On the First Law of Thermodynamics in Time-Dependent Open Quantum Systems

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In this work, we give a definitive argument determining the internal energy operator of an interacting time-dependent open quantum system arrived at using insights from Mesoscopics. Fully general expressions for the heat current and the power delivered by various agents are derived using the formalism of Non-Equilibrium Green's Functions (NEGF), thus establishing a First Law of Thermodynamics for Open Quantum Systems. Numerics implementing our formal results for a strongly-driven model quantum machine operating as an electrochemical pump and a heat engine are presented. Finally, we analyze the spatial distribution of the internal energy, which is concentrated within the system and along the system-reservoir interface.

Introduction

- Understanding control over quantum machines requires a careful thermodynamic analysis, yet broad consensus on such fundamental theoretical issues has been elusive.
- Our work aims to shed light on one such issue: How to establish an experimentally meaningful and quantum mechanically consistent division of the energy of a far-from-equilibrium quantum system into its Internal Energy, the Work done by the different agents acting on it and the Heat flowing from it.
- We utilize the Nonequilibrium Green's function method (NEGF) to compute all of the thermodynamic quantities of the open quantum system, and illustrate the power of our approach by simulating a model far-from-equilibrium quantum machine.

Divergent Points of View

A 'Hamiltonian of Mean Force' approach introduces an ambiguity in the definition of Internal Energy and concludes that a First Law can't be formulated, even on average.[1] There is also the proposal of dividing up the coupling energy half and half between the system and the environment.[2;3] Others still conclude from Master equation approach that the full Coupling should be put with the System.[4] A comparative study has also recently emerged.[5]

Open Quantum System

We work in the Open Quantum System paradigm where a fairly general Hamiltonian for a time-dependent Fermionic system can be written in second quantized notation as

$$H(t) = H_S(t) + \underbrace{\sum_{\alpha}\sum_{k\in\alpha} \epsilon_k c_k^\dagger c_k}_{H_B} + \underbrace{\sum_{\alpha}\sum_{k\in\alpha,n} (V_{kn} c_k^\dagger d_n + h.c.)}_{H_{SB}}$$

where

$$H_S(t) = \sum_{n,m}\left([H_S^{(1)}(t)]_{nm} d_n^\dagger d_m + [H_S^{(2)}]_{nm} d_n^\dagger d_m^\dagger d_m d_n \right)$$

allowing for explicit **Time-Dependence** *and* **Inter-Particle Interactions** in the System.

What we seek: Non-Equilibrium Thermodynamic quantities

The Work done by External forces

$$\dot{W}_{ext} \equiv \frac{d}{dt}\langle H(t)\rangle = \frac{d}{dt}\langle H_S(t) + H_{SB} + H_B\rangle = \langle \dot{H}_S(t)\rangle$$

Applying the Quasi-Equilibrium thermodynamic identity $TdS = dE - \mu dN$ to the Reservoirs, we identify

$$\frac{d}{dt}\langle H_B\rangle = \underbrace{\sum_{\alpha} \mu_\alpha I_\alpha^N(t)}_{-\text{Electrochemical Power}} + \underbrace{\sum_{\alpha} I_\alpha^Q(t)}_{\text{Heat Current}}$$

where

$$I_\alpha^N(t) \equiv \frac{d}{dt}\langle N_\alpha\rangle,\ I_\alpha^Q(t) = \frac{d}{dt}\langle H_{B,\alpha}\rangle - \mu_\alpha \frac{d}{dt}\langle N_\alpha\rangle$$

The Role of Reservoirs

- Heat is a quantity whose definition $đQ = TdS$ is only valid for processes involving systems infinitesimally perturbed from equilibrium. Furthermore, it must be accounted for as an irreversible flow of energy, and as such, must be accounted for carefully in strongly-driven systems.
- The requirements imposed due to this are met exactly by the semi-infinite Fermionic reservoirs to which the nonequilibrium system is coupled. These properties of the reservoir model have been long established in Mesoscopics and Quantum Transport literature,[6;7;8] where they enforce an Ordering of Limits such that one must take the limit of the Reservoirs going to infinity *before* the limit of the adiabatic perturbation switch-on time going to infinity or $L \to \infty > t_{adiab} \to \infty$

The First Law of Quantum Thermodynamics

$$\underbrace{\frac{d}{dt}\langle H_S(t) + H_{SB}\rangle}_{\text{Rate of Change of Internal Energy}} = \underbrace{(\dot{W}_{ext} + \overbrace{\dot{W}_{elec}}^{(\sum_\alpha -\mu_\alpha I_\alpha^{(0)}(t))})}_{\text{Rate of Work done}} + \underbrace{\overbrace{\dot{Q}}^{(\sum_\alpha -I_\alpha^{(1)}(t))}}_{\text{Rate of Heat flow}}$$

With the Internal Energy Operator $U(t) = H_S(t) + H_{SB}$

Where each RHS term has been evaluated using the Nonequilibrium Green's Function **(NEGF)** formalism, in terms of the System Green's function as

$$\dot{W}_{ext} = -i\mathbb{Tr}(\dot{H}_S^{(1)}(t) G^<(t,t))$$

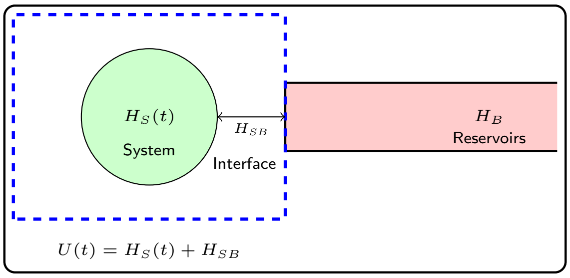
$$I_\alpha^{(\nu)}(t) = \frac{2}{\hbar}\int_{-\infty}^{\infty}\frac{dE}{2\pi}\int_{-\infty}^{t} dt_1 (E-\mu_\alpha)^\nu \mathbb{Im}\mathbb{Tr}\{e^{-iE(t_1-t)}\Gamma_\alpha(E) [G^<(t,t_1) + f_\alpha(E) G^R(t,t_1)]\}$$

where $\Gamma_\alpha(E) \equiv$ Tunneling Width Matrix and $f_\alpha(E) \equiv$ Fermi-Dirac distribution of α^{th} lead.
$\nu = 0$ gives the particle current and $\nu = 1$ gives the heat current.

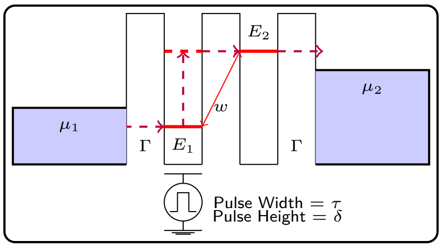
Similarly, Internal Energy $\langle U(t)\rangle = \langle H_S(t) + H_{SB}\rangle$ can be evaluated with

$$\langle H_S(t)\rangle = -i\mathbb{Tr}(H_S^{(1)}(t) G^<(t,t)),$$

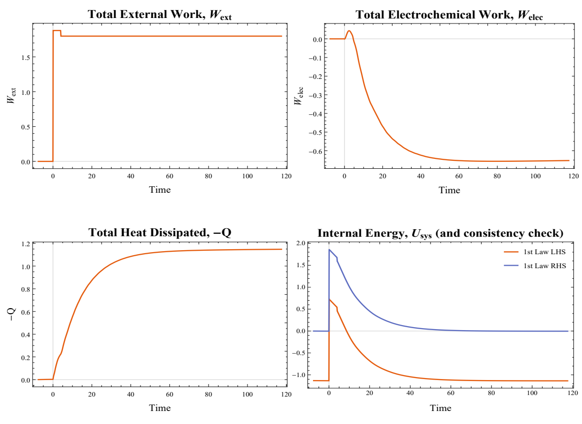
$$\langle H_{SB}\rangle = \frac{2}{\hbar}\int_{-\infty}^{\infty}\frac{dE}{2\pi}\int_{-\infty}^{t} dt_1 \mathbb{Re}\mathbb{Tr}\{e^{-iE(t_1-t)}\Gamma_\alpha(E) [G^<(t,t_1) + f_\alpha(E) G^R(t,t_1)]\}.$$



Proof of Concept: Electrochemical Pump from Rabi Oscillations

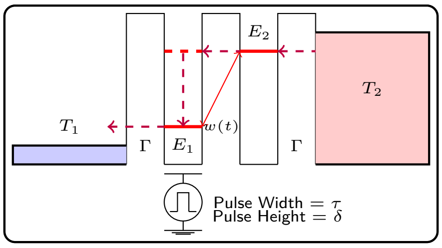


$$\hbar = 1; \Delta E = 2, w = \Delta E/5; \Gamma = w/5;$$
$$-\mu_1 = \mu_2 = 0.5; \delta = \Delta E, \tau = \pi/2w$$

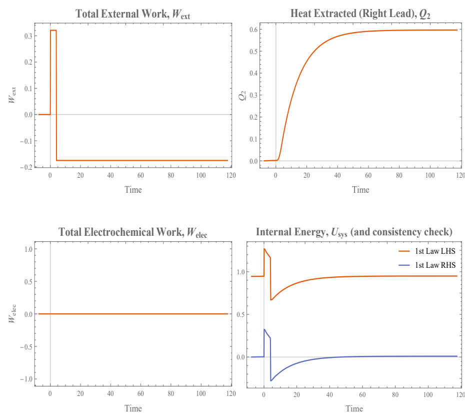


$$\eta = \frac{|W_{elec}(\infty)|}{|W_{ext}(\infty)|} = 36.5\%$$

Proof of Concept: Heat Engine from Rabi Oscillations

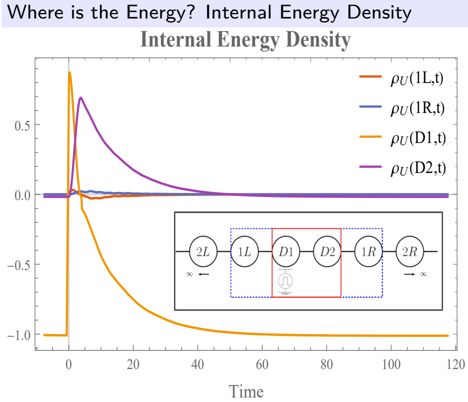


$$\hbar = 1; \Delta E = 2, w = \Delta E/5; \Gamma = w/5;$$
$$T_1 = 0.5, T_2 = 3.6; \delta = \Delta E, \tau = \pi/2w$$



$$\eta = \frac{|W_{ext}(\infty)|}{|Q_2(\infty)|} = 46.6\% = 53\%\eta_{Carnot}$$

Where is the Energy? Internal Energy Density



Reservoirs modeled as tight-binding chains (inset) for the system operating as electrochemical pump, exactly as before. All other sites have zero contribution from $U(t)$.

Summary and Extensions

- With a clear conception of Heat and critical evaluation of the role of Reservoirs, we established an unambiguous Internal energy operator of a time-dependent Open Quantum System, $U(t) = H_S(t) + H_{SB}$ and consequently the First Law.
- All First Law quantities are computed in terms of the System Green's Function and the formal results have been simulated on a strongly driven model quantum machine. Also find that the internal energy is concentrated within the System and along the System-Reservoir Interface.
- We have also extended the results to the fully time-dependent Coupling and Reservoirs case; and included Phonons and Electron-Phonon interactions.

References and Acknowledgements

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