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THERMODYNAMIC LIMITS FOR SOLAR ENERGY CONVERSION BY A QUANTUM-THERMAL HYBRID SYSTEM

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NOMENCLATURE

E_0	energy threshold of a quantum device
$\dot{E}$	incident radiation energy flux
$\dot{E}'$	re-radiated energy flux
$\dot{F}$	free energy flux of the incident radiation field
$\dot{F}'$	free energy flux of the re-radiated field
h	Planck's constant
k	Boltzmann's constant
q	electronic charge
$\dot{Q}$	heat flux
$\dot{S}$	incident radiation entropy flux
$\dot{S}'$	re-radiated entropy flux
$\dot{S}^{int}$	entropy flux arising from internal irreversibilities
T	absolute temperature
T_C	ambient temperature
T_R	quantum device operating temperature
T_S	source temperature
$\dot{W}$	flux of useful work
Δ	difference operator
η_1	maximum thermodynamic efficiency of a quantum device
η_2	maximum thermodynamic efficiency of a heat engine
η_H	maximum efficiency of a solar-driven heat engine in a hybrid system
η_{TOTAL}	maximum efficiency of a solar quantum-thermal hybrid system
ν_0	radiation frequency at threshold energy

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SUMMARY

The thermodynamic limits to power conversion efficiency for a general quantum-thermal hybrid system are presented for air mass 1.5 conditions. A maximum conversion efficiency of 74 percent is thermodynamically achievable for the quantum device operating at 3500 K and the heat engine in contact with a reservoir at 0 K. The efficiency drops to 56 percent for a cold reservoir at approximately room temperature conditions. Hybrid system efficiencies exceed 50 percent over receiver temperatures ranging from 1400 K to 4000 K, suggesting little benefit is gained in operating the system above 1400 K. The results are applied to a system consisting of a photovoltaic solar cell in series with a heat engine.

INTRODUCTION

Hybrid systems consisting of a quantum device, such as a photovoltaic cell coupled to a heat engine are capable of utilizing the available solar flux with an efficiency which is greater than a system consisting of a quantum device alone. The addition of the thermal engine powered by the heat rejected from the threshold device in a bottoming cycle is an attempt to lower the cost of the power produced from the incident solar flux. The analysis of the efficiency and cost of such hybrid systems are usually based on the efficiency of a specific threshold device (such as a GaAs or a Si photovaltaic cell) and its thermal characteristics and the efficiency of the heat engine. The efficiency of the heat engine is sometimes taken to be the Carnot efficiency, which is unrealistically high, or an estimated fraction of the Carnot efficiency based on experience. In a previous report (ref. 1), the authors presented an analysis (based on the first and second law of thermodynamics) giving the limiting or maximum power conversion efficiency of a general threshold device for air mass zero (AM Ø), air mass 1.5 (AM 1.5), and a blackbody source at 5800 K (the temperature of a blackbody radiator resulting in the solar constant at 1 AU). The results of their analyses are applicable to any quantum device having a single threshold and operating at any temperature. The limiting efficiency of their system depends on the two device parameters: (1) threshold energy of the device; and (2) the device operating temperature.

We extend their analysis of limiting efficiency to a hybrid system consisting of a generalized quantum device coupled to a Carnot engine in a bottoming cycle. We require, however, that the Carnot engine operate in a maximum power mode. This requirement results in limiting efficiencies which are more realistic than those based on the classical Carnot efficiency, and eliminates the arbitrary nature of the estimates made for the efficiency of the heat engine.

In this report we will first briefly review the thermodynamic analysis which results in the limiting efficiency of a general single threshold quantum device; then discuss the analysis (following Curzon and Ahlborn (ref. 2) of the operation of a heat engine with the requirement that the power delivered be a maximum; followed by a discussion of the solar conversion efficiency of a general quantum-thermal hybrid system; and finally an application of these results to a solar-driven hybrid system previously considered.

MAXIMUM EFFICIENCY FOR A QUANTUM DEVICE

Analyses of the solar energy conversion efficiency of quantum devices with a single threshold energy have previously been made for the specific device such as photovoltaic cells, photobiological, photochemical, and photoelectrochemical systems (ref. 3). In a recent paper (ref. 4), the ultimate conversion efficiency of radiation from a blackbody source by a quantum device with a characteristic threshold energy and an operating temperature was determined using general thermodynamic principles. The approach is outlined here for completeness.

Radiation incident on an energy converter which is operating at a constant temperature, T_R, is characterized by an energy flux, $\dot{E}$, and an entropy flux $\dot{S}$ (see fig. 1). A portion of the incident energy is converted to useful work characterized by the work flux $\dot{W}$, and a portion appears as a flux of heat $\dot{Q}$ to a thermal reservoir used to maintain the conversion device at a constant temperature. There is a re-radiated flux of energy $\dot{E}'$ and entropy $\dot{S}'$ and in general, an entropy flux due to internal irreversible processes $\dot{S}^{int}$. The balance equation for the energy flux gives

$$\dot{E} = \dot{E}' + \dot{Q} + \dot{W} \tag{1}$$

and the corresponding entropy flux balance is

$$\dot{S} = \dot{S}' + \frac{\dot{Q}}{T_R} - \dot{S}^{int} \tag{2}$$

To determine the amount of power derived from the radiation field, we eliminate $\dot{Q}$ from equations (1) and (2) to obtain

$$\dot{W} = (\dot{E} - T_R \dot{S}) - (\dot{E}' - T_R \dot{S}') - T_R \dot{S}^{int} \tag{3}$$

We identify the free energy flux of the incident and emergent radiation as

$$\dot{F} = \dot{E} - T_R \dot{S} \tag{4}$$

and

$$\dot{F}' = \dot{E}' - T_R \dot{S}^{int} \tag{5}$$

with the result that equation (3) can be written as

$$\dot{W} = -\Delta \dot{F} - T_R \dot{S}^{int} \tag{6}$$

The second law of thermodynamics demands that

$$T_R \dot{S}^{int} \geq 0 \tag{7}$$

giving rise to a limit in the amount of power that can be derived from the radiation field, or

$$\dot{W} \leq - \Delta \dot{F} \tag{8}$$

This states that the maximum power to be obtained from a quantum device is simply the change in free energy flux of the incident radiation field.

We consider here a quantum device characterized by a single energy threshold, E_0, capable of absorbing photons with energy $h\nu \geq E_0$ and converting their energy to useful work at a potential E_0/q. Photons having energies $h\nu < E_0$ do not contribute to the power delivered by the conversion device. The maximum thermodynamic efficiency is given by

$$\eta_1 = \frac{-\int_{\nu_0}^{\infty} \frac{h\nu_0}{h\nu} \Delta\dot{F} \, d\nu}{\int_0^{\infty} \dot{E} \, d\nu} \tag{9}$$

where we have defined

$$E_0 = h\nu_0 \tag{10}$$

Equation (9) is a general expression applicable to any radiation energy conversion system characterized by a threshold energy and an operating temperature. The integrals were evaluated in reference 1 for two radiation fields (AM Ø and AM 1.5), and in reference 4 for the flux from any blackbody radiator. The curve labeled "quantum device" in figure 2 is the locus of efficiency maxima for a quantum device and AM 1.5 radiation as a function of the receiver (device) temperature normalized to the source temperature, T_S = 5792 K. The maximum conversion efficiency for a quantum device is about 48 percent and occurs for a device operating at 0 K. This efficiency maximum decreases to zero with increasing temperature. These efficiency maxima are the upper limits to the conversion efficiency for any quantum device. We emphasize that these results apply to any quantum device with a threshold energy such as a photovoltaic solar cell, a photoelectrochemical cell, a photobiological cell, a photochemical cell, etc.

MAXIMUM EFFICIENCY FOR A THERMAL ENGINE

We now couple a thermal engine to this quantum device in a bottoming cycle which will utilize the flux of heat $\dot{Q}$ rejected by the quantum device. This situation is shown schematically in figure 3. The flux $\dot{Q}$ coming from the quantum device operating at a temperature T_R is used to heat a fluid from which a Carnot engine extracts an additional amount of useful energy. The Carnot engine is taken to operate between the reservoir at a temperature T_R and a cold reservoir at a temperature T_C. We demand, following Curzon and Ahlborn (ref. 2), that the Carnot engine deliver maximum power. This requirement restricts the maximum power efficiency of a thermal engine to values more realistic than the classical Carnot efficiency.

The classical Carnot expression for the efficiency of a heat engine applies to a cycle bounded by two adiabats and two isotherms. The operation of this thermal engine along the isotherms must be done infinitely slow to obtain the classical Carnot efficiency. This, however, results in a null power output and maximum energy conversion efficiency. To extract finite power requires that energy be withdrawn from the working fluid along the isotherms in finite time. The analysis carried out by Curzon and Ahlborn (ref. 2) shows that the power output is limited by the rate of energy transferred to and from the working fluid and that the efficiency at maximum power output is given by the surprisingly simple and useful relationship

$$\eta_2 = 1 - \sqrt{\frac{T_C}{T_R}} \tag{11}$$

Only the fraction $\dot{Q}/\dot{E}$ of the total solar flux is available for processing by a heat engine. An upper limit to this availability fraction can be determined from equation (2), i.e.,

$$\frac{\dot{Q}}{T_R} = \dot{S} - \dot{S}' + \dot{S}^{int} > \dot{S} - \dot{S}' \tag{12}$$

because the second law of thermodynamics requires that the entropy change due to irreversible processes be positive. Integrating over the entire solar spectrum assuming the Sun and receiver to behave as blackbodies, this availability fraction is specified by the temperatures of the source T_S and receiver T_R as

$$\frac{\dot{Q}}{\dot{E}} = \frac{T_R\,(\dot{S} - \dot{S}')}{\dot{E}} \longrightarrow \frac{4}{3}\left[\frac{T_R}{T_S} - \frac{T_R^4}{T_S^4}\right] \tag{13}$$

The net efficiency of the heat engine η_H in the hybrid configuration shown in figure 3 is

$$\eta_H = \frac{4}{3}\left[\frac{T_R}{T_S} - \frac{T_R^4}{T_S^4}\right] \cdot \eta_2 \qquad (14)$$

The efficiency, η_H, of the heat engine for this system is given in figure 4 as a function of the temperature ratio T_R/T_S and for parametric values of the ambient temperature T_C. A maximum efficiency of about 63 percent is realized by the heat engine if operated near $T_R/T_S \approx 0.6$ and in an ambient of absolute zero. A more realistic operating condition for this heat engine is given by the $T_C/T_S = 0.05$ curve which represents an ambient temperature near room temperature. An efficiency maximum of 45 percent can be realized by the heat engine. The efficiency continues to decrease for any given receiver temperature as the ambient temperature increases. It should be noted also from figure 4 that the point where the efficiencies of the quantum device and heat engine are equal moves to higher receiver temperatures as the ambient temperature increases. However, the efficiencies of quantum devices such as photovoltaic solar cells and photoelectrochemical cells are expected to be near zero for temperature ratios $T_R/T_S \geq 0.1$ (refs. 5-8).

MAXIMUM EFFICIENCY OF THE QUANTUM-THERMAL HYBRID SYSTEM

The thermodynamic maximum efficiency of a quantum-thermal hybrid system is the sum of the efficiencies given by equations (9) and (14),

$$\eta_{total} = \eta_1 + \eta_H \tag{15}$$

or

$$\eta_{total} = \eta_1 + \frac{4}{3}\left[\frac{T_R}{T_S} - \frac{T_R^4}{T_S^4}\right] \cdot \left[1 - \sqrt{\frac{T_C/T_S}{T_R/T_S}}\right] \tag{16}$$

where η_1 is the ultimate thermodynamic efficiency for the quantum device utilizing the AM 1.5 spectrum. (The efficiency maximum of η_1 occurs for threshold energies corresponding to about 1.1 eV, the bandgap of silicon for example.) The thermodynamic limit for quantum devices as a function of temperature is shown on figures 2, 4, and 5. Figure 2 also gives the dependence of the maximum efficiency for the heat engine and the limiting efficiency of the hybrid system for the condition that the ambient temperature T_C is 0 K. Figure 5 illustrates the effect of the ambient temperature on the limiting efficiency for the hybrid system. For practical ambient temperatures (T_C/T_S = 0.05) the maximum thermodynamic efficiency is 56 percent, and occurs at temperatures near $T_R/T_S \approx 0.5$. Hybrid system efficiencies exceed 50 percent over a wide temperature range ($0.24 < T_R/T_S < 0.7$), suggesting that little benefit is gained in operating a hybrid system above temperatures of $T_R/T_S \approx 0.24$ (1400 K).

AN APPLICATION

Studies of quantum-thermal hybrid solar systems have principally considered solar cells maintained at a constant operating temperature by a fluid which in turn supplies the thermal energy to drive a heat engine (refs. 6 and 9). System efficiency plays a major role in the capital cost analyses in these reports. It can be seen from figure 4 that the limiting efficiency of a photovoltaic cell operating at $T_R/T_S = 0.1$ (580 K) and AM 1.5 is 42 percent. The maximum power conversion efficiency for the thermal engine in contact with an ambient reservoir at $T_C/T_S = 0.05$ (290 K) is 4 percent, resulting in a 46 percent hybrid efficiency. To date, photovoltaic cells such as GaAs and Si operating at temperatures near 580 K have, at best, efficiencies [6,9] of about 10 percent, a factor of 4 smaller than the thermodynamic limit. This reduces this hybrid system efficiency to 14 percent. On the other hand, photovoltaic solar cells operating without concentrators at ambient temperatures have demonstrated efficiencies of 18 percent at AM Ø and 22 percent at AM 1 (ref. 10). Efficiencies are therefore degraded by attempting to employ a bottoming cycle in a hybrid configuration. Efficient high-temperature photovoltaic cells will be required in order that a hybrid system such as this be competitive with either a photovoltaic solar system or with a solar thermal engine.

CONCLUSIONS

An analysis of the efficiency of a quantum-thermal hybrid system based on the first and second laws of thermodynamics has been presented for an AM 1.5 solar spectrum. Hybrid system efficiencies approaching 75 percent are thermodynamically achievable for a quantum device having a threshold of about 1 eV and operating at 3500 K and a heat engine operating between a reservoir at 3500 K and a reservoir at 0 K. For a heat engine in contact with a cold reservoir at room temperature, the maximum system efficiency becomes 56 percent. For this condition, hybrid system limiting efficiencies exceed 50 percent for quantum device operating temperatures in the 1400 K $< T_R <$ 4000 K. Only a small gain in system efficiency is made operating the quantum device above 1400 K. The results of this analysis was applied to a hybrid system consisting of a photovoltaic cell operating at a high temperature maintained by a working fluid used to drive a heat engine in a bottoming cycle. Although the thermodynamically limiting efficiency for the ideal system is 46 percent for practical operating temperatures (≈580 K for the photovoltaic cell and ≈290 K for the cold reservoir), system efficiencies of about 14 percent might be achieved with available photovoltaic cells. This hybrid efficiency is less than efficiencies easily achievable by the separate systems.

Thermodynamically limiting efficiencies for the conversion of solar radiation by a general quantum-thermal hybrid system are larger than the efficiencies of the separate systems. Quantum-thermal hybrid systems should be considered when an efficient high-temperature quantum device is identified and developed.

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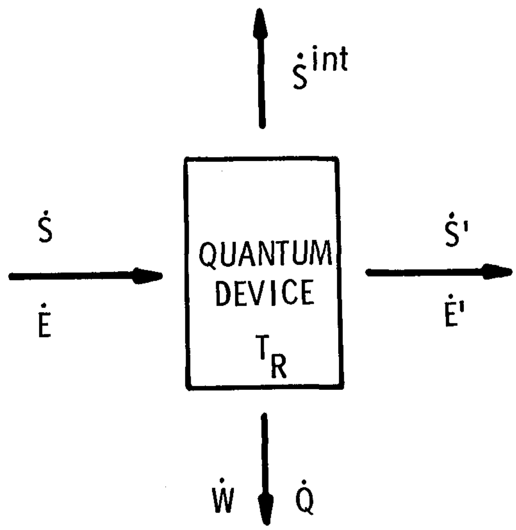

Figure 1. Schematic diagram of the energy, entropy, work and heat flux at a quantum device operating at a temperature T_R.

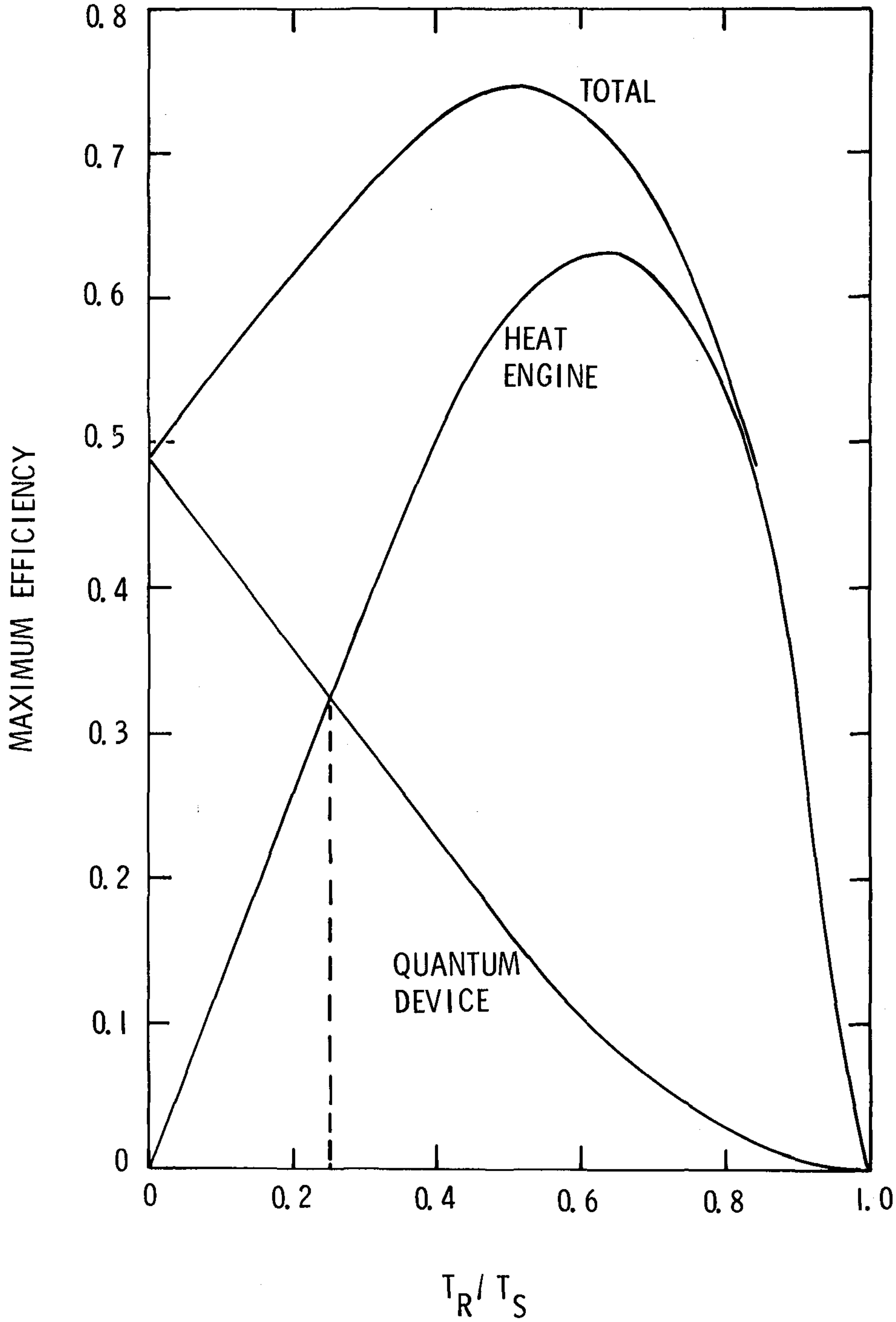

Figure 2. Effect of receiver temperature on the maximum efficiency of a quantum device, a heat engine and a hybrid system in contact with a reservoir at 0 K.

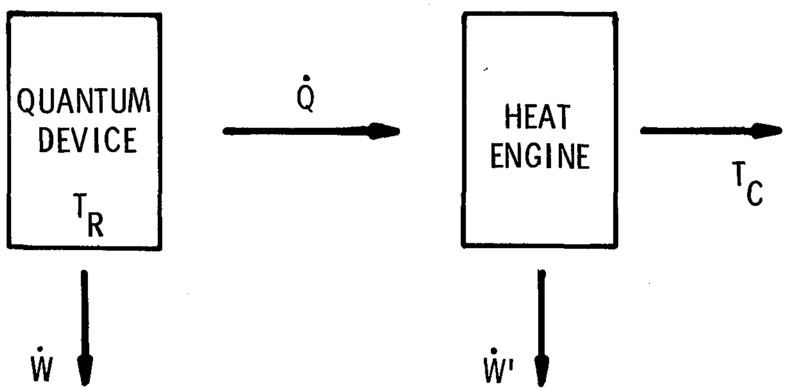

Figure 3. Schematic of the coupling of the heat engine to the thermal flux from the quantum device and the power produced by each. The heat engine is in contact with an ambient reservoir at temperature T_C.

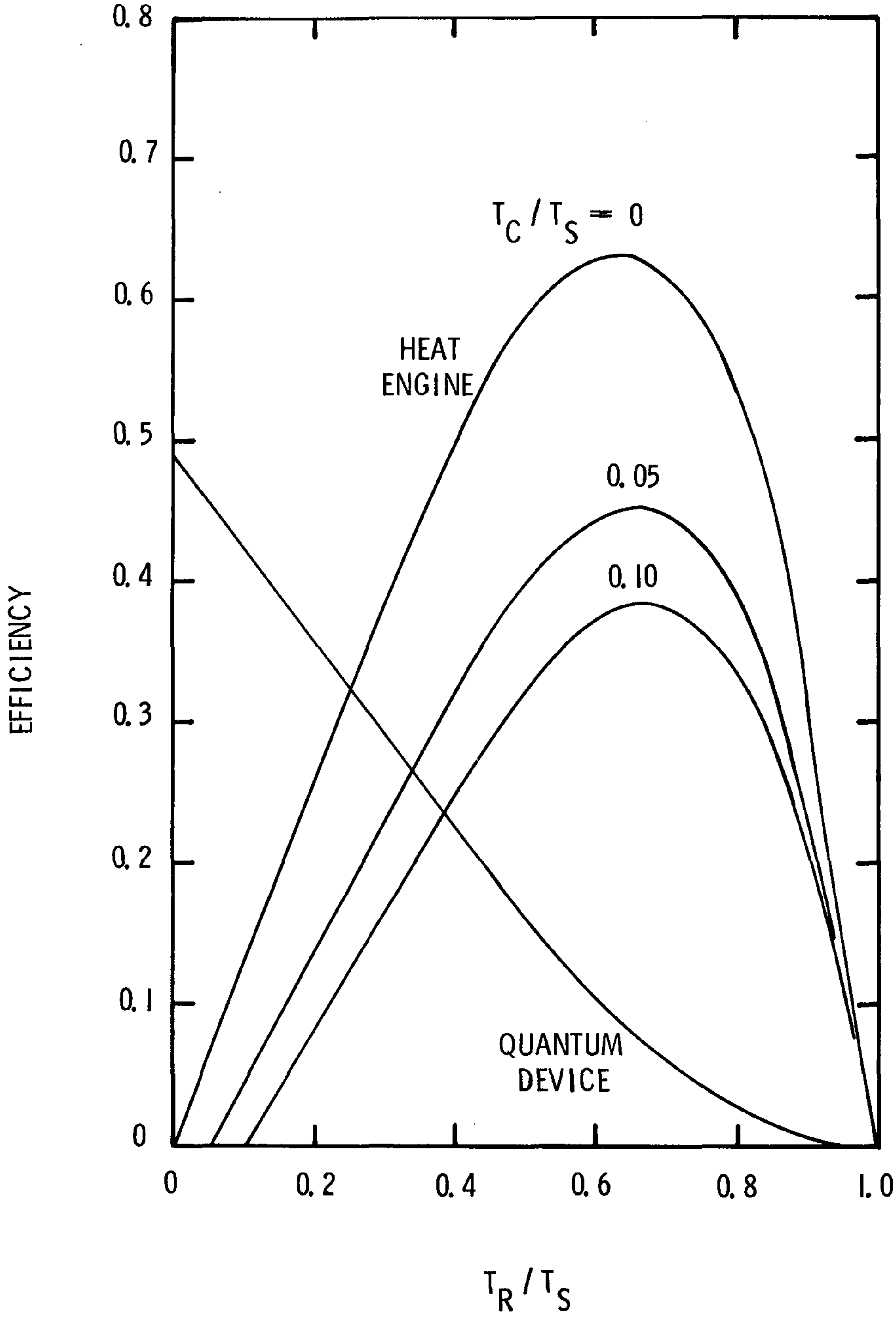

Figure 4. The maximum efficiency of the heat engine as a function of quantum device temperature T_R/T_S for ambient temperatures T_C=0 K, 0.05 T_S, and 0.10 T_S.

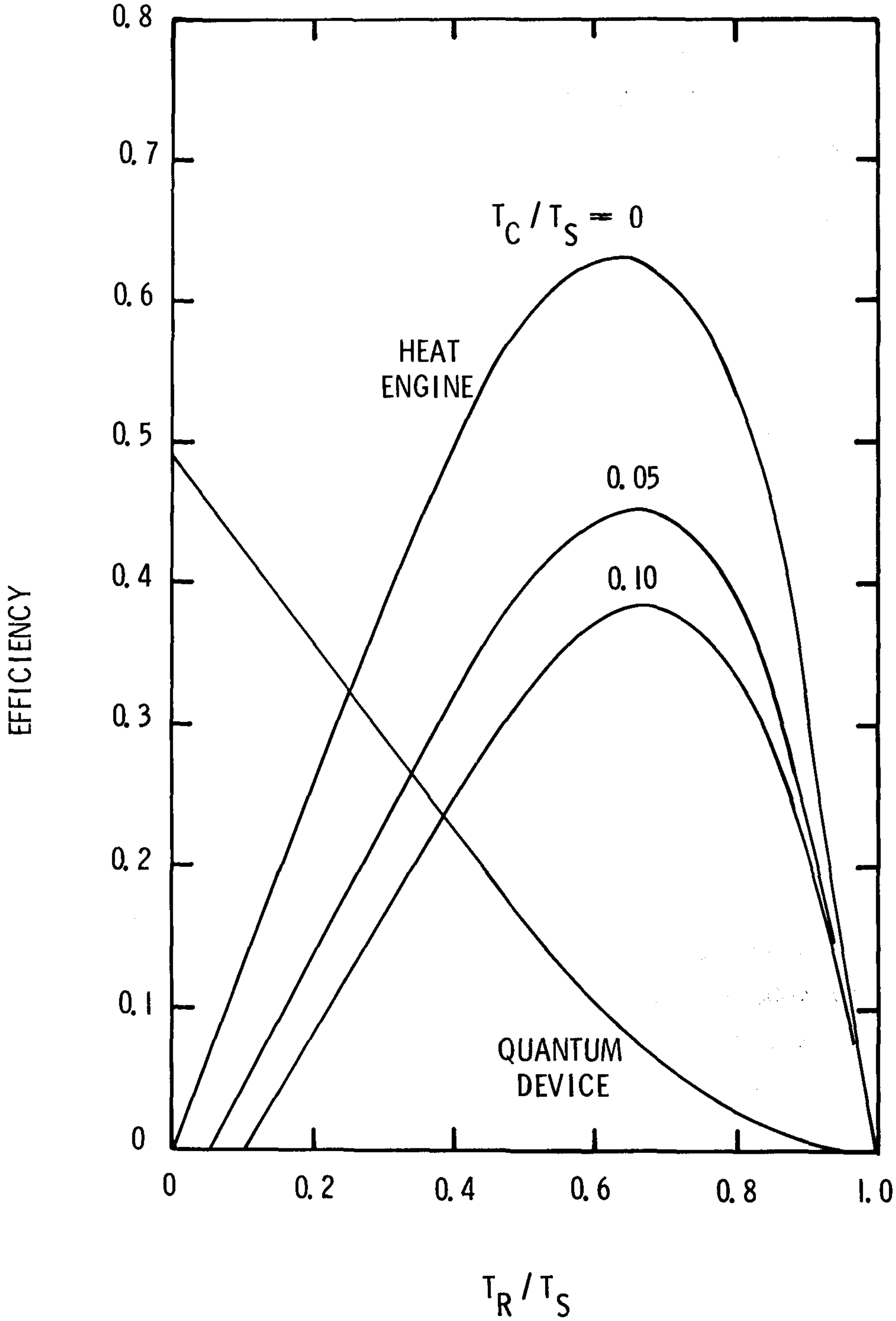

Figure 5. The maximum efficiency of a quantum-thermal hybrid system as a function of quantum device temperature T_R/T_S for ambient temperatures T_C = 0 K, 0.05 K and 0.10 K.

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16. Abstract

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