The roles of quantum coherence in thermodynamic processes

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Quantum coherence associated with the superpositions of two different sets of eigenbasis vectors has been regarded as essential in thermodynamics. It is found that coherent factors can be determined by writing observables as an expansion in the basis vectors of the systemic density operator and Hamiltonian. We reveal the roles of coherence in finite-time thermodynamic processes, such as the spin precession and the spontaneous emission of a photon. Results show that the work in the spin precession and the heat in the spontaneous emission process are mainly generated by coherence.

I. INTRODUCTION

The internal energy, heat, and work are fundamental quantities in thermodynamics, regardless of states in macro or micro. The first law of thermodynamics indicates that any change in the internal energy of a system is given by the sum of the heat flowing into the system and the work done by the surroundings. However, the division of the internal energy into heat and work has become a very controversial issue [1–5]. In classical thermodynamics, heat is usually defined as the flow of energy caused by the temperature difference between the system and its environment. On the other hand, work is performed by adjusting the state parameters of the system [8–14]. More recently, quantum thermodynamics is an emerging research field aiming to build the relation between thermodynamics and quantum mechanics [15–19]. One of the important tasks is to reveal the quantum version of first law [19]. Although there have been many progresses, it is impractical to create a unified definition of heat and work.

For a quasi-static reversible process, the change of occupation probabilities induces the heat transfer, while the shift of the eigenenergies of the Hamiltonian gives rise to the work [20, 21]. On the basis of the dissipative master equation, Pusz interpreted that the work done by the external agent is associated with the time derivative of the Hamiltonian of the working substance [22]. Alicki extended this concept and related the heat to the time derivative of the density operator [7, 23]. Pusz and Alicki’s definition has been broadly applied. For example, Su et al. proposed that quantum coherence represented by the transition between the different quantum states contributes to heat and work [24]. Vu revealed the heat dissipation in connection with finite-time information erasure and the influence of coherence in such process [25]. Cavina clarified the general bound of the efficiency of a low-dissipation quantum Carnot engine at the maximum power [26]. Tajima established a universal framework clarifying how coherence affects the current-dissipation trade-off relation and leads to quantum lubrication [27].

The application of quantum coherence has attracted interest from researchers. In order to probably unravel the role of coherence in a concrete thermodynamic process, it is essential to get the reliable definitions of heat and work in advance. We will start from Pusz and Alicki’s definition, because it has been validated in Markovian master equations with static Hamiltonian and adiabatically driven Hamiltonian [28]. The superpositions of two different sets of eigenbasis vectors have been pointed out to be one of the important coherence factors [20, 30]. For this reason, we are interested in addressing how this type of coherence exerts influence on the heat and work in the finite-time evolution of a quantum system.

In this work, we derive the coherent term in heat and work by writing observables as an expansion in the basis vectors of the system’s density operator and Hamiltonian. The contents are organized as follows: In Sec. II, we introduce the quantum version of the first law of thermodynamics for closed and open systems. In Sec. III, heat and work are written in terms of the diagonalizing bases of the density matrix and Hamiltonian, and their connections to coherence factors are revealed. In Sec. IV, we demonstrate that the decomposition of heat and work is agree with previous studies. Meanwhile, the effects of quantum coherence on the processes of spin precession and spontaneous emission are explored. Finally, the main conclusions are drawn.

II. THE FIRST LAW OF THERMODYNAMICS IN THE QUANTUM REGIME

For an open quantum system described by the time-dependent Hamiltonian $H$ and the density operator $\rho$, the internal energy is defined as

$$U = \text{Tr}[\rho H].$$

During an infinitesimal thermodynamic process, the time derivative of $U$ receives contributions from the variations of $\rho$ and $H$,

$$\dot{U} = \text{Tr}[\dot{\rho} H] + \text{Tr}[\rho \dot{H}].$$

On the other hand, the first law of thermodynamics asserts that $\dot{U}$ depend on the heat flux $\dot{Q}$ and power $\dot{W}$,
\[
\dot{U} = \dot{Q} + \dot{W}.
\]

(3)

Since \(\dot{Q}\) and \(\dot{W}\) are path functions, they will not correspond to observables.

If the quantum system is a closed system that undergoes a thermodynamic adiabatic process, the evolution of the density operator satisfies the Liouville–von Neumann equation [31]

\[
d\rho/dt = -i/\hbar [H, \rho],
\]

(4)

with \(\hbar\) being the reduced Planck's constant. Equation [4] and the invariant of trace under cyclic permutations imply that \(\text{Tr}[\rho H] = 0\). As the heat exchange does not exist as well, i.e., \(\dot{Q} = 0\) and \(\dot{W} = 0\). At the same time, the first term on Eq. [2] is missing and the heat flux is identified as

\[
\dot{Q} = \text{Tr}[\rho \dot{H}].
\]

(6)

When the system has an explicit time-dependent Hamiltonian \(H\) and is simultaneously weakly coupled to a thermal bath, the definitions of the heat flux and power rely on the road map of the evolution of open systems [32]. We enumerate two situations where Eqs. [4] and [6] are applicable.

For the quantum isothermal process, the Hamiltonian of the system is adjusted slowly enough, resulting in the fact that the system remains in equilibrium with the thermal bath at temperature \(T\). In such a quasi-static process, the heat flux and power are usually expressed as

\[
\dot{Q} = \sum_n P_n E_n \quad \text{and} \quad \dot{W} = \sum_n P_n \dot{E}_n
\]

[33, 34], where \(E_n\) and \(P_n = \exp[-E_n/(k_B T)]/\sum_n \exp[-E_n/(k_B T)]\) are, respectively, the eigenenergy and the occupation probability of eigenstate \(|n\rangle\) of \(H\), and \(k_B\) is the Boltzmann constant. Therefore, the rearrangement of the occupation probabilities induces the heat transfer between the system and the bath, while the variation of the eigenenergy gives rise to the work performed. As the system maintains in the state of equilibrium, the Hamiltonian and the density operator can be written as

\[
H = \sum_n E_n |n\rangle \langle n| \quad \text{and} \quad \rho = \sum_n P_n |n\rangle \langle n|.
\]

It is understandable that the heat flux and power in the quantum isothermal process are in line with Eqs. [4] and [6].

If the Hamiltonian changes slowly in time, the adiabatic perturbation theory can be applied to determine the evolution equation of the density matrix for the open system [28, 35, 36]. It has been found that Eqs. [4] and [6] continue to be true for any adiabatic driving system, where the Hamiltonian associated with the interaction with the external field must be incorporated in \(H\).

In some cases, however, the definitions of \(\dot{Q}\) and \(\dot{W}\) need appropriate modifications. For the system with a weakly driven Hamiltonian, the heat has a unique definition by applying two successive energy measurements to the environment [28]. For the regime of a system subjected to a periodic driving, heat currents flow in channels corresponding to quasi Bohr frequencies based on the Floquet-Markov master equation [37, 39]. In the regime of strong system-bath interaction, a controversial issue is how to deal with the interaction energy and one needs to reexamine the meaning of heat and work [40, 42].

Because this work focuses on rewriting Eqs. [4] and [6] using the representation based on the instantaneous eigenstate basis of the density operator. The following discussion will be limited to the conditions where the heat flux and power defined by Eqs. [4] and [6] can be applied.

III. HEAT AND WORK IN TERMS OF DIAGONALIZING BASES OF THE DENSITY MATRIX AND HAMILTONIAN

In order to reveal the roles of the coherence in thermodynamics, Eqs. [4] and [6] are usually written in a matrix form with respective to a complete set of basis vectors. For the eigenket \(|n\rangle\) in the energy representation, non-zero off-diagonal element of the density matrix \(\rho_{nn'} = \langle n|\rho|n'\rangle\) is referred to coherence factors [24, 27]. More recently, the factor \(c_{nk} = \langle n|k\rangle\), which corresponds to the inner product of the basis vector \(|n\rangle\) of the Hamiltonian \(H\) and the basis vector \(|k\rangle\) of the density operator \(\rho\), has been considered as an important factor to measure the coherence effect [28, 30]. On the other hand, the time derivative of the von Neumann entropy of the system is usually written as

\[
\dot{S} = -k_B \text{tr}[\rho \log \rho] = -k_B \sum_k \dot{P}_k \log P_k,
\]

(7)

where \(\rho = \sum_k P_k |k\rangle \langle k|\) with \(P_k = \langle k|\rho|k\rangle\). The entropy \(S\) is closely related to the eigenvalue \(P_k\) of \(\rho\).

For the above reasons, it will be interesting to know how the coherence factor \(c_{nk}\) affects \(\dot{Q}\) and \(\dot{W}\). Rewriting Eqs. [4] and [6] based on the instantaneous eigenstate bases of \(\rho\) and \(H\), we obtain (Appendix A)

\[
\dot{W} = \sum_{n,k} P_k \dot{E}_n c_{kn} c_{nk} + \sum_{n,k} P_k E_n (\langle \dot{n}|c_{nk}) + H.c.)
\]

(8)

\[
= \dot{W}_d + \dot{W}_c
\]
\[ \dot{Q} = \sum_{n,k} \hat{P}_k E_n c_{nk} c_{nk} + \sum_{n,k} P_k E_n (n) c_{nk} + H.c. \]
\[ = \dot{Q}_d + \dot{Q}_c, \tag{9} \]

where \( H.c. \) stands for the abbreviation for the Hermitian conjugate.

\( \dot{W}_d \) and \( \dot{W}_c \) are, respectively, the first term and the second term in the first equality of Eq. (5). \( \dot{Q}_d \) and \( \dot{Q}_c \) are, respectively, the first term and the second term in the first equality of Eq. (6). \( \dot{W}_d \) is the power corresponding to the change of the eigenenergy \( \dot{E}_n \), which is originated from the variation of the external field. \( \dot{Q}_d \) depends on the derivative of the distribution over time \( \dot{P}_k \) and is accompanied by the entropy change as \( \dot{S} \neq 0 \). \( \dot{W}_c \) and \( \dot{Q}_c \) are, respectively, caused by the basis vectors \( |n\rangle \) and \( |k\rangle \). Essentially, they are both connected with the coherence factor \( c_{nk} \). The sum of \( \dot{W}_c \) and \( \dot{Q}_c \) is equal to \( \sum_{n,k} P_k E_n d(c_{nk} c_{kn})/dt \), which is exactly the same as the change of the internal energy due to the dynamics of coherence energy defined in Ref. 23. In this work, it is clearly shown that the coherence energy may simultaneously make contributions to the heat and work. As the discussion in Sec. II, Eq. (4) could tell us that \( \dot{Q}_d = -\dot{Q}_c \), when the system undergoes a adiabatic process without the heat transfer.

IV. RESULTS AND DISCUSSION

Because the density operator has two equivalent expressions \( \rho = \sum_k P_k |k\rangle \langle k| = \sum_{n,n'} \rho_{nn'} |n\rangle \langle n'| \), Eqs. (5) and (6) are converted into

\[ \dot{W} = \sum_n \rho_{nn} \dot{E}_n + \sum_{n \neq n'} \rho_{nn'} \langle n'| \partial H/\partial t |n\rangle \tag{10} \]

and

\[ \dot{Q} = \sum_n \dot{p}_n E_n - \sum_{n \neq n'} \rho_{nn'} \langle n'| \partial H/\partial t |n\rangle, \tag{11} \]

where the relations \( \langle n'| n\rangle = -\langle n| n'\rangle = \langle n'| n\rangle \partial \dot{H}/\partial t |n\rangle/(E_n - E_{n'}) \) have been applied. These findings give the heat flux and power accounting the spectral decomposition of the time-dependent Hamiltonian, and are in complete agreement with previous studies 24, 25.

As an application of illustrating the effects of quantum coherence on thermodynamic processes, we first explore the adiabatic evolution of the spin precession in a rotating magnetic field. The Hamiltonian of the system takes the matrix form \( H_1 = \hbar \omega_0 \left( \begin{array}{cc} \cos \alpha & \sin \alpha e^{-i\omega t} \\ \sin \alpha e^{i\omega t} & -\cos \alpha \end{array} \right) \), where \( \omega_0 \) is the frequency depending on the magnitude of the magnetic field, and the field rotates around the direction of the Pauli-Z operator at an angular velocity \( \omega \) and a tilt angle \( \alpha \). The normalized eigenvectors of \( H_1 \) are given by \( |n_+\rangle = \cos \frac{\omega_0}{2} |e\rangle + e^{i\omega t} \sin \frac{\omega_0}{2} |g\rangle \) and \( |n_-\rangle = e^{-i\omega t} \sin \frac{\omega_0}{2} |e\rangle - \cos \frac{\omega_0}{2} |g\rangle \) with the orthonormal basis \( |e\rangle = \left( \begin{array}{c} 1 \\ 0 \end{array} \right) \) and \( |g\rangle = \left( \begin{array}{c} 0 \\ 1 \end{array} \right) \). The eigenvalue corresponding to state \( |n_\pm\rangle \) is \( E_\pm = \pm \hbar \omega_0 \). Given an initial state \( \rho_0 \), the density operator as a function of time \( \rho = U \rho_0 U^\dagger \), where the evolution operator \( U = \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} \) with \( U_{11} = \cos \frac{\omega t}{2} - i \frac{\omega_0 \sin \alpha}{2} e^{i\omega t} \sin \frac{\omega_0}{2} e^{i\omega t} \), \( U_{12} = \sin \frac{\omega t}{2} + i \frac{\omega_0 \sin \alpha}{2} e^{i\omega t} \sin \frac{\omega_0}{2} e^{i\omega t} \), \( U_{21} = -i \frac{\omega_0 \sin \alpha}{2} e^{-i\omega t} \sin \frac{\omega_0}{2} e^{-i\omega t} \), and \( \Omega = \sqrt{(\omega_0 \sin \alpha - \omega)^2 + \omega_0^2 \sin^2 \alpha} \). The Liouville–von Neumann equation [Eq. (1)] indicates \( \dot{P}_k = 0 \). From Eqs. (11) and (12), it is concluded that the unitary evolution of a closed system leads to \( \dot{Q}_d = 0 \) and \( \dot{S} = 0 \). \( \dot{Q}_c \) is a zero value as well, because the term inside the parentheses in Eq. (9) equals zero by considering the differential equation \( i \dot{\rho} U = H(U) \). Therefore, the spin carries out a thermodynamic adiabatic evolution without the heat exchange. The detailed proofs of \( \dot{P}_k = 0 \) and \( \dot{Q}_c = 0 \) are left for Appendix B. For the resource of the power, the partial power \( \dot{W}_d \) is not involved in the change of the internal energy, as the eigenvalues \( E_\pm \) are time independent. The power of the model is completely generated by the coherence term \( \dot{W}_c = \hbar \omega_0 \omega^2 \sin^2 \alpha |\cos(\Omega t) - 1|/(2\Omega^2) \).

In the next, the spontaneous emission of a photon implemented by a two-level system interacting with the electromagnetic field is considered. The bare Hamiltonian of the system is given by \( H_2 = E_0 |e\rangle \langle e| + E_g |g\rangle \langle g| \) with \( E_0 \) being the energy level of the excited state \( |e\rangle \) and \( E_g \) being the energy level of the ground state \( |g\rangle \). Assuming that the system starts from state \( \rho_0 = \frac{1}{2} \left( \begin{array}{cc} 1 & 1 \\ 1 & 1 \end{array} \right) \). By using the schematic model of the amplitude-damping channel, the matrix form of the time-dependent density operator \( \rho = \frac{1}{2} \left( \begin{array}{cc} 2 - e^{-\gamma t} & e^{-\gamma/2} \\ e^{\gamma/2} & e^{-\gamma t} \end{array} \right) \) with \( \gamma \) being the decay rate. The detailed derivation has been presented in Refs. 25, 26. The eigenvalues of \( \rho \) are found to be \( \rho_1 = \frac{1}{2} e^{-\gamma t} (\gamma t + a) \) and \( \rho_2 = \frac{1}{2} e^{-\gamma t} (\gamma t - a) \) with \( a = \sqrt{e^{2\gamma t} - e^{\gamma t} + 1} \), while their respective eigenvectors are \( |e_1\rangle = \frac{e^{-\gamma t} (\gamma t + a) + |e\rangle}{\sqrt{e^{-\gamma t} (\gamma t + a) + e^{\gamma t} (\gamma t - a) + 1}} \) and \( |e_2\rangle = \frac{e^{-\gamma t} (\gamma t - a) + |e\rangle}{\sqrt{e^{-\gamma t} (\gamma t - a) + e^{\gamma t} (\gamma t + a) + 1}} \). For the spontaneous emission process, no power is generated by the system, because the time-independent eigenvalues and eigenvectors of Hamiltonian \( H_2 \) make the partial powers \( \dot{W}_d = \dot{W}_c = 0 \) [Eq. (5)]. As a result, the work \( W \) (solid line) as a function of \( t \) is a horizontal line crossing the zero point at the vertical axis, as shown in Fig. 1. By applying Eq. (11) and integrating \( \dot{Q}_d \) and \( \dot{Q}_c \) over the interval \([0, t]\), Fig. 1 also presents the total heat exchange \( Q = \dot{Q}_d + \dot{Q}_c \) (dashed line) as a function of \( t \). The
The heat $Q$ (dashed line) and $W$ (solid line) as functions of time $t$ by integrating $\dot{Q}$ and $\dot{W}$ over the interval $[0, t]$. The dash-double-dotted line and dash-dotted line are, respectively, the heat $Q$ and work $W$ defined in Ref. [29] as functions of time $t$.

In summary, the results draw a clear distinction between the definitions of heat flux and power in quasi-static processes and those in non-quasi-static processes. The heat flux and power in non-quasi-static processes are further reformulated by using the basis vectors of the density matrix and the Hamiltonian, and their connections to the coherence are revealed. It is demonstrated that the power is completely generated by the coherence work in the spin precession process and the heat is mainly determined by the coherence heat in the spontaneous emission process. This method established here may pave the theoretical foundation for further exploring the coherence effects in quantum thermodynamics.

V. CONCLUSIONS

In the spontaneous emission process, the time derivative of the density matrix $\dot{\rho}$ is defined in Ref. [29], which states of $H$.

\begin{align*}
\dot{W} &= \text{Tr}[\rho \dot{H}] \\
&= \text{Tr}[\sum_k P_k |k\rangle \langle k| \frac{d}{dt} E_n |n\rangle \langle n|] \\
&= \sum_{n,k,k'} \langle k'| (P_k |k\rangle \langle k| \hat{E}_n |n\rangle \langle n| + P_k |k\rangle \langle k| E_n |n\rangle \langle n| \\
&\quad + P_k |k\rangle \langle k| \hat{n} |n\rangle \langle n|) |k'\rangle \\
&= \sum_{n,k,k'} (\dot{P}_k E_n (|k| |n\rangle \langle n| |k'\rangle \langle k'| + P_k E_n (|k| |n\rangle \langle n| |k'\rangle \langle k'| \\
&\quad + P_k E_n (|\hat{n}| |n\rangle \langle n| |k'\rangle \langle k'| + P_k E_n (|\hat{n}| |n\rangle \langle n| |k'\rangle \langle k'|) \\
&= \sum_{n,k} (\dot{P}_k E_n (|k| |n\rangle \langle n| + P_k E_n (|k| |n\rangle \langle n| \hat{k} \\
&\quad + P_k E_n (|\hat{n}| |n\rangle \langle n|)) \\
&= \sum_{n,k} (\dot{P}_k E_n (|k| |n\rangle \langle n| |k'\rangle \langle k'| + P_k E_n (|\hat{n}| |n\rangle \langle n| |k'\rangle \langle k'| + P_k E_n (|\hat{n}| |n\rangle \langle n|) \\
&\quad + P_k E_n (|\hat{n}| |n\rangle \langle n|) \\
&= \sum_{n,k} \dot{P}_k E_n (|k| |n\rangle \langle n| c_{kn} + \sum_{n,k} P_k E_n (|k| |n\rangle \langle n| c_{kn} + H.c.).
\end{align*}

Here, the unit operator $I = \sum_{k'} |k'\rangle \langle k'|$ is introduced for obtaining the penultimate step of Eq. (13). Note that the calculations of the traces with the aid of the basis states of $H$ will obtain the same results.

APPENDIX A: THE EXPANSION OF THE HEAT FLUX AND POWER

In the following steps, the heat flux and the power are written as an expansion in the basis states $|k\rangle$ of $\rho$ and $|n\rangle$ of $H$:

\begin{align*}
\dot{W} &= \text{Tr}[\rho \dot{H}] \\
&= \text{Tr}[\sum_k P_k |k\rangle \langle k| \frac{d}{dt} E_n |n\rangle \langle n|] \\
&= \sum_{n,k,k'} \langle k'| (P_k |k\rangle \langle k| \hat{E}_n |n\rangle \langle n| + P_k |k\rangle \langle k| E_n |n\rangle \langle n| \\
&\quad + P_k |k\rangle \langle k| \hat{n} |n\rangle \langle n|) |k'\rangle \\
&= \sum_{n,k,k'} (\dot{P}_k E_n (|k| |n\rangle \langle n| |k'\rangle \langle k'| + P_k E_n (|k| |n\rangle \langle n| |k'\rangle \langle k'| \\
&\quad + P_k E_n (|\hat{n}| |n\rangle \langle n| |k'\rangle \langle k'| + P_k E_n (|\hat{n}| |n\rangle \langle n| |k'\rangle \langle k'|) \\
&= \sum_{n,k} (\dot{P}_k E_n (|k| |n\rangle \langle n| + P_k E_n (|k| |n\rangle \langle n| \hat{k} \\
&\quad + P_k E_n (|\hat{n}| |n\rangle \langle n|)) \\
&= \sum_{n,k} (\dot{P}_k E_n (|k| |n\rangle \langle n| |k'\rangle \langle k'| + P_k E_n (|\hat{n}| |n\rangle \langle n| |k'\rangle \langle k'| + P_k E_n (|\hat{n}| |n\rangle \langle n|) \\
&\quad + P_k E_n (|\hat{n}| |n\rangle \langle n|) \\
&= \sum_{n,k} \dot{P}_k E_n (|k| |n\rangle \langle n| c_{kn} + \sum_{n,k} P_k E_n (|k| |n\rangle \langle n| c_{kn} + H.c.).
\end{align*}

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APPENDIX B: THE PROOF OF $\dot{P}_k = 0$ AND $\dot{Q}_k = 0$ IN THE SPIN PRECESSION PROCESS

In the spin precession process, the time derivative of the eigenvalue $P_k$ of the density matrix $\rho$ is demonstrated
to be zero as follows
\[ P_k = \langle k | \hat{\rho} | k \rangle + \langle k | \hat{\rho} | k \rangle + \langle k | \hat{\rho} | k \rangle \]
\[ = -\frac{i}{\hbar} [\langle k | H, \hat{\rho} | k \rangle + P_k (\langle k | k \rangle + \langle k | k \rangle)] \]
\[ = -\frac{i}{\hbar} \sum_{k,k'} E_{n,k'} \langle k | n \rangle \langle n | k \rangle \langle k' | k \rangle \]
\[ - \langle k | k \rangle \langle k' | n \rangle \langle n | k \rangle = 0, \]
where the Liouville–von Neumann equation [Eq. (11)] and \( \frac{d}{dt} (k) = \langle k | + \langle k | k \rangle = 0 \) have been applied in the second equality.

During the unitary evolution, the system changes into the state \( \rho = U \rho_0 U^\dagger = \sum_k P_k U | k_0 \rangle \langle k_0 | U^\dagger = \sum_k P_k | k \rangle \langle k | \), where the diagonalized form of the initial state \( \rho_0 = \sum_k P_k | k_0 \rangle \langle k_0 | \). Therefore, \( | k \rangle = U | k_0 \rangle \) can be regarded as the basis vector \( | k \rangle \) of \( \rho \) at time \( t \) with a constant occupation probability \( P_k \), and its time derivative \( \dot{k} = U | k_0 \rangle \). Consequently, the heat flux \( Q_c \) associated with coherence is rearranged into
\[ \dot{Q}_c = \sum_{n,k} P_k E_n (\langle k | n \rangle c_{nk} + H.c.) \]
\[ = \sum_{n,k} P_k E_n | \langle k_0 | \dot{U}^\dagger | n \rangle \langle n | U | k_0 \rangle + H.c.] \]
\[ = \sum_k P_k | \langle k_0 | \dot{U}^\dagger H | k_0 \rangle + \langle k_0 | U^\dagger H \dot{U} | k_0 \rangle \rangle \]
\[ = \sum_k P_k [i\hbar \langle k_0 | \dot{U}^\dagger \dot{U} | k_0 \rangle - i\hbar \langle k_0 | U^\dagger \dot{U} | k_0 \rangle] \]
\[ = 0, \]
where the summation \( \sum_n E_n | n \rangle \langle n | \) is replaced by the Hamiltonian \( H \) in the third equality, and the equation \( U = -\frac{i}{\hbar} H \) has been applied in the fifth step.

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