The heat and work of quantum thermodynamic processes with quantum coherence

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Energy is often partitioned into heat and work by two independent paths corresponding to the change in the eigenenergies or the probability distributions of a quantum system. The discrepancies of the heat and work for various quantum thermodynamic processes have not been well characterized in literature. Here we show how the work in quantum machines is differentially related to isochoric, isothermal, and adiabatic processes. We prove that the energy exchanges during the quantum isochoric and isothermal processes are simply depending on the change in the eigenenergies or the probability distributions. However, for a time-dependent system in a non-adiabatic quantum evolution, the transitions between the different quantum states representing the quantum coherence can affect the essential thermodynamic properties, and thus the general definitions of the heat and work should be clarified with respect to the microscopic generic time-dependent system.

I. INTRODUCTION

Thermodynamics is reputed to have the ability to deal with the energy transfer and work utilizing an extremely small number of variables. Numerous quantum devices that are related to harnessing energy focus on pioneering concepts and unexplored mechanisms. They are exemplified by artificial photosynthesis [1], quantum information heat engines [2–4], quantum thermodynamic cycles [5–8], and photovoltaic cells [7, 8]. The design of an improved heat engines [2–4], quantum thermodynamic cycles [5, 6], and photovoltaic cells [7, 8]. The design of an improved heat engines [2–4], quantum thermodynamic cycles [5, 6], and photovoltaic cells [7, 8]. The design of an improved heat engines [2–4], quantum thermodynamic cycles [5, 6], and photovoltaic cells [7, 8]. The design of an improved heat engines [2–4], quantum thermodynamic cycles [5, 6], and photovoltaic cells [7, 8]. The design of an improved heat engines [2–4], quantum thermodynamic cycles [5, 6], and photovoltaic cells [7, 8]. The design of an improved heat engines [2–4], quantum thermodynamic cycles [5, 6], and photovoltaic cells [7, 8]. The design of an improved heat engines [2–4], quantum thermodynamic cycles [5, 6], and photovoltaic cells [7, 8]. The design of an improved heat engines [2–4], quantum thermodynamic cycles [5, 6], and photovoltaic cells [7, 8].

According to the first and second laws of thermodynamics, the infinitesimal internal energy variation of a quantum system is

\[ dU = dQ + dW = \sum_n (E_n d\rho_{nn} + \rho_{nn} dE_n), \]  

where \( E_n \) and \( \rho_{nn} \) are the eigenenergy and the occupation probability of the \( n \)-th eigenstate, respectively. The work done \( dW \) and the heat exchange \( dQ \) during an infinitesimal thermodynamic process are often identified as

\[ dW = \sum_n \rho_{nn} dE_n \]  

and

\[ dQ = \sum_n E_n d\rho_{nn}. \]

These imply that the work has to be done by changing the generalized coordinates of the system, while the heat transfer between the quantum system and the heat bath induces the rearrangement of the occupation probabilities [11, 12]. However, these forms of identification are not strictly comfortable with rigorous mathematical proof. Questions inevitably arise when one is faced with a system undergoing different thermodynamic processes studied commonly. In fact, it may induce doubts whether the above definitions of the heat and work are applicable for any process.

Based on the dissipative master equation, the heat and work relevant to the open quantum system with time-dependent Hamiltonian were introduced in the pioneering research of Alicki [13, 14]. Kosloff et al. implemented Alicki’s formulas and systematically studied quantum heat engine cycles working with harmonic oscillators and spins [15–17]. Here, writing the heat and work in term of the systemic instantaneous orthonormal basis, we show that quantum coherence characterized by the off-diagonal elements of the density matrix stimulates additional energy changes in thermodynamic processes. The quantum effects make the heat and work of quantum isochoric, quantum isothermal, and thermodynamic adiabatic processes different from one another. The exactly solvable dynamics of high-spin precession will be used to prove that quantum coherence guarantees the thermodynamic adiabatic evolution of time-dependent system.

II. EXPRESSIONS OF HEAT AND WORK IN QUANTUM THERMODYNAMIC PROCESSES

For a general quantum system, an external driving field gives rise to a time-dependent Hamiltonian \( \hat{H}(t) \). According to the microscopic description of the first law of thermodynamics, the change in the internal energy of the
system can be split into two separate parts, i.e.,

$$\dot{U} = Tr \left( \dot{\hat{\rho}} \hat{H} \right) + Tr \left( \dot{\hat{\rho}} \hat{\rho} \hat{H} \right),$$

(4)

where the dot denotes the time derivative and \( \dot{\hat{\rho}} \) is the density operator corresponding to the ensemble [13] [18] [19].

Let \( \{ |m(t)\rangle, m = 1, 2, \ldots \} \) be a complete instantaneous orthonormal basis of \( \hat{H}(t) \), we can write the Hamiltonian and the density operator in a matrix form, that is

$$\hat{H}(t) = \sum_m E_m(t) |m(t)\rangle \langle m(t)|$$

(5)

and

$$\dot{\rho}(t) = \sum_{nm} \rho_{nm}(t) |n(t)\rangle \langle m(t)|,$$

(6)

where \( E_m(t) \) is the eigenvalue of the state \(|m(t)\rangle\) at any particular instant and \( \rho_{nm}(t) = \langle n(t) | \hat{\rho} | m(t) \rangle \) represents the density matrix element. For the sake of simplicity, time \( t \) is omitted in the notation. Note that the off-diagonal element \( \rho_{nm} (n \neq m) \) exists, meaning that \( \hat{\rho} \) and \( \hat{H} \) do not have a common orthonormal basis. With the help of Eqs. (5) and (6), we have

$$Tr \left( \dot{\hat{\rho}} \hat{H} \right) = \sum_n \rho_{nn} E_n - \sum_{n \neq m} \rho_{nm} \langle m | \frac{\partial \hat{H}}{\partial t} | n \rangle,$$

and

$$Tr \left( \dot{\hat{\rho}} \hat{\rho} \hat{H} \right) = \sum_n \rho_{nn} \dot{E}_n + \sum_{n \neq m} \rho_{nm} \langle m | \frac{\partial \hat{H}}{\partial t} | n \rangle$$

(Appendix A). The rate of change of the internal energy becomes

$$\dot{U} = \sum_n \rho_{nn} E_n - \sum_{n \neq m} \rho_{nm} \langle m | \frac{\partial \hat{H}}{\partial t} | n \rangle$$

$$+ \sum_n \rho_{nn} \dot{E}_n + \sum_{n \neq m} \rho_{nm} \langle m | \frac{\partial \hat{H}}{\partial t} | n \rangle,$$

(7)

which are classified into four different categories. The second and fourth terms representing the quantum coherence have the same magnitude but different signs. They would cancel each other resulting in the consistency between Eq. (7) and Eq. (1). However, we find that the connection between the quantum coherence and the infinitesimal increments of the heat and work exists. For a closed system subjected to a time-dependent force, the unawareness of the quantum coherence may violate the first law of thermodynamics.

In thermodynamics, an adiabatic process in a closed system occurs when the transfer of heat and matter between the thermodynamic system and its surrounding is avoided. The evolution of the density operator during the adiabatic process is unitary. Based on the Liouville-von Neumann equation [20]

$$\dot{\rho} = -\frac{i}{\hbar} \left[ \hat{H}, \rho \right]$$

(8)

and the derivative of the density matrix formula, we have (see Appendix B)

$$\sum_n \rho_{nn} E_n = \sum_{n \neq m} \rho_{nm} \langle m | \frac{\partial \hat{H}}{\partial t} | n \rangle,$$

(9)

which indicates that \( Tr \left( \dot{\hat{\rho}} \hat{H} \right) = 0 \). According to the first law of thermodynamics, the internal energy in an adiabatic process is transferred only as work, and the rate of work performed in this process is given by

$$\dot{W} = \sum_n \rho_{nn} \dot{E}_n + \sum_{n \neq m} \rho_{nm} \langle m | \frac{\partial \hat{H}}{\partial t} | n \rangle.$$

(10)

The rate of the heat transfer should have the following form

$$\dot{Q} = \sum_n \rho_{nn} E_n - \sum_{n \neq m} \rho_{nm} \langle m | \frac{\partial \hat{H}}{\partial t} | n \rangle.$$

(11)

Only when the quantum coherence, represented by \( \sum_{n \neq m} \rho_{nm} \langle m | \frac{\partial \hat{H}}{\partial t} | n \rangle \), is considered, the absence of the heat loss to the surroundings in the adiabatic process is guaranteed. The above description of the heat and work are compatible with Alicki and Kieu’s definitions and can be generalized to open quantum system dynamics [13] [21].

For the combined system bath scenario, the quantum master equation is described explicitly as

$$\dot{\rho} = -\frac{i}{\hbar} \left[ \hat{H}, \rho \right] + {\mathcal{L}}_D (\rho),$$

where \( {\mathcal{L}}_D (\rho) \) is the dissipative superoperator responsible for the interaction of a quantum system with its environment. Straightforwardly, we obtain

$$Tr \left( \dot{\hat{\rho}} \hat{H} \right) = Tr \left( {\mathcal{L}}_D (\dot{\rho}) \hat{H} \right),$$

which demonstrates that all dissipative parts due to the heat exchange are contained in Eq. (11). Equations (10) and (11) give the general definitions of the heat and work in quantum thermodynamic processes. The first part of Eq. (10) indicates that the work done on or by a system can be obtained through dynamic processes. The first part of Eq. (11) shows that the heat transfer is related to a change in the occupation probabilities \( \rho_{nn} \). The second terms in Eqs. (10) and (11) imply that both the heat transfer and the work done in a microscopic process are closely related to the quantum coherence. Considering other specific types of thermodynamic processes, we will find that the heat transfer rate and the work flux may have different characteristics.

When the external field is fixed and the quantum system is put into contacting with a thermal bath at a cer-
tained temperature, an isochoric evolution can be carried out. Since \( \frac{dH}{dt} = 0 \) and the eigenvalues of the Hamiltonian operator \( E_n \) remain constant throughout the isochoric process, no external work is performed \( (W = 0) \), leading to the sole change in the internal energy due to the heat exchange. The heat transfer rate between the system and the thermal bath under this condition can be calculated as \( Q = \sum \rho_{nn} E_n \), which is simply depending on a change in the population of the microstates.

The quantum isothermal processes typically occur when a system is kept in contact with a thermal bath. The system is capable of performing positive work to the outside, and meanwhile absorbs heat from the bath. Both the eigenvalues \( E_n \) and the occupation probabilities \( \rho_{nn} \) need to be changed simultaneously. This operation will occur slowly enough to allow the system to remain in equilibrium with the thermal bath at every instant. The density operator at thermal equilibrium is characterized by thermally distributed populations in the quantum states \( \hat{\rho}(t) = 1/Z \sum_m \exp[-E_m(t)/(k_B T)] | m(t) \rangle \langle m(t) | \) with \( Z = \sum_m \exp[-E_m(t)/(k_B T)] \) being the canonical partition function. Since the system approaches thermal equilibrium without a typical relaxation time due to the bath-system interactions, quantum coherence vanishes, i.e., \( \rho_{nm} = 0 \) \((n \neq m) \). The heat transfer rate and the work flux in the quantum isothermal processes can be expressed as \( Q = \sum \rho_{nn} E_n \) and \( W = \sum \rho_{nn} E_n \), respectively. Because the adiabatic process does not require the second terms in Eqs. (10) and (11) to be a zero value, the general expressions of the rates of the work performed and the heat transfer are different from the counterparts in the isothermal and isochoric processes. Examples of illustrating the valid arguments of the above discussion will be given in the following sections.

\[ \hat{H}_c(t) = -\hat{\mu} \cdot \mathbf{B}(t) = \frac{\hbar \omega}{2} [\sin \alpha \cos(\omega t) \hat{\sigma}_x + \sin \alpha \sin(\omega t) \hat{\sigma}_y + \cos \alpha \hat{\sigma}_z], \]

where \( \omega_1 = eB_0/m; \hat{\sigma}_i \,(i = x, y, \text{and } z) \) are the usual Pauli spin matrices; and \( \hbar \) equals the Planck constant divided by \( 2\pi \).

The wave function for the two-state system is a linear combination of the normalized eigenvectors \( | \chi_+ (t) \rangle \) and \( | \chi_- (t) \rangle \), i.e.,

\[ | \chi (t) \rangle = \left[ \cos \frac{\lambda t}{2} - i \frac{\omega_1 - \omega \cos \alpha}{\lambda} \sin \frac{\lambda t}{2} \right] e^{-i\omega t/2} | \chi_+ (t) \rangle + i \left[ \omega \sin \alpha \sin \frac{\lambda t}{2} \right] e^{i\omega t/2} | \chi_- (t) \rangle, \]

where \( \lambda = \sqrt{\omega^2 + \omega_1^2 - 2\omega_1 \cos \alpha} \) (see Appendix C). The density matrix operator can be written as \( \hat{\rho} = | \chi (t) \rangle \langle \chi (t) | \). Taking the matrix elements, we get \( \rho_{++} = \langle \chi_+ (t) | \hat{\rho} | \chi_+ (t) \rangle, \rho_{--} = \langle \chi_- (t) | \hat{\rho} | \chi_- (t) \rangle, \rho_{+-} = \langle \chi_+ (t) | \hat{\rho} | \chi_- (t) \rangle, \) and \( \rho_{-+} = \langle \chi_- (t) | \hat{\rho} | \chi_+ (t) \rangle \).

It is obvious that \( \rho_{++} \) and \( \rho_{--} \) are the probabilities of being in the spin up and spin down states along \( \mathbf{B}(t) \) and are, respectively, given by

\[ \rho_{++} = \cos^2 \frac{\lambda t}{2} + \frac{(\omega_1 - \omega \cos \alpha)^2}{\lambda^2} \sin^2 \frac{\lambda t}{2}, \]

and

\[ \rho_{--} = \left[ \frac{\omega \sin \alpha \sin \frac{\lambda t}{2}}{\lambda} \right]^2. \]

Most existing literatures studied the thermodynamic properties of the quantum systems with time-independent Hamiltonian. Thus, the heat exchange rate and the work flux in a thermodynamic process can be simplified as \( Q = \sum \rho_{nn} E_n \) and \( W = \sum \rho_{nn} E_n \). These indicates that only the population transfer results in the microscopic realization of the heat exchange, while the
work merely depends on the energy change generated by the external field. However, for the electron-spin system driven by a rotating magnetic field, the eigenvalues corresponding to the instantaneous eigenstates \( |\chi_+ (t)\rangle \) and \( |\chi_- (t)\rangle \) are time independent (see Appendix C). If the work flux in the adiabatic evolution process remains being computed by \( W = \sum_n \rho_{nn} E_n \), we have \( W = 0 \). It means that no work can be done by the magnetic field \( \mathbf{B} (t) \), which is an apparent contradiction in physical reality. In addition, according to the time derivative of \( \rho_{++} \) and \( \rho_{--} \) from Eqs. (14) and (15), the heat exchange rate \( \dot{Q} = \dot{\rho}_{++} E_+ + \dot{\rho}_{--} E_- = -\frac{\hbar \omega}{2\lambda} \sin^2 \alpha \sin (\lambda t) \). As \( \dot{Q} \) is a non-zero value, it is a paradox that there exists heat transfer between the system and the environment in the thermodynamic adiabatic process.

In the present studies, we emphasize that the quantum coherence effects are necessary for reclaiming the validity of the first law of thermodynamics when a quantum system with time-dependent Hamiltonian is considered. Making use of Eq. (13) and taking the off-diagonal elements of the density operator, one readily get

\[
\sum_n \rho_{nn} \langle m | \frac{\partial \hat{H}_e}{\partial t} | n \rangle = \rho_{++} \langle \chi_+ | \frac{\partial \hat{H}_e}{\partial t} | \chi_+ \rangle + \rho_{--} \langle \chi_- | \frac{\partial \hat{H}_e}{\partial t} | \chi_- \rangle = -\frac{\hbar \omega}{2\lambda} \omega^2 \sin^2 \alpha \sin (\lambda t). \tag{16}
\]

It is observed that \( \sum_n \dot{\rho}_{nn} E_n = \sum_{n \neq m} \rho_{nm} \langle m | \frac{\partial \hat{H}_e}{\partial t} | n \rangle \). According to this and Eq. (11), we ensure that the heat transfer rate \( \dot{Q} \) of the two-state system in the adiabatic evolution process equals zero and the corresponding power generated by the external field \( \dot{W} = -\frac{\hbar \omega}{2\lambda} \omega^2 \sin^2 \alpha \sin (\lambda t) \).

### IV. TEST OF THE THERMODYNAMIC ADIABATIC PROCESS VIA THE EXACTLY-SOLVABLE DYNAMIC OF HIGH-SPIN PRECESSION

In this section, we consider a neutral particle with a magnetic moment and arbitrary spin \( j \) in a harmonically-changing external magnetic field \( \mathbf{B} (t) = B_0 \left[ \sin \theta \cos (\omega t), \sin \theta \sin (\omega t), \cos \theta \right] \). The magnetic field rotates around the \( z \)-axis with frequency \( \omega \) and is inclined at a constant angle \( \theta \). The system Hamiltonian is time dependent and is given by

\[
\hat{H}_J (t) = \gamma \mathbf{B} (t) \cdot \mathbf{J} \tag{17}
\]

\[
= \gamma B_0 \left[ J_x \sin \theta \cos (\omega t) + J_y \sin \theta \sin (\omega t) + J_z \cos \theta \right],
\]

where \( \gamma \) is the coupling parameter and \( \mathbf{J} \) is the total angular momentum vector. The operators \( J_x, J_y, \) and \( J_z \) represent three Cartesian components of the angular momentum. Learning the thermodynamic behavior of high-spin precession faces a demand with the exact solution for the wave function. The Schrödinger equation with the time-dependent Hamiltonian is usually difficult to deal with. However, it can be reduced to a Schrödinger-like equation with a time-independent effective Hamiltonian by invoking quantum rotation transformation in angular momentum theory \cite{23}.

If the system is placed initially in an instantaneous eigenstate of \( H_J (0) \), i.e.,

\[
|\psi (0)\rangle = \hat{R}_z (0) \hat{R}_y (\varphi) |j, M\rangle = \sum_{m'} d^j_{m'M}(\beta) |j, m' (\varphi)\rangle,
\]

the exact solution of the time-dependent wavefunction becomes

\[
|\psi (t)\rangle = \sum_{mm'} d^j_{m'M}(\beta) d^\dagger_{m'm'} (\varphi) e^{-im'm't} e^{-ij_j \omega t / \hbar} |j, m\rangle, \tag{19}
\]

where \( \lambda_0 = \frac{\omega}{\gamma B_0}; \omega_0^2 = (\gamma B_0)^2 \left( 1 - 2\lambda_0 \cos \theta + \lambda_0^2 \right) \); and \( \beta = \varphi - \theta \). \( \hat{R}_z (\omega t) = e^{-ij_j \omega t / \hbar} \) and \( \hat{R}_y (\varphi) = e^{-ij_j \varphi / \hbar} \) are the rotation operators. \( |j, m (\varphi)\rangle = \hat{R}_y (\varphi) |j, m\rangle \) \((m = j, j - 1, \ldots, -j)\) are the rotations of the standard angular momentum basis \( |j, m\rangle \). \( d^j_{m'm'} (\varphi) = \langle j, m' | e^{-ij_j \varphi / \hbar} | j, m \rangle \) represents an element of Wigner’s d-matrix. Details of the algorithm are given in Appendix D. The wavefunction \( |\psi (t)\rangle \) is a linear combination of the eigenstates \( |\psi_n\rangle \). As the density operator \( \hat{\rho} = |\psi (t)\rangle \langle \psi (t)| \), we can explicitly carry out its matrix elements

\[
\rho_{nm} (t) = \langle \psi_n | \hat{\rho} | \psi_m \rangle = \sum_{mm'} e^{-i(m-m')\omega t} d^j_{m'M}(\beta) d^\dagger_{m'm'} (\beta) d^j_{m'm} (\beta) \cdot \tag{20}
\]

Similar to the previous model, the dynamic evolution of high-spin precession can also be visualized as an adiabatic process in which no heat is gained or lost by the system. Accordingly, using Eq. (11), we will show that the high-spin system is hardly thermally isolated unless the quantum coherence is considered. From Eqs. (11) and (20), we immediately have

\[
\sum_n \dot{\rho}_{nn} E_n = -i \omega_0 \gamma B_0 \hbar \sum_{mm'} (m - m') ne^{-i(m-m')\omega t} \times d^j_{m'M}(\beta) d^\dagger_{m'm'} (\beta) d^j_{m'm} (\beta). \tag{21}
\]

Knowing that

\[
\langle \psi_m | \frac{\partial \hat{H}_J}{\partial t} | \psi_n \rangle = \frac{\gamma B_0 \hbar \sin \theta}{2i} [\sqrt{(j-n)(j+n+1)} \delta_{m,n+1} - \sqrt{(j+n)(j-n+1)} \delta_{m,n-1}], \tag{22}
\]
implies that momentum, the recursion relation for Wigner’s d-matrix in the computation. In the quantum theory of angular
magnetic field. As an interesting application of the exact
abatic processes. The microscopic expressions are thermodynamic adiabatic regardless of the spin quantum numbers of any particles. The proof is straightforward, which can be done by substituting Eqs. (21) and (23) into Eq. (11).

When \( m = m' \), we have \( \sum_m \rho_{nm} \langle \psi_m | \partial H / \partial t | \psi_n \rangle = 0 \). Only the terms with \( m \neq m' \) need to be considered in the computation. In the quantum theory of angular momentum, the recursion relation for Wigner’s d-matrix implies that \( \gamma \) \( \text{[24]} \[26] \)

\[
\frac{m + n \cos \beta}{\sin \beta} d_{mn}^\beta (\beta) = \frac{1}{2} 
\begin{align*}
&d_{mn+1}^\beta (\beta) \sqrt{(j - n)(j + n + 1)} \\
&+ d_{mn-1}^\beta (\beta) \sqrt{(j + n)(j - n + 1)}.
\end{align*}
\]

Combining the relation between \( d_{mn}^\beta (\beta) \) and \( d_{mn\pm 1}^\beta (\beta) \) and the usual index transformation, one can derive the following invariant sum which gives the coupling rules relating to the direct product of two rotation matrices

\[
\sum_n (m - m') n d_{mn}^\beta (\beta) d_{m'n}^\beta (\beta) = \frac{\sin \beta}{2} \sum_n d_{mn}^\beta (\beta)
\begin{align*}
&x [d_{mn-1}^\beta (\beta) \sqrt{(j + n)(j - n + 1)} \\
&- d_{m'n+1}^\beta (\beta) \sqrt{(j - n)(j + n + 1)}].
\end{align*}
\]

The detail calculations are given in the Appendix E. Applying the invariant sum to Eqs. (21) and (23), we can verify that \( \sum_n \rho_{nm} E_n = \sum_{n \neq m} \rho_{nm} \langle \psi_m | \partial H / \partial t | \psi_n \rangle \) for an instantaneous state. As the heat exchange rate \( \dot{Q} = 0 \), the spin system exchanges no mass or heat energy with its environment. The change in its internal energy is merely due to the work done by the external magnetic field. Once again, the analysis demonstrates that the unitary evolution of a closed system with time-dependent Hamiltonian is equivalent to a thermodynamic adiabatic process when the quantum coherence is taken into account.

If a system starts in an eigenstate of the initial Hamiltonian, the quantum adiabatic theorem states that the system will remain in the corresponding instantaneous eigenstate of the final Hamiltonian when a given perturbation acting on it is slowly enough \( \gamma \) \( \text{[27]} \[28] \). The adiabatic approximation holds when the time derivative of Hamiltonian is extremely small and the dimensionless adiabatic parameter \( \tau = \hbar (m | \partial H / \partial t | n) / (E_n - E_m)^2 \ll 1 \) \( (n \neq m) \). However, the above analysis shows that the thermodynamic adiabatic processes do not require the quantum adiabatic approximation to be satisfied. Quantum adiabatic process certainly results in a thermodynamic adiabatic process, but not all thermodynamic adiabatic processes are due to the quantum-mechanical adiabatic processes.

V. CONCLUSIONS

In summary, we found that the heat and work in microscopic processes are closely related to the transition between different quantum states. The energy exchanges during the quantum isochoric and isothermal processes are simply depending on the change in the eigenenergies or the probability distributions. However, for a closed system with a time-dependent driving, the unitary evolution is equivalent to a thermodynamic adiabatic process only when the quantum coherence is taken into account. Under this consideration, one can ensure that no heat is lost to or gained from the surroundings in the case of quantum-spin precession. The microscopic expressions for thermodynamic quantities are applicable to both the thermal equilibrium case and the nonequilibrium case.

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[2] A. B. Boyd and J. P. Crutchfield, Phys. Rev. Lett. 116, 190601 (2016).
Using Eq. (A1), we obtain the trace of $\dot{\rho} \hat{H}$ as

$$\text{Tr} \left( \dot{\rho} \hat{H} \right) = \sum_{m'} \langle m' | \dot{\rho} E_{m'} | m' \rangle$$

$$= \sum_{m'} \sum_{n m} E_{m'} \rho_{nm} \langle m' | n \rangle \langle m | m' \rangle$$

$$+ \sum_{m'} \sum_{n m} E_{m'} \rho_{nm} \langle \hat{n} | m \rangle \langle m | m' \rangle$$

$$+ \sum_{m} \sum_{n m} E_{m} \rho_{nm} \langle m' | n \rangle \langle m | m \rangle$$

$$+ \sum_{m} \sum_{n \neq m} \rho_{nm} \langle \hat{n} | n \rangle \langle m | n \rangle$$

$$= \sum_{n} \rho_{nn} E_{n} - \sum_{n \neq m} \rho_{nm} \langle m | \hat{n} \rangle \langle \hat{n} | n \rangle.$$

(A2)

In the last step, the relation [22]

$$\langle m | \hat{n} \rangle = - \langle \hat{n} | n \rangle = \langle m | \frac{\partial \hat{H}}{\partial t} | n \rangle / (E_{n} - E_{m}) \ (n \neq m)$$

(A3)

has been applied.

Next, we consider the trace formula $\text{Tr} \left( \dot{\rho} \hat{H} \right)$. The time derivative of the systemic Hamiltonian in Eq. (5) reads

$$\dot{\hat{H}} = \sum_{\alpha} \dot{E}_{\alpha} | \alpha \rangle \langle \alpha | + \sum_{\alpha} E_{\alpha} | \alpha \rangle \langle \alpha | + \sum_{\alpha} E_{\alpha} | \alpha \rangle \langle \alpha |$$

(A4)

With the help of Eqs. (A3) and (A4), it is reasonable to expect that

$$\text{Tr} \left( \dot{\rho} \hat{H} \right) = \sum_{n m} \rho_{nm} \langle m | \dot{\hat{H}} | n \rangle$$

$$= \sum_{n m} \rho_{nm} \sum_{\alpha} \dot{E}_{\alpha} \langle m | \alpha \rangle \langle \alpha | n \rangle$$

$$+ \sum_{n m} \rho_{nm} \sum_{\alpha} E_{\alpha} \langle m | \alpha \rangle \langle \alpha | n \rangle$$

$$+ \sum_{n m} \rho_{nm} \sum_{\alpha} E_{\alpha} \langle m | \alpha \rangle \langle \alpha | n \rangle$$

$$= \sum_{n} \rho_{nn} \dot{E}_{n} + \sum_{n \neq m} \rho_{nm} \langle m | \hat{n} \rangle \langle \hat{n} | n \rangle$$

$$+ \sum_{n \neq m} \rho_{nm} \langle m | \frac{\partial \hat{H}}{\partial t} | n \rangle.$$

(A5)

### Appendix A: Expressing $\text{Tr}(\dot{\rho} \hat{H})$ and $\text{Tr}(\dot{\rho} \hat{H})$ in Terms of the Instantaneous Orthonormal Basis of $\hat{H}$.

From Eq. (6), the time derivative of the density operator is given by

$$\dot{\rho} = \sum_{n m} \left( \rho_{nm} | m \rangle \langle m | + \rho_{nm} | \hat{n} \rangle \langle \hat{n} | + \rho_{nm} | m \rangle \langle m | \hat{n} \rangle \right).$$

(A1)

Using Eq. (A1), we obtain the trace of $\dot{\rho} \hat{H}$ as
Appendix B: TIME DEPENDENCE OF THE DENSITY MATRIX IN AN ADIABATIC PROCESS.

By invoking Eqs. (5) and (6) in the main text, the Poisson bracket \( [\hat{H}, \hat{\rho}] \) is expanded as follows,

\[
[\hat{H}, \hat{\rho}] = \hat{H} \hat{\rho} - \hat{\rho} \hat{H} = \sum_{nm'} E_{nm'} |m'\rangle \langle m'| \sum_{nm} \rho_{nm} |n\rangle \langle m| - \sum_{nm} \rho_{nm} |n\rangle \langle m| \sum_{m'} E_{nm'} |m'\rangle \langle m'| = \sum_{nm} (E_n - E_m) \rho_{nm} |n\rangle \langle m|. \tag{B1}
\]

Substituting Eq. (B1) into the Liouville-von Neumann equation, we obtain

\[
\sum_{nm} (\dot{\rho}_{nm} |n\rangle \langle m| + \rho_{nm} \dot{|n\rangle} \langle m| + \rho_{nm} |n\rangle \langle m| \dot{|n\rangle} = -\frac{i}{\hbar} \sum_{nm} (E_n - E_m) \rho_{nm} |n\rangle \langle m|. \tag{B2}
\]

Multiplying both sides of Eq. (B2) by a bra \( \langle k | \) on the left and a ket \( | l \rangle \) on the right yields

\[
\dot{\rho}_{kl} = -\frac{i}{\hbar} (E_k - E_l) \rho_{kl} - \sum_{m} (\rho_{ml} \langle k | \dot{|m\rangle} + \rho_{km} \langle m | \dot{|l\rangle}) . \tag{B3}
\]

When \( k = l = n \) and considering \( \langle m | \dot{|n\rangle} = -\langle \dot{|m\rangle} | n\rangle = (\frac{\partial \hat{H}}{\partial \gamma} | n\rangle / (E_n - E_m) \langle n | m\rangle \neq m \), one readily finds the equality of Eq. (9).

Appendix C: ELECTRON SPIN PRECESSION IN AN ADIABATICALLY ROTATING ELECTRIC FIELD.

Considering the orthonormal bases \( |\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \) and \( |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \), we have the normalized eigenvectors of \( \hat{H}_e(t) \) as

\[
|\chi_+(t)\rangle = \cos \frac{\alpha}{2} |\uparrow\rangle + e^{i\omega t} \sin \frac{\alpha}{2} |\downarrow\rangle , \tag{C1}
\]

and

\[
|\chi_-(t)\rangle = e^{-i\omega t} \sin \frac{\alpha}{2} |\uparrow\rangle - \cos \frac{\alpha}{2} |\downarrow\rangle , \tag{C2}
\]

which represent the spin up and spin down, respectively, along the instantaneous direction of \( \mathbf{B}(t) \). The corresponding eigenvalues are

\[
E_{\pm} = \pm \frac{\hbar \omega}{2} . \tag{C3}
\]

When the electron starts out with spin up along \( \mathbf{B}(t) \), the system is initially in a state of superposition and is given by \(|\chi (0)\rangle = \cos \frac{\alpha}{2} |\uparrow\rangle + \sin \frac{\alpha}{2} |\downarrow\rangle \). The Schrödinger equation can be integrated formally to give the time-dependent wave function \(|\chi (t)\rangle = \hat{U}(t) |\chi (0)\rangle \), where the unitary time-evolution operator is solved by \( i\hbar \frac{\partial}{\partial t} \hat{U}(t) = \hat{H}_e(t) \hat{U}(t) \).

Appendix D: EXACTLY-SOLVABLE DYNAMICS OF HIGH-SPIN PRECESSION.

Moving to a rotating frame using \( \hat{H}_R = \hat{R}_z(\omega t)^\dagger \hat{H}_f(t) \hat{R}_z(\omega t) - i\hbar \hat{R}_z(\omega t)^\dagger \frac{\partial}{\partial \gamma} \hat{R}_z(\omega t) \) with \( \hat{R}_z(\omega t) = e^{-iJ_z\omega t/\hbar} \), one has

\[
\hat{H}_R = \hat{R}_z(\omega t)^\dagger \hat{\omega}_0 (\hat{J}_z \sin \varphi + \hat{J}_x \cos \varphi) , \tag{D1}
\]

where \( \sin \varphi = \frac{\sin \theta}{\sqrt{1 - 2\lambda_0 \cos \theta + \lambda_0^2}} \) and \( \cos \varphi = \frac{\cos \theta - \lambda_0}{\sqrt{1 - 2\lambda_0 \cos \theta + \lambda_0^2}} \). Obviously, the effective Hamiltonian \( \hat{H}_R \) contains no explicit time dependence in the rotating frame. The corresponding rotated wavefunction is

\[
|\phi (t)\rangle = \hat{R}_z(\omega t)^\dagger |\psi (t)\rangle . \tag{D2}
\]

Invoking the transformation \( \hat{R}_y(\varphi) = e^{-iJ_y\varphi/\hbar} \), one can rewrite \( \hat{H}_R \) as

\[
\hat{H}_R = \hat{R}_y(\varphi) \omega_0 \hat{J}_z \hat{R}_y(\varphi)^\dagger . \tag{D3}
\]

It’s reasonable to expect that \( \hat{H}_R \)'s eigenstates \(|j, m(\varphi)\rangle = \hat{R}_y(\varphi) |j, m\rangle \) \( (m = j, j - 1, \ldots, -j) \) are the rotations of the standard angular momentum basis \(|j, m\rangle \). Therefore, when the initial state of the system is \(|\psi (0)\rangle\), the exact wavefunction is straightforwardly given by

\[
|\psi (t)\rangle = \sum_{mm'} (j, m \langle \psi (0) \rangle |d_{m',m}(\varphi) e^{-im\omega_{m'}t} \times e^{-iJ_z\omega t/\hbar} |j, m'\rangle . \tag{D4}
\]

Starting from \( \hat{J}_z |j, m\rangle = \hbar |j, m\rangle \) and remembering that \( e^{-iJ_y\varphi/\hbar} \hat{J}_z e^{iJ_y\varphi/\hbar} = \hat{J}_z \cos \varphi + \hat{J}_x \sin \varphi \) and \( e^{-iJ_z\omega t/\hbar} \hat{J}_x e^{iJ_z\omega t/\hbar} = \hat{J}_z \cos \omega t + \hat{J}_y \sin \omega t \), we recognize the following relation

\[
\hat{H}_f(t) \hat{R}_z(\omega t) \hat{R}_y(\varphi) |j, m\rangle = \gamma B_0 \hat{R}_z(\omega t) \hat{R}_y(\varphi) \hat{J}_z |j, m\rangle . \tag{D5}
\]

It indicates that \( \psi_m = \hat{R}_z(\omega t) \hat{R}_y(\varphi) |j, m\rangle \) is the eigenstate of \( \hat{H}_f(t) \) and its corresponding eigenvalue is \( m\gamma B_0 \hbar \).
Appendix E: PROOF OF THE COUPLING RULES RELATING TO THE DIRECT PRODUCT OF TWO ROTATION MATRICES.

In angular momentum theory, one has the relations between $d^j_{m(m')n}(\beta)$ and $d^j_{m(m')n \pm 1}(\beta)$ as [24][26]

$$-m + n \cos \beta \overline{d}_m^j (\beta) = \frac{1}{2} [d^j_{m+1} (\beta) \sqrt{(j-n)(j+n+1)}$$
$$+ d^j_{m-1} (\beta) \sqrt{(j+n)(j-n+1)}],$$

(E1)

and

$$-m' + n \cos \beta \overline{d}_m^j (\beta) = \frac{1}{2} [d^j_{m'+1} (\beta) \sqrt{(j-n)(j+n+1)}$$
$$+ d^j_{m'-1} (\beta) \sqrt{(j+n)(j-n+1)}].$$

(E2)

Multiplying each of them by $d^j_{m'n}(\beta)$ and $d^j_{m'n}(\beta)$, respectively, yields

$$-m + n \cos \beta \overline{d}_m^j (\beta) d^j_{m'n}(\beta)$$
$$= \frac{1}{2} [d^j_{m'+1} (\beta) d^j_{m'n}(\beta) \sqrt{(j-n)(j+n+1)}$$
$$+ d^j_{m'-1} (\beta) d^j_{m'n}(\beta) \sqrt{(j+n)(j-n+1)}],$$

(E3)

and

$$-m' + n \cos \beta \overline{d}_m^j (\beta) d^j_{m'n}(\beta)$$
$$= \frac{1}{2} [d^j_{m'+1} (\beta) d^j_{m'n}(\beta) \sqrt{(j-n)(j+n+1)}$$
$$+ d^j_{m'-1} (\beta) d^j_{m'n}(\beta) \sqrt{(j+n)(j-n+1)}].$$

(E4)

Subtracting Eq. (E4) from Eq. (E3) to eliminate the term $\frac{n \cos \beta}{\sin \beta} d^j_{m'n}(\beta) d^j_{m'n}(\beta)$ and multiplying both sides of the equation by $n$, we arrive at a summation formula

$$\sum_n \frac{(m-m') n}{\sin \beta} d^j_{m'n}(\beta) d^j_{m'n}(\beta)$$
$$= \frac{1}{2} \sum_n [d^j_{m'n+1}(\beta) d^j_{m'n}(\beta) n \sqrt{(j-n)(j+n+1)}$$
$$- d^j_{m'n-1}(\beta) d^j_{m'n}(\beta) n \sqrt{(j+n)(j-n+1)}$$
$$+ d^j_{m'n-1}(\beta) d^j_{m'n}(\beta) n \sqrt{(j+n)(j-n+1)}$$
$$- d^j_{m'n+1}(\beta) d^j_{m'n}(\beta) n \sqrt{(j-n)(j+n+1)}].$$

(E5)

According to the usual rules of arithmetic,

$$\sum_n d^j_{m'n}(\beta) d^j_{m'n+1}(\beta) (n+1) \sqrt{(j-n)(j+n+1)},$$

(E6)

and

$$\sum_n d^j_{m'n+1}(\beta) d^j_{m'n-1}(\beta) (n-1) \sqrt{(j+n)(j-n+1)}.$$

(E7)

As a direct consequence of Eqs. (E5)-(E7), the following invariant sum is obtained

$$\sum_n \frac{(m-m') n}{\sin \beta} d^j_{m'n}(\beta) d^j_{m'n}(\beta)$$
$$= \frac{1}{2} \sum_n [d^j_{m'n+1}(\beta) \sqrt{(j-n)(j+n+1)}$$
$$- d^j_{m'n-1}(\beta) \sqrt{(j+n)(j-n+1)}$$
$$- d^j_{m'n+1}(\beta) \sqrt{(j-n)(j+n+1)}].$$

(E8)