existence introduces very little error. The terms \( V_j^+ \rho V_j \), instead, would rapidly populate such irrelevant unpopulated eigenstates and void the validity of our so successful simple models, unless we deliberately overlook this instability problem by highly ad-hoc assumption, e.g., by forcing the \( V_j \)'s to be such that \( (V_j)_{nr} = 0 \) whenever either \( \rho_n = 0 \) or \( \rho_r = 0 \), in which case, however, we can no longer claim true linearity with respect to \( \rho \).

To avoid the unnatural implications of this seldom recognized problem of linear evolution equations of form (A1), we consider in this paper only equations of form (2). We do not exclude that it may be interesting to investigate also the behavior of equations that include nonlinear terms of the form \( V_j^+ \rho V_j \). However, at least when the system is strictly isolated, the operator-functions \( V_j(\rho) \) should be such that \( (V_j(\rho))_{nr} = 0 \) whenever either \( \rho_n = 0 \) or \( \rho_r = 0 \).

Another important general physical reason why we exclude terms that generate nonzero rates of change of zero eigenvalues of \( \rho \), is that if such terms are construed so as to conserve positivity in forward time, in general they cannot maintain positivity in backward time. The view implicitly assumed when Eq. (A1) is adopted, is that the model is “mathematically irreversible” (a distinguishing feature if not a starting point of the theory of completely positive linear dynamical semigroups on which it is based), in the sense that neither uniqueness of solutions in forward time nor existence in backward time are required (and granted). Such mathematical irreversibility of the initial value problem, is often accepted, presented and justified as a natural counterpart of physical irreversibility. However, it is more related to the principle of causality than to physical irreversibility. The strongest form of the non-relativistic principle of causality, a cornerstone of traditional physical thought, requires that future states of a system should unfold deterministically from initial states along smooth unique trajectories in state domain defined for all times (future as well as past). Accepting mathematical irreversibility of the model dynamics, implies giving up such causality requirement. But it is not strictly necessary to describe physical irreversibility, at least not if we are willing to give up linearity instead. The proof of this statement is our Eq. (2) which, together with the additional assumptions made in Section VII to describe relaxation within an isolated system, is mathematically reversible, in the sense that it features existence and uniqueness of well-defined solutions both in forward and backward time, and yet it does describe physically irreversible time evolutions, in the sense that the physical property described by the entropy functional \( -k_B \text{Tr}(\rho \ln \rho) \) is a strictly increasing function of time for all states except the very restricted subset defined by Eq. (B8), where it is time invariant.

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(\(f, g\)) = \(\text{Tr}(f^g)\), we note that (\(f, f\)) = (\(f|f\)) and obtain the inequality (\(f|f\)(\(g|g\)) ≥ (\(f|g\))^2 and (\(g|g\)) and hence inequality (1) by setting \(f = \sqrt{\rho}F\) and \(g = \sqrt{\rho}G\). Note that the strict equality in (1) holds iff \(\sqrt{\rho}F = c\sqrt{\rho}G\) for some scalar \(c\) (in which case we have \(|F|G⟩/2i = 0\) iff either \(c^* = c\) or \(\sqrt{\rho}F = 0\) or both). For further inequalities in the case of position and momentum operators see V. V. Dodonov, J. Opt. B, bf 4, S98 (2002) and references therein.

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FIG. 1: (Color online) See text; $\tau$ assumed constant.
FIG. 2: See text; $\tau$ assumed constant.
FIG. 3: (Color online) See text; $\tau$ assumed according to (89).
FIG. 4: See text; $\tau$ assumed according to (89).