Quantum Equivalent of the Carnot Cycle

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The concept of a *quantum heat pump* is proposed as a convenient model in the thermodynamic interpretation of certain multilevel processes. The *ideal quantum heat engine* is defined as an idealization of realistic pumped multilevel systems in much the same way that the well-known Carnot cycle is an idealization of physically realizable, *classical* processes or engines. There is evidence that the conventional Carnot cycle can be operated only between reservoirs at absolute temperatures of identical sign. No such restriction applies, however, to the quantum heat engine. Thus it may be used to calibrate negative absolute temperatures by relating them directly to positive temperatures. Negative efficiencies or efficiencies greater than unity have particularly simple interpretations in the quantum-heat-engine model. An important application of these concepts is in the calculation of optical *maser* parameters.

I. THE CONCEPT OF NEGATIVE ABSOLUTE TEMPERATURES

THE concept of a negative absolute temperature was first associated with "inverted" systems (that is, systems where higher energy levels possess greater populations than those below) by Pound and Purcell.[1] Later the maser principle was realized experimentally by Townes and co-workers.[2] Since then the terms "negative temperature" and "maser action" have become more or less synonymous for the emissive state shown by pairs of energy levels with inverted populations. Obviously, both terms emphasize different aspects of this state; the first relates primarily to the thermodynamics, statistical mechanics, and perhaps to the form of Planck's radiation law that is applicable, while the second emphasizes the possibility of obtaining amplification or oscillation.

A thermodynamic justification of the negative-temperature definition was given in a most stimulating paper by Ramsey.[3] He named the conditions under which systems such as nuclear or electronic spins are able to assume a positive or negative temperature (a "spin temperature") different from the necessaryily positive temperature of the surrounding lattice. He indicated the changes necessary in the classical formulations of the three laws of thermodynamics if they should remain valid for negative temperatures, too. He showed that the conventional thermodynamical functions like entropy, internal energy, and specific heat can be derived without difficulty from statistical mechanics. Entropy and specific heat are even functions of temperature, the internal energy odd, provided the Hamiltonian of the spin system is written to have a vanishing trace.

Following Ramsey's publication, several authors examined the concept of spin temperature as distinct from lattice temperature and, especially, negative absolute temperatures. The term "spin temperature," of course, derives from nuclear spin systems which historically were the first to show negative temperatures. Since then, the evolution of the maser field, especially in the optical range, has shown that many other systems can be made to show negative temperatures. Abragam and Proctor[4–6] discussed the usefulness of the spin-temperature concept and demonstrated it experimentally by a kind of spin calorimetry. Fick[7,8] showed that one is entitled to distinguish spin and orbit temperatures as independent parameters for particles obeying Boltzman statistics whereas thermodynamic functions for Fermi or Bose particles involve both parameters owing to the requirement of over-all symmetric or antisymmetric wave functions. Coleman and Noll[9] proved that at negative absolute temperatures an equilibrium is defined by maximum entropy at given energy or maximum energy at given entropy. This second condition is opposite to what is valid at positive temperatures. Hecht[10] derived that internal energy, enthalpy, Helmholtz and Gibbs free energy are maximal at negative temperatures and given entropy. Landsberg[11] pointed out that negative temperatures can be accommodated without inconsistency in Carathéodory's axiomatic thermodynamics. Desloge and Barker[12] were critical of the spin-temperature concept and proposed to describe the spectroscopic situation by chemical potentials and ambient temperature.

Another field where the concept of a negative temperature proves rather useful and meaningful is in discussions of noise generation due to spontaneous emission from inverted systems. It was proved in the original treatments of maser noise by Pound,[13] Shimoda,

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[1] E. M. Purcell and R. V. Pound, Phys. Rev. **81**, 279 (1951).
[2] J. P. Gordon, H. J. Zeiger, and C. H. Townes, Phys. Rev. **95**, 282 (1954).
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[4] A. Abragam and W. G. Proctor, Phys. Rev. **106**, 106 (1957).
[5] A. Abragam and W. G. Proctor, Compt. Rend. **245**, 1048 (1957).
[6] A. Abragam and W. G. Proctor, Phys. Rev. **109**, 1441 (1959).
[7] E. Fick, Z. Physik **157**, 407 (1960).
[8] E. Fick, Z. Physik **163**, 481 (1961).
[9] B. D. Coleman and W. Noll, Phys. Rev. **115**, 262 (1959).
[10] C. E. Hecht, Phys. Rev. **119**, 1443 (1960).
[11] P. T. Landsberg, Phys. Rev. **115**, 518 (1959).
[12] E. A. Desloge and W. A. Barker, Phys. Rev. **108**, 924 (1957).
[13] R. V. Pound, Ann. Phys. (N. Y.) **1**, 24 (1957).

Takahasi, and Townes,[14] and Strandberg[15] that this emission is still governed by the Planck radiation law. In the Planck formula, however, the negative spin temperature of the transition under consideration has to be entered. A seeming paradox exists since the emission according to this formula is negative for negative temperatures. The absorption coefficient associated with the transition, however, also changes sign as the temperature becomes negative and since the observed power is always the product of absorption coefficient and the specific emission, the observed power is necessarily positive as it should be.[16]

The present discussion is in response to Ramsey's statement[3] that "no means has yet been devised by which a Carnot cycle can be operated between positive and negative temperatures . . . . As a result, the ratio of a positive temperature to a negative one has not been determined by operating a Carnot cycle between the two temperatures." Schöpf[17] presents an even stronger statement based on a discussion using the methods of axiomatic thermodynamics. He showed that no Carnot cycle can be constructed with one isotherm at a positive, the other at a negative absolute temperature.

In this paper we wish to demonstrate a cyclic process which, although different in many ways from a Carnot cycle, still has important features in common with it. Most important, however, it exceeds the capabilities of the Carnot cycle in that it can operate between reservoirs of positive and negative temperatures.

Our process is basically an idealization of the three-level maser scheme due independently to Basov and Prokhorov[18] and, in a form more suited for experimental realization, to Bloembergen.[19] The most general form of our process may be called a heat pump and it consists of a three-level scheme connected selectively, for each of the three transitions, to three heat reservoirs at different temperatures. The identification of three (or more) level systems with heat pumps offers a rather direct approach for evaluating maser efficiency and it provides, in the case of optically pumped lasers, a method of determining the minimum pump color temperature needed to obtain oscillation or a given amount of gain from a particular maser material. This is of some significance since many optical masers are limited in their performance by the equivalent black-body temperature of available pump lamps. Such a treatment also makes apparent the features required in an efficient maser meterial, some of which are at variance with widely held notions. Similarly, it suggests ways to predict the performance of real maser materials in view of their realistic, less-than-optimum characteristics.[20] Recently, it was shown that the color temperature of the pump lamp needed for oscillation threshold can be accurately predicted from such heat-pump considerations.[21] Furthermore, for a nearly ideal laser crystal, i.e., one that is nearly reversible in the thermodynamic sense, such as Nd^{3+} in yttrium-aluminum garnet, one concludes that it should be able to function as the working substance in a refrigerator. In this type of operation, the crystal is made to absorb laser radiation from a similar crystal, it emits what would normally be called pump radiation, and in the process it will cool down its crystal lattice.

In the following, we outline definitions of classical cyclic processes such as the heat pump, the heat engine, and the refrigerator, in a form suitable for the subsequent discussion. We then introduce their quantum counterparts, in particular the quantum heat engine, and discuss its operation between reservoirs at positive and negative temperatures.

II. CLASSICAL HEAT-PUMP AND HEAT-ENGINE CYCLES

As sketched in Fig. 1(a), a heat pump is a device connected to three reservoirs a, b, c, being, respectively, at the temperatures T_a, T_b, T_c. The heat pump is cycled through a sequence of processes. Ideally, the processes

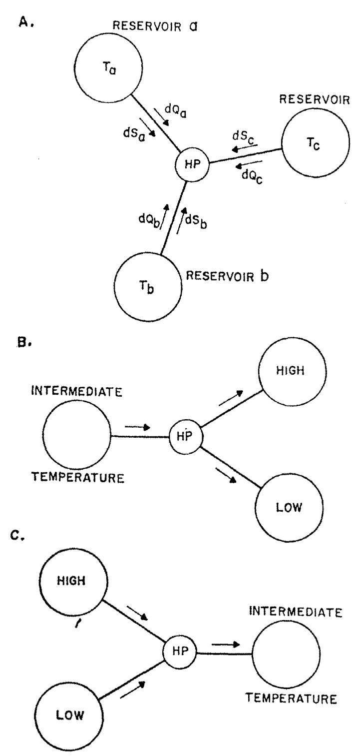

FIG. 1. Operation of the classical heat pump. (a) Schematic diagram of heat and entropy flow; (b) distributive operation; (c) combinatory operation.

[14] K. Shimoda, H. Takahasi, and C. H. Townes, J. Phys. Soc. Japan **12**, 686 (1957).
[15] M. W. P. Strandberg, Phys. Rev. **107**, 1483 (1957).
[16] E. O. Schulz-DuBois, in *Progress in Cryogenics* (Heywood and Company, Ltd., London, 1960), Vol. 2, p. 173.
[17] H. G. Schöpf, Ann. Phys. (Leipzig) **9**, 107 (1961).
[18] N. G. Basov and A. M. Prokhorov, Zh. Eksperim. i Teor. Fiz. **27**, 431 (1954).
[19] N. Bloembergen, Phys. Rev. **104**, 324 (1956).
[20] J. E. Geusic and H. E. D. Scovil, Rept. Progr. Phys. **27**, 241 (1964).
[21] J. E. Geusic (unpublished).

are either isothermal or adiabatic. Through this operation, amounts of heat dQ_a, dQ_b, dQ_c are accepted or rejected by the pump from the respective reservoirs. As a convention, heat going to the pump is considered positive, that leaving it negative. Energy conservation requires

$$dQ_a+dQ_b+dQ_c=0. \tag{1}$$

Note that by the convention adopted in this equation, one or two terms in the sum are necessarily negative. Concurrent with the flow of heat, there is a flow of entropy,

$$dS_i=dQ_i/T_i, \quad i=a, b, c. \tag{2}$$

With classical heat pumps, the temperature is restricted to positive values so that heat and entropy both flow in the same direction. The second law of thermodynamics requires

$$dS_a+dS_b+dS_c\geq 0. \tag{3}$$

The equality sign applies if the heat pump is ideal, that is, reversible. For the following we are concerned exclusively with reversible cycles. There are two modes of operation for the heat pump. The first may be called distributive. As indicated in Fig. 1(b), heat is extracted from a reservoir at intermediate temperature and is distributed to two reservoirs, one each at a lower and a higher temperature. The reverse operation may be called combinatory and it is shown in Fig. 1(c). Heat both from a high- and a low-temperature reservoir is combined and passed on to one at intermediate temperature.

A limiting case of a heat pump is the heat engine. It is obtained by letting the hot reservoir assume infinite temperature. Heat transferred to or from a reservoir at infinite temperature is equivalent to work. This can be appreciated directly by noting that the transfer of this type of heat is not accompanied by entropy flow, or it can be verified indirectly by assuming an additional ideal Carnot engine connected to the heat pump. This Carnot engine accepts heat from the reservoir at infinite temperature as input quantity and it is connected to an additional reservoir at a finite temperature. Thus it is able to convert the input heat with unity efficiency into work.

The reversible heat engine is, of course, equivalent to the Carnot engine. One can define various efficiencies for it, depending on the mode of operation and on the (somewhat arbitrary) selection of two of the connections as output and input ports. The distributive mode of operation is the usual heat-engine sketched in Fig. 2(a). Heat dQ_1 is taken from the hot reservoir at T_1; part of it leaves the device in terms of heat $-dQ_0$ at temperature T_0 and part of it is work $-dW$. In the usual efficiency definition, dQ_1 is the input quantity and $-dW$ the useful output. In this case, one obtains from (1),

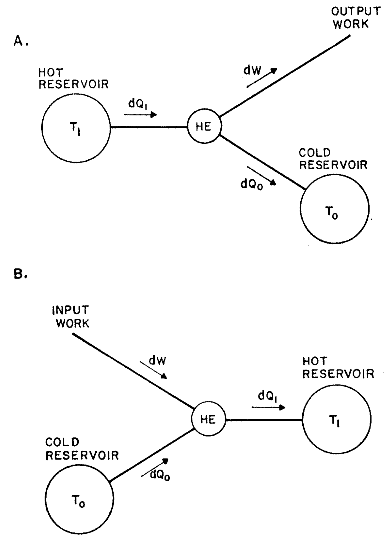

FIG. 2. Operation of the classical heat engine or Carnot cycle. (a) Distributive operation or operation as an engine; (b) combinatory operation which also may be called operation as a refrigerator (the cold reservoir is cooled further) or as a heater (the hot reservoir is heated further).

(2), and (3) the Carnot efficiency

$$\eta_c=\frac{-dW}{dQ_1}=\frac{T_1-T_0}{T_1}. \tag{4a}$$

The device run in reverse is a refrigerator. Work, i.e., heat at an infinite temperature, and heat from the low-temperature reservoir enter the engine and are discharged in combination as heat at the higher temperature, as indicated in Fig. 2(b). Two kinds of efficiencies are conveniently defined. The cooling efficiency as a refrigerator would be the heat extracted at the low temperature related to the input work,

$$\eta_R=\frac{dQ_0}{dW}=\frac{T_0}{T_1-T_0}. \tag{4b}$$

Similarly the efficiency as a heater is the amount of heat at the higher temperature obtained from the input work,

$$\eta_H=\frac{-dQ_1}{dW}=\frac{T_1}{T_1-T_0}=1+\eta_R=\frac{1}{\eta_c}. \tag{4c}$$

For positive finite temperatures and with the convention $T_1>T_0$, one has $0<\eta_c<1$, $\eta_H>1$, and $\eta_R>0$.

The general heat pump of Fig. 1(a) is equivalent to a tandem arrangement of two heat engines, one run as an engine, the other as a refrigerator as shown in Fig. 3. If one considers dQ_a as input quantity and $-dQ_c$ as the useful output, the efficiency can be evaluated either directly from (1), (2), and (3) or by considering the equivalent scheme of Fig. 3 and the applicable efficiency formulas (4a) and (4c). The resulting heat pump efficiency is

$$\eta_{\mathrm{HP}}=-\frac{dQ_c}{dQ_a}=\frac{T_a-T_b}{T_a}\frac{T_c}{T_c-T_b}. \tag{5}$$

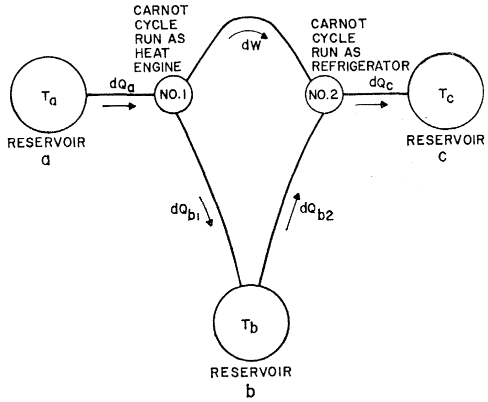

FIG. 3. Equivalence of a heat pump with the tandem arrangement of two Carnot cycles. Arrows show the flow of heat and work for the case where T_b is the lowest temperature and heat flows from a and toward c.

This expression may assume any positive or negative value depending on the choice of T_a, T_b, T_c. A negative efficiency indicates that dQ_a and dQ_c simultaneously flow either to or from the heat pump.

III. THE QUANTUM HEAT-PUMP AND HEAT-ENGINE CYCLES

Consider an ensemble of particles which are able to occupy one of a number of energy levels and which obey Boltzmann statistics. The ensemble may be represented by an energy-level diagram such as shown in Figs. 4(a) and 4(b). Here, as usual, the vertical spacing of the lines is made proportional to the energy-level separation. As an additional convention, the length of the horizontal lines is drawn proportional to the logarithm of the average population (ensemble or time average) of that level. This choice results in a graph where the endpoints of the energy-level lines lie on a straight line if the ensemble is in the thermal equilibrium. An example

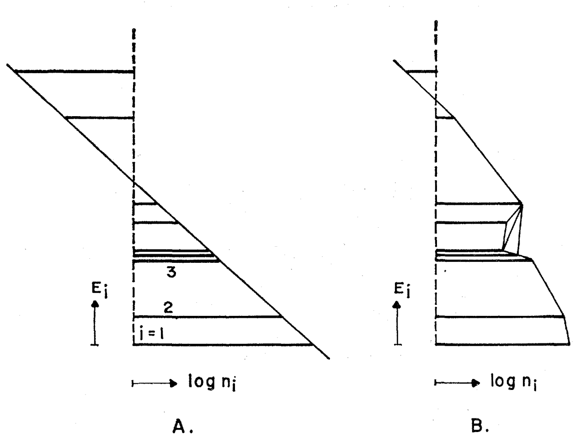

FIG. 4. Diagram of a multilevel system. (a) In thermal equilibrium at a single temperature; (b) not in thermal equilibrium—note transitions that are appreciably colder and hotter than average.

for this is shown in Fig. 4(a). Clearly, the connecting line becomes steeper for higher temperatures when the populations tend to differ less.

Figure 4(b) shows the diagram of an ensemble not in thermal equilibrium. The study of ensembles in thermal nonequilibrium is perhaps more important than that of ensembles in equilibrium because it is only in the former situation that nontrivial energy-transfer processes occur. Under natural or experimental conditions a nonequilibrium situation can be maintained in the steady state only if there are at least two reservoirs at different temperatures, which, in maintaining the steady state, supply or withdraw energy quanta to or from the ensemble.

To illustrate this point, we may mention two typical systems which are also important for laser purposes. One is a gas-discharge plasma, and the other is a crystal containing impurities with optical transitions. The ensemble of particles able to occupy quantized energy levels is, in one case, the atoms, molecules, or ions in the discharge, and, in the other case, the impurity ions within the crystal. The hot reservoir should be identified with the collection of free electrons in the discharge whose Maxwell temperature may easily reach several thousand degrees, or alternatively, with the radiation of a pump lamp of a high equivalent black-body temperature. Similarly, the cold reservoir is represented by the cold wall of the discharge vessel or the cold lattice of the host crystal.

In the discussion of such systems, it is convenient although necessarily somewhat arbitrary to distinguish between three classes of transitions. Transitions which predominantly interact with the hot reservoir tend to assume its temperature. The resulting "hot" transitions are usually characterized by high transition frequencies and large electron collision or optical cross sections, for the two systems discussed. Similarly, transitions which predominantly interact with the cold reservoir tend to assume its temperature. These transitions usually have a lower transition frequency, and it is interesting to note that their mode of interaction with the reservoir is also typically different from that of the hot transitions. In the discharge, these transitions interact through wall or neutral-gas collisions, and in the illuminated crystal, the interaction is via phonons. The remaining third class of transitions may be called "uncommitted." Their interaction with either the hot or cold reservoir is weaker than the interactions taking place in the other transitions. As a result, the populations of the two terminal states of such an uncommitted transition are not related to any physical temperature which would be "seen" by this transition. It is therefore possible, for example, that such a transition may assume a temperature substantially lower than that of the cold reservoir. This possibility is the essence of the Overhauser effect[22] and the term "spin refrigeration"

[22] A. W. Overhauser, Phys. Rev. **92**, 411 (1953).

has been used for such a process applied to electron spins in ruby.[23] Another possibility is the opposite case where the uncommitted transition assumes a temperature substantially higher than the hot reservoir. This includes the possibility of a negative temperature which, as pointed out by Ramsey, should be considered hotter than any positive temperature. This situation is commonly referred to as "population inversion" and it is the prerequisite for maser action.

A. The Quantum Heat Pump

For a discussion of the quantum heat pump we consider a system capable of occupying three energy levels as shown in Fig. 5. A greater number of levels is frequently involved in cases of practical interest. In an earlier evaluation of maser pumping efficiency[20] it was convenient to consider four-level systems and there the extension to the general multilevel case was clearly indicated. However, three levels suffice to demonstrate the principle. It is assumed that the three-level system is not in thermal equilibrium at a single temperature and, further, that there are no phase-coherent transitions between the levels, i.e., that the off-diagonal elements of the density matrix for the three level system be negligible.

It is further assumed that the widths of the energy levels and, correspondingly, the linewidths of the transitions are vanishingly small. This idealization is consistent with the reversible operation of a heat pump: Reversibility requires that energy is exchanged at a vanishingly slow rate, hence the transition frequencies may be arbitrarily sharp. In a more practical sense, it is adequate for our considerations if the linewidths are small compared to the line frequencies.

Under these circumstances, the state of the three-level system is described by the level populations n_i, $i=1, 2, 3$. The population ratio for any one of the transitions $i \rightarrow j$ with transition frequency $\nu_{ij}=-\nu_{ji}$ may then formally be related to a temperature $T_{ij}=T_{ji}$ by a Boltzmann relation

$$n_i/n_j=\exp(h\nu_{ij}/kT_{ij}), \quad i, j=1, 2, 3. \tag{6}$$

In addition there is the identity relation

$$\frac{n_1}{n_2}\frac{n_2}{n_3}\frac{n_3}{n_1}=1. \tag{7}$$

At this point it may be argued that the temperatures T_{ij} thus introduced are fictitious quantities. Notice, however, that it is the temperature T_{ij} which governs the interaction of radiation of frequency ν_{ij} with the three-level system. More specifically, T_{ij} determines the relative strengths of stimulated absorption, stimulated emission, and spontaneous emission.

[23] J. E. Geusic, R. W. DeGrasse, E. O. Schulz-DuBois, and H. E. D. Scovil, J. Appl. Phys. **30**, 1113 (1959).

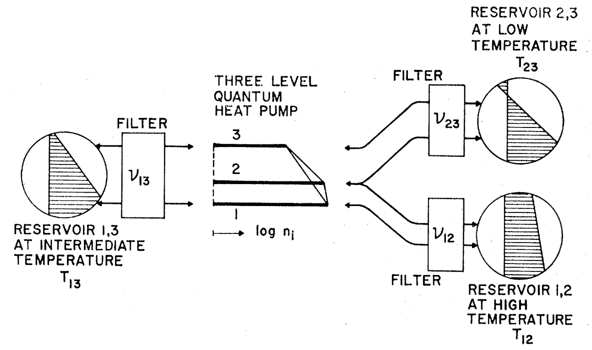

FIG. 5. Schematic illustration of a three-level quantum heat pump whose transitions are selectively in equilibrium with three thermal reservoirs at different temperatures.

Even more significance is given to this temperature concept if the three-level system is assumed to be in contact with three heat reservoirs as sketched in Fig. 5. Note that one is not at liberty to choose the three temperatures arbitrarily; rather the third temperature is given by the other two and the transition frequencies in terms of relation (9) below. With this proviso, it is clear that in the situation depicted, the temperature of each one of the transitions and the corresponding reservoir will become equal under steady-state conditions if a direct exchange of quanta is possible only between each one of the transitions in the three-level system with the corresponding reservoir. This requires an idealized three-level system in which there are no nonradiative transitions or interactions other than these with the respective reservoirs.

With these idealizations the scheme of Fig. 5 performs as a reversible heat pump. From self-consistency considerations we have the relation

$$\nu_{ik}+\nu_{kl}+\nu_{li}=0, \tag{8}$$

where f, k, l assume the values 1, 2, 3 in some cyclic fashion. Notice that the convention adopted in Eq. (8) makes one or two frequencies negative. This equation, by multiplication with Planck's constant, will be interpreted as energy conservation in the cyclic heat-pump process in which one particle in the ensemble of three-level systems is taken just once through the three levels. Thus relation (8) is analogous to (1). From (7) we find, by forming the logarithm and observing (6),

$$\frac{h\nu_{ik}}{T_{ik}}+\frac{h\nu_{kl}}{T_{kl}}+\frac{h\nu_{li}}{T_{li}}=0. \tag{9}$$

This relation is analogous to (3) and it expresses the fact that entropy is conserved in an ideal, i.e., reversible, heat pump.

As with the classical heat pump, there are two modes of operation, the distributive one and the combinatory one. In the distributive mode, heat flows from left to right in the arrangement of Fig. 5. In the cyclic process, a particle in the three-level system is raised from level 1 to 3 by absorbing a quantum $h\nu_{13}$ from the black-body spectrum of reservoir 1,3. Subsequently it rejects quanta $h\nu_{23}$ and $h\nu_{12}$ into the reservoirs 2,3 and 1,2, respectively, by first dropping to level 2 and then back to 1. In the combinatory mode, this sequence is reversed and heat flows from right to left in the diagram.

From Eqs. (8) and (9) we can obtain the efficiency of the quantum heat pump. In the operation of the pump cycle, one quantum of one frequency is exchanged for one quantum of another frequency. Thus the efficiency is simply given by a frequency ratio. The sign of the efficiency is determined by the convention that a positive efficiency relates a useful output quantity to the necessary input quantity. This requirement produces the negative sign in the following Eq. (10) for the efficiency of the quantum heat pump:

$$\eta_{\mathrm{HP}}=-\frac{\nu_{li}}{\nu_{ik}}=\frac{T_{ik}-T_{kl}}{T_{ik}}\,\frac{T_{li}}{T_{li}-T_{kl}}. \qquad (10)$$

Again there is analogy with Eq. (5) for a classical heat pump. In Eq. (10), the indices i, k, l may be identified with any permutation of 1, 2, 3.

The quantum heat engine[24] is a special case of the heat pump with one of the transitions at infinite temperature. For example, let $T_{li}\rightarrow\infty$. Then the quantum $h\nu_{li}$ is a quantum of work and the efficiency of the quantum heat engine is

$$\eta_{\mathrm{HE}}=-\frac{\nu_{li}}{\nu_{ik}}=\frac{T_{ik}-T_{kl}}{T_{ik}}. \qquad (11)$$

Note that

$$-\frac{\nu_{li}}{\nu_{ik}}=\frac{\nu_{il}}{\nu_{ik}}=\frac{\nu_{li}}{\nu_{ki}}.$$

In the following this formula is applied to situations where T_{ik} and T_{kl} are both positive, or positive and negative, or both negative. Before doing that, however, it may be well to add some remarks on nonideal heat pumps.

For the proposed embodiment of a heat pump, it is particularly easy to see why practical heat pumps have less than the optimum thermodynamic efficiency. One reason is the unavoidable presence of processes by which energy is given to or accepted from reservoirs other than the three considered. Some of these interactions would be described by friction or leakage in a classical system. These interactions essentially violate the energy conservation (1) or (8) within the cycle. Another and perhaps more fundamental limitation is related to loading of the heat pump. This refers to the requirement that the pump should deliver a certain amount of heat in a finite time to one of the reservoirs. The efficiency (5) can be realized only in the adiabatic sense, i.e., if finite amounts of heat are delivered in infinite time. From heat-conduction considerations it is clear that, for example in the distributive mode of operation discussed with Fig. 5, a finite power flow from the reservoir 1,3 to the transition $1\rightarrow3$ will take place only if the former is hotter. Similarly, the transitions $1\rightarrow2$ and $2\rightarrow3$ should be hotter than the corresponding reservoirs to guarantee appreciable heat transfer. This then has the consequence that the entropy balance (9), written with the *temperatures of the reservoirs*, exceeds zero. Thus the process is not isentropic, hence it is irreversible and less efficient than indicated by (5). At the same time, however, the three-level system itself is still reversible having an entropy balance of zero in (9), when the *actual transition temperatures* are used in this expression. In view of the temperature differences between the reservoirs and the corresponding transitions, it is clear that the operation of the loaded heat pump involves nonisothermal interactions. We thus have a result which is well known for classical heat pumps. By loading the heat pump, i.e., by extracting finite amounts of power, the device becomes less efficient than indicated in Eq. (10), it becomes irreversible, and it does that by violating simultaneously two conditions, namely that the cyclic operation consists of *isothermal* and of *isentropic* interactions.

B. The Quantum Heat Engine Operating between Reservoirs at Positive Temperatures

We consider a three-level system with one transition at infinite temperature and the remaining two transitions at positive finite temperatures. There are only two ways in which this situation can be realized and they are illustrated in Figs. 6(a) and 6(b). We may introduce maser terminology by identifying the outer "hot" transition with the pump transition so that the pump

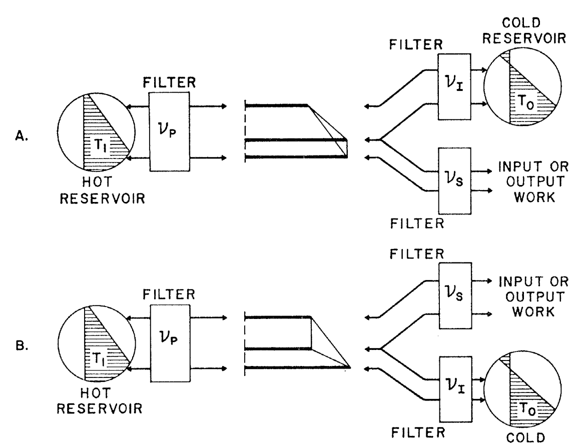

FIG. 6. Schematic illustration of three-level systems operating as quantum heat engines. In (a) the transition exchanging work is the bottom one; in (b), the top one.

[24] H. E. D. Scovil and E. O. Schulz-DuBois, Phys. Rev. Letters 2, 262 (1959).

frequency is $\nu_P=\nu_{13}$. Similarly we identify the transition at infinite temperature with the signal transition so that the signal frequency is $\nu_S=\nu_{12}$ in the situation of Fig. 6(a) or $\nu_S=\nu_{23}$ in the situation of Fig. 6(b). Finally the remaining "cold" transition is identified as the idler with frequency ν_I. In agreement with thermodynamic usage we call the temperature of the pump reservoir T_1 and that of the idler reservoir T_0. It is understood that $T_1>T_0$.

By applying Eq. (11), we obtain the efficiency of the quantum heat engine

$$\eta_{\mathrm{HE}+}=\frac{\nu_S}{\nu_P}=\frac{T_1-T_0}{T_1}. \tag{11'}$$

Numerically $\eta_{\mathrm{HE}+}$ is positive and smaller than unity.

Relation (11′) allows a direct calibration for the temperature of a transition and thus, in a more general sense, the establishment of a temperature scale as one or more parameters are varied. In practice the calibration procedure will primarily involve spectroscopic measurements. We wish to outline the type of measurements required in terms of a rather general example. Referring to Fig. 6(b) we assume that it is possible to determine in some direct way the hotter temperature, T_1, and we propose to use the calibration procedure for a determination of the temperature T_0 of the lower transition.

The calibration procedure involves four separate statements. Two of them are frequency measurements, namely measurements of ν_S and ν_P. The other two statements specify the state of the corresponding transitions, $2\leftrightarrow 3$ and $1\leftrightarrow 3$, respectively. In the simplest case the statements would be that the signal transition is with sufficient accuracy at infinite temperature and that the pump transition is with sufficient accuracy at the temperature of a macroscopic reservoir such as a crystalline lattice or a cryogenic bath which may be determined with a thermometer. The infinite-temperature condition of the signal transition can be verified experimentally. It manifests itself by complete transparency of the three-level material for signal-frequency radiation, i.e., by mutual cancellation of stimulated emission and absorption. Note, however, that spontaneous emission is still observed under these circumstances. If it is not possible to realize the infinite-temperature condition with sufficient accuracy, then a correction should be introduced through the heat-pump formula (10).

The identification of the temperature T_1 of the pump transition with that of a macroscopic reservoir is adequate only if there is a sufficiently strong coupling between the two, for example by the exchange of phonons. If this is not the case, it may be necessary to determine T_1 by a direct measurement. The measurement procedure to be discussed is possible, at least in principle, if the pump transition is radiative. If that is the case, it is possible to arrange the host material of the heat-engine three-level system in such a way that radiation of pump frequency is completely absorbed within the three-level system, if only for one mode. For this mode the three-level material, therefore, acts as a blackbody and radiates, according to Planck,

$$\rho_P=\frac{1}{\exp(h\nu_P/kT_1)-1} \tag{12}$$

photons per cycle, second and mode. If the radiation mode is terminated in a thermally insulated, frequency filtered, low-heat-capacity absorber, the absorber material will under equilibrium conditions assume the temperature T_1 which then may be determined by any conventional thermometer. The function of the absorber just discussed is, of course, that of a radiation detector and in fact any radiation detector capable of absolute calibration can be used instead. Notice that this calibration procedure for T_1 is applicable only for T_1 in the positive-temperature regime. The reason is that the Planck formula (12) is valid only for blackbodies, i.e., bodies where incident radiation of the same frequency is completely absorbed. Since transitions at negative temperatures emit rather than absorb, incident radiation leaves a material with negative-temperature interaction (maser material) substantially unaltered except for amplification and addition of noise, and thus it should be characterized as optically thin as opposed to optically thick or black.

C. The Quantum Heat Engine Operating between Reservoirs at Absolute Temperatures of Opposite Sign

The heat reservoirs used in the quantum heat engine are not necessarily restricted to the positive-temperature regime. We are at liberty to consider a three-level quantum heat engine with one transition in equilibrium with a reservoir at a positive temperature, the other with a reservoir at a negative temperature. The situation is sketched in Fig. 7. While the positive-temperature reservoir and interaction can be realized in many ways and without restrictions, this is not true for the negative-temperature reservoir and interaction mechanism. As Ramsey has pointed out, the number of physical systems capable of assuming a negative temperature is limited to systems with a finite number of energy levels and sufficient thermal insulation from positive-temperature reservoirs. We like to add that the equilibrating interaction between systems at negative temperatures is also limited in kind. Bosons such as photons or phonons are by themselves reservoirs characterized by a necessarily positive temperature and thus must be excluded as intermediaries between systems at negative temperatures. One may, however, revert to a more direct energy exchange such as that provided by resonant dipolar coupling. Although the latter involves electric or magnetic fields, these are of

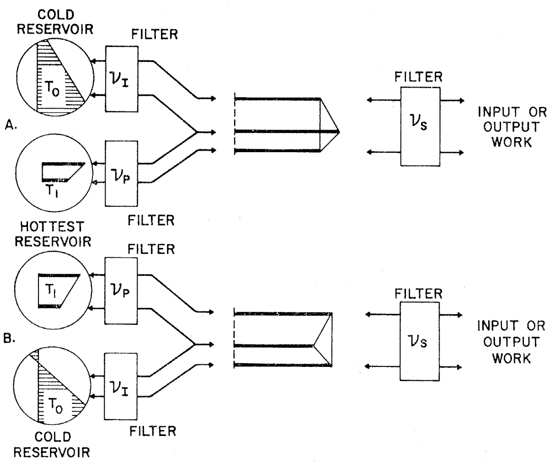

FIG. 7. Schematic illustration of three-level systems operating as quantum heat engines between reservoirs at absolute temperatures of opposite sign. This operation may be used to calibrate negative temperatures directly against positive ones. Since the signal quantum or quantum of work is bigger than the pump quantum, the efficiency is greater than unity.

the induction type and thus do not permit a photon description.

As shown in Fig. 7, work is extracted at the outer transition while the input quantities are heat at a positive and negative temperature. In reversing this cycle we obtain the operation of the three-level maser scheme in the microwave range. There work or, more realistically, heat at a very high equivalent radiation temperature is used to bring the level pair 1,3 essentially to population equalization. This then may produce one transition at a negative temperature, the other at a positive one. By realizing that the positive temperature transition cannot be colder than the crystal lattice or an equivalent heat sink, one may arrive at realistic limits for three-level maser performance.

In defining the efficiency there is some choice. We follow the convention of associating T_1 and ν_P with the hottest reservoir (provided the temperature T_1 is not infinite). And we follow Ramsey in recognizing that a negative temperature must be considered hotter than any positive temperature. The illustrations of Fig. 7 reflect this choice. The resulting heat-engine efficiency

$$\eta_{\mathrm{HE}\pm}=\frac{\nu_S}{\nu_P}=\frac{T_1-T_0}{T_1} \qquad (11'')$$

is identical with (11′) where here, however, the efficiency is positive and greater than unity. This is in agreement with the fact that the quantum of output work $h\nu_S$ is greater than the quantum of input heat $h\nu_P$.

Equation (11″) may be used to calibrate a negative temperature by relating it directly to a positive one. The calibration procedure is essentially the same as that in the positive-temperature case. The four separate statements needed are measurements of the frequencies ν_S and ν_P, establishment of the fact that the signal transition is transparent, that is at infinite temperature, and an absolute determination of the positive temperature T_0.

D. The Quantum Heat Engine Operating between Reservoirs at Negative Absolute Temperatures

This operation is possible and it is illustrated in Fig. 8. As in Fig. 6 before, the transition at infinite temperature may be the upper or lower one and both versions of Fig. 8 are simply upside-down versions of Fig. 6.

In defining the efficiency we again follow the convention that T_1 and ν_P apply to the hottest transition (provided T_1 is not infinite). And we again follow Ramsey in recognizing that, of two negative temperatures, the one with the smaller absolute value is the hotter one. This choice makes $|T_1|<|T_0|$ and the resulting associations are shown in Fig. 8.

For the efficiency one finds

$$\eta_{\mathrm{HE}-}=-\frac{\nu_S}{\nu_P}=\frac{T_1-T_0}{T_1}, \qquad (11''')$$

a formula that differs by a sign from (11′) and (11″). The efficiency is negative and may assume any value between 0 and $-\infty$. The negative efficiency indicates that one has to supply input heat from the hottest reservoir and simultaneously input work in order to obtain heat output at the idler frequency ν_{13}. One recognizes this type of heat-pump operation as the combinatory one in which heat from the hottest reservoir (at T_1) and the coldest one (i.e., work from a reservoir

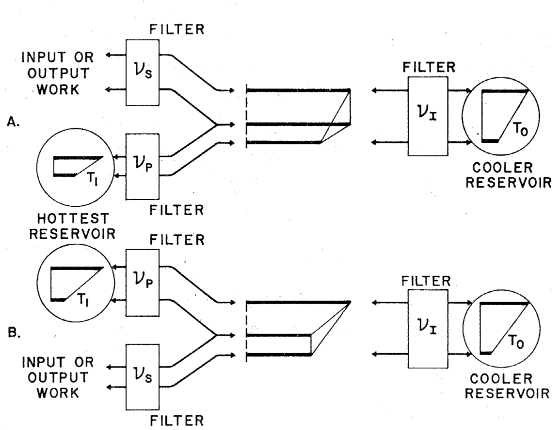

FIG. 8. Schematic illustration of three-level systems operating as quantum heat engines between reservoirs of negative absolute temperatures. Note that work and pump quanta flow simultaneously to or from the engine, thus leading to a negative value of efficiency. Also note the different symbol used for the reservoirs; it points to the fact that a reservoir at negative temperature can only be realized by a system of a limited number of energy levels, while a positive temperature reservoir (see preceding figures) may be realized by a system having an infinite number of levels such as harmonic oscillators.

effectively at infinite temperature) combine to produce heat at an intermediate temperature (at T_0). This relation of input work to input heat through a negative efficiency is in contrast to the more usual relation of output work to input heat through a positive efficiency.

IV. SUMMARY

The proposed quantum heat engine appears to be a quantum equivalent of the well-known Carnot cycle. The efficiency expression for both is formally the same. Unlike the classical Carnot engine, however, which operates only between reservoirs at temperatures of the same sign, the quantum engine is capable of operation between reservoirs at temperatures of opposite sign. This capability would appear to make possible the calibration of negative absolute temperatures in a procedure through which one establishes a ratio of a negative to a positive temperature in much the same way that a Carnot cycle permits the evaluation of a ratio between two positive temperatures.

Ramsey[3] has shown that the description of certain classes of physical systems by a temperature variable of negative absolute value is compatible with the traditional framework of classical thermodynamics. At that time, however, no Carnot cycle or equivalent process was known which would permit the calibration of a negative temperature by determining a direct relation between a positive and a negative temperature. This gap seems to be filled by the quantum heat engine.

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Drift Velocity and Energy of Electrons in Liquid Argon*

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Measurements are reported of the energy required for injection of an electron into liquid argon and of the drift velocity of electrons in liquid argon at moderate field strength. It is found that the barrier to electron injection is -0.33 eV, in moderately good agreement with a theoretical estimate of -0.45 eV. The observed field dependence of the drift velocity is in good agreement with the recent calculations of Lekner.

THIS paper reports on measurements of the field dependence of the drift velocity and on a photoelectric determination of the binding energy of electrons injected into liquid argon. The drift-velocity measurements are an extension to lower and higher fields of the recent work of Schnyders, Rice, and Meyer.[1] The photoelectric method of determining the energy required to inject electrons into liquids has been used by Woolf and Rayfield[2] in liquid helium, but has not been applied to other systems.

The drift-velocity measurements were made by the electronic-gate method previously employed.[1] The only modification in the present experiment is the use of a glass apparatus of about 4-liter volume, containing mass-spectrometer grade argon. The argon was specified as having 3 ppm N_2, and no other detectable impurities. Further purification inside the sealed glass system was provided by a tantalum getter. A field-emission microscope incorporated into the system enabled a visual test[3] for purity to be made. The impurity level was estimated to be less than 10^{-3} ppm. Measurements were made with two drift tubes, both with a 5-mm drift space and 1-mm spacing between grids. The grids were 85% transmission nickel electromesh spot-welded to stainless-steel rings of 12-mm i.d. Electrons were produced in the liquid by field emission from tungsten tips. Currents of 10^{-13} to 10^{-11} A were obtained at the collector, that is, after passing through five grids. The results obtained with the two drift tubes are compared with previous data and with theory in Fig. 1. The theoretical line is derived from the solution of the Boltzmann equation in the single-scatterer approximation,[4] as described in Ref. 5. We see that nonohmic behavior does indeed set in at fields of about 200 V/cm, as predicted.[4] The dashed line gives the drift velocity in the ohmic region, corrected for multiple scattering (energy renormalization and effective mass) following Wigner and Seitz and Bardeen, taken from Ref. 5.

The photoelectric measurements were made with a similar glass system, again with mass-spectrometer grade argon and tantalum getter. The cathode and

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