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Thermodynamic length for far-from-equilibrium quantum systems

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We consider a closed quantum system initially at thermal equilibrium and driven by arbitrary external parameters. We derive a lower bound on the entropy production which we express in terms of the Bures angle between the nonequilibrium and the corresponding equilibrium state of the system. The Bures angle is an angle between mixed quantum states and defines a thermodynamic length valid arbitrarily far from equilibrium. As an illustration, we treat the case of a time-dependent harmonic oscillator for which we obtain analytic expressions for generic driving protocols.

I. INTRODUCTION

Thermodynamics provides a generic framework to describe properties of systems at or close to equilibrium. On the other hand, for systems which are far from equilibrium; that is, beyond the linear response regime, no unified formalism has been developed so far. Recently, however, a number of cold-atom experiments have been able to investigate quantum processes which occur far from thermal equilibrium [1–4]; they underline the need for general characterizations of quantum processes that take place beyond the range of linear response theory. In thermodynamics, nonequilibrium phenomena are associated with a nonvanishing entropy production, $\langle\Sigma\rangle = \Delta S - \langle Q\rangle/T \geqslant 0$, defined as the difference between the change of entropy and the (mean) heat divided by temperature [5,6]. The positivity of the (mean) entropy production is an expression of the second law of thermodynamics and follows from the Clausius inequality. The entropy production $\langle\Sigma\rangle$ is expected to be larger the further away from equilibrium a system operates. However, it is not possible to compute $\langle\Sigma\rangle$, nor to derive a useful, process-dependent lower bound for it within equilibrium thermodynamics.

For classical systems near equilibrium, such a lower bound was obtained using a geometric approach and expressed in terms of the thermodynamic length [7–9]. The latter defines a thermodynamic Riemannian metric which measures the distinguishability of equilibrium and nonequilibrium distributions [10]. In the linear regime, the entropy production is bounded from below by the square of the thermodynamic length $\langle\Sigma\rangle \gtrsim \ell^2$. The thermodynamic length plays an important role in finite-time thermodynamics, where it provides limits on the efficiency of thermal machines [11,12]. Methods on how to measure ℓ have been discussed in Refs. [13,14]. Interestingly, the length ℓ is identical to the statistical distance introduced by Wootters to distinguish two pure quantum states [15]: the angle in Hilbert space between two wave vectors ψ_1 and ψ_2 is given by $\ell(\psi_1,\psi_2) = \arccos \int dx \sqrt{p_1(x)p_2(x)}$, with the two probability distributions $p_1(x) = |\psi_1(x)|^2$ and $p_2(x) = |\psi_2(x)|^2$. Recently, we have extended the notion of thermodynamic length to closed quantum systems driven arbitrarily far from equilibrium [16]. To this end, we have generalized the length ℓ by the Bures angle $\mathcal{L}$ [17–21] between the nonequilibrium and the corresponding equilibrium density

operators of the system. The Bures metric is a generalization of Wootters' metric to mixed quantum states and plays a major role in quantum information theory [22,23]. Using the Bures angle, we have derived a generalized Clausius inequality with a process-dependent lower bound, $\langle\Sigma\rangle \geqslant (8/\pi^2)\mathcal{L}^2$, that is valid for arbitrary nonequilibrium driving beyond the linear response. This bound, however, corresponds to the lowest-order term of a systematic series expansion as a function of the Bures length. Our aim in this paper is to extend our previous findings and derive a sharper lower bound on the entropy production $\langle\Sigma\rangle$ by evaluating the contribution of higher-order terms. We then apply this result to the case of a quantum parametric harmonic oscillator, a model for a driven trapped ion [24,25], for which we find exact analytical expressions for the angle $\mathcal{L}$ for arbitrary driving protocol. We furthermore compare these results with those obtained with the trace distance, a non-Riemannian quantum metric [22,23]. Finally, we derive an upper bound for the quantum entropy production in the appendix.

II. GEOMETRIC ANGLE BETWEEN MIXED QUANTUM STATES

The Bures angle $\mathcal{L}$ is implied by the Bures metric, which formally quantifies the infinitesimal distance between two mixed quantum states described by the density operators ρ and $\rho + d\rho$ as $\mathcal{L}^2(\rho + \delta\rho, \rho) = \mathrm{tr}\{\delta\rho G\}/2$, where the operator G obeys the equation $\rho G + G\rho = \delta\rho$ [23]. In the orthonormal basis $|i\rangle$ that diagonalizes $\rho = \sum_i p_i |i\rangle\langle i|$, an explicit expression of the Bures metric is given by $\mathcal{L}^2(\rho + \delta\rho, \rho) = (1/2) \sum_{i,j} |\langle i|d\rho|j\rangle|^2/(p_i + p_j)$. In the limit of pure quantum states, the Bures metric reduces to Wootters' statistical distance, $\ell^2(p, p + dp) = (1/4)\sum_i (dp_i)^2/p_i$ [21]. Wootters' distance is equal to the angle in Hilbert space between two state vectors, and is the only monotone Riemannian metric (up to a constant factor) which is invariant under all unitary transformations [15]. It is therefore a natural metric on the space of pure states. The Bures metric, on the other hand, being the generalization of Wootters' metric to mixed quantum states, represents a natural, unitarily invariant Riemannian metric on the space of impure density matrices [23].

For any two density operators ρ_1 and ρ_2, the finite Bures angle $\mathcal{L}$ is given by

$$\mathcal{L}(\rho_1,\rho_2) = \arccos\left(\sqrt{F(\rho_1,\rho_2)}\right), \qquad (1)$$

where the fidelity F is defined for an arbitrary pair of mixed quantum states as [19,20]

$$F(\rho_1,\rho_2) = [\mathrm{tr}\{\sqrt{\sqrt{\rho_1}\rho_2\sqrt{\rho_1}}\}]^2. \qquad (2)$$

The fidelity is a symmetric, nonnegative and unitarily invariant function, which is equal to one only if the two states ρ_1 and ρ_2 are identical. For pure quantum states, $\rho_i = |\psi_i\rangle\langle\psi_i|$, the fidelity reduces to their overlap, $F(\rho_1,\rho_2) = \mathrm{tr}\{\rho_1\rho_2\} = |\langle\psi_1|\psi_2\rangle|^2$. It is worth emphasizing that the Bures angle (1) is the natural distance quantifying the distinguishability of two density operators. We shall use this property in the following to quantify the distance between a nonequilibrium state and the equilibrium state corresponding to the same configuration of the system. With the help of this thermodynamic length, we will also obtain a lower bound on the nonequilibrium quantum entropy production.

III. THERMODYNAMIC LENGTH AND GENERALIZED CLAUSIUS INEQUALITY

We consider a quantum system whose Hamiltonian $H = H_t$ is varied during a finite time interval τ. We assume that the system is initially let to equilibrate with a thermal reservoir at inverse temperature $\beta = 1/T$, before an external control parameter is modified. We further assume that the system is quasi-isolated during the finite driving time τ so that relaxation is negligible and the dynamics is unitary to an excellent approximation. This corresponds to a realistic experimental situation. For an infinitely large driving time, much larger than the relaxation time induced by the weak coupling to the reservoir, the transformation is quasistatic and the system remains in an equilibrium state at all times. During such a slow, equilibrium transformation, the change in free energy $\Delta F = \Delta E - T\Delta S$ is equal to the average work $\langle W \rangle$ done on the quantum system, $\langle W \rangle = \Delta F$. Here $\Delta E = \langle H_\tau \rangle - \langle H_0 \rangle$ is the (internal) energy difference. For a fast, nonequilibrium transformation, work is larger than the free energy difference. Using the first law, $\Delta E = \langle W \rangle + \langle Q \rangle$, we can rewrite the nonequilibrium entropy production $\langle \Sigma \rangle = \Delta S - \langle Q \rangle/T$ as

$$\langle \Sigma \rangle = \beta(\langle W \rangle - \Delta F). \qquad (3)$$

The nonequilibrium entropy production $\langle \Sigma \rangle$ is thus proportional to the difference between the nonequilibrium and the equilibrium work done on the system. Equation (3) is valid for both open and closed dynamics for which $\langle Q \rangle = 0$. Being a mechanical quantity, it is worth noticing that work is always defined, even for far-from-equilibrium processes.

Let us denote the density operator of the system at time t by $\rho_t = U_t\rho_0 U_t^\dagger$, where U_t is the unitary evolution operator. The initial equilibrium density operator is then $\rho_0 = \exp(-\beta H_0)/Z_0$, where $Z_0 = \mathrm{tr}\{\exp(-\beta H_0)\}$ is the initial partition function. The equilibrium density operator at the final time τ is similarly given by $\rho_\tau^{\mathrm{eq}} = \exp(-\beta H_\tau)/Z_\tau$ with Z_τ being the corresponding partition function. To obtain a microscopic expression for the entropy production, we

use $\Delta E = \mathrm{tr}\{\rho_\tau H_\tau\} - \mathrm{tr}\{\rho_0 H_0\}$ and note that $-\beta H_{0,\tau} = \ln\rho_{0,\tau} + \ln Z_{0,\tau}$. Combined with the expression $-\beta\Delta F = -\ln(Z_\tau/Z_0)$ for the free-energy difference, we find

$$\langle \Sigma \rangle = S(\rho_\tau||\rho_\tau^{\mathrm{eq}}) = \mathrm{tr}\{\rho_\tau \ln\rho_\tau - \rho_\tau \ln\rho_\tau^{\mathrm{eq}}\}, \qquad (4)$$

where $S(\rho_\tau||\rho_\tau^{\mathrm{eq}})$ is the quantum relative entropy [26,27]. Note that the latter is different from the entropy variation $\mathrm{tr}\{\rho_\tau \ln\rho_\tau - \rho_\tau^{\mathrm{eq}} \ln\rho_\tau^{\mathrm{eq}}\}$. Equation (4) is an exact expression for the nonequilibrium entropy production for closed quantum systems driven by an external parameter, and a quantum generalization of the classical results presented in Refs. [28,29] (see also Ref. [30]). We note, however, that the relative entropy is not a true metric, as it is not symmetric and does not satisfy the triangle inequality; it can therefore not be used as a proper quantum distance [31]. We next derive a lower bound for the quantum entropy production which we express in terms of the Bures angle (1).

Inequalities are important tools of classical and quantum information theory, as they allow us to express "impossibilities;" that is, things that cannot happen [31]. An elementary example is Klein's inequality, $S(\rho_1||\rho_2) \geqslant 0$, which expresses the nonnegativity of the quantum relative entropy [22]. Combined with Eq. (4), it immediately leads to the usual Clausius inequality. A generalized Clausius inequality can be derived by noting that the quantum relative entropy satisfies (Ref. [32], Theorem 4),

$$S(\rho_1||\rho_2) \geqslant s\left(\frac{d(\rho_1,\rho_2)}{d(e^{1,1},e^{2,2})}\right), \qquad (5)$$

if $d(\rho_1,\rho_2)$ is an unitarily invariant norm. Furthermore, $e^{i,j} = |i\rangle\langle j|$ is the matrix with i,j elements equal to 1 and all other elements 0. The lower bound (5) has been derived with the help of optimization theory and is therefore as sharp as possible. The function $s(x)$ is explicitly given by the expression [32]

$$s(x) = \min_{x<r<1}\left\{(1-r+x)\ln\left(1+\frac{x}{1-r}\right) \right.$$
$$\left. + (r-x)\ln\left(1-\frac{x}{r}\right)\right\}. \qquad (6)$$

The first five nonzero terms in a series expansion around the origin $x = 0$ read

$$s(x) = 2x^2 + \frac{4}{9}x^4 + \frac{32}{135}x^6 + \frac{992}{5103}x^8 + \frac{6656}{32805}x^{10} + O(x^{12}). \qquad (7)$$

Applying inequality (5) to the unitarily invariant Bures angle $\mathcal{L}$, we obtain a process-dependent lower bound on the nonequilibrium entropy production. Taking into account that $\mathcal{L}(e^{1,1},e^{2,2}) = \pi/2$, since the two matrices $e^{1,1}$ and $e^{2,2}$ are orthogonal [$F(e^{1,1},e^{2,2}) = 0$], we find

$$\langle \Sigma \rangle \geqslant s\left(\frac{2}{\pi}\mathcal{L}(\rho_\tau,\rho_\tau^{\mathrm{eq}})\right) \geqslant \frac{8}{\pi^2}\mathcal{L}^2(\rho_\tau,\rho_\tau^{\mathrm{eq}}). \qquad (8)$$

The first-order term in the expansion (7) yields the generalized Clausius inequality, $\langle \Sigma \rangle \geqslant (8/\pi^2)\mathcal{L}^2$, derived in Ref. [16]. Since the terms in the expansion (7) are positive, an increasingly sharper lower bound can be obtained by taking more
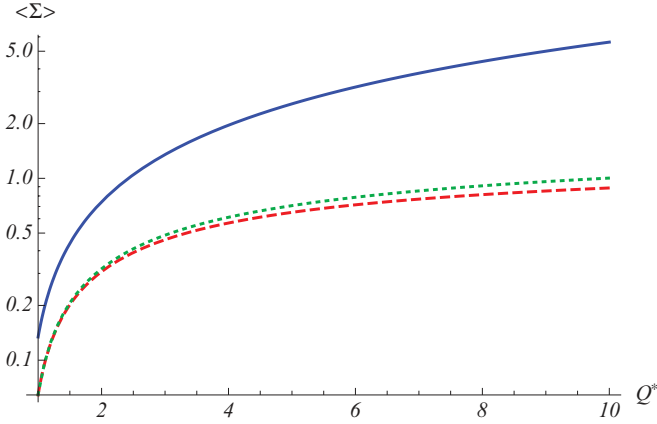
FIG. 1. (Color online) Irreversible entropy production $\langle \Sigma \rangle$ (25) (blue, solid line) together with the lower bound (8) corresponding to the lowest-order term of the expansion (7) (red, dashed line), or the exact function $s(x)$ (6) (green, dotted line), as a function of the (numerical) adiabaticy parameter Q^* (13). Parameters are $\hbar = 1$, $\beta = 1.2$, $\omega_0 = 0.9$, $\omega_1 = 0.5$.

terms into account [33]. An illustration for the case of a quantum harmonic oscillator with time-dependent frequency, to be discussed in detail in the next section, is shown in Fig. 1.

Equation (8) indicates that the nonequilibrium entropy production $\langle \Sigma \rangle$ is bounded from below by a function of the geometric distance between the actual density operator ρ_τ of the system at the end of the driving and the corresponding equilibrium operator ρ_τ^{eq}, as measured by the Bures angle. Thus the Bures angle provides a natural scale to compare with $\langle \Sigma \rangle$ and quantifies in a precise manner the notion that the entropy production is larger when a system is driven farther away from equilibrium.

In the classical limit, where nonequilibrium and equilibrium states are diagonal in the energy basis, the Bures angle reduces to Wootters' statistical distance. As a result, Eq. (8) yields a lower bound to the classical nonequilibrium entropy production that is valid for any nonequilibrium driving beyond the linear-response regime,

$$\langle \Sigma \rangle_{\mathrm{cl}} \geqslant s\left(\frac{1}{2\pi} \ell\left(p_\tau, p_\tau^{\mathrm{eq}}\right)\right) \geqslant \frac{2}{\pi^2} \ell^2\left(p_\tau, p_\tau^{\mathrm{eq}}\right). \qquad (9)$$

Moreover, when nonequilibrium and equilibrium states are infinitesimally close, Eq. (9) takes the form $\langle \Sigma \rangle_{\mathrm{cl}} \geqslant (2/\pi^2) d\ell^2$, which has been obtained in Refs. [7–9]. It is worth emphasizing that the latter was derived by expanding the entropy around equilibrium to second order; it is therefore only valid in the linear-response regime.

IV. PARAMETRIC HARMONIC OSCILLATOR

Let us now apply the generalized Clausius inequality (8) to the case of a time-dependent harmonic oscillator. The latter provides an important physical model for many quantum systems (for example, ultracold trapped ions [24,25]) and is furthermore analytically solvable. We will, in particular, evaluate the Bures angle (1) for a nontrivial quantum time evolution. Explicit expressions for $\mathcal{L}$ are in general only

known for low-dimensional systems [34–36]. The difficulty arises from the operational square roots in the definition of the quantum fidelity (2). For Gaussian states, however, the expression for the fidelity simplifies and can be written in closed form [37].

The Hamiltonian of the parametric quantum harmonic oscillator is of the usual form (M denotes the mass),

$$H_t = \frac{p^2}{2M} + \frac{M}{2}\omega_t^2 x^2. \qquad (10)$$

We assume that the time-dependent frequency ω_t starts with initial value ω_0 at $t = 0$ and ends with final value ω_1 at $t = \tau$. Due to the quadratic form of the Hamiltonian (10), the wave function of the oscillator is Gaussian for any driving protocol ω_t. By introducing the Gaussian wave-function ansatz [38],

$$\psi_t(x) = \exp\left[\frac{i}{2\hbar}(a_t x^2 + 2b_t x + c_t)\right], \qquad (11)$$

the Schrödinger equation for the quantum oscillator can be reduced to a system of three coupled differential equations for the time-dependent coefficients a_t, b_t, and c_t,

$$\frac{1}{M}d_t a_t = -\frac{a_t^2}{M^2} - \omega_t^2, \qquad (12a)$$

$$d_t b_t = -\frac{a_t}{M}b_t, \qquad (12b)$$

$$d_t c_t = i\hbar \frac{a_t}{M} - \frac{1}{M}b_t^2. \qquad (12c)$$

The nonlinear equation (12a) is of the Riccati type. It can be mapped onto the equation of motion of a classical, force free, time-dependent harmonic oscillator via the transformation $a_t = M\dot{X}_t/X_t$. The resulting equation reads $\ddot{X}_t + \omega_t^2 X_t = 0$. Equations (12b)–(12c) can be solved once the solution of Eq. (12a) has been determined. With the solutions of the three equations (12a)–(12c) known, the Gaussian wave function $\psi_t(x)$ (11) is fully characterized by the time-dependence of the angular frequency ω_t. It can be shown that the dynamics is completely determined by the function Q^* introduced by Husimi [38–40],

$$Q^* = \frac{1}{2\omega_0\omega_1}\left[\omega_0^2(\omega_1^2 X_\tau^2 + \dot{X}_\tau^2) + (\omega_1^2 Y_\tau^2 + \dot{Y}_\tau^2)\right], \qquad (13)$$

where X_t and Y_t are the solutions of the force-free classical oscillator equation satisfying the boundary conditions $X_0 = 0$, $\dot{X}_0 = 1$ and $Y_0 = 1$, $\dot{Y}_0 = 0$. The function $Q^* \geqslant 1$ is a measure of the adiabaticy of the process: it is equal to one for adiabatic transformations and increases with the degree of nonadiabaticy. In particular, the final mean energy of the quantum oscillator is given by Ref. [40]

$$\langle H_\tau \rangle = \frac{\hbar\omega_1}{2}Q^* \coth(\beta\hbar\omega_0/2), \qquad (14)$$

and thus linearly increases with Q^*.

To evaluate the Bures angle (1) for the parametric harmonic oscillator, the quantum fidelity (2) has to be written in closed form. For Gaussian states such an explicit form is known: for two arbitrary (nondisplaced) Gaussian density operators ρ_1

and ρ_2, the fidelity reads [37]

$$F(\rho_1, \rho_2) = \frac{2}{\sqrt{\Delta + \delta} - \sqrt{\delta}}. \qquad (15)$$

The two parameters $\Delta = \det(A_1 + A_2)$ and $\delta = [\det(A_1) - 1][\det(A_2) - 1]$ are completely determined by the covariance matrices A_i (matrices of the variances of position and momentum) of the quantum oscillator,

$$A_i = \begin{pmatrix} a_{xx}^i & a_{xp}^i \\ a_{xp}^i & a_{pp}^i \end{pmatrix}. \qquad (16)$$

The matrix elements a^i are explicitly given by

$$a_{xx}^i = 2(\langle x_i^2 \rangle - \langle x_i \rangle^2), \qquad (17a)$$

$$a_{pp}^i = \frac{2}{\hbar^2}(\langle p_i^2 \rangle - \langle p_i \rangle^2), \qquad (17b)$$

$$a_{xp}^i = \frac{2}{\hbar}\left(\frac{1}{2}\langle x_i p_i + p_i x_i \rangle - \langle x_i \rangle \langle p_i \rangle\right). \qquad (17c)$$

To evaluate the terms appearing in the Clausius inequality (8), we make use of the explicit expressions of the initial, ρ_0, and final density operators, ρ_τ and ρ_τ^{eq}, of the oscillator in coordinate representation, as given in Appendix C. In particular, the final equilibrium density operator ρ_τ^{eq} has the same form as Eq. (C1), replacing ω_0 by ω_1. Accordingly, the

corresponding equilibrium mean and variances are $\langle x \rangle_\tau^{\text{eq}} = \langle p \rangle_\tau^{\text{eq}} = \langle xp + px \rangle_\tau^{\text{eq}} = 0$, and

$$\langle x^2 \rangle_\tau^{\text{eq}} = \frac{\hbar}{2M\omega_1} \coth(\beta\hbar\omega_1/2), \qquad (18a)$$

$$\langle p^2 \rangle_\tau^{\text{eq}} = \frac{\hbar\omega_1 M}{2} \coth(\beta\hbar\omega_1/2). \qquad (18b)$$

On the other hand, for the final nonequilibrium state ρ_τ, we have $\langle x \rangle_\tau = \langle p \rangle_\tau = 0$, and

$$\langle x^2 \rangle_\tau = \frac{\hbar}{2M\omega_0}(Y_\tau^2 + \omega_0^2 X_\tau^2)\coth(\beta\hbar\omega_0/2), \quad (19a)$$

$$\langle p^2 \rangle_\tau = \frac{\hbar M}{2\omega_0}(\dot{Y}_\tau^2 + \omega_0^2 \dot{X}_\tau^2)\coth(\beta\hbar\omega_0/2). \qquad (19b)$$

The cross correlation function can be evaluated by exploiting the fact that $\langle xp + px \rangle_\tau = Md_t\langle x^2 \rangle_\tau$ and reads

$$\langle xp + px \rangle_\tau = \frac{\hbar}{\omega_0}(Y_\tau\dot{Y}_\tau + \omega_0^2 X_\tau\dot{X}_\tau)\coth(\beta\hbar\omega_0/2). \qquad (20)$$

The analytic expression of the quantum fidelity function $F(\rho_\tau, \rho_\tau^{\text{eq}})$ between nonequilibrium and equilibrium oscillator states at the end of the driving can be finally obtained by evaluating the determinants Δ and δ in Eq. (15) using Eqs. (18a)–(20), with the help of the relation $\dot{X}_t Y_t - X_t \dot{Y}_t = 1$ [38] and the definition of the function Q^* given in Eq. (13). We find

$$F(\rho_\tau, \rho_\tau^{\text{eq}}) = \frac{2}{\sqrt{\text{ct}^2(\beta\varepsilon_0/2) + \text{ct}^2(\beta\varepsilon_1/2) + 2Q^*\text{ct}(\beta\varepsilon_0/2)\text{ct}(\beta\varepsilon_1/2) + \text{c}^2(\beta\varepsilon_0/2)\text{c}^2(\beta\varepsilon_1/2)} - \text{c}(\beta\varepsilon_0/2)\text{c}(\beta\varepsilon_1/2)}, \qquad (21)$$

with the notation $\text{c}(.) = \text{csch}(.)$ and $\text{ct}(.) = \coth(.)$, and the energies $\varepsilon_i = \hbar\omega_i$. The Bures angle $\mathcal{L}$ then directly follows from Eq. (1), and the lower bound to the nonequilibrium entropy production $\langle\Sigma\rangle$ can be determined, to any order, with the help of the expansion (7).

To get more physical insight, let us evaluate the limiting expressions of the fidelity (21) in the low-temperature (quantum) and high-temperature (classical) regimes. An expansion of the hyperbolic cosine and cotangent functions in the zero-temperature limit, $\hbar\beta \to \infty$, leads to

$$F(\rho_\tau, \rho_\tau^{\text{eq}}) \xrightarrow{\hbar\beta \to \infty} \sqrt{\frac{2}{1 + Q^*}}. \qquad (22)$$

In the adiabatic limit $Q^* \to 1$, the fidelity thus tends to one; that is, the Bures angle approaches zero, indicating that the system ends in an equilibrium state, as expected. For strongly nonadiabatic processes, $Q^* \gg 1$, on the other hand, the fidelity tends to zero as $1/\sqrt{Q^*}$. Here the Bures angle tends to $\pi/2$, showing that ρ_τ and ρ_τ^{eq} are maximally distinguishable (orthogonal).

Equation (22) can also be derived directly by noting that, in the zero-temperature limit, the harmonic oscillator is initially in a pure state $|0_0\rangle$. The initial equilibrium density operator is, hence, $\rho_0|_{T=0} = |0_0\rangle\langle 0_0|$ and analogously for $\rho_\tau^{\text{eq}}|_{T=0}$. Since these states are pure, the fidelity simplifies to their overlap, and we have $F(\rho_\tau, \rho_\tau^{\text{eq}})|_{T=0} = \text{tr}\{\rho_\tau\rho_\tau^{\text{eq}}\} = p_{0,0}^\tau$, where $p_{0,0}^\tau$ is the

probability for the system to start and end in the corresponding ground state. The latter is given by the expression [40]

$$p_{0,0}^\tau = \sqrt{\frac{2}{1 + Q^*}}, \qquad (23)$$

and we thus recover Eq. (22).

In the classical limit, $\hbar\beta \to 0$, by repeating the same analysis, the fidelity (21) simplifies to

$$F(\rho_\tau, \rho_\tau^{\text{eq}}) \xrightarrow{\hbar\beta \to 0} \frac{4\omega_0\omega_1}{\omega_0^2 + 2Q^*\omega_0\omega_1 + \omega_1^2}. \qquad (24)$$

For an adiabatic frequency change, $Q^* \to 1$, the fidelity reduces to $F(\rho_\tau, \rho_\tau^{\text{eq}}) \simeq 4\omega_0\omega_1/(\omega_0 + \omega_1)^2$. Therefore, as noticed in Ref. [39] (see also Ref. [41]), a unitary process can only be quasistatic in the thermodynamic sense, $F(\rho_\tau, \rho_\tau^{\text{eq}}) \simeq 1$, if $|\omega_1 - \omega_0|/\omega_0 \ll 1$. Indeed, according to the quantum adiabatic theorem, the occupation probabilities remain constant during a quasistatic process. As a result $\rho_\tau = \exp(-\beta H_\tau)/Z_0$ which is different from $\rho_\tau^{\text{eq}} = \exp(-\beta H_\tau)/Z_\tau$, except for infinitesimal frequency changes. We note additionally that in the classical limit the fidelity vanishes for large values of Q^* as $1/Q^*$; that is, much faster than in the low-temperature regime. The density operators ρ_τ and ρ_τ^{eq} thus become orthogonal ($\mathcal{L} = \pi/2$) much faster as a function of the degree of nonadiabaticy.

For the parametric quantum oscillator, the nonequilibrium entropy production (5) can be determined exactly, allowing to

test the generalized Clausius inequality (8). It is given by [39]

$$\langle\Sigma\rangle = \frac{\beta}{2}(Q^*\hbar\omega_1 - \hbar\omega_0)\coth(\beta\hbar\omega_0/2)$$
$$- \ln\left(\frac{\sinh(\beta\hbar\omega_1/2)}{\sinh(\beta\hbar\omega_0/2)}\right), \quad (25)$$

where we used $\langle H_0\rangle = (\hbar\omega_0/2)\coth(\beta\hbar\omega_0/2)$ and Eq. (14). Figure 1 shows the nonequilibrium entropy production $\langle\Sigma\rangle$ as a function of the measure of adiabaticity Q^*, together with the lower bound obtained with the first term in the expansion (7) and the exact function $s(x)$ (6) (the latter is indistinguishable from the expression including the first five nonzero terms of the expansion). We see that the first term in the expansion provides a good lower bound in many cases.

V. LOWER BOUND BASED ON TRACE DISTANCE

As discussed in Sec. I, the Bures angle $\mathcal{L}$, being the extension of Wootters' statistical distance to mixed states, possesses a simple interpretation as the geometric angle between two density operators. However, Eq. (5) shows that the nonequilibrium entropy production $\langle\Sigma\rangle$ is bounded by many unitarily invariant distances, albeit with possibly less natural physical interpretation. To elucidate this point, we discuss the concrete case of the trace norm, which has been reported to yield the largest lower bound on the relative entropy [32] (a further comparison of $\mathcal{L}$ with the Bures distance $\mathcal{D}$ is given in Appendix A). The trace distance between two density operators ρ_1 and ρ_2 is defined as [22,23]

$$\mathcal{T}(\rho_1, \rho_2) = \tfrac{1}{2}\mathrm{tr}\{|\rho_1 - \rho_2|\} = \tfrac{1}{2}\mathrm{tr}\{\sqrt{(\rho_1 - \rho_2)^2}\}. \quad (26)$$

Contrary to the Bures angle (or the Bures distance), it is not a Riemannian distance—however, both are monotone. The trace distance between nonequilibrium and equilibrium states of the parametric quantum oscillator (10) can be evaluated for arbitrary driving with the help of the explicit expressions of ρ_τ and ρ_τ^{eq} given in Appendix C: we have $\mathcal{T}(\rho_\tau, \rho_\tau^{\mathrm{eq}}) = (1/2)\sum_i |\lambda_i|$, where λ_i are the eigenvalues of $\rho_\tau - \rho_\tau^{\mathrm{eq}}$. Unlike for the Bures angle, it does not seem to be possible to express $\mathcal{T}$ as a function of the adiabaticy parameter Q^* alone (the density operators ρ_τ and ρ_τ^{eq} depend on the two functions X_t and Y_t and not on Q^* directly). To circumvent this problem, we have numerically evaluated the trace distance for the case of a sudden switching of the frequencies for which $Q^* = (\omega_0^2 + \omega_1^2)/(2\omega_0\omega_1)$. Figure 2 shows the corresponding entropy production $\langle\Sigma\rangle$ (25) and the lower bound (8) for the Bures angle, $s(2\mathcal{L}/\pi)$, and for the trace distance, $s(\mathcal{T})$, as a function of Q^* for fixed β and ω_0. Contrary to Fig. 1, where both ω_0 and ω_1 are fixed, for the sudden frequency switch $Q^*(\omega_1)$ is a function of ω_1.

We observe that the lower bound based on the trace distance is sharper than the one obtained using the Bures angle. However, the two bounds appear largely equivalent, reflecting the fact that $\mathcal{L}$ and $\mathcal{T}$ are closely related (see, e.g., Refs. [22,23]). We stress that the trace distance lacks the simple interpretation of the Bures angle as the angle between density operators. Moreover, in the classical limit the bound based on the trace distance does not reduce to the known bound on the entropy production derived in linear-response theory [7–9].
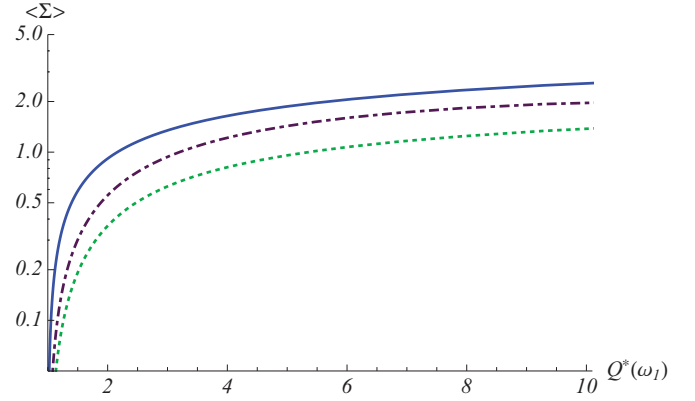

FIG. 2. (Color online) Irreversible entropy production $\langle\Sigma\rangle$ (25) (blue, solid line) together with the lower bound (8) evaluated for the Bures angle $\mathcal{L}$ (1) (green, dotted line) and the trace distance $\mathcal{T}$ (26) (purple, dot-dashed line), as a function of the (numerical) adiabaticy parameter (13) for the sudden switch $Q^*(\omega_1) = (\omega_0^2 + \omega_1^2)/(2\omega_0\omega_1)$. Parameters are $\hbar = 1$, $\beta = 4.8$, $\omega_0 = 0.9$.

VI. CONCLUSIONS

The Bures angle between the nonequilibrium and the corresponding equilibrium state of a driven closed quantum system defines a thermodynamic length that is valid arbitrarily far from equilibrium. The latter can be used to characterize the departure from equilibrium for generic driving. We derived a lower bound on the nonequilibrium entropy production, which we expressed as a function of the Bures angle, by using a sharp lower bound on the quantum relative entropy. In such a way, we obtained a generalized Clausius inequality, with a process-dependent lower bound that holds beyond the range of linear-response theory. As an illustration, we treated the case of a time-dependent harmonic oscillator for which we derived analytic expressions for the Bures angle. We further compared the lower bound obtained with the Bures angle with the one based on the trace distance. While the trace distance offers a slightly sharper bound, the two appear to be largely equivalent.

APPENDIX A: LOWER BOUND BASED ON BURES DISTANCE

To evaluate the changes induced by the choice of another unitarily invariant distance on the lower bound (8), we present in this appendix an alternative constructive derivation of the lowest-order estimation of the nonequilibrium entropy production $\langle\Sigma\rangle$. Let us begin by introducing the Hellinger distance [42,43],

$$\mathcal{H}^2(p_1, p_2) = \int dx(\sqrt{p_1(x)} - \sqrt{p_2(x)})^2, \quad (A1)$$

for two (classical) probability distributions $p_1(x)$ and $p_2(x)$. The Hellinger distance is another measure of the

distinguishability of two probability distributions. It is a true distance which fulfills symmetry, nonnegativity, and the triangle inequality. Expression (A1) can be rewritten in terms of the classical fidelity function, $f(p_1, p_2) = \int dx \sqrt{p_1(x)p_2(x)}$, to yield

$$\mathcal{H}(p_1, p_2) = \sqrt{2 - 2f(p_1, p_2)}. \qquad \text{(A2)}$$

By using the inequality $\sqrt{y} - 1 \geqslant 1/2 \ln(y)$, we have

$$\sqrt{\frac{p_2(x)}{p_1(x)}} - 1 \geqslant \frac{1}{2} [\ln p_2(x) - \ln p_1(x)]. \qquad \text{(A3)}$$

Averaging Eq. (A3) over the probability distribution $p_1(x)$ results in

$$2\left(1 - \left\langle \sqrt{\frac{p_2(x)}{p_1(x)}} \right\rangle_{p_1}\right) \leqslant \langle \ln p_1(x) - \ln p_2(x) \rangle_{p_1}, \qquad \text{(A4)}$$

from which we deduce the inequality

$$D(p_1 || p_2) \geqslant 2 - 2f(p_1, p_2) = \mathcal{H}^2(p_1, p_2). \qquad \text{(A5)}$$

Here $D(p_1 || p_2)$ denotes the classical Kullback-Leibler divergence between p_1 and p_2. The classical result (A5) can be extended to quantum states by considering the quantum version of the Hellinger distance, which is the Bures distance between density operators ρ_1 and ρ_2 [20]:

$$\mathcal{D}^2(\rho_1, \rho_2) = 2(1 - \sqrt{F(\rho_1, \rho_2)}). \qquad \text{(A6)}$$

Note the difference in the definitions of the classical and quantum fidelity. By combining Eqs. (4), (A5), and (A6), we then find the generalized Clausius inequality,

$$\langle \Sigma \rangle \geqslant \mathcal{D}^2(\rho_\tau, \rho_\tau^{\text{eq}}). \qquad \text{(A7)}$$

The above lower bound on the entropy production corresponds to the lowest-order term in the expansion (7) when the Bures distances is chosen instead of the Bures angle in Eq. (5), since $\mathcal{D}(e^{1,1}, e^{2,2}) = \sqrt{2}$. Figure 3 shows the Bures angle $\mathcal{L}$ and the Bures distance $\mathcal{D}$ as a function of the quantum fidelity F. We observe that $\mathcal{D} \geqslant \mathcal{L}$ so that the Bures distance offers a (slightly) sharper bound to the entropy production than the Bures angle, to lowest order. However, the distance $\mathcal{D}$ bears the disadvantage that the intuitive, physical interpretation as
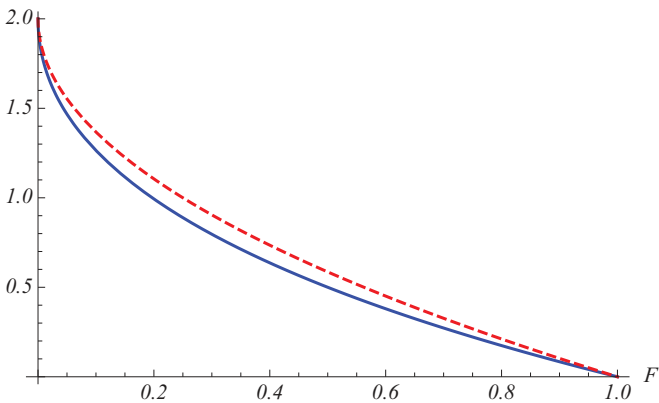

FIG. 3. (Color online) Lower bounds for the nonequilibrium entropy production based on the Bures angle, $(8/\pi^2)\mathcal{L}^2$ (8) (blue solid), and on the Bures distance, $\mathcal{D}^2$ (A7) (red dashed), as a function of the fidelity F.

an angle between mixed states is lacking. Moreover, the Bures distance does not reduce to the classical thermodynamic length derived in Refs. [7–9] in the appropriate limit, in contrast to the Bures angle.

APPENDIX B: ANALYTIC UPPER BOUND FOR QUANTUM RELATIVE ENTROPY

Due to the importance of the relative entropy in physics and mathematics, and the complexity to evaluate it, accurate approximations and bounds are essential. While a lower bound has been obtained for unitarily invariant norms in the form of Eq. (5) [32], upper bounds are much more difficult to find. Recently, a general upper bound was proposed in terms of the eigenvalues of the density operators [44]. In the present thermodynamic context, we may, however, derive a simpler upper bound. We start with the inequality [45],

$$\text{tr}\{\rho_1 \ln \rho_1 - \rho_1 \ln \rho_2\} \leqslant \frac{1}{\nu} \text{tr}\{\rho_1^{1+\nu} \rho_2^{-\nu} - \rho_1\}, \qquad \text{(B1)}$$

which is true for all positive definite operators ρ_1, ρ_2 and $\nu > 0$. We shall here concentrate on the final nonequilibrium and equilibrium density operators, ρ_τ and ρ_τ^{eq}. By choosing $\nu = 1$ and using the normalization condition $\text{tr}\{\rho\} = 1$, we obtain the upper bound, $\langle \Sigma \rangle \leqslant \text{tr}\{\rho_\tau^2 (\rho_\tau^{\text{eq}})^{-1}\} - 1$. In order to further simplify the bound and derive an expression which does not depend on the off-diagonal matrix elements in energy representation of the density operators, we use the inequality [46]

$$|\text{tr}\{\rho_1 \rho_2\}| \leqslant \sum_{r=1}^{n} \sigma_r^1 \sigma_r^2, \qquad \text{(B2)}$$

which holds for any complex $n \times n$ matrices ρ_1 and ρ_2 with descending singular values, $\sigma_1^1 \geqslant \cdots \geqslant \sigma_n^1$ and $\sigma_1^2 \geqslant \cdots \geqslant \sigma_n^2$. The singular values of an operator A acting on a Hilbert space are defined as the eigenvalues of the operator $\sqrt{A^\dagger A}$. If ρ_1 and ρ_2 are density operators acting on the same Hilbert space Eq. (B2) remains true for arbitrary dimensions, and the singular values are identically given by the eigenvalues [47,48]. As a result, we obtain the upper bound for the entropy production $\langle \Sigma \rangle$:

$$\langle \Sigma \rangle \leqslant \sum_n \frac{(p_n^\tau)^2}{p_n^{\text{eq}}} - 1. \qquad \text{(B3)}$$

APPENDIX C: EXPLICIT EXPRESSIONS OF DENSITY OPERATORS

The evaluation of the covariance matrix (16) requires the expressions of the density operators ρ_0^{eq}, ρ_τ^{eq}, and ρ_τ in coordinate representation. We collect them in this Appendix for completeness. The initial equilibrium density operator ρ_0^{eq} is given by Ref. [49]

$$\rho_0^{\text{eq}}(x, y) = \sqrt{\frac{M\omega_0}{\pi\hbar} \tanh(\beta\hbar\omega_0/2)} \exp\left(-\frac{M\omega_0}{2\hbar}\coth(\beta\hbar\omega_0)\right.$$
$$\left. \times [x^2 + y^2 - 2\text{sech}(\beta\hbar\omega_0)xy]\right). \qquad \text{(C1)}$$

The final equilibrium density operator ρ_τ^{eq} has the same form as Eq. (C1) with the replacement ω_0 by ω_1. On the other hand, the final nonequilibrium operator ρ_τ can be derived

from Eq. (C1) by noting that $\rho_\tau(x,x') = \int dy \int dy' U_\tau(x,y)$ $\rho_0^{\mathrm{eq}}(y,y') U_\tau^*(y',x')$. The propagator $U_\tau(x,x_0)$ can be determined from the wave function (11) with $\psi_\tau(x) = \int dx_0 U_\tau(x,x_0) \psi_{t_0}(x_0)$ and reads [38]

$$U_\tau = \sqrt{\frac{M}{2\pi i\hbar X_\tau}} \exp\left(\frac{iM}{2\hbar X_\tau}\left[\dot{X}_\tau x^2 - 2xx_0 + Y_\tau x_0^2 \right] \right).$$

(C2)

The functions X_τ and Y_τ are solutions of the force-free harmonic oscillator satisfying the boundary conditions

$X_0 = 0$, $\dot{X}_0 = 1$ and $Y_0 = 1$, $\dot{Y}_0 = 0$. A direct evaluation of the Gaussian integrals leads to the expression

$$\rho_\tau(x,y) = \sqrt{\frac{M\omega_0}{\pi\hbar} \frac{\tanh(\beta\hbar\omega_0/2)}{Y_\tau^2 + \omega_0^2 X_\tau^2}} \exp\left(-\frac{M\omega_0}{2\hbar} \frac{1}{Y_\tau^2 + \omega_0^2 X_\tau^2} \right.$$

$$\times \left\{ \coth(\beta\hbar\omega_0)[x^2 + y^2 - 2\mathrm{sech}(\beta\hbar\omega_0)xy] \right.$$

$$\left. \left. + i(x^2 - y^2)(\omega_0^2 \dot{X}_\tau X_\tau + \dot{Y}_\tau Y_\tau) \right\} \right).$$

(C3)

[1] T. Kinoshita, T. Wenger, and D. Weiss, Nature (London) **440**, 900 (2006).

[2] S. Hofferberth, I. Lesanovsky, B. Fischer, T. Schumm, and J. Schmiedmayer, Nature (London) **449**, 324 (2007).

[3] S. Trotzky, Y-A. Chen, A. Flesch, I. P. McCulloch, U. Schollwöck, J. Eisert, and I. Bloch, Nat. Phys. **8**, 325 (2012).

[4] M. Gring, M. Kuhnert, T. Langen, T. Kitagawa, B. Rauer, M. Schreitl, I. Mazets, D. Adu Smith, E. Demler, and J. Schmiedmayer, Science **337**, 1318 (2012).

[5] S. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (Dover Publications, Inc., New York, 1984).

[6] D. Kondepudi and I. Prigogine, *Modern Thermodynamics* (John Wiley, Chichester, 1999).

[7] P. Salamon and R. S. Berry, Phys. Rev. Lett. **51**, 1127 (1983).

[8] P. Salamon, J. Nulton, and R. Berry, J. Chem. Phys. **82**, 2433 (1984).

[9] J. Nulton, P. Salamon, B. Andresen, and Qi Anmin, J. Chem. Phys. **83**, 334 (1985).

[10] G. Ruppeiner, Rev. Mod. Phys. **67**, 605 (1995).

[11] B. Andresen, P. Salamon, and R. S. Berry, Phys. Today **37**, 62 (1984).

[12] B. Andresen, Angew. Chem., Int. Ed. **50**, 2690 (2011).

[13] G. E. Crooks, Phys. Rev. Lett. **99**, 100602 (2007).

[14] E. H. Feng and G. E. Crooks, Phys. Rev. E **79**, 012104 (2009).

[15] W. K. Wootters, Phys. Rev. D **23**, 357 (1981).

[16] S. Deffner and E. Lutz, Phys. Rev. Lett. **105**, 170402 (2010).

[17] S. Kakutani, Ann. Math. **49**, 214 (1948).

[18] D. Bures, Trans. Am. Math. Soc. **135**, 199 (1969), http://www.jstor.org/stable/1995012.

[19] A. Uhlmann, Rep. Math. Phys. **9**, 273 (1976).

[20] R. Jozsa, J. Mod. Opt. **41**, 2315 (1994).

[21] S. L. Braunstein and C. M. Caves, Phys. Rev. Lett. **72**, 3439 (1994).

[22] M. A. Nielsen and I. L. Chuang, *Quantum Computation and Quantum Information* (Cambridge University Press, Cambridge, 2000).

[23] I. Bengtsson and K. Życzkowski, *Geometry of Quantum States*, (Cambridge University Press, Cambridge, 2006).

[24] D. Leibfried, R. Blatt, C. Monroe, and D. Wineland, Rev. Mod. Phys. **75**, 281 (2003).

[25] G. Huber, F. Schmidt-Kaler, S. Deffner, and E. Lutz, Phys. Rev. Lett. **101**, 070403 (2008).

[26] S. Kullback, *Information Theory and Statistics* (Peter Smith, Gloucester, 1978).

[27] H. Umegaki, Kodai Math. Sem. Rep. **14**, 59 (1962).

[28] R. Kawai, J. M. R. Parrondo, and C. Vanden Broeck, Phys. Rev. Lett. **98**, 080602 (2007).

[29] S. Vaikuntanathan and C. Jarzynski, Europhys. Lett. **87**, 60005 (2009).

[30] S. Deffner and E. Lutz, Phys. Rev. Lett. **107**, 140404 (2011).

[31] R. W. Yeung, *A First Course in Information Theory*, (Kluwer Academic, New York, 2002).

[32] K. Audenaert and J. Eisert, J. Math. Phys. **46**, 102104 (2005).

[33] All the coefficients in the expansion are not positive; the first negative one is the coefficient of x^{62} [32].

[34] M. Hübner, Phys. Lett. A **163**, 239 (1992).

[35] P. B. Slater, J. Phys. A **29**, L271 (1996).

[36] J. Dittmann, J. Phys. A: Math. Gen. **32**, 14 (1999).

[37] H. Scutaru, J. Phys. A: Math. Gen. **31**, 3659 (1998).

[38] K. Husimi, Prog. Theor. Phys. **9**, 381 (1953).

[39] S. Deffner and E. Lutz, Phys. Rev. E **77**, 021128 (2008).

[40] S. Deffner, O. Abah, and E. Lutz, Chem. Phys. **375**, 200 (2010).

[41] A. E. Allahverdyan and Th. M. Nieuwenhuizen, Phys. Rev. E **71**, 046107 (2005).

[42] E. Hellinger, J. Reine und Angewandte Mathematik **136**, 210 (1909).

[43] O. Abah, J. Rossnagel, G. Jacob, S. Deffner, F. Schmidt-Kaler, K. Singer, and Eric Lutz, Phys. Rev. Lett. **109**, 203006 (2012).

[44] K. Audenaert and J. Eisert, J. Math. Phys. **52**, 112201 (2011).

[45] W. Hebisch, R. Olkiewicz, and B. Zegarlinski, Lin. Alg. Appl. **329**, 89 (2001).

[46] L. Mirsky, Monatsh. Math. **79**, 303 (1975).

[47] R. Grigorieff, Math. Nachr. **151**, 327 (1991).

[48] S. Dragomir, M. Schloz, and J. Sunde, Comp. Math. Appl. **39**, 91 (2000).

[49] W. Greiner, L. Neise, and H. Stöcker *Thermodynamics and Statistical Mechanics* (Springer, New York, 1995).