Supplementary Information for Quantum heat engines: A thermodynamic analysis of power and efficiency

Upendra Harbola
Department of inorganic and physical chemistry,
Indian Institute of Science, Bangalore, 560012, India.

Saar Rahav
Schulich Faculty of Chemistry, Israel Institute of Technology, Haifa 32000, Israel.

Shaul Mukamel
Department of chemistry, University of California, Irvine, USA.
(Dated: June 1, 2012)
I. THE LINDBLAD EQUATIONS AND THE STEADY STATE POWER OUTPUT

We derive the Lindblad equations for our four-level QHE model and compute the power output in the steady state. The Hamiltonian is, $H_T = H_0 + H + \hat{V}$, where the three terms are given in Eqs. (1)-(3) of the main text. The time evolution of the total density matrix $\hat{\rho}_T(t)$ is given by ($\hbar = 1$),

$$\dot{\hat{\rho}}_T(t) = e^{-iH_Tt}\hat{\rho}_T e^{iH_Tt}. \tag{S-1}$$

Tracing over the reservoirs and the cavity modes, and defining the reduced system density matrix $\hat{\rho}(t) = \text{Tr}_R\{\hat{\rho}_T(t)\}$, we get

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -i\text{Tr}_R\{[\hat{H}_S, \hat{\rho}(t)] - \hat{\rho}(t)\hat{H}_S\} \tag{S-2}$$

To second order in the coupling to the reservoirs and the cavity mode, and assuming the Markovian approximation, the right hand side gives,

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -i[H_0, \hat{\rho}(t)] - \Omega_{ph}\pi \sum_{\nu, i'} \left[ g_{i\nu} g_{i'\nu}^* \left\{ \hat{B}_{ai} \hat{B}_{a'i'}^\dagger \hat{\rho}(t) \bar{n}_h(\omega_{ai'}) \hat{B}_{a'i'} - \bar{n}_h(\omega_{ai'}) \hat{B}_{ai} \hat{B}_{a'i'}^\dagger \hat{\rho}(t) \right\} + g_{i'\nu} g_{i\nu}^* \left\{ \bar{n}_h(\omega_{ai'}) \hat{B}_{a'i'} \hat{B}_{ai} \hat{\rho}(t) \hat{B}_{a'i'}^\dagger \hat{\rho}(t) \hat{B}_{ai} \right\} \right] \nonumber$$

where we have indicated the couplings with the hot and the cold baths by subscript $h$ and $c$, respectively, $\omega_{ij} = E_i - E_j$. The mode populations are $\bar{n}_x = \text{Tr}\{a_x^\dagger a_x \hat{\rho}(t)\}$, where $x$ corresponds to either hot ($x = h$), cold ($x = c$) reservoirs, or the cavity mode ($x = t$), and $\bar{n}_x = 1 + n_x$. $\Omega_{ph}$ is the density of states of thermal reservoirs which is assumed to be independent of energy and identical for the two reservoirs.

We next define the matrix element, $\rho_{ij} \equiv \langle i | \hat{\rho} | j \rangle$. A coupled set of equations describing the time evolution of the populations, $\rho_{ii}$, and the real part of the coherence $\rho_{12}$ is obtained as follows.

$$\frac{\partial}{\partial t} \rho_{11} = - (\gamma_{1c}\bar{n}_c(\omega_1) + \gamma_{1h}\bar{n}_h(\omega_1)) \rho_{11} + \gamma_{1h}\bar{n}_h(\omega_1)\rho_{aa} + \gamma_{1c}\bar{n}_c(\omega_1)\rho_{bb} - (\gamma_{1c}\bar{n}_c(\omega_2) + \gamma_{1h}\bar{n}_h(\omega_2)) \rho_{1d} \tag{S-4}$$

$$\frac{\partial}{\partial t} \rho_{22} = - (\gamma_{2c}\bar{n}_c(\omega_2) + \gamma_{2h}\bar{n}_h(\omega_2)) \rho_{22} + \gamma_{2h}\bar{n}_h(\omega_2)\rho_{aa} + \gamma_{2c}\bar{n}_c(\omega_2)\rho_{bb} - (\gamma_{2c}\bar{n}_c(\omega_1) + \gamma_{2h}\bar{n}_h(\omega_1)) \rho_{1d} \tag{S-5}$$

$$\frac{\partial}{\partial t} \rho_{aa} = \gamma_{1h}e^{-i\omega_1} \bar{n}_h(\omega_1)\rho_{11} + \gamma_{2h}e^{-i\omega_2} \bar{n}_h(\omega_2)\rho_{22} - (\gamma_{1h}\bar{n}_h(\omega_1) + \gamma_{2h}\bar{n}_h(\omega_2)) \rho_{aa} + \gamma_{12h}(\bar{n}_h(\omega_1) + \bar{n}_h(\omega_2))\rho_{12} + g^2\bar{n}_t(\omega_2)\rho_{bb} \tag{S-6}$$

$$\frac{\partial}{\partial t} \rho_{ab} = \gamma_{1c}\bar{n}_c(\omega_1)\rho_{11} + \gamma_{2c}\bar{n}_c(\omega_2)\rho_{22} + g^2\bar{n}_t(\omega_2)\rho_{aa} + \gamma_{1c}(\bar{n}_c(\omega_1) + \bar{n}_c(\omega_2))\rho_{12} - (\gamma_{1c}\bar{n}_c(\omega_1) + \gamma_{2c}\bar{n}_c(\omega_2) + g^2\bar{n}_t(\omega_2))\rho_{bb} \tag{S-7}$$

and

$$\frac{\partial}{\partial t} \rho_{12} = -\frac{1}{2} (\gamma_{12h}\bar{n}_h(\omega_1) + \gamma_{12c}\bar{n}_c(\omega_1))\rho_{11} - \frac{1}{2} (\gamma_{12h}\bar{n}_h(\omega_2) + \gamma_{12c}\bar{n}_c(\omega_2))\rho_{22} + \frac{1}{2} \gamma_{12h}(\bar{n}_h(\omega_1) + \bar{n}_h(\omega_2))\rho_{aa} + \frac{1}{2} \gamma_{12c}(\bar{n}_c(\omega_1) + \bar{n}_c(\omega_2))\rho_{bb} - i\omega_{12}\rho_{12} - \Gamma\rho_{12} \tag{S-8}$$
where we have added a decoherence rate $\Gamma$ due to the environment effects [1] and defined the couplings,

$$\gamma_{1x} = \frac{\pi \Omega_{ph}}{2} |g_{1x}|^2, \gamma_{12x} = \frac{\pi \Omega_{ph}}{2} g_{1x} g_{2x}.$$  \hfill (S-9)

Note that $\gamma_{1x} (\gamma_{2x})$ is proportional to the modulus square of the transition dipole between the states 1,2 [1] and $|a\rangle$ or $|b\rangle$, and defines the rate of transition between these states. On the other hand, $\gamma_{12x}$, which defines the strength of coherences, is proportional to the square-root of the scalar product of the transition dipoles between these states and therefore depends also on the relative orientation of the transition dipole vectors. We can change $\gamma_{12x}$ by manipulating the relative orientation, without affecting the transition rates. The maximim value of $\gamma_{12x} = \sqrt{\gamma_{1x} \gamma_{2x}}$ [1].

For symmetric couplings $\gamma_{1x} = \gamma_{2x} = \gamma$ and degenerate levels $E_1 = E_2$, we can rewrite above equation in a matrix form,

$$\dot{\rho}(t) = \gamma \mathcal{M} \rho(t),$$  \hfill (S-10)

where

$$\mathcal{M} = \begin{pmatrix}
-(n_c + n_h) & 0 & (1 + n_h) & (1 + n_c) & -(n_c + r n_h) \\
0 & -(n_c + n_h) & (1 + n_h) & (1 + n_c) & -(n_c + r n_h) \\
n_h & n_h & -2(1 + n_h) - \frac{2c}{r} (1+n_l) & \frac{2c}{r} n_l & 2r n_h \\
-\frac{1}{2}(n_c + r n_h) & -\frac{1}{2}(n_c + r n_h) & r (1+n_h) & (1+n_c) & -(n_c + n_h) - \frac{r}{\gamma}
\end{pmatrix}. \hfill (S-11)
$$

where $r = \gamma_{12}/\gamma$.

Thus the matrix $\mathcal{M}$ describes the time evolution of the system density matrix. Various terms depending on $n_x$, $x = h, c, l$, represent effects of thermal baths and the cavity. At steady state, $\dot{\rho}(t) = 0$, and the set of coupled linear equations (S-10) can be solved to obtain the steady state probabilities $\rho_{ij}^s$. The rate of change in the photon number of the cavity mode can be computed by calculation the rate of change of the energy of the system due to interaction with the cavity mode. This is same as the rate of the work done, i.e., the power ($P$) of the system. We get,

$$P(t) = (E_a - E_b) g^2 (\rho_{aa}(t)(1+n_l) - \rho_{bb}(t) n_l).$$  \hfill (S-12)

Equation (S-12) has a simple interpretation. The bracketed quantity on the right hand side containing the probabilities and the cavity occupation is the detail balance between the transition processes between the states $|a\rangle$ and $|b\rangle$. Thus power is proportional to the breacking of the detail balance. At the equilibrium, $P = 0$, the two transition processes cancel each other.

Substituting the steady state values for $\rho_{aa}^s$ and $\rho_{bb}^s$, and taking the large $g$ limit, we obtain expression given in Eq. (5) in the main text.

### II. VARIATION OF $r^*$ AND THE FRACTIONAL POWER CHANGE WITH RESPECT TO THE CAVITY PHOTON OCCUPATION

Here we show that the optimal value of $r$ in Eq. (9) in the main text, is always an increasing function of the cavity occupation ($n_l$), that is, the derivative of $r^*$ with respect to $n_l (x_l)$ is always positive (negative). The derivative with respect to $n_l$ and $x_l$ are related as,

$$\frac{dA}{dx_l} = -n_l \frac{dn_l}{dn_l}.$$  \hfill (S-13)

Taking derivative of $r^*$ with respect to $x_l$ in Eq. (9), we get,

$$\frac{dr^*}{dx_l} = \frac{r^3}{27 \gamma} f_3 f_4^2 + \frac{r^3}{27 \gamma} a'$$ \hfill (S-14)

where $a$ is defined through Eq. (9). $a'$ and $f_3^*$ are the derivatives of $a$ and $f_3$ with respect to $x_l$. We get,

$$a' = f_3^* = \frac{e^{x_l}(e^{x_h} - 1)[e^{x_h} + e^{x_c} + 2e^{x_c+x_h}]}{[1 + e^{x_h} + e^{x_c} + e^{x_c+x_h}]^2}.$$  \hfill (S-15)
If $dr^*/dn \leq 0$, we must have,

$$1 + \frac{\Gamma}{\gamma} \left( f_3 - \frac{(e^{x_h} - 1)(e^{x_e} - e^{x_h-x_l})}{1 + e^{-x_l} + e^{x_e} + e^{x_h-x_l}} \right) \geq 0. \quad (S-16)$$

Substituting value of $f_3$ from Eq. (10), we find that inequality (S-16) is satisfied over the whole range of parameters.

$$1 + \frac{\Gamma}{\gamma} f_3 \left( \frac{1 + e^{-x_l} + e^{x_e} + e^{x_h-x_l}}{1 + e^{-x_l/2} + 2e^{x_e}} \right) \geq 0, \quad (S-17)$$

where $f_3 > 0$. Thus $dr^*/dn \leq 0$, which using (S-13) implies,

$$\frac{dr^*}{dn} \geq 0. \quad (S-18)$$

Thus $r^*$ is an increasing function of the population in the cavity mode. In fact, using the condition $0 \leq r^* \leq 1$ in (S-14), we obtain,

$$0 \leq \frac{dr^*}{dn} \leq \frac{f_3}{f_3} e^{-x_l}(e^{x_l} - 1)^2. \quad (S-19)$$

We next show that the fractional gain in the power at the optimal value of $r$, $\lim_{r \to r^*}(f_1/(1 - f_2))$ decreases as occupation in the cavity mode increases. To that end, we first express $\Delta P = P/P_0$ in Eq. (5) in a slightly modified form.

$$\lim_{r \to r^*} \Delta P = \frac{f_1}{1 - f_2} \equiv \frac{f_1}{d} \quad (S-20)$$

where $f_1$ is the same as given in Eq. (6) with $r$ replaced by $r^*$ and

$$f = \frac{r^*(e^{x_e} - 1) + e^{x_h} - 1}{N} \quad (S-21)$$

$$g_1 = \frac{1}{e^{x_l} - 1} \left( \frac{1 + e^{x_l} + 2e^{x_e + x_l}}{e^{x_e} - 1} + \frac{r^*(1 + e^{x_l} + 2e^{x_h})}{e^{x_h} - 1} \right) \quad (S-22)$$

$$g_2 = \frac{1}{e^{x_l} - 1} \left( \frac{1 + e^{x_l} + 2e^{x_e + x_l}}{e^{x_e} - 1} + \frac{1 + e^{x_l} + 2e^{x_h}}{e^{x_h} - 1} \right) \quad (S-23)$$

with $N = e^{x_h} + e^{x_e} - 2 + (\Gamma/\gamma)(e^{x_h} - 1)(e^{x_e} - 1)$, independent on the cavity occupation. Note that,

$$1 \geq \frac{g_1}{g_2} \geq r^*. \quad (S-24)$$

The first inequality in (S-24) is obvious since $r^* \leq 1$. For second inequality, we note that $g_1 - r g_2 \geq 0.

The derivative of $f_1$ with respect to the occupation of the cavity mode, $n_l$, is,

$$f'_1 = -\frac{2r^* e^{-x_l}(e^{x_e} - 1)}{N} \quad (S-25)$$

Since $r'' \geq 0$, $f_1$ decays with increasing $n_l$.

We next compute the derivatives of functions $g_1$ and $g_2$ in Eqs. (S-21). These are given by,

$$g'_1 = \frac{1}{e^{x_h} - 1} \left[ \frac{2((1 + r^*)(e^{x_h + x_e} - 1) + (1 - r)(e^{x_h} - 1))}{e^{x_e} - 1} + \frac{r^*(1 + e^{x_l} + 2e^{x_h})}{e^{x_l} - 1} \right] \quad (S-26)$$

and $g'_2$ is obtained from (S-26) by substituting $r^* = 1$ and $r'' = 0$. We note that $g'_1$, $g'_2$, and $f'$ [see Eq. (S-21)] are all positive, i.e., these functions increase with $n_l$. Since $r'' \to 0$ as $r^* \to 1$, we find that

$$\frac{g'_1}{g'_2} \geq r^*. \quad (S-27)$$

The derivative of the denominator is,

$$d' = \left[ f' \frac{g_1}{g_2} + f \frac{g'_1}{g_2} \left( \frac{g'_1}{g_2} - \frac{g_1}{g_2} \right) \right] \quad (S-28)$$
If the quantity inside the bracket is negative, then the denominator increases with \( n_l \), hence \( \Delta P \) decreases with increasing \( n_l \). On the other hand, if the bracketed quantity is positive, the denominator decreases with \( n_l \). We now show that even for \( d' < 0 \) the fractional gain decreases with increasing cavity occupation.

From (S-28) and (S-24), we have

\[
d' \geq - \left[ f' \frac{g_1}{g_2} + f' \frac{g_2}{g_1} \left( \frac{g_1}{g_2} - r^* \right) \right].
\]

(S-29)

Since (S-29) is valid in general, it must also be valid when the r.h.s. function is at minimum. Thus substituting for minimum values from (S-24) and (S-27), we find that,

\[
d' \geq - \frac{r^* r + (e^{x_e} - 1)}{N}.
\]

(S-30)

Taking differentiation of (S-20) with respect to \( n_l \), we get

\[
(\Delta P)' = \frac{1}{d^2}(d f'_1 - f_1 d').
\]

(S-31)

Since \( f'_1 < 0 \) and \( d' < 0 \), we can write

\[
(\Delta P)' = \frac{1}{d^2}(f_1 |d'| - d |f'_1|),
\]

(S-32)

where \( |f| \) denotes the absolute value of the \( f \). Then if \( (\Delta P)' < 0 \), we must have

\[
\frac{d}{f_1} > \frac{|d'|}{|f'_1|}.
\]

(S-33)

Using (S-30) and (S-20), and for \( d' \leq 0 \), the maximum value of the right hand side is 1/2. Thus, we must have \( d > f_1/2 \), which implies,

\[
\frac{g_1}{g_2} < \frac{1 - f_1/2}{f}.
\]

(S-34)

Since the maximum value of the left side is \( r^* \), Eq. (S-24), we must have

\[
\frac{r^*}{f} \leq \frac{1 - f_1/2}{f} = 1 + \frac{\frac{e^{x_e}}{e^{x_e}} + (1 - r^* + r^{*2})(e^{x_e} - 1)}{e^{x_e} - 1 + r^*(e^{x_e} - 1)}.
\]

(S-35)

Since the last term on the right hand side is always positive, the inequality is trivially satisfied. We thus have \( \lim_{r \to r^*} (\Delta P)' < 0 \), i.e., fractional gain decreases with increasing occupation in the cavity mode.