Heat engines in finite time governed by master equations

Tova Feldmann, Eitan Geva, and Ronnie Kosloff
Department of Physical Chemistry, The Hebrew University, Jerusalem 91904, Israel

Peter Salamon
Department of Mathematical Sciences, San Diego State University, San Diego, California 92182

(Received 10 April 1995; accepted 29 June 1995)

A simple example of a four-stroke engine operated in finite-time is analyzed. The working medium consists of noninteracting two-level systems or harmonic oscillators. The cycle of operation is analogous to a four-stroke *Otto* cycle. The only source of irreversibility is due to the finite rate of heat transfer between the working medium and the cold and hot baths. The dynamics of the working medium is governed by a master equation. The engine is shown to settle to a stable limit cycle for *given* contact periods with the hot and cold baths. The operation of the engine is analyzed subject to a fixed cycle time. The time allocation between the hot and cold branches that maximizes the work output is considered. Analytical results are obtained when the relaxation is very slow, very fast, or when the relaxation rates along the hot and cold branches are equal. Numerical results are presented for the general case. A maximization of the power with respect to the cycle time leads to a finite optimal cycling frequency provided the adiabatic branches are allotted finite durations. © *1996 American Association of Physics Teachers.*

I. INTRODUCTION

The traditional bounds imposed on the performance of energy conversion processes correspond to the reversible limit. The classic example of such a bound is the Carnot efficiency. Note however that reversible processes involving any type of transport require infinite time.[1] Infinite duration is not tolerable in real applications; hence the motivation for studying limits to the finite rate performance of engines and similar devices. The finite time performance of engines has been intensively studied in recent years, thereby yielding many interesting new results[2–17] which form the core of the new field of finite time thermodynamics. The goal of this field is to seek bounds on the performance of thermodynamic processes operating in finite time.

To define a finite time thermodynamics problem, traditional thermodynamics must be augmented by a dynamical theory. In most of the previous studies, the dynamics was provided by phenomenological rate equations. A typical example is Newton's law of cooling, which postulates that the heat flow across an interface is proportional to the temperature difference. It has been shown that the specific dynamical law has a considerable effect upon the operation of the engine.[13,14] This fact supplies our motivation to examine a rather different dynamical law at the mesoscopic level of description.

The literature contains many previous analyses of finite time thermodynamic heat engines at the macroscopic level. A more recent analysis at the quantum mechanical level treated the finite time thermodynamics of heat transfer via quantum master equations.[18–21] These equations can be derived from the underlying microscopic theory of the system and the coupled reservoirs.[22–24] The situation is considerably simplified if the off-diagonal terms of the density matrix are eliminated, leading to an analysis based only on the energy level populations. In such a case the Pauli master equation can be used, and this mesoscopic approach is the one adopted here.[25–27]

Our engine is similar to the spin-1/2 engine of Ref. 19, and the harmonic oscillator engine of Ref. 20. However, it corresponds to a different mode of operation and the optimization procedure is of a different type. The dynamical model is based on the probability distribution of occupancy of the energy levels $\{p_n\}$ evolving according to a Pauli master equation. Quantum interference effects are unimportant in this case.[19] Another considerable simplification of the present mode of operation over previous ones[18–21] is that thermal relaxation occurs under the influence of a *constant* external field. It therefore avoids the difficulty of considering a master equation for systems subject to *time dependent* fields.[28] The models analyzed obey canonical invariance,[29] which allows the internal temperature of the working medium to remain well defined. Having a well-defined temperature simplifies the interpretation although it is not necessary for the analysis of operation. Such analysis could be performed directly at the level of the probability distribution $\{p_n\}$.

The paper is organized in the following manner. In Sec. II we consider the basic components of the engine, i.e., the working medium, cycle of operation and the dynamics induced by the master equations. The finite time thermodynamic analysis of the engine is presented in Sec. III, where the work output is maximized with respect to the time allocation. It is possible to push the analysis through analytically for the limits of slow and fast relaxation, and in the case of equal relaxation rates. The general case is analyzed numerically. The results are discussed and the main conclusions are pointed out in Sec. IV.

II. THE ENGINE

For our present purposes, an engine is characterized by its working medium, the cycle of operation, and the dynamics that specify how the working medium traverses the cycle. In the present section we introduce these three constituents for our engine.

A. The working medium

The working medium consists of either many noninteracting two-level systems (TLSs) or of many noninteracting harmonic oscillators (HOs). For simplicity we carry out

the analysis for the former and show in the Appendix how the latter case proceeds completely analogously.

For the sake of concreteness it is useful to envision the TLSs as spin-1/2 systems. The lack of spin–spin interactions allows us to treat the energy exchange between the working medium and the surroundings in terms of a single TLS. The energy exchange for the working medium as a whole is then obtained by multiplying the energy exchange for a single spin by the total number of spins within the working medium. The state of the system is then defined by the occupation probabilities P_+ and P_- corresponding to the energies $\frac{1}{2}\omega$ and $-\frac{1}{2}\omega$ where ω is the energy gap between the two levels. The average energy per spin is given by

$$E=P_+\cdot(\tfrac{1}{2}\omega)+P_-\cdot(-\tfrac{1}{2}\omega). \tag{2.1}$$

The polarization, S, is defined by

$$S=\tfrac{1}{2}(P_+-P_-), \tag{2.2}$$

and thus the energy can be written as $E=\omega S$.

In the language of magnetic resonance, $\omega=-\gamma B_z$, where γ is the gyromagnetic ratio and B_z is the longitudinal component of the magnetic field (there is no transverse driving field). Furthermore, S corresponds to the magnetization per spin along the direction of the magnetic field: $S=\langle S_z\rangle$.[24]

The energy of the working medium may change either by population transfer from one level to the other or by changing the energy gap between the two levels. The former corresponds to changing S, while the latter corresponds to changing ω. Hence,

$$dE=S\,d\omega+\omega\,dS. \tag{2.3}$$

In the case of spin-1/2 systems, a change in S is associated with "spin–lattice relaxation," whereas ω can vary by altering the magnitude of the longitudinal magnetic field. These two distinct agents for energy exchange with the environment may now be cast in terms of the thermodynamic heat and work by identifying Eq. (2.3) with the first law of thermodynamics:

$$dE=D\mathscr{W}+D\mathscr{Q}, \tag{2.4}$$

where $D\mathscr{W}$ is the work differential and $D\mathscr{Q}$ is the heat differential. Population transfer is the microscopic manifestation of heat exchange, whereas energy change caused by varying an external field is associated with work.[19,30] Hence,

$$D\mathscr{W}\equiv S\,d\omega;\quad D\mathscr{Q}\equiv\omega\,dS. \tag{2.5}$$

Note that our convention is such that $D\mathscr{Q}$ is positive if heat flows into the working medium and $D\mathscr{W}$ is positive if work is performed on the working medium.

Finally, in the TLS, the internal temperature, T', is always defined via the relation

$$S=-\frac{1}{2}\tanh\left(\frac{\omega}{2k_BT'}\right). \tag{2.6}$$

Equation (2.6) reflects the fact that if the working medium is coupled with a bath of temperature T', no heat will flow between the two systems [cf. Eq. (2.12)]. Note that S is negative as long as the temperature is kept positive. There is a similar relation between temperature and population for the harmonic oscillator [see Eq. (A8)].

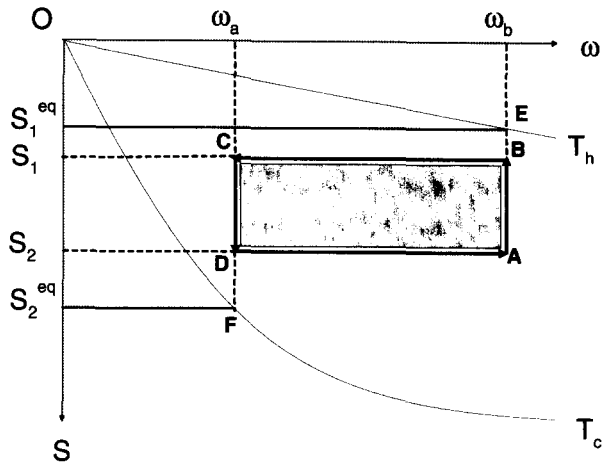

Fig. 1. A schematic view of the cycle of operation ($A\rightarrow B\rightarrow C\rightarrow D\rightarrow A$) in the ($\omega$,$S$) plane. The working medium is coupled to a hot bath of temperature T_h along the branch $A\rightarrow B$, and to a cold bath of temperature T_c along the branch $C\rightarrow D$. The branches $B\rightarrow C$ and $D\rightarrow A$ are adiabatic. The vertices of the cycle are defined by the extreme polarizations S_1 and S_2 and external fields ω_a and ω_b. Also indicated are the *reversible* isotherms at temperatures T_c and T_h. The relaxation along the $A\rightarrow B$ branch drives the system toward the equilibrium state at point E, and the relaxation along the $C\rightarrow D$ branch drives the system toward the equilibrium state at point F. The points E and F are associated with the polarizations S_1^{eq} and S_2^{eq} which would be realized in equilibrium with the baths at T_h and T_c, respectively.

B. The cycle of operation

The cycle of operation in the (S,ω) plane is schematically shown in Fig. 1. This is an *irreversible* four-stroke cycle, consisting of two "thermal branches" ($A\rightarrow B$ and $C\rightarrow D$), connected by two adiabats ($B\rightarrow C$ and $D\rightarrow A$). The direction of motion along the cycle is chosen such that net work is produced in each cycle. The work and heat transfer along each branch are given in Table 1. We next consider each of the four branches in some detail.

On the first (thermal) branch, $A\rightarrow B$, the working medium is coupled to a hot bath of temperature T_h while the energy gap is kept fixed at the value ω_b. The initial state (A) is not in thermal equilibrium with the hot bath. Thermal equilibrium in this case corresponds to point E, lying on the hot isotherm, where $S=S_1^{eq}$ (cf. Fig. 1). This means that the internal temperature of the working medium along the branch $A\rightarrow B$ is always lower than the temperature of the hot bath, i.e., $T'<T_h$ along this branch. Hence, population transfer is induced from the lower level to the upper one, thereby diminishing the population difference between the two levels and making S less negative. Allowing this process to continue for a sufficiently long time would result in thermal equilibration with the bath. However, in our case the working medium is coupled to the hot bath for a *finite* period of time, τ_h. Hence, the final state (B) does not correspond to thermal

Table I. Work and heat exchange along the different branches.

Branch	Work	Heat
$A\rightarrow B$	0	$\mathscr{Q}_h=\omega_b(S_1-S_2)>0$
$B\rightarrow C$	$S_1(\omega_a-\omega_b)>0$	0
$C\rightarrow D$	0	$\mathscr{Q}_c=\omega_a(S_2-S_1)<0$
$D\rightarrow A$	$S_2(\omega_b-\omega_a)<0$	0

equilibrium; namely S_1 is still more negative than S_1^{eq} and the internal temperature of the working medium is still cold relative to T_h. Since ω is kept fixed along this branch, no work is done, and the only form of energy transfer is the heat $\omega_b(S_1-S_2)$ absorbed by the working medium from the hot bath (cf. Table I).

On the second (adiabatic) branch, $B\rightarrow C$, the working medium is decoupled from the hot bath and the energy gap is varied from ω_b to ω_a. Adiabaticity dictates that no change in probabilities should occur, hence S remains constant and equal to its initial value, S_1. The faster this branch is, the more time we are able to allocate to heat transfer. Except for the discussion in Sec. III E, we take the adiabatic branches to be infinitely fast, i.e., of a negligible duration relative to the thermal branches.[19,20] Hence, no heat transfer is involved, and the only form of energy exchange is the work $(\omega_a-\omega_b)S_1$ done on the working medium by the external field (cf. Table I). For a constant S, Eq. (2.6) shows that the change in temperature has the same sign as the change in ω. Thus, the internal temperature of the working medium at the final state (C) is lower than its initial temperature was at (B).

The third (thermal) branch, $C\rightarrow D$, is similar to the first. The working medium is now coupled to a cold bath of temperature T_c and the energy gap is kept fixed at the value ω_a. The initial state (C) corresponds to an internal temperature *hotter* than T_c. Population transfer from the upper to the lower level is induced, thereby restoring the population difference between the two levels and making S more negative. The coupling with the cold bath is maintained until the original value of $S=S_2$, is restored. The finite time period associated with this branch is denoted τ_c. The only form of energy exchange is the heat $\omega_a(S_2-S_1)$ flowing out of the working medium and into the cold bath (cf. Table I).

The fourth (adiabatic) branch, $D\rightarrow A$, closes the cycle, and is similar to the second branch. The working medium is decoupled from the cold bath, and the energy gap is restored to its original value, ω_b, whereas the populations in the two levels remain fixed at $S=S_2$. The time duration of this branch relative to the thermal branches is neglected as for the second branch. This branch involves no heat transfer, and the only form of energy exchange is the work $(\omega_b-\omega_a)S_2$ done by the working medium on the surroundings (cf. Table I). The internal temperature of the working medium at the final state (A) is higher than it was at state (D).

The only reversible cycle for an environment containing only two baths at fixed temperatures is the Carnot cycle,[19] in which the adiabats are connected by isotherms rather than by branches with fixed energy gap ω. Hence, the cycle described above cannot run reversibly, and the only "reversible limit" is to spend the entire time τ at equilibrium with one of the two heat baths, i.e., to do nothing. The cycle we describe may be considered to be the TLS analog of the Otto cycle,[19] which is usually discussed in terms of volume work. Recall that in the Otto cycle, the working medium traverses two isochores and two adiabats. The external field in our case is the energy gap (ω) rather than the volume. To run the Otto cycle (or our engine) reversibly, a continuum of heat baths would be required with temperatures that range from T_c to T_h.[1]

C. Dynamics of the working medium

The state of the working medium is completely characterized by the population difference, S, and the energy gap, ω. On the adiabatic branch the polarization is constant since population transfer can only be induced by the bath. Constant population implies constant entropy, and therefore the adiabatic branches are reversible. For most of the discussion below, we will assume that it is possible to perform these adiabatic changes in the energy gap ω instantaneously. In Sec. III E, however, we will briefly explore the effect of finite duration for these branches.

The dynamics along the heat exchange branches needs to be specified in detail. Recall that along these branches ω is constant. Accordingly, we will focus on the dynamics of S, a TLS coupled to a heat bath.

We describe the dynamics of the populations at the two levels, P_+ and P_-, via a master equation

$$\begin{cases} \dfrac{dP_+}{dt}=-k_\downarrow P_+ + k_\uparrow P_-, \\ \dfrac{dP_-}{dt}=k_\downarrow P_+ - k_\uparrow P_-, \end{cases} \tag{2.7}$$

where $k_\downarrow$ and $k_\uparrow$ are the respective transition rates from the upper to the lower level and vice versa. As $t\rightarrow\infty$, thermal equilibrium with the bath of temperature T should be obtained, corresponding to a Boltzmann distribution. In this limit the derivatives in Eq. (2.7) vanish and

$$k_\downarrow P_+^{eq}=k_\uparrow P_-^{eq}. \tag{2.8}$$

This is the familiar condition of detailed balance giving

$$\frac{k_\downarrow}{k_\uparrow}=e^{\omega/k_BT}, \tag{2.9}$$

where ω corresponds to the (fixed) energy gap between the two levels. Using the definition of S [Eq. (2.2)] and conservation of probabilities $(P_++P_-=1)$, the equation of motion for S is obtained from Eq. (2.7) as

$$\frac{dS}{dt}=-\Gamma(S-S^{eq}), \tag{2.10}$$

where

$$\Gamma=k_\downarrow+k_\uparrow, \tag{2.11}$$

and

$$S^{eq}=-\frac{1}{2}\frac{k_\downarrow-k_\uparrow}{k_\downarrow+k_\uparrow}=-\frac{1}{2}\tanh\left(\frac{\omega}{2k_BT}\right). \tag{2.12}$$

The last equality in Eq. (2.12) is obtained by utilizing detailed balance [Eq. (2.9)]. Note that for a spin-1/2 system, Γ is usually denoted by $1/\tau_1$, were τ_1 is the spin–lattice, or longitudinal, relaxation time constant.[22] Similar equations are found for the harmonic oscillator in the appendix where S in Eq. (2.10) is replaced by $\langle n\rangle$ [see Eq. (A7)].

The general solution of Eq. (2.10) is straightforward:

$$S(t)=S^{eq}+(S(0)-S^{eq})e^{-\Gamma t}. \tag{2.13}$$

Employing Eq. (2.13) along the hot branch $(A\rightarrow B$ in Fig. 1) we obtain

$$S_1=S_1^{eq}+(S_2-S_1^{eq})e^{-\Gamma_h\tau_h}. \tag{2.14}$$

Similarly, employing Eq. (2.13) along the cold branch $(C\rightarrow D$ in Fig. 1) we obtain

$$S_2=S_2^{eq}+(S_1-S_2^{eq})e^{-\Gamma_c\tau_c}. \tag{2.15}$$

Note that Γ_h and Γ_c are the values of the relaxation rate constant Γ for the hot and cold baths respectively. Also, S_1^{eq} and S_2^{eq} correspond to different temperatures and energy gaps:

$$S_1^{eq}=-\frac{1}{2}\tanh\left(\frac{\omega_b}{2k_BT_h}\right), \tag{2.16}$$

$$S_2^{eq}=-\frac{1}{2}\tanh\left(\frac{\omega_a}{2k_BT_c}\right). \tag{2.17}$$

The central quantity of interest for the analyses in this paper is the polarization difference S_1-S_2 (cf. Sec. III). The latter can be obtained from Eq. (2.14) and (2.15) as

$$S_1-S_2=(S_1^{eq}-S_2^{eq})\frac{(1-e^{-\Gamma_h\tau_h})(1-e^{-\Gamma_c\tau_c})}{1-e^{-\Gamma_h\tau_h}e^{-\Gamma_c\tau_c}}. \tag{2.18}$$

Defining new variables:

$$x=e^{-\Gamma_c\tau_c},\quad y=e^{-\Gamma_h\tau_h}, \tag{2.19}$$

S_1-S_2 may be written as

$$S_1-S_2=(S_1^{eq}-S_2^{eq})\cdot F(x,y), \tag{2.20}$$

where

$$F(x,y)=\frac{(1-x)(1-y)}{1-xy}. \tag{2.21}$$

As we shall see, the optimizations discussed in the next section reduce to the maximization of $F(x,y)$ with respect to x and y, subject to the constraint of a given cycle duration.

$$\tau=-\frac{1}{\Gamma_c}\ln(x)-\frac{1}{\Gamma_h}\ln(y). \tag{2.22}$$

D. The limit cycle

An interesting feature of this engine is that regardless of its initial polarization, it will settle to a limit cycle imposed by the constraints of operation. This limit cycle is identical to the one described in Sec. II B.

Consider the following parameters as fixed: T_h, T_c, ω_a, ω_b, Γ_h, Γ_c and also τ_h,τ_c. Let the initial polarization $S^{(0)}$ reside *anywhere* on the hot branch ($\omega=\omega_b$, cf. Fig. 1). According to Eq. (2.13), the polarization $S^{(1)}$ after the contact period τ_h with the hot bath becomes

$$S^{(1)}=B+S^{(0)}y, \tag{2.23}$$

where $B=S_1^{eq}(1-y)$ [the parameters x and y are defined by Eqs. (2.19)]. Adiabatically moving to the cold branch keeps the polarization constant. The polarization $S^{(2)}$ at the end of the cold branch will then be:

$$S^{(2)}=A+S^{(1)}x=A+Bx+S^{(0)}yx, \tag{2.24}$$

where $A=S_2^{eq}(1-x)$. The next step is adiabatic, changing ω back to its initial value ω_b and keeping $S^{(2)}$ constant. Note that $S^{(2)}$ does not close the cycle ($S^{(2)}\neq S^{(0)}$) (see Fig. 2).

By iteration the polarization at the beginning of the hot branch after n loops becomes:

$$S^{(2n)}=S^{(0)}x^ny^n+(A+Bx)\sum_{i=0}^{n-1}x^iy^i. \tag{2.25}$$

x and y are always smaller than one, cf. (2.19) hence in the limit $n\to\infty$, the first term on the rhs of Eq. (2.25) vanishes,

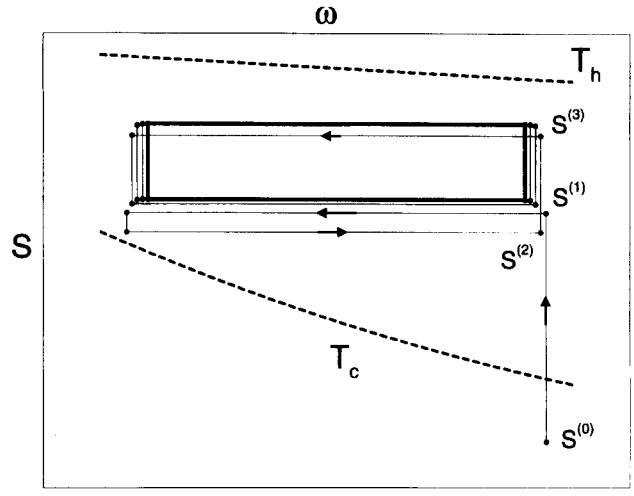

Fig. 2. The approach to the limit cycle. The operation of the engine is initiated at the polarization, $S^{(0)}$. It is then put in contact with the hot bath for a period τ_h leading to $S^{(1)}$. The working medium is adiabatically shifted to $\omega=\omega_a$. It is then put in contact with the cold bath for a period τ_c, leading to $S^{(2)}$. The working medium is then adiabatically shifted back to $\omega=\omega_b$. This procedure is repeated, eventually leading to the limit cycle (heavy line). For clarity, the thermal branches are successively shifted. In reality, they all lie on two vertical lines at ω_a and ω_b.

while the second term is an infinite geometric series leading to

$$S^{(2n\to\infty)}=\frac{(A+Bx)}{1-xy}=\frac{S_1^{eq}(1-y)x+S_2^{eq}(1-x)}{1-xy}, \tag{2.26}$$

which is the value of S_2 for which the cycle is closed as obtained from Eqs. (2.14) and (2.15). Similarly, $S^{(2n+1\to\infty)}=S_1$. Hence, the cycle of operation described in Sec. II B is indeed the limit cycle for given τ_c and τ_h.

III. FINITE TIME THERMODYNAMIC ANALYSIS

A. Constraints, controls, and objective function

An optimization problem is defined by the constraints imposed on the system, the adjustable control parameters and the quantity to be optimized, i.e., the objective function. In this subsection we define the optimization problem of interest in the present paper.

In the analysis the parameters describing the environment are kept constant. They include the bath temperatures: T_h and T_c, the two extreme energy gaps: ω_a and ω_b, and the coupling mechanism as represented by the relaxation rates: Γ_h and Γ_c. No attempt at optimization with respect to these parameters is carried out. This set of variables nicely characterizes the environment of the TLS system and leaves us with the problem of characterizing the optimal behavior of the TLS system in this setting. We therefore treat the bath temperatures, the energy gaps, and the relaxation rates as fixed.

The TLS is free then to couple to either heat reservoir and to switch its energy gap at will between ω_a and ω_b. We impose the condition that the TLS undergo a cyclic process in time τ with the four branches as described in the previous section. The only remaining degree of freedom is associated with the ability to allocate the overall time period of the cycle, τ, between the hot and cold branches, i.e., to τ_h and

τ_c. Hence, this time allocation will serve as our control. It should be noted that to each time allocation there corresponds a *different* limit cycle. The maximization of the work output corresponds to finding the limit cycle with the maximum area.

The objective function considered is the work output per cycle which is to be maximized (cf. Table I):

$$\mathscr{W}_{\text{cycle}} = \oint D\mathscr{W} = (\omega_b - \omega_a)(S_1 - S_2) > 0. \tag{3.1}$$

Note that $\mathscr{W}_{\text{cycle}}$ is defined as a positive quantity when the working medium performs net work on the external field. Since ω_a and ω_b are fixed, the quantity that we really need to maximize is the polarization difference $S_1 - S_2$, given in terms of our parameters x and y in Eqs. (2.18) and (2.20). Since ω_a, ω_b, T_h, and T_c are fixed, so are S_1^{eq} and S_2^{eq}. Finally, note that x and y are monotonic functions of τ_c and τ_h, respectively. Hence, the maximization of the work output with respect to τ_c and τ_h is equivalent to the maximization of $F(x,y)$ with respect to x and y.

It is interesting to consider at this point three other thermodynamic quantities: the efficiency, the entropy production per cycle, and the cycle averaged power. The efficiency

$$\eta = \frac{\mathscr{W}_{\text{cycle}}}{Q_h} = 1 - \frac{\omega_a}{\omega_b} \tag{3.2}$$

only depends on the constraints ω_a and ω_b and is therefore fixed for all time allocations and cycle durations. It must be smaller than the efficiency obtained from a reversible Carnot cycle operated between the same two heat baths: $\eta_{\text{Carnot}} = 1 - T_c/T_h$. This demand is equivalent to requiring that the entropy production per cycle be positive. This in turn is equivalent to the requirement that $S_2^{\text{eq}} < S_1^{\text{eq}}$.

Minimizing the entropy production (cf. Table I),

$$\Delta\mathscr{S}^u_{\text{cycle}} = -\left(\frac{Q_h}{T_h} + \frac{Q_c}{T_c}\right) = \left(\frac{\omega_a}{T_c} - \frac{\omega_b}{T_h}\right)(S_1 - S_2), \tag{3.3}$$

would yield the trivial minimal value of zero when the system does nothing, i.e., corresponding to the time allocations $\{\tau_c = 0,\ \tau_h = \tau\}$, or $\{\tau_c = \tau,\ \tau_h = 0\}$. In such a case $S_1 = S_2$, and the cycle shrinks to a line of zero area.

The cycle averaged power output is

$$\mathscr{P} = \frac{\mathscr{W}_{\text{cycle}}}{\tau}. \tag{3.4}$$

For the optimization with τ as a constraint, the maximization of $\mathscr{W}_{\text{cycle}}$ is equivalent to the maximization of power. For most of our discussion, we consider cycles with fixed τ. In Sec. III E, we briefly discuss dropping the constraint of a given τ.

One interesting and at first surprising feature of our engine is that since both the work output and the entropy production are positive constants multiplied by $S_1 - S_2$, the maximization of the former immediately implies the maximization of the latter. Thus, the objectives of maximum work output and minimum entropy production seem to be diametrically opposed in this example! This is very much in opposition to statements in Ref. 8 where it is claimed that maximum power is always equivalent to *minimum* entropy production.

We are indebted to Raj Pathria for pointing out that our "surprising feature" is explained by the fact that the efficiency is externally fixed for our problem. In fact it follows generally from the first half of Eqs. (3.2) and (3.3) that

$$\Delta\mathscr{S}^u_{\text{cycle}} = (\eta_{\text{Carnot}} - \eta)\frac{\mathscr{W}_{\text{cycle}}}{\eta T_c}. \tag{3.5}$$

Thus, provided η, T_h, and T_c are kept fixed, $\Delta\mathscr{S}^u_{\text{cycle}}$ and $\mathscr{W}_{\text{cycle}}$ are proportional with a positive constant of proportionality; maximizing one means maximizing the other.

B. Maximization of work output

We have shown that the maximization of the work output with respect to the time allocation is equivalent to maximizing $F(x,y)$ with respect to x and y, subject to the constraint $\tau_c + \tau_h = \tau$.

The Lagrangian is therefore

$$\mathscr{L}(x,y,\lambda) = F(x,y) + \lambda\left(\tau + \frac{1}{\Gamma_c}\ln(x) + \frac{1}{\Gamma_h}\ln(y)\right), \tag{3.6}$$

where λ is a Lagrange multiplier, and τ_c and τ_h are defined in terms of x and y respectively. Note that the only parameters that enter this reduced problem are the relaxation rates, Γ_c and Γ_h, and thus only these parameters can affect the optimal time allocation. Equating the partial derivatives of $\mathscr{L}(x,y,\lambda)$, with respect to x and y, to zero yields the following condition for the optimal time allocation:

$$\Gamma_c\, x(1-y)^2 = \Gamma_h y(1-x)^2. \tag{3.7}$$

Equation (3.7), supplemented by the constraint $\tau = \tau_c + \tau_h$, cannot be solved in closed form for the general case. We therefore proceed by examining certain interesting special cases and limits of this equation followed by numerical optimization of the time allocation in the general case.

C. Special cases and limits

1. Equal relaxation rates

In this case $\Gamma_c = \Gamma_h = \Gamma$. Hence, $y = \exp(-\Gamma\tau)/x$. Implementing this equality into Eq. (3.7) reduces it to

$$x^2 = e^{-\Gamma\tau}, \tag{3.8}$$

which implies that the optimal time allocation is

$$\tau_c = \tau_h = \tau/2. \tag{3.9}$$

2. Limit of fast relaxation

In this limit $\Gamma_c\tau_c,\ \Gamma_h\tau_h \gg 1$. It could equivalently be characterized as the long time limit. Equation (3.7) then reduces to

$$\Gamma_c\, x = \Gamma_h y. \tag{3.10}$$

Utilizing the constraint $\tau = \tau_c + \tau_h$ one obtains for the optimal time allocation:

$$\tau_c^{\text{opt}} = \frac{1}{\Gamma_c + \Gamma_h}\left[\Gamma_h\tau + \ln\left(\frac{\Gamma_c}{\Gamma_h}\right)\right] \approx \frac{\Gamma_h\tau}{\Gamma_c + \Gamma_h}, \tag{3.11}$$

$$\tau_h^{\text{opt}} = \frac{1}{\Gamma_c + \Gamma_h}\left[\Gamma_c\tau + \ln\left(\frac{\Gamma_h}{\Gamma_c}\right)\right] \approx \frac{\Gamma_c\tau}{\Gamma_c + \Gamma_h}. \tag{3.12}$$

The optimal time ratio in this case is given by

$$\frac{\tau_c^{\text{opt}}}{\tau_h^{\text{opt}}} = \frac{\Gamma_h}{\Gamma_c}. \tag{3.13}$$

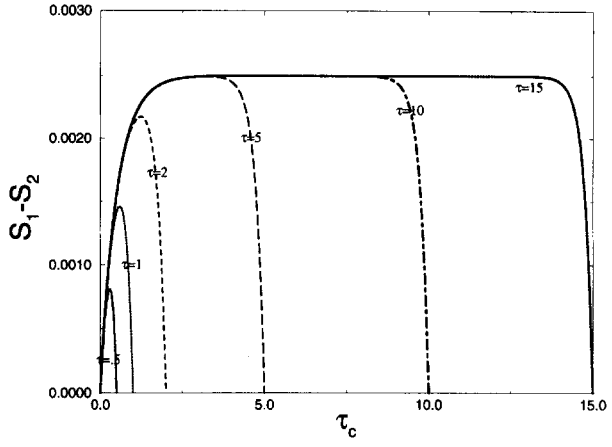

Fig. 3. The polarization difference S_1-S_2 vs the contact time with the cold branch, τ_c, for fixed Γ_c and Γ_h. $\Gamma_c=1.0$, $\Gamma_h=2.0$, $\omega_b/\omega_a=0.25$, $T_c/T_h=0.2$, for $\tau=0.5$, 1, 2, 5, 10, and 15.

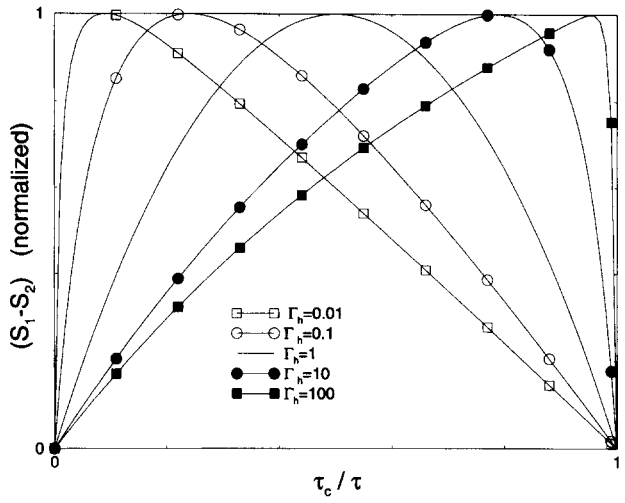

Fig. 4. The normalized polarization difference vs the relative contact time with the cold bath, τ_c/τ. All plots correspond to $\Gamma_c=1/\tau$ and various values of Γ_h (in units of $1/\tau$).

3. *Limit of slow relaxation*

In this limit $\Gamma_c\tau_c$, $\Gamma_h\tau_h \ll 1$. It could equivalently be characterized as the short time limit. Equation (3.7) then reduces to

$$\Gamma_h\tau_h^2=\Gamma_c\tau_c^2. \tag{3.14}$$

The optimal time allocation therefore becomes:

$$\frac{\tau_c^{\mathrm{opt}}}{\tau_h^{\mathrm{opt}}}=\sqrt{\frac{\Gamma_h}{\Gamma_c}}. \tag{3.15}$$

It is interesting to compare the optimal time ratios in the two extreme limits of slow and fast relaxation, Eqs. (3.13) and (3.15). Both depend solely on the ratio Γ_h/Γ_c, with and without a square root. Hence, as expected, the optimal strategy allocates more time to the slow branch. As Γ_h/Γ_c approaches unity, the optimal time allocation of both limits approach one another, as predicted for the case $\Gamma_h=\Gamma_c$.

D. The general case

Figure 3 shows the polarization difference S_1-S_2 as a function of τ_c for different total time durations. The curves are not symmetric due to the fact that Γ_h is larger than Γ_c. As τ increases beyond the relaxation time constant $(1/\Gamma_c)$ the curve's maximum saturates leading to a tablelike shape. This corresponds to the long time limit close to equilibrium. S_1-S_2 vanishes at the extremes since the time spent along either the hot or the cold branches vanishes there, and the cycle shrinks to a line. To show the relative effect of time allocation we show in Fig. 4 S_1-S_2, normalized with respect to its maximum value. It is seen that the larger the relaxation rate along one thermal branch relative to the other, the smaller the optimal time spent along this branch. This is reasonable, since more time is allocated this way to the slower process, thereby allowing it to change S by a similar amount. When the two rates exactly balance each other, i.e., $\Gamma_c=\Gamma_h$, the same time is spent along each of the thermal branches, as predicted in the previous subsection.

In Fig. 5 the polarization difference S_1-S_2, normalized with respect to its maximum value, was plotted against the time along the cold branch, τ_c/τ, for the case of equal relaxation rates $\Gamma_c=\Gamma_h=\Gamma$. The different plots correspond to different values of Γ, measured in units of $1/\tau$. It is seen that the "sharpness" of the maximum is lost as the relaxation becomes faster. This is reasonable since for fast relaxation $(\Gamma\tau\gg1)$ S_1 and S_2 almost converge to S_1^{eq} and S_2^{eq} respectively, unless the allocation is such that τ_c or τ_h drop below values on the order of $1/\Gamma$. Hence, the optimization is especially important for slow relaxation or, equivalently, for short cycle duration.

E. Optimization over τ

Finally, we explore the consequences of releasing the constraint on the overall cycle duration, τ. Whatever the value of τ, the time allocation for the contact between the two heat baths should be optimal. After substituting this optimal time allocation into the work output, one can maximize with respect to τ.[6,20] For the work output such an optimization yields a trivial result, namely $\tau\to\infty$. This is due to the fact

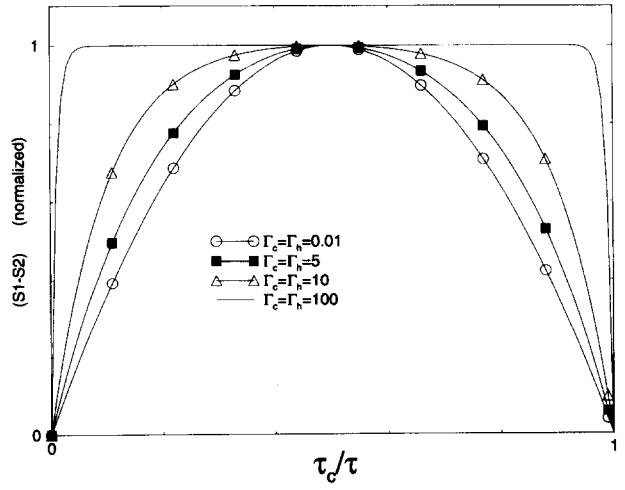

Fig. 5. The normalized polarization difference vs the relative contact time with the cold bath, τ_c/τ in the case $\Gamma_c=\Gamma_h=\Gamma$. The plots correspond to different values of Γ (in units of $1/\tau$).

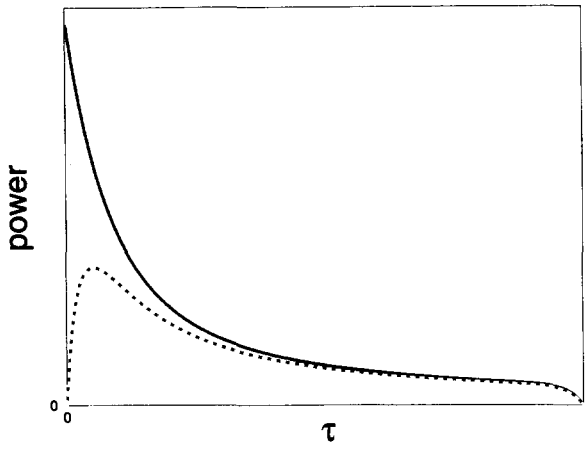

Fig. 6. The effect of finite duration on the adiabats on the power. The solid line corresponds to infinitely fast adiabats where maximum power is obtained when $\tau \to 0$. The dashed line corresponds to a finite duration on the adiabatic branches showing a maximum in power.

that the longer the duration, the larger the area of the cycle and thus more work is produced. This is however *not* the optimal use of the time as we can see by examining the power, which is the work output divided by the duration. Plotting the maximum power as a function of τ reveals that it is monotonic decreasing in τ, i.e., it takes on its maximum value only in the limit as $\tau \to 0$! It should be emphasized that the power is *finite* in this limit since both work and τ decay to zero. In this short time limit, the exponents in F can be expanded and using Eq. (3.15) one obtains:

$$\frac{F}{\tau}=\frac{\Gamma_h\Gamma_c}{(\sqrt{\Gamma_h}+\sqrt{\Gamma_c})^2}. \tag{3.16}$$

It follows that the maximum work in a given time τ is obtained by running many cycles of infinitely small period. This is the bang-bang solution which gives

$$\mathscr{W}^{\max}=(\omega_a-\omega_b)\cdot(S_1^{\mathrm{eq}}-S_2^{\mathrm{eq}})\cdot\frac{\Gamma_h\Gamma_c}{(\sqrt{\Gamma_h}+\sqrt{\Gamma_c})^2}\cdot\tau. \tag{3.17}$$

We conclude the present line of analysis by noting that if one drops the assumption that the adiabatic branches can be achieved instantaneously, the resulting power (while smaller) is maximum for a finite (i.e., nonzero) τ. This is demonstrated in Fig. 6.

IV. DISCUSSION AND CONCLUSIONS

The model analyzed in this paper is probably the simplest possible example of the optimization of the performance of a heat engine governed by a master equation. It is meant to demonstrate how finite time thermodynamics can be extended to treat systems which are quite remote from the traditional thermodynamic agenda, and for which master equations are most natural. It is conjectured that the results of this analysis hold generally for systems whose dynamics obey canonical invariance.[31] Although oversimplified and not directly related to any specific application, this model, together with the studies in Refs. 18–21, enabled us to present the basic conceptual tools for the treatment of more involved systems. The main advantage of this model over the ones analyzed in Refs. 18–21 lies in the fact that it does not involve relaxation under the influence of a time-dependent field where the evaluation of thermodynamically consistent master equations turns out to be quite a delicate task.

The engine analyzed above differs from previous studies in that the thermal contact to the reservoirs obeys dynamics given by a Pauli master equation. A nice feature of this engine is that it settles to a limit cycle irrespective of its initial conditions, which also means that the cycle is stable to any perturbation. It displays two additional interesting features not previously reported in finite time thermodynamic analyses. The minimization of entropy production and maximization of power always correspond to opposing strategies.[6,10] The present model brings this observation to an extreme since maximizing work is the complete antithesis of minimizing entropy production. The second feature is the fact that the power is a monotonically decreasing function of the cycle time, thereby maximizing work for a given allocated time in the limit of infinite cycling frequency.

ACKNOWLEDGMENTS

P. S. gratefully acknowledges support from the Danish Research Council and the Fritz Haber Center for Molecular Dynamics which made it possible for him to visit Jerusalem and begin the collaboration leading to this manuscript. We also want to thank Bjarne Andresen for extremely useful discussions and hospitality during the Danish–Israeli symposium, and Jeff Gordon and Raj K. Pathria for helpful remarks. This research was supported by the Israel Science Foundation administered by the Israel Academy of Science. The Fritz Haber Research Center is supported by the Minerva Gesellschaft für die Forschung, GmbH München, FRG.

APPENDIX A: WORKING MEDIUM CONSISTING OF HARMONIC OSCILLATORS

Consider a working medium consisting of many noninteracting HOs. Energy exchange between the working medium and the surroundings is then cast in terms of a single HO. The total energy is obtained by multiplying by the total number of HOs.

Ignoring zero-point energy, the energy levels, $\{E_n\}$, of the HO are given by

$$E_n=n\omega, \quad n=0,1,2,\ldots, \tag{A1}$$

where ω is the oscillator's frequency (in units where $\hbar=1$). The average energy of the system at any time is given by

$$\langle E\rangle(t)=\sum_{n=0}^{\infty}P_n(t)E_n=\omega\sum_{n=0}^{\infty}P_n(t)n=\omega\langle n\rangle, \tag{A2}$$

where $P_n(t)$ is the probability for finding the oscillator in the nth level at time t.

Thus, the energy of the working medium may change by either changing the frequency, ω, or the population, $\langle n\rangle$:

$$d\langle E\rangle=\langle n\rangle d\omega+\omega d\langle n\rangle. \tag{A3}$$

In analogy with the case of the TLS, the first term in the right-hand side of Eq. (A3) is associated with work and the second term with heat:

$$D\mathscr{W}=\langle n\rangle d\omega; \quad D\mathscr{Q}=\omega d\langle n\rangle. \tag{A4}$$

If we only allow transitions such that $\Delta n=\pm 1$, the master equation for the HOs populations reads

$$\frac{dP_n}{dt}=k_{\uparrow}nP_{n-1}+k_{\downarrow}(n+1)P_{n+1}$$

$$-[k_{\downarrow}n+k_{\uparrow}(n+1)]P_n. \tag{A5}$$

Montroll and Schuler[31] proved that Eq. (A5) retains canonical invariance. Thus, if the initial distribution is Boltzmannian, corresponding to a temperature $T'(0)$, it retains the Boltzmannian form throughout the relaxation, with $T'(0)$ changing in time until it reaches the bath temperature, T. Thus, assuming we start with a Boltzmann distribution, we may unambiguously associate a unique internal temperature with the working medium. Detailed balance is obtained by requiring that

$$k_{\uparrow}/k_{\downarrow}=e^{-\omega/k_BT}. \tag{A6}$$

The differential equation for the first moment, $\langle n\rangle$, is obtained from Eq. (A5):

$$\frac{d\langle n\rangle}{dt}=-\Gamma'[\langle n\rangle-\langle n\rangle_{\rm eq}], \tag{A7}$$

where, $\Gamma'=k_{\downarrow}-k_{\uparrow}$ and

$$\langle n\rangle_{\rm eq}=\frac{k_{\uparrow}}{k_{\downarrow}-k_{\uparrow}}=\frac{1}{e^{\omega/k_BT}-1}. \tag{A8}$$

Equation (A7) is equivalent to Eq. (2.10), where $\langle n\rangle$ is analogous to S. Thus, the rest of the analysis is exactly the same as in the TLS case.

[1]H. B. Callen, *Thermodynamics* (Wiley, New York, 1960).

[2]F. L. Curzon and B. Ahlborn, "Efficiency of a Carnot Engine at Maximum Power Output," Am. J. Phys. **43**, 22–24 (1975).

[3]B. Andresen, P. Salamon, and R. S. Berry, "Thermodynamics in Finite Time III: Extremals for Imperfect Heat Engines," J. Chem. Phys. **66**, 1571–1577 (1977).

[4]M. Rubin, "Optimal Configuration of a Class of Irreversible Heat Engines," Phys. Rev. A **19**, 1272–1276 (1979).

[5]P. Salamon, A. Nitzan, B. Andresen, and R. S. Berry, "Thermodynamics in Finite Time IV: Minimum Entropy Production in Heat Engines," Phys. Rev. A **21**, 2115–2129 (1980).

[6]P. Salamon and A. Nitzan, "Finite Time Optimizations of a Newton's Law Carnot Cycle," J. Chem. Phys. **74**, 3546–3560 (1981).

[7]L. I. Rozonoer and A. M. Tsirlin, "Optimal Control of Thermodynamic Processes. I, II, and III," Avtomat. Telemekh. **1**, 70–79 (1983); **2**, 88–101 (1983); **3**, 50–64 (1983).

[8]A. Bejan, *Entropy Generation Through Heat and Fluid Flow* (Wiley, New York, 1982).

[9]P. Salamon and R. S. Berry, "Thermodynamic Length and Dissipated Availability," Phys. Rev. Lett. **51**, 1127–1130 (1983).

[10]B. Andresen, P. Salamon and R. S. Berry, "Thermodynamics in Finite Time," Phys. Today **37**, 62–70 (Sept. 1984).

[11]B. Andresen, R. S. Berry, M. J. Ondrechen, and P. Salamon, "Thermodynamics for Processes in Finite Time," Acc. Chem. Res. **17**, 266–271 (1984).

[12]T. Feldmann, B. Andresen, A. Qi, and P. Salamon, "Thermodynamic Lengths and Intrinsic Time Scales in Molecular Relaxation," J. Chem. Phys. **83**, 5849–5853 (1985).

[13]L. Chen and Z. Yan, "The Effect of Heat Transfer Law on Performance of a Two-Heat-Source Endoreversible Cycle," J. Chem. Phys. **90**, 3740–3743 (1989).

[14]J. M. Gordon, "Observations on the Efficiency of Heat Engines Operating at Maximum Power," Am. J. Phys. **58**, 370–375 (1990).

[15]V. N. Orlov and R. S. Berry, "Power Output from an Irreversible Heat Engine with a Non-uniform Working Fluid," Phys. Rev. A **42**, 7230–7235 (1990).

[16]R. K. Pathria, J. D. Nulton, and P. Salamon, "Carnot-like Processes in Finite Time II: Applications to Model Cycles," Am. J. Phys. **61**, 916–924 (1993).

[17]S. Sieniutycz and P. Salamon (Ed.), *Finite Time Thermodynamics and Thermoeconomics*, Advances in Thermodynamics, Vol. 4 (Taylor & Francis, London, 1991).

[18]R. Kosloff, "A Quantum Mechanical Open System as a Model of a Heat Engine," J. Chem. Phys. **80**, 1625–1631 (1984).

[19]E. Geva and R. Kosloff, "A Quantum-Mechanical Heat Engine Operating in Finite Time. A Model Consisting of Spin-1/2 Systems as the Working Fluid," J. Chem. Phys. **96**, 3054 (1992).

[20]E. Geva and R. Kosloff, "On the Classical Limit of Quantum Thermodynamics in Finite Time," J. Chem. Phys. **97**, 4398–4412 (1992).

[21]E. Geva and R. Kosloff, "Three Level Quantum Amplifier as a Heat Engine: a Study in Finite Time Thermodynamics," Phys. Rev. E **49**, 3903–3918 (1994).

[22]A. Abragam, *The Principles of Nuclear Magnetism* (Oxford, 1961).

[23]W. H. Louisell, *Quantum Statistical Properties of Radiation* (Wiley, New York, 1990).

[24]R. Alicki and K. Lendi, *Quantum Dynamical Semigroups and Applications* (Springer-Verlag, Berlin, 1987).

[25]I. Oppenheim, K. E. Shuler, and G. H. Weiss, *Stochastic Processes in Chemical Physics: The Master Equation* (MIT, Cambridge, MA, 1977).

[26]F. Schlogl, *Probability and Heat* (Vieweg & Sohn, 1989).

[27]N. Van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1992).

[28]E. Geva, R. Kosloff, and J. L. Skinner, "On the Relaxation of a Two Level System Driven by a Strong Electromagnetic Field," J. Chem. Phys. **102**, 8541–8561 (1995).

[29]H. C. Andersen, I. Oppenheim, K. E. Shuler, and G. H. Weiss, "Exact Conditions for the Preservation of a Canonical Distribution in Markovian Relaxation Processes," J. Math. Phys. **5**, 522–536 (1964).

[30]N. R. Davidson, *Statistical Mechanics* (McGraw-Hill, New York, 1962).

[31]E. W. Montroll and K. E. Shuler, "Studies in Nonequilibrium Rate Processes. I. The Relaxation of a System of Harmonic Oscillators," J. Chem. Phys. **26**, 454–464 (1957).

NATURA NON FACIT SALTUS

After the conceptual cataclysm evoked by [matrix mechanics] it seemed as if Schrödinger's return to quasi-classical conceptions reinstated continuity. Those who in their yearning for continuity hated to renounce the classical maxim *natura non facit saltus* acclaimed Schrödinger as the herald of a new dawn. In fact, within a few brief months Schrödinger's theory "captivated the world of physics" because it seemed to promise "a fulfillment of that long-baffled and insuppressible desire." Einstein was "enthusiastic" about it, Planck reportedly declared, "I am reading it as a child reads a puzzle," and Sommerfeld was exultant.

Max Jammer, *The Conceptual Development of Quantum Mechanics* (McGraw-Hill, New York, 1966), p. 271.