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# Unified Quantum Model of Work Generation in Thermoelectric Generators, Solar and Fuel Cells

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**Abstract:** In the previous papers, the idea of “hidden oscillations” has been applied to explain work generation in semiconductor photovoltaic cells and thermoelectric generators. The aim of this paper is firstly to extend this approach to fuel cells and, secondly, to create a unified quantum model for all types of such devices. They are treated as electron pumps powered by heat or chemical engines. The working fluid is electron gas and the necessary oscillating element (“piston”) is provided by plasma oscillation. Those oscillations are localized around the junction that also serves as a diode rectifying fast electric charge oscillations and yielding a final output direct current (DC). The dynamics of the devices are governed by the Markovian master equations that can be derived in a rigorous way from the underlying Hamiltonian models and are consistent with the laws of thermodynamics. The new ingredient is the derivation of master equations for systems driven by chemical reactions.

**Keywords:** quantum open systems; quantum heat engines; photovoltaic cells; thermoelectric generators; fuel cells

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## 1. Introduction

Photovoltaic cells, thermoelectric generators and fuel cells (PTFs) are devices that produce electric current from light, heat and chemical energy, respectively. Although all of them were developed over hundred years ago, the explanations of their operation principle that can be found in numerous textbooks and popular accounts cannot be complete. While for a battery or a capacitor the electric current, which can yield work, is produced by a charge flow from the place with a higher electrochemical potential to the place with a lower one in PTFs, the electric current flows always in a closed circuit. Therefore, by the very definition of *potential*, it cannot be driven by a time-independent *electrochemical potential* as usually claimed in the literature.

The PTF should rather be treated as a heat engine which powers a pump, in this case pumping electron gas (or fluid) in the external circuit [1–3]. The macroscopic heat motors or turbines contain always periodically moving elements like pistons, flywheels or rotors, which perform periodic motion at the expense of heat or chemical energy provided by the external reservoir. Such self-oscillatory mechanisms that rely on the feedback are an essential part of the operation of heat engines [4,5].

Another argument supporting the presence of “hidden” self-oscillations in PTFs stem from the theoretical studies of quantum heat engines within the formalism of quantum open systems [6–15]. It was shown, using a number of different models appropriate for various regimes, that the very process of work extraction needs a system of a single degree of freedom executing an oscillatory motion. This system, called a work reservoir, or simply a “piston”, operates in the semi-classical limit and, usually, can be replaced by a periodic external driving. Only the presence of such a system can synchronize the individual motions of microscopic subsystems forming PTFs and produce work

that is a macroscopic and deterministic form of energy (the different approach to work generation in photovoltaic devices and photosynthesis processes is advocated, e.g., in [16]).

The aim of this paper is to present a universal quantum model of PTF that generalizes and simplifies the previous proposals for photovoltaic cells and thermoelectric generators. It consists of two “bands” occupied by electrons in which energy spectrum can be controlled by a certain collective degree of freedom. This oscillatory degree of freedom acts as a piston and in all PTFs can be identified with a sort of plasma oscillation. Those self-oscillations of plasma are powered by the coupling of the electron gas to a non-equilibrium stationary environment. Moreover, a diode mechanism rectifying the oscillations of electric current is built in the system in a form of non-ohmic junction. The cooperation of the oscillating piston and the diode mechanism “pumps” the electron gas in the external circuit similarly to a piston water pump [3].

## 2. Model of PTF

The aim of this section is to develop a unified general model of heat or chemical engine valid as an idealized theoretical scheme for all types of PTF devices. All formulas will be written in the natural units of energy, frequency and temperature such that  $\hbar = k_B = 1$ . The working medium is an electron gas occupying effective single-electron states distributed in two bands  $A$  and  $B$ . The electrons interact with the *cold bath* at the temperature  $T$  which drives them into the Gibbs state at the same temperature. Another reservoir called *hot bath* is either a heat bath at the temperature  $T_1 > T$  or a chemical bath supplying chemical energy to the electronic system. Both types of hot bath can be described by the universal model of a chemical bath characterized by the temperature  $T_1$  and the chemical potentials  $\mu_1, \mu_2, \dots, \mu_K$ .

The other important ingredient is the presence of a collective, essentially macroscopic degree of freedom, called *work reservoir* or *piston*, which can execute oscillatory motion. In all PTFs, this motion is attributed to plasma oscillations, which are universal phenomena in the presence of freely moving charges in the background of fixed opposite charges and the boundaries separated materials with different charge densities. To generate electric current, which can perform work, one needs a positive feedback mechanism that stimulates the oscillatory motion of the piston at the expense of energy flow from the hot bath.

### 2.1. Model Hamiltonians

The electrons distributed in two bands  $A$  and  $B$  are described by two sets of the annihilation and creation operators,  $a_k, a_k^\dagger$  and  $b_l, b_l^\dagger$ , respectively, subject to canonical anticommutation relations. The electrons are treated as non-interacting fermions moving in a self-consistent potential with the unperturbed Hamiltonian:

$$H_0 = \sum_k E_a(k) a_k^\dagger a_k + \sum_l E_b(l) b_l^\dagger b_l. \quad (1)$$

The system of electrons creates an equilibrium charge distribution which minimizes free energy. The collective perturbation of this distribution produces macroscopic charge oscillations called plasma oscillations with the frequency  $\Omega$  described by a single collective variable  $\xi(t) = g \sin \Omega t$ . The coupling of this collective mode with individual electrons in bands is given by Coulomb and exchange interactions and can be described by a mean field modulation Hamiltonian:

$$H_{mod} = \xi N_a = \xi \sum_k a_k^\dagger a_k. \quad (2)$$

Here, the parameter  $\xi$  absorbs all relevant coupling constants and hence can be interpreted as a shift of the single electron energy in a band  $A$ . The coupling Equation (2) involves only the number of electrons in the  $A$ -band because the total number of electrons in both bands is a constant of motion and hence the number of electrons in  $B$ -band can be eliminated at the cost of an overall shift of the energy scale.

The system of electrons perturbed periodically by the piston interacts with a non-equilibrium environment composed at least of two baths. One of these baths is assumed to be a thermal reservoir at the device ambient temperature  $T$ . We assume also that, practically, this cold bath can cause only *intraband transitions* and serves as a dump for a part of the supplied energy. The corresponding interaction Hamiltonian can be written as:

$$H_{intra} = \sum_{kk'} a_k^\dagger a_{k'} \otimes R_{kk'}^{(a)} + \sum_{ll'} b_l^\dagger b_{l'} \otimes R_{ll'}^{(b)}, \tag{3}$$

where  $R_{kk'}^{(a)}, R_{ll'}^{(b)}$  are hermitian matrices consisting of operators acting on the baths Hilbert spaces.

The second component of the environment is the source of energy either in the form of heat supplied at the higher temperature  $T_1 > T$ , or chemical energy. In this case, the interaction Hamiltonian reads:

$$H_{inter} = \sum_{kl} (a_k^\dagger b_l + b_l^\dagger a_k) \otimes R_{kl}^{(ab)} \tag{4}$$

and describes the *interband transitions*.

### 2.2. Markovian Master Equations

A generic quantum open system coupled to a stationary environment is described by the “bare” system Hamiltonians  $H^0$ , the bath Hamiltonian  $H_R$ , and the weak interaction Hamiltonian:

$$H_{int} = S \otimes R. \tag{5}$$

( $S$  ( $R$ ) is a Hermitian system (reservoir) operator) and the stationary state of the reservoir satisfying

$$[\rho_R, H_R] = 0, \text{Tr}(\rho_R R) = 0. \tag{6}$$

The Schroedinger picture Markovian Master equation (MME) for the system reduced density matrix has the following standard form:

$$\frac{d\rho}{dt} = -i[H, \rho] + \frac{1}{2} \sum_{\{\omega \geq 0\}} \left\{ G(\omega) ([S_\omega, \rho S_\omega^\dagger] + [S_\omega \rho, S_\omega^\dagger]) + G(-\omega) ([S_\omega^\dagger, \rho S_\omega] + [S_\omega^\dagger \rho, S_\omega]) \right\}, \tag{7}$$

where

$$S(t) = e^{iHt} S e^{-iHt} = \sum_{\{\omega \geq 0\}} (e^{-i\omega t} S_\omega + e^{i\omega t} S_\omega^\dagger), \tag{8}$$

with  $\{\omega \geq 0\}$  denoting the set of all non-negative Bohr frequencies.

Notice, that  $S(t)$  is defined with respect to the renormalized, *physical* Hamiltonian  $H$  containing *Lamb-shift* corrections. The influence of the reservoir on the relaxation processes is entirely described by the coupling spectrum defined as:

$$G(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} \text{Tr}(\rho_R R(t)R) dt, \quad R(t) = e^{iH_R t} R e^{-iH_R t}. \tag{9}$$

The term in Equation (7) proportional to  $G(\omega)$  characterizes the dissipation rate of energy  $\omega$  into bath, while the term proportional to  $G(-\omega)$  is the reverse process of excitation.

The generalization of the form of MME to more complicated interactions like, e.g., Equation (3) or Equation (4) is straightforward.

### 2.3. Thermal and Chemical Baths

Two particular types of baths are important for the models of PTF—a thermal bath and a chemical bath.

A thermal bath is described by the Gibbs state at the temperature  $T$  given by the density matrix

$$\rho_R = Z^{-1} \exp\left\{-\frac{1}{T}H_R\right\}. \tag{10}$$

The so-called Kubo–Martin–Schwinger condition (KMS) implied by the form Equation (10) and valid in the thermodynamic limit leads to the following relation (detailed balance) satisfied by the coupling spectrum

$$G(-\omega) = e^{-\omega/T}G(\omega). \tag{11}$$

Under the condition Equation (11), the Gibbs state at the same temperature  $T$  is a stationary solution of the MME Equation (7).

A chemical bath is a collection of  $K$  separated baths each consisting of many molecules of a given type. The whole bath is described by the density matrix corresponding to the grand canonical ensemble at the temperature  $T_1$  and the chemical potentials  $\mu_j$

$$\tilde{\rho}_R = Z^{-1} \exp\left\{-\frac{1}{T_1}\left(H_R - \sum_{j=1}^K \mu_j N_j\right)\right\} \tag{12}$$

Here,  $N_j$  is the operator describing the number of  $j$ -type molecules in the bath and  $H_R$  is the total Hamiltonian of the chemical bath satisfying

$$[N_j, H_R] = 0, \text{ for all } j = 1, 2, \dots, K. \tag{13}$$

The Condition (13) means that the molecules in the chemical bath do not undergo chemical reactions unless they became coupled by the quantum system. This coupling can be described by the rotating-wave approximation version of the Hamiltonian Equation (5):

$$H_{int} = S^- \otimes R^+ + S^+ \otimes R^-, \quad S^+ = (S^-)^\dagger, R^+ = (R^-)^\dagger. \tag{14}$$

Here,  $S^+$  increases the energy of the system and the operator  $R^-$  describes the possible transitions from higher to lower energy levels of the bath including chemical reactions. One can think about  $R^-$  as a sum of products of operators describing transitions preserving all numbers of molecules, “annihilation operators” corresponding to reactants and “creation operators” corresponding to reaction products, respectively. Hence,  $R^-$  satisfies the following relation

$$\left[\sum_{j=1}^K \mu_j N_j, R^-\right] = \left(\sum_{j=1}^K v_j \mu_j\right)R^-, \tag{15}$$

where  $v_j$  are stoichiometric coefficients, negative for reactants and positive for reaction products. The sum

$$\sum_{j=1}^K v_j \mu_j = \Delta g \tag{16}$$

can be interpreted as the Gibbs free energy released in a single reaction. Obviously, the operator  $S^- \otimes R^+$  describes the reverse processes consuming energy from the system. If the operators  $R^\pm$  commute with all number operators  $N_j$ , then  $\Delta g = 0$ , no chemical reactions occur, and the bath acts as a purely thermal bath at the temperature  $T_1$ .

Applying again the standard derivation of the MME, one obtains the Equation (7) with  $G(\omega)$  ( $\omega > 0$ ) replaced by the relaxation coefficient:

$$G(\omega) \rightarrow \gamma_\downarrow(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} \text{Tr}(\tilde{\rho}_R R^-(t)R^+) dt, \tag{17}$$

and  $G(-\omega)$  ( $\omega > 0$ ) is replaced by the excitation coefficient:

$$G(\omega) \rightarrow \gamma_{\uparrow}(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} \text{Tr}(\tilde{\rho}_R R^+(t)R^-) dt. \quad (18)$$

The fictitious dynamics governed by the *extended Hamiltonian*  $\tilde{H}_R = H_R - \sum_{j=1}^K \mu_j N_j$  and applied to the operators  $R^{\pm}$  yields:

$$\tilde{R}^{\pm}(t) = e^{i\tilde{H}_R t} R^{\pm} e^{-i\tilde{H}_R t} = R^{\pm}(t) e^{\mp i\Delta g t}. \quad (19)$$

Using Equation (19) and the KMS condition again for the grand canonical ensemble  $\tilde{\rho}_R$  treated as an “extended” Gibbs state and the “extended” operators  $\tilde{R}^{\pm}(t)$ , one obtains the following relation:

$$\gamma_{\uparrow}(\omega) = \exp\left\{-\frac{1}{T_1}(\omega + \Delta g)\right\} \gamma_{\downarrow}(\omega), \quad (20)$$

which generalizes the detailed balance Condition (11) to chemical baths. A chemical bath is more general than a thermal one and reduces to the latter for  $\Delta g = 0$ , hence it will be used as a universal model of the hot bath for PTFs.

#### 2.4. A Generic Model of a Quantum Engine

In the PTF model, the electron gas, interacting with a stationary environment and collective degree of freedom (plasma oscillation), can be considered as a particular example of slowly driving quantum open system. In other words, it can be interpreted as a version of the generic quantum heat engine model introduced in [6] (compare also [7]) and successfully used in the context of solar cells [1] and thermoelectric generators [2].

In this scheme, the quantum system corresponding to “working medium” interacts weakly with a stationary non-equilibrium environment typically, but not always, consisting of two heat baths at different temperatures. The external periodic driving  $H_{mod}(t)$  added to the free Hamiltonian  $H_0$  of the system describes the action of a macroscopic piston which supplies and extracts work. If the average net power extracted from the working medium is positive, then the oscillations of the piston are self-sustained (self-oscillations), and the whole system acts as an engine yielding useful work.

Under certain standard assumptions: (i) weak system-environment coupling; (ii) ergodic properties of the stationary environment; (iii) slowly varying  $H_{mod}(t)$  in comparison to the fast internal dynamics; the irreversible evolution of the reduced density matrix  $\rho(t)$  of the working medium satisfies the Markovian master equation (MME) of the following form:

$$\frac{d}{dt}\rho(t) = -i[H(t), \rho(t)] + \mathcal{L}(t)\rho(t). \quad (21)$$

Here,  $H(t) = H_0 + H_{mod}(t)$  is the total Hamiltonian of the working medium and  $\mathcal{L}(t)$  describes the influence of an environment.

If the modulation part  $H_{mod}(t)$  is also “small”, in comparison to  $H_0$ , we can assume that, according to the standard perturbation theory, in the lowest order approximation,  $H_{mod}(t)$  commutes with  $H_0$ . Then, assuming also harmonic oscillations, we can put

$$H_{mod}(t) = \zeta(t)M = g(\sin \Omega t) M, \quad [H_0, M] = 0, \quad (22)$$

where  $g$  is a “small” amplitude of oscillations.

The dissipative generator  $\mathcal{L}(t)$  obtained by the standard weak coupling limit procedure is a function of the magnitude of perturbation  $\zeta$  and can be written as

$$\mathcal{L}(t) \equiv \mathcal{L}[\zeta(t)]. \quad (23)$$

Under natural ergodic assumptions, the generator  $\mathcal{L}[\zeta]$  possesses a unique stationary state  $\bar{\rho}[\zeta]$  satisfying the identities:

$$\mathcal{L}[\zeta]\bar{\rho}[\zeta] = 0, \quad \mathcal{L}'[\zeta]\bar{\rho}[\zeta] = -\mathcal{L}[\zeta]\bar{\rho}'[\zeta], \tag{24}$$

where  $\mathcal{L}'[\zeta] \equiv \frac{d}{d\zeta}\mathcal{L}[\zeta]$ ,  $\bar{\rho}'[\zeta] \equiv \frac{d}{d\zeta}\bar{\rho}[\zeta]$ . As discussed in [6], the power  $P(t)$  provided by the engine and the net heat current  $J(t)$  supplied by the environment are defined as:

$$P(t) = -\text{Tr}\left(\rho(t)\frac{dH(t)}{dt}\right), \quad J(t) = \text{Tr}\left(H(t)\frac{d\rho(t)}{dt}\right). \tag{25}$$

The definitions of the above are consistent with the first and second law of thermodynamics, and the time-dependence of the Hamiltonian is necessary to define work. The stationary average power output given by the time averaging of  $P(t)$  reads:

$$\bar{P} = -g\Omega \lim_{t_0 \rightarrow \infty} \frac{1}{t_0} \int_0^{t_0} \text{Tr}\left(\rho(t)M\right) \cos \Omega t dt. \tag{26}$$

For the reader's convenience, the following second order approximation with respect to a small parameter  $g$  is derived in the Appendix (compare [1]):

$$\bar{P} = -\frac{1}{2}g^2\text{Tr}\left(\bar{\rho}'[0]\frac{\Omega^2}{\Omega^2 + \mathcal{L}^{*2}[0]}\mathcal{L}^*[0]M\right), \tag{27}$$

where  $\mathcal{L}^*[0]$  is the Heisenberg picture counterpart of the Schroedinger picture generator  $\mathcal{L}[0]$ . If, additionally, the modulation frequency  $\Omega$  is much higher than the relaxation rate of the observable  $M$  then, we can use the following compact expression

$$\bar{P} = -\frac{1}{2}g^2\text{Tr}\left(\bar{\rho}'[0]\mathcal{L}^*[0]M\right). \tag{28}$$

The lowest order Formula (28) is still consistent with thermodynamics [1] and is the basic one for the further analysis of PTF. The stationary output power is proportional to the square of the amplitude of piston oscillations, which is a free parameter. This amplitude is determined by the energy flux from the environment and the load attached to the piston, e.g., the resistance, electric motor or battery in the case of PTF.

### 2.5. MME for the PTF

The general framework of the previous section can be applied to the PTF model described by the Hamiltonians Equations (1)–(4). The first element is the MME generator  $\mathcal{L}[0]$  computed under the absence of modulation. It is a sum of two generators corresponding to statistically independent processes of intraband transitions induced by the thermal cold bath at the ambient temperature  $T$  and the interband transitions induced by the chemical hot bath characterized by the temperature  $T_1$  and the Gibbs free energy excess  $\Delta g$ . The detailed structure of the generators is the following:

$$\mathcal{L}[0] = \mathcal{L}^{intra}[0] + \mathcal{L}^{inter}[0], \tag{29}$$

$$\mathcal{L}^{intra}[0] = \sum_{\{kk'\}} \mathcal{L}_{kk'}^{(a)} + \sum_{\{ll'\}} \mathcal{L}_{ll'}^{(b)}, \tag{30}$$

$$\mathcal{L}^{inter}[0] = \sum_{\{kl\}} \mathcal{L}_{kl}^{(ab)}, \tag{31}$$

$$\begin{aligned} \mathcal{L}_{kk'}^{(a)} \rho = & \frac{1}{2} \Gamma_{kk'}^{(a)} \left( [a_k a_{k'}^\dagger, \rho, a_{k'} a_k^\dagger] + [a_k a_{k'}^\dagger, \rho, a_{k'} a_k^\dagger] \right. \\ & \left. + e^{-(E_a(k) - E_a(k')/T)} ([a_k^\dagger a_{k'} \rho, a_{k'}^\dagger a_k] + [a_k^\dagger a_{k'} \rho, a_{k'}^\dagger a_k]) \right), \end{aligned} \tag{32}$$

$$\begin{aligned} \mathcal{L}_{ll'}^{(b)} \rho = & \frac{1}{2} \Gamma_{ll'}^{(b)} \left( [b_l b_{l'}^\dagger, \rho, b_{l'} b_l^\dagger] + [b_l b_{l'}^\dagger, \rho, b_{l'} b_l^\dagger] \right. \\ & \left. + e^{-(E_b(l) - E_b(l')/T)} ([b_l^\dagger b_{l'} \rho, b_{l'}^\dagger b_l] + [b_l^\dagger b_{l'} \rho, b_{l'}^\dagger b_l]) \right), \end{aligned} \tag{33}$$

$$\begin{aligned} \mathcal{L}_{kl}^{(ab)} \rho = & \frac{1}{2} \gamma_{kl} \left( [a_k b_l^\dagger, \rho, b_l a_k^\dagger] + [a_k b_l^\dagger, \rho, b_l a_k^\dagger] \right. \\ & \left. + e^{-(E_a(k) - E_b(l) + \Delta g)/T_1} ([a_k^\dagger b_l \rho, b_l^\dagger a_k] + [a_k^\dagger b_l \rho, b_l^\dagger a_k]) \right), \end{aligned} \tag{34}$$

where the summations in the formulas of the above are performed over the sets of indices:  $\{kk'\} = \{kk'; E_a(k) - E_a(k') \geq 0\}$ ,  $\{ll'\} = \{ll'; E_b(l) - E_b(l') \geq 0\}$ ,  $\{kl\} = \{kl; E_a(k) - E_b(l) > 0\}$ .

The term in Equations (32) and (33) describes the following intraband processes:

- (a) Band A (B) electron relaxation from the state  $k$  ( $l$ ) to the state  $k'$  ( $l'$ ) accompanied by a positive energy release to the heat bath at the ambient temperature;
- (b) The inverse process of electron transfer from the lower energy state to the higher energy one with the probability suppressed by the Boltzmann factor.

The term in Equation (34) describes the following interband processes:

- (c) Electron transfer from the higher energy state  $k$  in the band A to the lower energy state  $l$  in the band B;
- (d) The inverse process of electron transfer with the probability suppressed or enhanced by suitable Boltzmann factors including chemical energy.

The analysis of the stationary state for the MME governed by the generator Equation (29) is based on the following facts:

- (i) The intraband thermalization processes governed by Equations (32) and (33) preserve the number of electrons in each band and for a fixed initial numbers of electrons drive the system into a product of two canonical Gibbs states at the temperature  $T$ ;
- (ii) The interband transitions described by Equation (34) preserve the total number of electrons but modify the relative occupation of both bands;
- (iii) Because the number of electrons in a macroscopic PTF device is very large, we can use the equivalence of canonical and grand canonical ensembles to derive the approximate form of the stationary state for  $\mathcal{L}[0]$ ;
- (iv) Due to the form of the modulation Equation (2), the stationary state of the generator  $\mathcal{L}[\xi]$  can be obtained from the stationary state of the generator  $\mathcal{L}[0]$  by replacing the single electron energy  $E_a(k)$  by  $E_a(k) + \xi$ .

Taking (i)–(iv) into account, one concludes that the approximate stationary state of the generator  $\mathcal{L}[\xi]$  has a form of the product of grand canonical ensembles at the ambient temperature  $T$  but with two different electrochemical potentials  $\mu_a, \mu_b$ :

$$\bar{\rho}[\xi] = \frac{1}{Z[\xi]} \exp \left\{ -\frac{1}{T} \left[ \sum_k (E_a(k) + \xi - \mu_a) a_k^\dagger a_k + \sum_l (E_b(l) - \mu_b) b_l^\dagger b_l \right] \right\}. \tag{35}$$

The electro-chemical potentials  $\mu_a, \mu_b$  are determined by the average numbers of electrons in both bands. Therefore, they are functions of the hot bath temperature  $T_1$ , the density of electrons in the material and the load which is attached to the device. This load might be described by the additional generator which takes into account the exchange of electrons between the PTF device and the external circuit. This generator does not depend on  $\xi$  and hence does not explicitly enter the formula for the

power output Equation (28) (see Equation (24) for the explanation), but contributes to the form of the stationary state. Therefore, the electro-chemical potentials  $\mu_a, \mu_b$  may be treated as adjustable parameters depending on the external load.

The difference of electro-chemical potentials between bands can be interpreted as the measured voltage  $V$  of the PTF device, *i.e.*,

$$\mu_a - \mu_b = eV. \quad (36)$$

Indeed, the band  $A$  supplies electrons to the external circuit at the higher energy  $\mu_a$  per electron while the band  $B$  accepts electrons at the lower energy  $\mu_b$  per electron.

## 2.6. The Formula for the Output Power

The results of the previous section can be inserted into the general formula for power output Equation (28). The derivative  $\bar{\rho}'[0]$  is given by

$$\bar{\rho}'[0] = -\frac{Z'[0]}{Z[0]}\bar{\rho}[0] - \frac{1}{T}N_a\bar{\rho}[0]. \quad (37)$$

Inserting Equation (37) into Equation (28) and remembering that now  $M = N_a = \sum_k a_k^\dagger a_k$  one can simplify the expression for power,

$$\bar{P} = -\frac{1}{2}g^2\text{Tr}\left(\bar{\rho}'[0]\mathcal{L}^*[0]M\right) = \frac{1}{2T}g^2\text{Tr}\left(\bar{\rho}[0]N_a\mathcal{L}^*[0]N_a\right) = \frac{1}{2T}g^2\text{Tr}\left(\bar{\rho}[0]N_a\mathcal{L}^{inter*}[0]N_a\right), \quad (38)$$

where one uses the fact that the intraband relaxation does not change the number of electrons in each band.

The further computation involves the action of the Heisenberg picture generator on  $N_a$  for the chemical hot bath:

$$\begin{aligned} \mathcal{L}^{(ab)*}_{kl}N_a &= \gamma_{kl}\left([b_l a_k^\dagger, N_a]a_k b_l^\dagger + b_l a_k^\dagger[N_a, a_k b_l^\dagger]\right) \\ &\quad + e^{-(E_a(k)-E_b(l)+\Delta g)/T_1}\left([b_l^\dagger a_k, N_a]a_k^\dagger b_l + b_l^\dagger a_k[N_a, a_k^\dagger b_l]\right) \\ &= \gamma_{kl}\left(e^{-(E_a(k)-E_b(l)+\Delta g)/T_1}n_l^{(b)}(1-n_k^{(a)}) - n_k^{(a)}(1-n_l^{(b)})\right), \end{aligned} \quad (39)$$

where  $n_k^{(a)} = a_k^\dagger a_k$  and  $n_l^{(b)} = b_l^\dagger b_l$ .

After inserting Equation (39) into Equation (38), one can use the properties of quantum grand canonical ensembles Equation (35) and reduce the averages of even products of annihilation and creation fermionic operators into sums of products of the only non-vanishing two-point correlations:

$$\begin{aligned} \langle a_k^\dagger a_{k'} \rangle_0 &= \delta_{kk'} f_c(k), & \langle a_k a_{k'}^\dagger \rangle_0 &= \delta_{kk'} (1 - f_c(k)), \\ \langle b_l^\dagger b_{l'} \rangle_0 &= \delta_{ll'} f_b(l), & \langle b_l b_{l'}^\dagger \rangle_0 &= \delta_{ll'} (1 - f_b(l)). \end{aligned} \quad (40)$$

Here,  $\langle \dots \rangle_0$  denotes the quantum average with respect to the state  $\bar{\rho}[0]$  given by Equation (35), and  $f_a(k)$  and  $f_b(l)$  are the Fermi–Dirac statistical distribution functions:

$$f_a(k) = \frac{1}{e^{\beta(E_a(k)-\mu_a)} + 1}, \quad f_b(l) = \frac{1}{e^{\beta(E_b(l)-\mu_b)} + 1}, \quad (41)$$



with  $\beta = 1/T$ . The straightforward computation yields the leading order term

$$\begin{aligned}\bar{P} &= \frac{g^2}{T} \langle N_a \rangle_0 \sum_{\{kl\}} \gamma_{kl} \left( e^{-(E_a(k) - E_b(l) - \Delta g)/T_1} [1 - f_a(k)] f_b(l) - [1 - f_b(l)] f_a(k) \right) \\ &= \frac{g^2}{T} \langle N_a \rangle_0 \sum_{\{kl\}} G_{kl} \left( \exp \left\{ \frac{1}{T} \left( \left[ 1 - \frac{T}{T_1} \right] (E_a(k) - E_b(l)) - \frac{T}{T_1} \Delta g - eV \right) \right\} - 1 \right),\end{aligned}\quad (42)$$

where

$$G_{kl} = \gamma_{kl} [1 - f_b(l)] f_a(k). \quad (43)$$

The presence of the factor Equation (43) in the sum Equation (42) essentially restricts the range of positive energy differences  $E_a(k) - E_b(l)$  which can be replaced in the exponent by a single ‘‘average’’ denoted by  $E_g$ . This leads to the following final formula for the output power:

$$\bar{P} = \frac{g^2}{T} \langle N_a \rangle_0 \bar{G} \left( \exp \left\{ \frac{1}{T} \left( \left[ 1 - \frac{T}{T_1} \right] E_g - \frac{T}{T_1} \Delta g - eV \right) \right\} - 1 \right), \quad (44)$$

where  $\bar{G} = \sum_{kl} G_{kl}$ .

A direct consequence of the formula Equation (44) is the condition for work generation in PTF devices:

$$eV < eV_{oc} = (E_g + \Delta g) \left( 1 - \frac{T}{T_1} \right) - \Delta g. \quad (45)$$

Here,  $V_{oc}$  can be interpreted as an *open-circuit voltage* because, when the external circuit is closed, the voltage is reduced and the positive output power maintains collective plasma oscillations (positive feedback). These charge oscillations are subsequently rectified by the diode mechanism due to the build-in non-ohmic junctions, which are present in all PTF devices.

For a purely thermal hot bath, the Carnot factor  $1 - T/T_1$  also suggests the interpretation of the Equation (45) in terms of thermodynamical efficiency. A single electron excited from the band  $B$  to  $A$  requires, on average,  $E_g$  of thermal energy extracted from the hot bath. Then, a part of  $E_g$  is transformed into useful work, equal at most to  $eV_{oc}$  per single electron flowing in the external circuit. For a purely chemical hot bath, in principle, the whole Gibbs energy can be transformed into work.

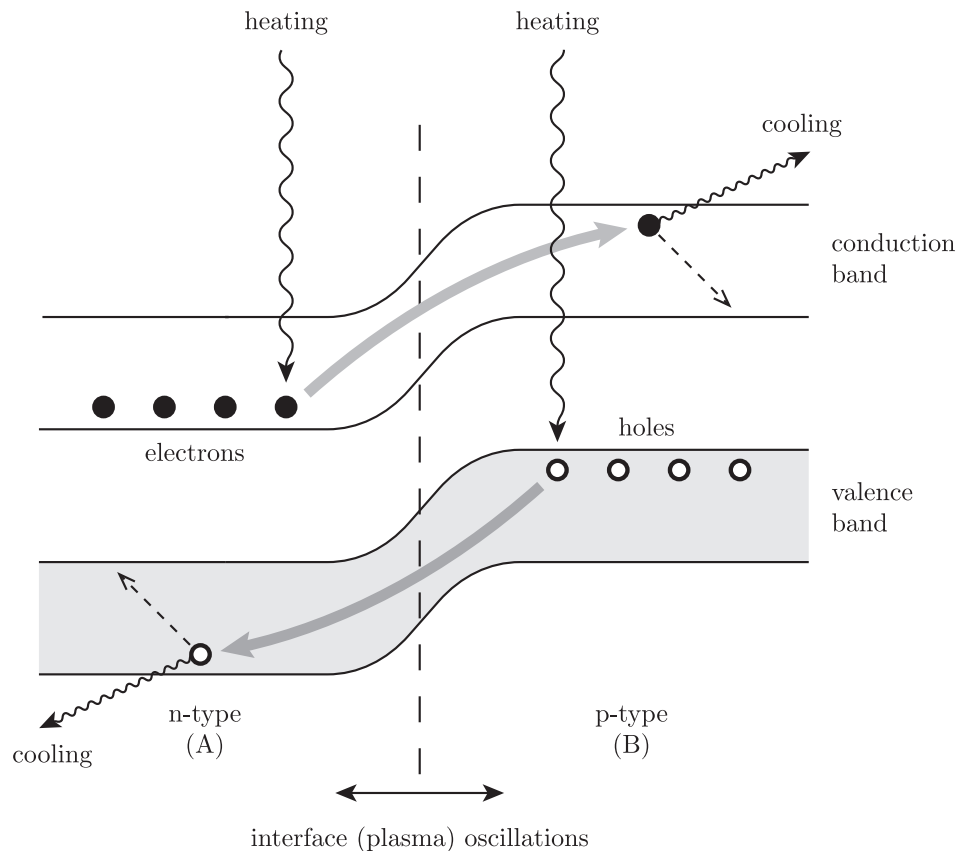
Obviously, for real systems, the efficiency is much smaller than the theoretical bound because heat conductivity and damping of plasma oscillations dissipate a large portion of the supplied thermal and chemical energy.

### 3. Implementations of the Model

The general universal model of PTFs presented above can be used as an idealized model of thermoelectric generators, photovoltaic cells and fuel cells.

#### 3.1. Thermoelectric Generators

The idealized model of a thermoelectric generator is a special case of the PTF model developed in the previous section (see Figure 1). Consider first the case of a semiconductor device composed of two semiconductors of  $p$ -type and  $n$ -type. They are connected by a conducting material which is heated by a thermal bath at the temperature  $T_1$  higher than the ambient temperature  $T$ . A finite heat conductivity is neglected and the electrons in bulk are assumed to thermalize quickly to the temperature  $T$  by the electron-phonon interactions.



**Figure 1.** Operation principles of a semiconductor thermoelectric generator ( $x$ -axis represents position,  $y$ -axis represents electronic energy): (i) a  $pn$ -junction is heated by a hot bath increasing the rate of transition over the built-in potential barrier; (ii) the electrons and holes in bulk are cooled down by a cold bath; (iii) the excess electrons and holes modify the shape of the built-in potential supporting self-oscillations of the interface; (iv) periodic oscillations of the charge density are rectified by the  $pn$ -diode, the averaged direct current (DC) flows in the outer circuit from the right contact to the left one.

The electronic states in  $n$ -type material form the band  $A$ , while those in  $p$ -type the band  $B$ . Here, both valence and conduction bands are included in a single band  $A$  or  $B$ . In the formed  $pn$ -junction, a built-in potential produces the energy barrier  $E_g$  separating the  $A$ -electrons from  $B$ -electrons. The notation  $E_g$  is consistent with that used in Equation (44) because most of the thermally induced transitions from the band  $B$  to  $A$  satisfy the relation  $E_a(k) - E_b(l) \simeq E_g$ . Therefore, one can apply the Equation (45) with  $\Delta g = 0$  and express the open circuit voltage as

$$V_{oc} = \frac{E_g}{eT_1} \Delta T, \quad \Delta T = T_1 - T, \quad (46)$$

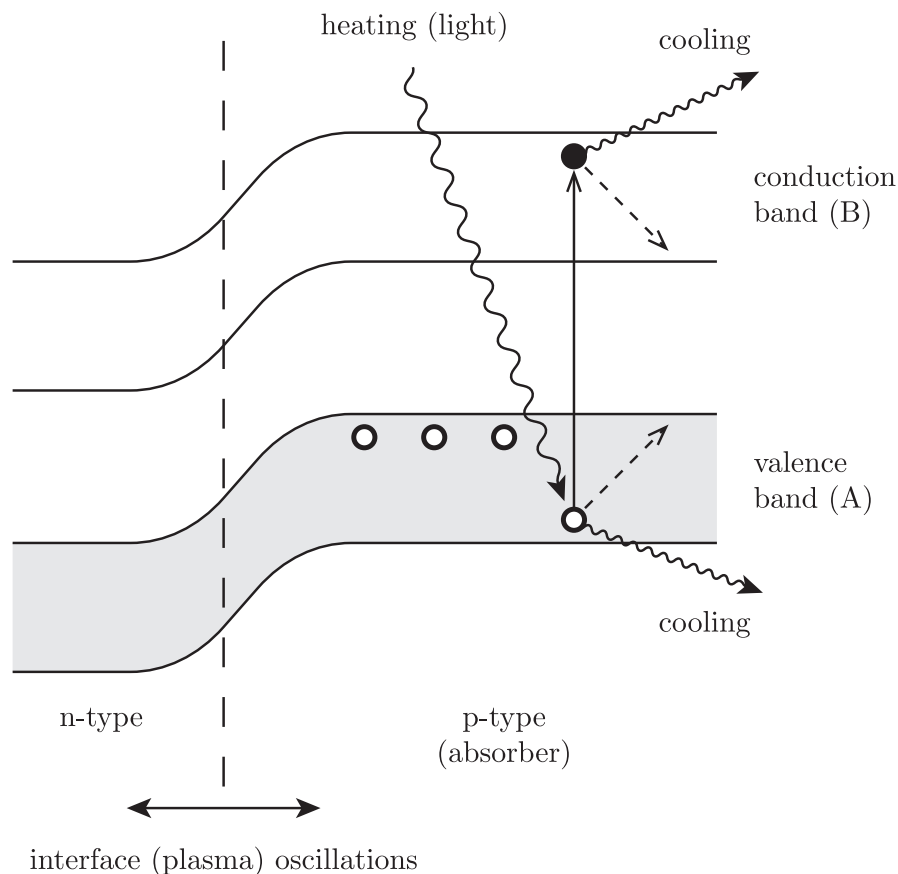
where  $\frac{E_g}{eT_1}$  can be interpreted as the *relative Seebeck coefficient*. Indeed, for a typical  $T_1 \sim 500$  K, the relative Seebeck coefficient given by Equation (46) is of the order of mV/K, which is comparable to the highest values obtained for some semiconductors.

The plasma oscillations in the THz domain of frequencies localized at the  $pn$ -junction were observed by several experimental groups [17,18]. They provide here the necessary macroscopic degree of freedom—a piston. The fast current oscillations are rectified by the  $pn$ -junction possessing diode characteristic of the voltage-current relation. Physically, this rectifying property is due to the built-in potential which acts similarly to a non-perfect one-way valve in a piston water pump.

For a bimetallic thermoelectric generator, the band *A* corresponds to the metal with a higher density of electrons in the conduction band while the band *B* to a lower density. Again, the energy barrier  $E_g$  appears at the metal–metal junction, which is also a source of its non-ohmic characteristic expected, at least, for high enough frequencies, leading to rectification of current oscillations. The origin of slow (THz) plasma oscillations at the metal–metal contact has been discussed in [2]. However, for metals, the neglected irreversible transport processes reduce the relative Seebeck coefficient by two or three orders of magnitude. As a consequence, the discussed model can give only a very rough qualitative picture in this case.

### 3.2. Photovoltaic Cells

The typical semiconductor solar cell consists of a moderately doped *p*-type absorber, on both sides of which a highly doped layer is formed, *n*-type on the top side and *p*-type on the back side, respectively (see Figure 2). The electronic bands *A* and *B* correspond to the absorber valence and conduction bands, respectively. The bands are separated by the semiconductor energy gap  $E_g$ .



**Figure 2.** Processes of work generation in the photovoltaic cell (*x*-axis represents position, *y*-axis represents electronic energy): (i) a photon is absorbed in the *p*-type phase of the semiconductor, generating a conducting pair (electron and hole); (ii) the pair thermalizes with the phonons in the lattice, dissipating the energy excess above the band gap; (iii) the photo-generated electrons and holes interact with the electrons in *n*-phase supporting self-oscillations of the interface; (iv) periodic oscillations of the charge density are rectified by the *pn*-diode, the averaged DC flows in the outer circuit from the right contact to the left one.

The incoming photon flux can be treated as a hot bath which is stationary but not equilibrium one. The hot bath is fully characterized by the frequency-dependent photon population number  $n(\omega)$ , which determines the *local temperature*  $T(\omega)$  by the following relation [19]:

$$e^{-\omega/T[\omega]} = \frac{n(\omega)}{1 + n(\omega)}. \quad (47)$$

For sunlight on Earth (neglecting the effect of the atmosphere), one can use the rough approximation

$$n_{sun}(\omega) = \frac{\lambda}{e^{\omega/T_s} - 1}, \quad (48)$$

where  $T_s \simeq 6000$  K is the temperature of the Sun surface and  $\lambda = [R_{sun}/R_{se}]^2 \simeq 2 \times 10^{-5}$  is the geometrical factor ( $R_{sun}$ —Sun radius,  $R_{se}$ —Sun-Earth distance), which takes into account the photon density reduction at a large distance from the source. For a typical semiconductor energy gap  $E_g \equiv \omega_0 \simeq 1$  eV, the effective temperature of sunlight  $T[\omega_0] \simeq 1000$  K. The cold bath is essentially a phonon bath at the ambient temperature  $T \simeq 300$  K.

The THz plasma oscillation at the *pn*-junction between the top *n*-type layer and the *p*-type absorber provides the self-oscillating piston interacting with the electron gas in the absorber. The junction acts also as a rectifier yielding, finally, a direct current.

One can apply the universal model of PTF, in particular Equation (45), which gives the formula for the open-circuit voltage:

$$V_{oc} = \frac{E_g}{e} \left(1 - \frac{T}{T_1}\right), \quad (49)$$

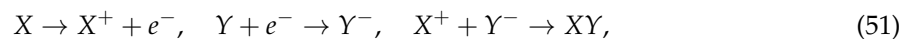
where  $T_1$  can be identified with  $T[\omega_0]$  averaged over the absorber. The Carnot factor in Equation (49) provides an upper bound on the thermodynamic efficiency of the solar cell and under standard illumination conditions agrees with the Shockley–Queisser (detailed balance) limit [1,20].

### 3.3. Fuel Cells

Fuel cell is an example of a PTF where the hot bath is a chemical reservoir at the ambient temperature. The basic chemical reaction for the hydrogen cell is



which takes several steps and is associated with the release of four electrons at the anode and absorption of four electrons at the cathode. The fundamental mechanism of work generation in a fuel cell does not change if we replace the actual reaction Equation (50) by the simpler fictitious one (see Figure 3)



which involves the chemical reservoir consisting of separated substances  $X, Y$ , and  $XY$  with the chemical potentials  $\mu_X, \mu_Y$  and  $\mu_{XY}$ , respectively.

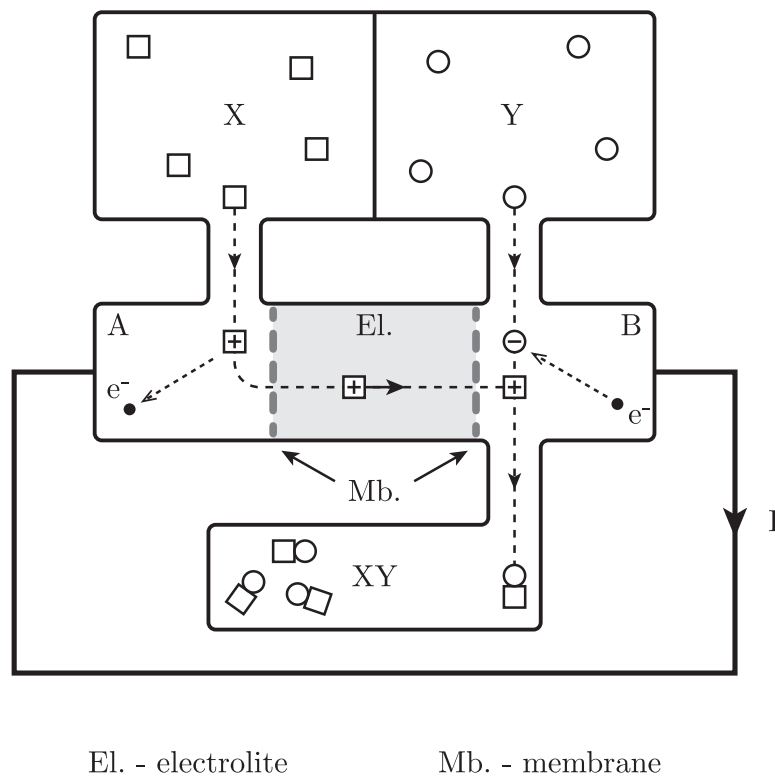
In the reduced description, the final effect of Equation (51) is a transfer of a single electron from the electronic state in the cathode (band  $B$ ) to the electronic state in the anode (band  $A$ ). Therefore, this process can be described by the generator Equation (34). For  $T_1 = T$ , one obtains from Equation (45) the formula for the open-circuit voltage

$$V_{oc} = -\frac{\Delta g}{e}, \quad \Delta g = \mu_{XY} - \mu_X - \mu_Y, \quad (52)$$

which agrees with the standard one for the ideal “reversible” voltage [21]. Obviously, a number of various types of losses reduces substantially the open-circuit voltage.

The question of the physical nature of a fuel cell piston is less clear than for the other instances of PTFs. However, the existence of plasma oscillations in electrolytes is discussed in a number of papers, and the frequencies of such oscillations are again placed in the far infrared region [22,23]. The role of interfaces between electrodes and electrolyte in the onset of plasma oscillations also needs further theoretical and experimental studies.

The electrolyte conducts only ions (protons in real devices) but not electrons and hence acts as a membrane that rectifies the self-oscillations of charge carriers.



**Figure 3.** Operation principles of a fuel cell illustrated by the model based on the simplified reaction  $X + Y \rightarrow XY$ : (i) the final effect of the reaction is the transport of a single electron from the cathode (band B) to the anode (band A); (ii) the excess heat is dissipated to the cold bath; (iii) the transferred electric charges modify the shape of the build-in potential supporting self-oscillations of the interface; (iv) periodic oscillations of the charge density are rectified by the semi-permeable membranes yielding an output DC.

#### 4. Conclusions

The aim of this paper is to show that there is a common mechanism of “hidden” plasma self-oscillations behind the operation principle of photoelectric cells, thermoelectric generators and fuel cells. This is illustrated by the idealized model in which thermal and chemical baths are treated on the same footing. The experimental tests of this theory could involve the detection of weak THz radiation emitted by the devices and proportional to the output power. Another possibility could be the observation of the resonant phenomena like the increased output power stimulated by the appropriate external and coherent THz radiation. It is also plausible that the similar models can explain work generation in biological systems fueled by radiation (photosynthesis) and chemical energy (proton pumps). The self-oscillation mechanism can be provided either by a sort of plasma oscillation or coherent molecular oscillation. The important role of the latter, played in the energy and charge transfer in biological systems, has been already noticed (see, e.g., [24,25]).

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### Appendix. Derivation of the Formula for Power Output

For the reader's convenience, the derivation of the basic formula Equation (27) for the model described in the Section 2.4 is outlined.

The lowest order expansion with respect to  $\xi$  of the total generator  $\mathcal{L}_{tot}[\xi] = -i[H[\xi], \cdot] + \mathcal{L}[\xi]$

$$\mathcal{L}_{tot}[\xi] = \mathcal{L}_{tot}[0] + \xi \mathcal{L}'_{tot}[0] + \mathcal{O}(\xi^2) \quad (\text{A1})$$

can be inserted into the MME Equation (21) yielding

$$\frac{d}{dt}\rho(t) = \mathcal{L}_{tot}[0]\rho(t) + \xi(t)\mathcal{L}'_{tot}[0]\rho(t). \quad (\text{A2})$$

The lowest order solution with respect to a small modulation amplitude reads

$$\rho(t) = e^{t\mathcal{L}_{tot}[0]}\rho(0) + \int_0^t \xi(s)e^{(t-s)\mathcal{L}_{tot}[0]}\mathcal{L}'_{tot}[0]e^{s\mathcal{L}_{tot}[0]}\rho(0) ds. \quad (\text{A3})$$

Each generator  $\mathcal{L}_{tot}[\xi]$  possesses a unique stationary state  $\bar{\rho}[\xi]$  hence

$$\lim_{t \rightarrow \infty} e^{t\mathcal{L}_{tot}[0]}\rho(0) = \bar{\rho}[0]. \quad (\text{A4})$$

In the formula for the stationary average power output (compare Equation (26))

$$\bar{P} = -g\Omega \lim_{t_0 \rightarrow \infty} \frac{1}{t_0} \int_0^{t_0} \text{Tr}(\rho_{as}(t)M) \cos \Omega t dt, \quad (\text{A5})$$

one can insert the asymptotic form of  $\rho(t)$  denoted by  $\rho_{as}(t)$  which is valid for  $t$  longer than any relevant relaxation time and for small  $g$

$$\rho_{as}(t) = \bar{\rho}[0] + g \left( \int_0^t e^{(t-s)\mathcal{L}_{tot}[0]} \sin(\Omega s) ds \right) \mathcal{L}'_{tot}[0]\bar{\rho}[0]. \quad (\text{A6})$$

The generator  $\mathcal{L}[\xi]$  is derived using a weak coupling limit approach and hence automatically commutes with the Hamiltonian part  $-i[H[\xi], \cdot]$ . As a consequence,  $e^{t\mathcal{L}_{tot}[0]} = e^{-it[H[0], \cdot]}e^{t\mathcal{L}[0]}$  and, when inserted into Equation (A5), can be replaced by  $e^{t\mathcal{L}[0]}$  because  $[H[0], M] = 0$ . For the same reason, in Equation (A5),  $\mathcal{L}'_{tot}[0]\bar{\rho}[0]$  can be replaced by  $\mathcal{L}'[0]\bar{\rho}[0]$ .

The integral in Equation (A6) (with  $\mathcal{L}_{tot}[0]$  replaced by  $\mathcal{L}[0]$ ) can be computed as follows:

$$\int_0^t e^{(t-s)\mathcal{L}[0]} \sin(\Omega s) ds = -[\mathcal{L}[0]^2 + \Omega^2]^{-1} (\sin(\Omega t)\mathcal{L}[0] + \Omega \cos(\Omega t) - \Omega e^{t\mathcal{L}[0]}). \quad (\text{A7})$$

The only term which survives the time-averaging procedure in Equation (A5) is that proportional to  $\cos(\Omega t)$  in Equation (A7) yielding

$$\bar{P} = \frac{1}{2}g^2\Omega^2 \text{Tr} \left( M[\mathcal{L}[0]^2 + \Omega^2]^{-1} \mathcal{L}'[0]\bar{\rho}[0] \right). \quad (\text{A8})$$

Using the identity  $\mathcal{L}'[0]\bar{\rho}[0] = -\mathcal{L}[0]\bar{\rho}'[0]$  (compare Equation (24)) and introducing the Heisenberg version of the generator, one obtains the final expression

$$\bar{P} = -\frac{1}{2}g^2\Omega^2 \text{Tr} \left( \bar{\rho}'[0] \frac{\Omega^2}{\Omega^2 + \mathcal{L}^{*2}[0]} \mathcal{L}^*[0]M \right). \quad (\text{A9})$$

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