A LETTERS JOURNAL EXPLORING
THE FRONTIERS OF PHYSICS

OFFPRINT

Finite-time availability in a quantum system

K. H. Hoffmann and P. Salamon

EPL, **109** (2015) 40004

A Letters Journal Exploring the Frontiers of Physics

February 2015

EPL, **109** (2015) 40004 www.epljournal.org
doi: 10.1209/0295-5075/109/40004

Finite-time availability in a quantum system

K. H. Hoffmann[1] and P. Salamon[2]

[1] *Department of Physics, Technische Universität Chemnitz - D-09107 Chemnitz, Germany*
[2] *Department of Mathematical Sciences, San Diego State University - San Diego, CA 92182, USA*

received 30 October 2014; accepted in final form 4 February 2015
published online 23 February 2015

PACS 05.70.-a – Thermodynamics
PACS 03.65.Yz – Decoherence; open systems; quantum statistical methods
PACS 03.67.Ac – Quantum algorithms, protocols, and simulations

Abstract – Classically, availability refers to the work available in any reversible process that brings about equilibrium between the system and its environment. Here we introduce an additional meaning of availability as the maximum work associated with the change of an external parameter in the Hamiltonian of a quantum system. This availability can be gained in a FEAT process and for times larger than or equal to the FEAT time, there exists an optimal control that achieves the available work. For shorter times, quantum friction effects are unavoidable and the available work is thereby lowered. This finite-time availability is quantified here as a function of the time available.

Availability as the quantification of available work from a thermodynamic system has been with us since Gibbs introduced the concept in 1873 [1]. While not being very prominent in physics and chemistry texts on the subject, it was enthusiastically revived in the engineering literature by Joseph Keenan [2] and has remained as an important cornerstone of engineering process analysis. Renamed exergy, it survives to this day with an extensive literature including a dedicated journal, the *International Journal of Exergy*. In both Gibbs' and Keenan's treatments, the concept perforce relates the work available from disequilibrium between the system of interest and an environment that acts as a bath with constant intensities. Classically, availability refers to the work available in any reversible process that brings about equilibrium between the system and such an environment.

During the last decades, the concept has been used to bound the work required to bring a system along a specified sequence of states in a given time using a macroscopic [3,4], or a microscopic [5] description of the process. More recently, availability loss and the closely related concept of entropy production have been discussed for applications to heat engines [6], and radiation [7,8], as well as from a more fundamental point of view [9]. And finally, the concept has attained considerable interest in connection with the work available from quantum systems, see, for instance, the work by Deffner and Lutz [10], Allahverdyan and collaborators [11–14], or Sivak and Crooks [15].

In a recent paper [16], we introduced an additional meaning of availability as the maximum work associated with the change of an external parameter in the Hamiltonian of a quantum system. The context of the problem discussed there, the change in the frequency of a harmonic oscillator, made the extension of the term natural since the associated availability in fact equaled the traditional availability of the initial state of the quantum system relative to an environment at the temperature of the final state. As shown in that work, there is a minimum time $t_{\min}$ and for times larger than $t_{\min}$, there exists a control of the frequency which achieves the available work. For shorter times quantum friction effects [17,18] are unavoidable and the available work is thereby lowered.

Similar results have been shown for a system of two interacting spin-$\frac{1}{2}$ particles in an external magnetic field [19]. Both examples achieved what traditional adiabatic switching could also achieve. However, they achieve the same final state in a much shorter time than adiabatic switching would require. Accordingly these minimum possible time processes have been dubbed *Fastest Effectively Adiabatic Transitions* or simply FEATs. The FEAT controls found in [19] extract an amount of work equal to the availability associated with the adiabatic change for any time greater than $t_{\mathrm{FEAT}} = t_{\min}$. What can be achieved for even shorter times is the topic of the present paper.

Effectively adiabatic processes have received considerable interest in the context of control of quantum systems [20–26] for instance to bring them close to the absolute zero of temperature [27,28]. Contrary to expectations, effectively adiabatic switching of external parameters has been shown to be possible much faster than traditional adiabatic switching arguments would lead one to expect for a large class of systems [28–37]. Often referred to as Shortcuts To Adiabaticity (STA) processes, they have become indispensable tools for manipulating Bose-Einstein condensates.

The implications of finite-time constraints for the concept of availability have been explored for more classical macroscopic systems [38–42]. Constraints on the process time in conjunction with finite transport rates will typically lead to increased dissipation. Thus, such constraints typically exclude reversible processes, thereby decreasing the amount of available work.

Transport rates are not the issue for the spin-$\frac{1}{2}$ systems considered here and the time dependence of the availability for times greater than t_{FEAT} is trivial —the availability is constant. While effectively adiabatic processes are reversible, for process times $t_{\mathrm{P}} < t_{\mathrm{FEAT}}$ such processes nonetheless excite certain so-called parasitic oscillations whose effects show up as a difference between the von Neumann entropy and the energy entropy of the system. This difference is responsible for the lost availability for shorter times and is our object of interest for times between the sudden process ($t_{\mathrm{P}} = 0$) and the effectively reversible process when $t_{\mathrm{P}} = t_{\mathrm{FEAT}}$.

Interacting spins. – The thermodynamic system we use to study finite-time availability is an ensemble of non-interacting systems, each consisting of two interacting spin-$\frac{1}{2}$-particles introduced in [18]. The Hamiltonian of these systems is

$$\mathcal{H} = \mathcal{H}^{\mathrm{int}} + \mathcal{H}^{\mathrm{ext}}(\omega), \tag{1}$$

where

$$\mathcal{H}^{\mathrm{int}} = \frac{1}{2}\hbar j(\sigma_x^1 \otimes \sigma_x^2 - \sigma_y^1 \otimes \sigma_y^2) =: \hbar j \mathcal{B}_2, \tag{2}$$

$$\mathcal{H}^{\mathrm{ext}} = \frac{1}{2}\hbar \omega(t)(\sigma_z^1 \otimes I^2 + I^1 \otimes \sigma_z^2) =: \hbar\omega(t)\mathcal{B}_1. \tag{3}$$

$\mathcal{H}^{\mathrm{int}}$ represents the interaction between the two spins and $\mathcal{H}^{\mathrm{ext}}$ the interaction of the spins with an external magnetic field ω. Here σ is the Pauli spin operator, j scales the strength of the inter-particle interaction and $\omega(t)$ is the time-dependent strength of the external magnetic field which is considered to be in the z-direction. The energy levels of one of the spin systems are

$$E_1 = -\hbar\Omega, \quad E_2 = E_3 = 0, \quad E_4 = \hbar\Omega \tag{4}$$

with $\Omega(t) = \sqrt{\omega(t)^2 + j^2}$. From here on we will set $\hbar = 1$.

The operators $\mathcal{B}_1$ and $\mathcal{B}_2$ together with $\mathcal{B}_3 = \frac{1}{2}(\sigma_y^1 \otimes \sigma_x^2 + \sigma_x^1 \otimes \sigma_y^2)$ form a closed $\mathfrak{su}(2)$ algebra [43]. This has the consequence that in the Heisenberg picture the time derivatives of these operators can be written as linear combinations of these same operators. Due to this linearity one obtains equivalent equations for the expectation values of the operators $b_i = \langle \mathcal{B}_i \rangle$ as can be seen by multiplying by the (constant) density matrix ρ and taking the trace

$$\dot{b_1} = f_1(\vec{b}, \omega) = 2jb_3, \tag{5}$$

$$\dot{b_2} = f_2(\vec{b}, \omega) = -2\omega b_3, \tag{6}$$

$$\dot{b_3} = f_3(\vec{b}, \omega) = -2jb_1 + 2\omega b_2. \tag{7}$$

Note that these equations imply that the Casimir companion [44]

$$X = b_1^2 + b_2^2 + b_3^2 \tag{8}$$

is a constant of the motion for an arbitrary control ω. The invariance of X is important —it sets the minimum energy achievable even without considering explicit controls.

The thermodynamic equilibrium conditions for this system coincide with the stationarity conditions obtained by setting (5)–(7) equal to zero. For constant ω, this leads to [18]

$$b_3^{\mathrm{eq}} = 0, \tag{9}$$

$$b_1^{\mathrm{eq}} j = b_2^{\mathrm{eq}} \omega. \tag{10}$$

The same conditions are alternatively obtained by maximizing the entropy while holding the energy constant. Since the entropy is a monotonic function of X [44] this can easily be seen by maximizing X in (8) with $E = jb_2 + \omega b_1$ constant.

Connecting thermodynamic equilibrium states in finite time. – For this system it is known [18,19] that one can connect two different thermodynamic equilibrium states without friction and in a finite time by appropriately controlling ω. The time-optimal controls, *i.e.* those generating the fastest transition between two different thermodynamic equilibrium states, have been determined [19]. The time needed to connect an initial to a final equilibrium state with $0 < \omega_{\mathrm{f}} \leq \omega_{\mathrm{i}}$ was obtained as

$$t_1 = \frac{1}{2\Omega_{\mathrm{f}}}\mathrm{acos}(\phi), \qquad t_2 = \frac{1}{2\Omega_{\mathrm{i}}}\mathrm{acos}(\phi), \tag{11}$$

$$\phi = \frac{\Omega_{\mathrm{i}}\Omega_{\mathrm{f}}(j^2 + \omega_{\mathrm{i}}\omega_{\mathrm{f}}) - (j^2 + \omega_{\mathrm{i}}\omega_{\mathrm{f}})^2}{j^2(\omega_{\mathrm{i}} - \omega_{\mathrm{f}})^2} \tag{12}$$

with the total time $t_{\mathrm{FEAT}} = t_1 + t_2$. For that result ω was limited to positive values with $0 < \omega_{\mathrm{f}} \leq \omega \leq \omega_{\mathrm{i}}$.

In conclusion one can state that for process times longer than the above-determined time t_{FEAT} all the availability of the transition can be extracted by appropriately chosen schedules for $\omega(t)$. The value of this maximum work follows from the invariance of the Casimir companion.

Maximum work in finite time. – We now turn to the problem to determine this maximum available work in an adiabatic process as a function of the process time t_{P}. We first note that the energy of the system can be expressed as

$$E(\vec{b}, \omega) = jb_2 + \omega b_1 \tag{13}$$

and thus $\dot{E} = j\dot{b}_2 + \dot{\omega} b_1 + \omega \dot{b}_1 = \dot{\omega} b_1$. The availability of a state $\vec{b}$ at frequency ω with respect to a reference state $\vec{b}_0$ at frequency ω_0 is in our context defined as $A(\vec{b}, \omega, \vec{b}_0, \omega_0) = E(\vec{b}, \omega) - E(\vec{b}_0, \omega_0)$. We note that the usual entropy terms are missing as we consider only reversible processes. The work W available in a reversible process leading from $\vec{b}_\mathrm{i}$ at frequency ω_i to another state $\vec{b}_\mathrm{f}$ at frequency $\omega_\mathrm{f} \leq \omega_\mathrm{i}$ is then given by the decrease of the availability,

$$\begin{aligned} W &= -\Delta A(\vec{b}_\mathrm{f}, \omega_\mathrm{f}, \vec{b}_\mathrm{i}, \omega_\mathrm{i}) \\ &= A(\vec{b}_\mathrm{i}, \omega_\mathrm{i}, \vec{b}_0, \omega_0) - A(\vec{b}_\mathrm{f}, \omega_\mathrm{f}, \vec{b}_0, \omega_0). \end{aligned} \tag{14}$$

The finite-time availability $A_\mathrm{P}(\vec{b}_\mathrm{i}, \omega_\mathrm{i}, \omega_\mathrm{f}; t_\mathrm{P})$ of a state $\vec{b}_\mathrm{i}$ at frequency ω_i is defined as the maximum of $\Delta A(\vec{b}_\mathrm{i}, \omega_\mathrm{i}, \vec{b}, \omega_\mathrm{f})$ over all states $\vec{b}$ which can be reached from $\vec{b}_\mathrm{i}$ with controls limited to the range $\omega_\mathrm{f} \leq \omega \leq \omega_\mathrm{i}$ within time t_P. Note that the index "P" stresses the fact, that the finite-time availability depends crucially on the process class, for which the maximization is carried out. In our case these are processes of duration t_P, with control $\omega(t)$ starting at ω_i, ending at ω_f, and limited to the range $\omega_\mathrm{f} \leq \omega \leq \omega_\mathrm{i}$. In the following we always assume that we start from an initial thermodynamic equilibrium state $(b_{1,\mathrm{i}}, b_{2,\mathrm{i}}) = (\omega_\mathrm{i}, j)/\sqrt{\omega_\mathrm{i}^2 + j^2}$; in order to shorten the notation we will suppress the dependence of the finite-time availability A_P on the initial state and on the initial and final frequencies and write $A_\mathrm{P}(t_\mathrm{P})$ for $A_\mathrm{P}(\vec{b}_\mathrm{i}, \omega_\mathrm{i}, \omega_\mathrm{f}; t_\mathrm{P})$.

Determining $A_\mathrm{P}(t_\mathrm{P})$ leads to an optimal control problem which can be cast in the following form:

$$\begin{aligned} A_\mathrm{P}(t_\mathrm{P}) &= \underset{\text{process class P}}{\textbf{Maximize}} \, \Delta A(\vec{b}_\mathrm{i}, \omega_\mathrm{i}, b(\vec{t}_\mathrm{P}), \omega_\mathrm{f}), \\ &= \underset{\text{process class P}}{\textbf{Maximize}} \int_0^{t_\mathrm{P}} \dot{\omega}(t) b_1(t) \mathrm{d}t, \end{aligned} \tag{15}$$

subject to the constraints set by the dynamics (5)–(7).

The result will be $A_\mathrm{P}(t_\mathrm{P})$ as a function of the process time t_P. However, as the objective contains the time derivative of the control this approach has technical difficulties. Here we avoid these by inverting the problem: Instead of finding A_P for a given t_P, we search for the minimum time needed to extract A_P from our quantum system. This leads to $t_\mathrm{P}(A_\mathrm{P})$ which can then readily be inverted to obtain the originally desired result. The advantage of the second approach is that the ensuing control problem is very similar to the one solved in [19] to find the minimal time needed to extract the full reversible availability $A_\mathrm{P}(t_\mathrm{P} = \infty) = A_\mathrm{P}(t_\mathrm{FEAT}) = A_\mathrm{FEAT}$.

Finding minimal time processes for given availabilty. – Below we review the approach taken in [19] to the extent needed here. Using optimal control theory, (see, for instance, [45]) the cost function

$$\tau = \int_{t_\mathrm{i}}^{t_\mathrm{f}} 1 \mathrm{d}t \tag{16}$$

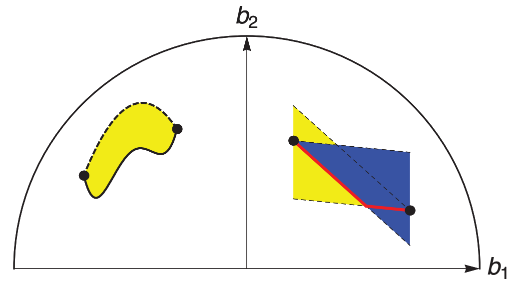

Fig. 1: (Colour on-line) In this figure the circle of thermal equilibrium states is shown. On the left two possible paths connecting the same initial and final points are depicted. The path represented by the solid black line is traversed in shorter time than the dashed path, as for all b_1 values the corresponding b_2^2 is always smaller for the solid path than for the dashed one. On the right the light cone represents the states which can be reached from the initial point; on the left, the dark cone shows states from which the final point can be reached. The overlap area is where possible paths connecting the initial and the final point can be located. The fastest path is the one with the smallest b_2^2 possible, here depicted by the solid line. This path consists only of boundary arcs.

was minimized under the constraints given by the equations of motion (5)–(7). The control is limited only by $\omega_\mathrm{f} \leq \omega(t) \leq \omega_\mathrm{i}$ without any continuity requirements as in [28]. The process starts at the initial time t_i in a given equilibrium state $\vec{b}_\mathrm{i}$ and finishes at the yet unknown final time t_f in a given equilibrium state $\vec{b}_\mathrm{f}$. For this problem the control Hamiltonian H_C turns out to be linear in ω, which up to so-called singular arcs requires a bang-bang control consisting of arcs with constant ω. Due to the existence of the Casimir companion X, a process can be described by a curve in the (b_1, b_2)-plane. b_3 can be regained at any instant from

$$b_3 = \hat{b}_3(b_1, b_2) = \pm\sqrt{X - (b_1^2 + b_2^2)}. \tag{17}$$

In the (b_1, b_2)-plane arcs with constant ω are represented by lines with constant slope due to

$$\frac{\mathrm{d}b_2}{\mathrm{d}b_1} = -\omega/j. \tag{18}$$

Also the total time for a process can be obtained from (5), (18), and the bang-bang nature of the optimal path by using

$$\frac{\mathrm{d}b_1}{\mathrm{d}t} = 2jb_3 \Rightarrow \tau = \frac{1}{2j} \int_{b_{1,\mathrm{i}}}^{b_{1,\mathrm{f}}} \frac{\mathrm{d}b_1}{\sqrt{X - (b_1^2 + b_2^2)}}. \tag{19}$$

In a fashion similar to [46] the time-optimal evolution can be seen geometrically by choosing paths which, for any given value of b_1, minimize the value of b_2^2 along the path.

In fig. 1 in the left part the graphical consequence of that fact is shown. The solid line represents a process path which takes less time than the dashed one. In our

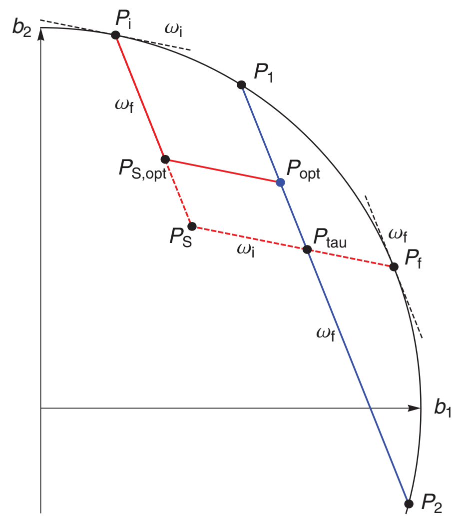

Fig. 2: (Colour on-line) This graph depicts the overall setting for determining the finite-time availability. A detailed description is given in the text.

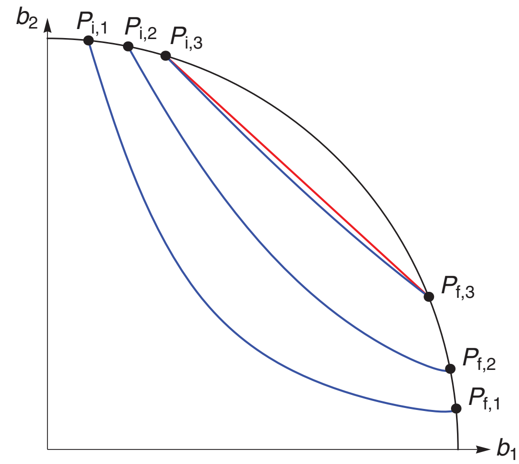

Fig. 3: (Colour on-line) The figure shows the location of those states $P_{\rm opt}$ which are reached by time-optimal processes with energies E between $E(\vec{b_{\rm f}}, \omega_{\rm f}) < E < E(\vec{b_{\rm i}}, \omega_{\rm i})$ for the three different $(\omega_{\rm i}, \omega_{\rm f})$ combinations used in fig. 4.

figures and numerical calculations ω is given in units of j, while in our equations we keep the j-dependence. In fig. 1 in the right part the graphical consequence is that the optimal path consists of boundary arcs.

The time-optimal path for connecting two equilibrium states characterized by $\omega_{\rm i}$ and $\omega_{\rm f}$ is now readily constructed as shown in fig. 2. The constraints on ω force the initial and final states to be within the first quadrant. The best path (red solid and red dashed lines) is to start in the initial state at $P_{\rm i}$ by switching from $\omega_{\rm i}$ to the largest magnetic-field strength $\omega_{\rm f}$. After waiting the time τ_1 one switches at the switch-point $P_{\rm S}$ to $\omega_{\rm i}$, waits the time τ_2, and finally switches at $P_{\rm f}$ to $\omega_{\rm f}$ thus reaching the final equilibrium state.

If the time available for the process $t_{\rm P}$ is shorter than $t_{\rm FEAT}$, we cannot reach the final equilibrium state $P_{\rm f}$. As described above, we then ask for the minimum time path to extract a given amount of work

$$E(\vec{b_{\rm i}}, \omega_{\rm i}) - E < A_{\rm FEAT}. \tag{20}$$

It follows from eq. (14) that a given value of E will be obtained for any state $\vec{b}$ on the line $jb_2 + \omega_{\rm f} b_1 = E$ shown in blue in the figure. It thus remains to find the state (b_1, b_2) on this line which can be reached in minimum time from our initial state $\vec{b_{\rm i}}$ using a bang-bang control. The choice of such an optimal state and the corresponding control which must again be of the two-arc form is shown in fig. 2 as the solid red line terminating at $P_{\rm opt}$ for one particular value of the final energy E. The numerical optimization requires a line search which calculates the times for the arcs using (19).

In fig. 3 the resulting locations of the $P_{\rm opt}$'s are shown for three different combinations of $(\omega_{\rm i}, \omega_{\rm f})$ as blue lines. The values are $(\omega_{\rm i,1}, \omega_{\rm f,1}) = (0.1, 10)$, $(\omega_{\rm i,2}, \omega_{\rm f,2}) = (0.2, 5)$, and $(\omega_{\rm i,3}, \omega_{\rm f,3}) = (0.3, 2.5)$. An interesting feature of the locations is that the closer the initial and final equilibrium states are the more this line approaches the straight line connecting those states, shown in red in fig. 3.

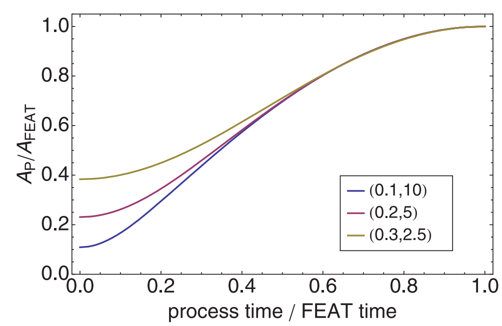

Fig. 4: (Colour on-line) The rescaled availabilty is shown as a function of the rescaled process time for the three different $(\omega_{\rm i}, \omega_{\rm f})$ combinations shown in the legend. Note how close the curves are to each other for values $t_{\rm P}/t_{\rm FEAT} \gtrsim 0.4$.

The relation between $t_{\rm P}$ and $A_{\rm P}$ is shown in fig. 4. For that figure we normalized the times by using the ratio $t_{\rm P}/t_{\rm FEAT}$. We also rescaled $A_{\rm P}$ by measuring it in units of $A_{\rm FEAT}$. The graph shows the results for the same three $(\omega_{\rm i}, \omega_{\rm f})$ combinations presented in fig. 3. One immediately notes that for times $t_{\rm P}/t_{\rm FEAT}$ close to one, *i.e.* in the vicinity of the reversible time, all three curves are very close together. This general behavior starts already for times as low as $t_{\rm P}/t_{\rm FEAT} = 0.4$ thus leading to a wide range of times, where the results deviate from each other by only a few percent. For short times the ratio $A_{\rm P}/A_{\rm FEAT}$ has of course to approach the work available from the sudden ($t_{\rm P} = 0$) value set by the initial and final frequency through

$$\frac{A_{\mathrm{P}}}{A_{\mathrm{FEAT}}} = \frac{1 + \Omega_{\mathrm{f}}/\Omega_{\mathrm{i}}}{1 + \omega_{\mathrm{f}}/\omega_{\mathrm{i}}}. \tag{21}$$

Discussion. – The extraction of work from quantum systems is a fascinating area of research of far-reaching importance. In the literature, for instance the consequences of the quantum nature of working fluids in "quantum refrigerators" [16], the efficiencies of quantum engines [12,14], or the work extraction using cyclic processes [13] have been discussed. In the present work we put our focus on a non-cyclic reversible work extraction process. Even though the processes considered proceed in *finite time*, they remain reversible at all times. Such processes can then be used to define the *finite-time availability* for quantum systems.

In particular we calculated the availability for a pair of interacting spin-$\frac{1}{2}$ systems for times shorter than the FEAT time t_{FEAT} by controlling the frequency which must remain between two given positive values ω_{i} and ω_{f}. Starting at a thermal equilibrium state at ω_{i}, processes with process times greater than t_{FEAT} allow the extraction of work equal to the availability of the initial state with respect to a thermal reservoir whose temperature equals the temperature of the final state. Furthermore, this temperature is the lowest we can achieve by the change of frequency ω from its initial to its final value. Going any faster while making the same change in ω extracts less work, and leaves the system in a non-equilibrium state. That state possesses a remnant availability with respect to the equilibrium state at ω_{f}. If and how this availability can be extracted, depends on the further fate of the system. If the system at ω_{f} is put into contact with a heat bath, then the excited parasitic oscillations will decay; the quantum friction turns the potential losses into real losses.

In the present work we expanded on the notion of availability as generalized in [16]: how much work can one extract from the change of an external parameter of a system in minimum time as a prelude to its contact with a thermal bath. Both the spin-$\frac{1}{2}$ systems considered here and the harmonic oscillators considered in [16] are able to reach a thermal equilibrium state at a minimum temperature through an adiabatic process. For these two systems, the maximum work that could be extracted given sufficient time is equal to the classic availability of Gibbs with respect to a thermal reservoir at the final temperature. These systems (and their FEAT processes) are special: for these two systems quantum adiabaticity coincides with thermodynamic adiabaticity. This is not the case for most systems; doing work changing the energy levels without changing the populations cannot in general lead to a thermal population at another temperature. Exploring the nature of the maximum work we can extract from a change in a parameter for a less special system remains an important open problem.

REFERENCES

[1] Gibbs J. W., *Trans. Conn. Acad. Arts Sci.*, **2** (1873) 382.
[2] Keenan J. H., *Br. J. Appl. Phys.*, **2** (1951) 183.
[3] Salamon P. and Berry R. S., *Phys. Rev. Lett.*, **51** (1983) 1127.
[4] Sivak D. A. and Crooks G. E., *Phys. Rev. Lett.*, **108** (2012) 190602.
[5] Schlögl F., *Z. Phys. B*, **59** (1985) 449.
[6] Izumida Y. and Okuda K., *Phys. Rev. Lett.*, **112** (2014) 180603.
[7] Badescu V., *J. Non-Equilib. Thermodyn.*, **38** (2013) 313.
[8] Madadi V., Tavakoli T. and Rahimi A., *J. Non-Equilib. Thermodyn.*, **39** (2014) 183.
[9] Lieb E. H. and Yngvason J., *Proc. R. Soc. London, Ser. A*, **469** (2013) 20130408.
[10] Deffner S. and Lutz E., *Phys. Rev. Lett.*, **107** (2011) 140404.
[11] Allahverdyan A. E. and Nieuwenhuizen T. M., *Phys. Rev. Lett.*, **85** (2000) 1799.
[12] Allahverdyan A. E., Johal R. S. and Mahler G., *Phys. Rev. E*, **77** (2008) 041118.
[13] Allahverdyan A. E. and Hovhannisyan K. V., *EPL*, **95** (2011) 60004.
[14] Allahverdyan A. E., Hovhannisyan K. V., Melkikh A. V. and Gevorkian S. G., *Phys. Rev. Lett.*, **111** (2013) 050601.
[15] Sivak D. A. and Crooks G. E., *Phys. Rev. Lett.*, **108** (2012) 150601.
[16] Salamon P., Hoffmann K. H., Rezek Y. and Kosloff R., *Phys. Chem. Chem. Phys.*, **11** (2009) 1027.
[17] Feldmann T., Geva E., Kosloff R. and Salamon P., *Am. J. Phys.*, **64** (1996) 485.
[18] Kosloff R. and Feldmann T., *Phys. Rev. E*, **82** (2010) 011134.
[19] Boldt F., Hoffmann K. H., Salamon P. and Kosloff R., *EPL*, **99** (2012) 40002.
[20] Rabitz H., de Vivie-Riedle R., Motzkus M. and Kompa K., *Science*, **288** (2000) 824.
[21] Shapiro M. and Brumer P., *Rep. Prog. Phys.*, **66** (2003) 859.
[22] Herek J. L., Wohlleben W., Cogdell R. J., Zeidler D. and Motzkus M., *Nature*, **417** (2002) 533.
[23] Boscain U. and Mason P., *J. Math. Phys.*, **47** (2006) 062101.
[24] Kosloff R., Rice S. A., Gaspard P., Tersigni S. and Tannor D. J., *Chem. Phys.*, **139** (1989) 201.
[25] Khaneja N., Brockett R. and Flaser S. J., *Phys. Rev. A*, **63** (2001) 032308.
[26] Ciampini D., Morsch O. and Arimondo E., *Int. J. Quantum Inf.*, **9** (2011) 139.
[27] Rezek Y., Salamon P., Hoffmann K. H. and Kosloff R., *EPL*, **85** (2009) 30008.
[28] Hoffmann K. H., Salamon P., Rezek Y. and Kosloff R., *EPL*, **96** (2011) 60015.
[29] Demirplak M. and Rice S. A., *J. Phys. Chem. A*, **107** (2003) 9937.
[30] Demirplak M. and Rice S. A., *J. Phys. Chem. B*, **109** (2005) 6838.
[31] Demirplak M. and Rice S. A., *J. Chem. Phys.*, **129** (2008) 154111.

[32] Chen X., Ruschhaupt A., Schmidt S., del Campo A., Guery-Odelin D. and Muga J. G., *Phys. Rev. Lett.*, **104** (2010) 063002.
[33] Muga J. G., Chen X., Ibez S., Lizuain I. and Ruschhaupt A., *J. Phys. B: At. Mol. Opt. Phys.*, **43** (2010) 085509.
[34] Stefanatos D., Ruths J. and Li J.-S., *Phys. Rev. A*, **82** (2010) 063422.
[35] del Campo A., *Phys. Rev. A*, **84** (2011) 031606(R).
[36] Torrontegui E., Ibez S., Chen X., Ruschhaupt A., Gury-Odelin D. and Muga J. G., *Phys. Rev. A*, **83** (2011) 013415.
[37] Campo A. d. and Boshier M. G., *Sci. Rep.*, **2** (2012) 648.
[38] Andresen B., Rubin M. H. and Berry R. S., *J. Phys. Chem.*, **87** (1983) 2704.
[39] Andresen B., Berry R. S., Ondrechen M. J. and Salamon P., *Acc. Chem. Res.*, **17** (1984) 266.
[40] Sieniutycz S., *Phys. Rev. E*, **56** (1997) 5051.
[41] Sieniutycz S. and von Spakovsky M. R., *Energy Convers.*, **39** (1998) 1423.
[42] Hoffmann K. H., Andresen B. and Salamon P., *Phys. Rev. A*, **39** (1989) 3618.
[43] Feldmann T. and Kosloff R., *Phys. Rev. E*, **68** (2003) 016101.
[44] Boldt F., Nulton J. D., Andresen B., Salamon P. and Hoffmann K. H., *Phys. Rev. A*, **87** (2013) 022116.
[45] Macki J. and Strauss A., *Introduction to Optimal Control Theory* (Springer) 1982.
[46] Tsirlin A. M., Salamon P. and Hoffmann K. H., *Automat. Remote Control*, **72** (2011) 1627.