

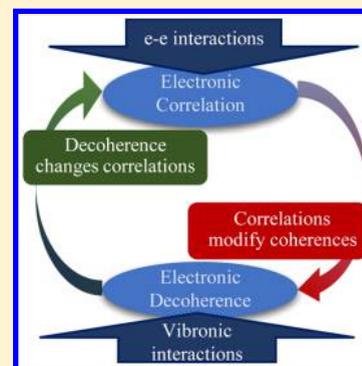
Understanding the Fundamental Connection Between Electronic Correlation and Decoherence

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S Supporting Information

ABSTRACT: We introduce a theory that exposes the fundamental and previously overlooked connection between the correlation among electrons and the degree of quantum coherence of electronic states in matter. For arbitrary states, the effects only decouple when the electronic dynamics induced by the nuclear bath is pure-dephasing in nature such that $[H^S, H^{SB}] = 0$, where H^S is the electronic Hamiltonian and H^{SB} is the electron–nuclear coupling. We quantitatively illustrate this connection via exact simulations of a Hubbard–Holstein molecule using the Hierarchical Equations of Motion that show that increasing the degree of electronic interactions can enhance or suppress the rate of electronic coherence loss.



Understanding the behavior of electrons in matter is fundamental to our ability to characterize, design, and control the properties of molecules and materials.^{1,2} Electronic correlations^{3,4} and decoherence^{5–7} are two basic properties that are ubiquitously used to characterize the nature and quality of electronic quantum states. Correlations among electrons arise due to their pairwise Coulombic interactions, that lead to a dependency of the motion of an electron with that of other surrounding electrons. These correlations determine the energetic properties of electrons in matter and the character of their energy eigenstates.^{8,9} In turn, decoherence in molecules typically arises due to the interactions of the electrons with the nuclear degrees of freedom.^{10–12} The nuclei act as an environment that induces a loss of phase relationship between quantum electronic states. Establishing mechanisms for electronic decoherence is central to our understanding of the excited state dynamics of molecules,^{13–16} to the development of useful approximations to model correlated electron–nuclear dynamics,^{17,18} and to the design of strategies to preserve electronic coherence that can subsequently be exploited in quantum technologies.^{19,20}

While electronic correlation and decoherence have been amply investigated separately, the connection between the two, if any, is not understood. This is partially due to the fact that usual definitions of electronic correlation, such as correlation energy²¹ or natural occupation numbers,²² are only applicable to pure electronic systems^{23,24} and do not allow addressing this fundamental question. For this reason, it is unclear whether decoherence can induce changes in correlation and, conversely, whether correlations can modify the coherence content of a quantum state.

Here we demonstrate that electronic correlation and decoherence are coupled physical phenomena that need to be considered concurrently. We do so by extending the concept of electronic correlation to open nonequilibrium quantum systems, and showing that the electronic correlation modulates the degree of entanglement between electrons and nuclei, and thus the degree of electronic decoherence. Conversely, we also show that the electronic decoherence modulates the degree of electronic correlation, as evidenced by the correlation energy. Further, we isolate conditions under which electronic correlation and decoherence can be considered as uncoupled physical phenomena and show that they are generally violated by molecules and materials, demonstrating that the connection between electronic correlation and decoherence is ubiquitous in matter. These formal developments are quantitatively illustrated via numerically exact computations in a Hubbard–Holstein molecule that show that increasing the electronic interactions can strongly modulate the rate of electronic coherence loss.

To proceed, consider a pure electron–nuclear system with Hamiltonian $\mathcal{H} = H^S + H^B + H^{SB}$, where H^S is the electronic Hamiltonian, H^B is the nuclear component, and H^{SB} is the electron–nuclear couplings. Here, H^{SB} is defined as the residual electron–nuclear interactions that arise when the nuclear geometry deviates from a given reference configuration (e.g., the optimal geometry). The electronic Hamiltonian $H^S = H_0^S + V^S$ can be further decomposed into single-particle contributions H_0^S (e.g., Hartree–Fock) and residual two-body terms V^S . The

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latter arise from Coulombic interactions that cannot be mapped into one-body terms and introduce correlations among the electrons. The associated noninteracting Hamiltonian is obtained when $V^S = 0$, and is given by $\mathcal{H}_0 = H_0^S + H^B + H^{SB}$.

To extend the concept of electronic correlation to open nonequilibrium quantum systems, we require a correlation metric and a reference uncorrelated state for each electron–nuclear state. To construct the reference state, we imagine a fictitious process where for each physical time t the V^S term in the Hamiltonian is turned off adiabatically slow along a fictitious time coordinate τ (see Figure S1 in the Supporting Information (SI)). Specifically, we suppose that the Hamiltonian of the system is of the form

$$\mathcal{H}_\epsilon(\tau) = \mathcal{H} - e^{-\epsilon|\tau|}V^S \quad (\epsilon > 0) \quad (1)$$

where the second term is considered as a perturbation to the \mathcal{H} -induced evolution. The physical evolution along t occurs at the $\tau = \tau_0 \rightarrow -\infty$ limit of the (t, τ) space for which the Hamiltonian is in its fully interacting form $\mathcal{H}_\epsilon(\tau_0) = \mathcal{H}$. In this limit, the state of the fully interacting system is given by

$$\hat{\rho}(t) = \sum_{i,j} \alpha_i(t)\alpha_j^*(t)|\psi_i\rangle\langle\psi_j| \quad (2)$$

where $|\psi_i\rangle$ are eigenstates of \mathcal{H} ($\mathcal{H}|\psi_i\rangle = E_i|\psi_i\rangle$). The uncorrelated reference state is generated by adiabatically turning off, in the Interaction picture, the V^S term in the Hamiltonian in the $\tau = \tau_0$ to $\tau = 0$ interval, i.e.,

$$\hat{\rho}^u(t) = \lim_{\epsilon \rightarrow 0} \lim_{\tau_0 \rightarrow -\infty} U_{e1}(\tau, \tau_0)\hat{\rho}(t)U_{e1}^\dagger(\tau, \tau_0) \quad (3)$$

where $U_{e1}(\tau, \tau')$ is the evolution operator in the Interaction picture. The latter is defined by the Dyson series⁴ $U_{e1}(\tau, \tau') = \mathbb{1} + \sum_{n=1}^{\infty} U_{e1}^{(n)}(\tau, \tau')$, where

$$U_{e1}^{(n)}(\tau, \tau') = -\frac{i}{\hbar} \int_{\tau'}^{\tau} d\tau_n e^{-\epsilon|\tau_n|} V_1(\tau_n) U_{e1}^{(n-1)}(\tau_n, \tau')$$

$V_1(\tau) = -U_0^\dagger(\tau)V^S U_0(\tau)$ is the $-V^S$ operator in Interaction picture, and $U_0(\tau) = e^{-i\mathcal{H}\tau/\hbar}$ is the perturbation-free evolution operator.

Equation 3 captures changes in $\hat{\rho}(t)$ that are generated by the process of turning off V^S in the presence of a nuclear environment. It has the desirable property that $\hat{\rho}^u(t) = \hat{\rho}(t)$ when $V^S = 0$, and it reduces to the usual adiabatic connection for isolated electronic systems when $H^{SB} = 0$. Note that we have chosen $U_{e1}(\tau)$ instead of the full evolution operator $U(\tau) = U_0(\tau)U_{e1}(\tau)$ to generate the uncorrelated states. This is because the $U_0(\tau)$ component of $U(\tau)$ leads to changes in $\hat{\rho}(t)$ due to electron–nuclear entanglements that are present even when $V^S = 0$. By contrast, $U_{e1}(\tau)$ solely captures electron–nuclear entanglements that can be modulated by the electron–electron interactions.

Switching off interactions adiabatically generates exact eigenstates of the noninteracting system from those of the interacting system via the Gell-Mann and Low theorem (GMLT).^{1,4} The GMLT states that, given an eigenstate $|\psi_i\rangle$ of the interacting \mathcal{H} , if the limit

$$\lim_{\epsilon \rightarrow 0} |\phi_i^\epsilon\rangle = \lim_{\epsilon \rightarrow 0} A_i^{-1} U_{e1}(0, -\infty) |\psi_i\rangle \quad (4)$$

(where $A_i = \langle\psi_i|U_{e1}(0, -\infty)|\psi_i\rangle / \langle\psi_i|U_{e1}(0, -\infty)|\psi_i\rangle$ and $|A_i|^2 = 1$ because the $|\phi_i\rangle$ are chosen to be normalized) exists, then

$\lim_{\epsilon \rightarrow 0} |\phi_i^\epsilon\rangle = |\phi_i\rangle$ is an eigenstate of the noninteracting \mathcal{H}_0 . Applying the GMLT in eq 3, we arrive at the uncorrelated reference state that corresponds to $\hat{\rho}(t)$ in eq 2,

$$\hat{\rho}^u(t) = \sum_{i,j} \alpha_i(t)\alpha_j^*(t)e^{i(\theta_i - \theta_j)} |\phi_i\rangle\langle\phi_j| \quad (5)$$

Here, we have assumed that $\lim_{\epsilon \rightarrow 0} A_i A_j^* = e^{i(\theta_i - \theta_j)}$ exists even when the phase factors $A_i \sim e^{i/\epsilon}$ are known to be ill-behaved as $\epsilon \rightarrow 0$.⁴ While the A_i introduce convergence issues at the wave function level, observable quantities, including the density operator, should remain finite during the unitary evolution.

As a physical measure of electronic correlation in electron–nuclear systems, we choose the energetic difference between the correlated and uncorrelated state:

$$E_{\text{cor}}(t) = \text{Tr}[\hat{\rho}(t)\mathcal{H}] - \text{Tr}[\hat{\rho}^u(t)\mathcal{H}_0] \quad (6)$$

This quantity measures energetic changes in the electron–nuclear system that are introduced by the process of turning off V^S during the adiabatic connection in eq 3, and parallels a common metric for correlation²¹ used in closed electronic systems. Note that any energetic measure of correlation based on the properties of the electronic subsystem alone is not appropriate since it will unavoidably include relaxation channels due to interactions with the bath. Further note that definitions of correlation based on the nonidempotency of the single-particle electronic density matrix^{22,25} are not applicable since the nonidempotency can arise due to correlation or due to decoherence²⁶ (see refs 27 and 28 for measures claimed to operate in open quantum systems).

As a basis-independent measure of decoherence, we employ the purity $P(t) = \text{Tr}[\hat{\rho}_e^2(t)]$, where $\hat{\rho}_e(t) = \text{Tr}_B[\hat{\rho}(t)]$ is the N -body electronic density matrix obtained by performing a partial trace over the nuclear bath. The purity $P = 1$ for pure states and $P < 1$ for mixed states. For pure electron–nuclear systems, the decoherence of the electronic (or nuclear) subsystem is solely due to electron–nuclear entanglement. Thus, in this regime, the decay of P also measures the degree of electron–nuclear entanglement.

In this context, it is now readily seen why correlation and decoherence are strongly connected. For this, first note that the coherence content of $\hat{\rho}_e(t)$ and $\hat{\rho}^u(t)$ are generally different. To see this, consider $\hat{\rho}(t) = |\Psi(t)\rangle\langle\Psi(t)|$ in eq 2 for which $|\Psi(t)\rangle = \sum_i \alpha_i(t)|\psi_i\rangle$. In light of the Schmidt decomposition,²⁰ $|\Psi(t)\rangle$ can be written as $|\Psi(t)\rangle = \sum_i \sqrt{\lambda_i(t)} |s_i(t)\rangle |b_i(t)\rangle$, where $|s_i(t)\rangle$ and $|b_i(t)\rangle$ are, respectively, orthonormal electron and nuclear states, and $\sqrt{\lambda_i}$ are the Schmidt coefficients ($\sum_i \lambda_i = 1$, $\lambda_i > 0$). In the Schmidt basis,

$$\hat{\rho}(t) = \sum_{i,j} \sqrt{\lambda_i \lambda_j} |s_i\rangle |b_i\rangle \langle b_j| \langle s_j| \quad (7)$$

In terms of $\{\lambda_i\}$, the purity of the electronic (or nuclear) subsystem is $P(t) = \sum_i \lambda_i^2(t)$. In turn, the uncorrelated state $\hat{\rho}^u(t) = |\Phi(t)\rangle\langle\Phi(t)|$ (eq 5) is associated with $|\Phi(t)\rangle \equiv \sum_i \alpha_i(t) e^{i\theta_i} |\phi_i\rangle$. Under the Schmidt decomposition, $|\Phi(t)\rangle = \sum_i \sqrt{\mu_i(t)} |S_i(t)\rangle |B_i(t)\rangle$ and the resulting purity is $P^u(t) = \sum_i \mu_i^2(t)$. Since $|\Phi(t)\rangle \neq |\Psi(t)\rangle$, the set $\{\mu_i\}$ is different from the set $\{\lambda_i\}$, and therefore the purity for the correlated state and its reference uncorrelated counterpart generally differ. That is, for $H^{SB} \neq 0$, V^S modulates the degree of coherence of electronic states.

Consider now the influence of H^{SB} on the correlation energy [eq 6],

$$E_{\text{cor}}(t) = \sum_i |\alpha_i(t)|^2 (E_i - \mathcal{E}_i) \quad (8)$$

where $\mathcal{H}\psi_i = E_i|\psi_i\rangle$ and $\mathcal{H}_0|\phi_i\rangle = \mathcal{E}_i|\phi_i\rangle$. For $V^{\text{S}} \neq 0$, E_{cor} will change if H^{SB} changes because E_i and \mathcal{E}_i vary differently as H^{SB} is modified. That is, H^{SB} influences E_{cor} because it modulates the response of the electron–nuclear system to V^{S} .

Decoherence and correlation decouple when

$$[H^{\text{S}}, H^{\text{SB}}] = 0 \quad (9)$$

for $V^{\text{S}} \neq 0$. When eq 9 holds, the H^{SB} does not introduce electronic relaxation, and the system–bath dynamics is pure dephasing. To see how this sufficient condition arises, consider the decoherence case first. For the purity of $\hat{\rho}_e(t)$ and $\hat{\rho}_e^{\text{u}}(t)$ to coincide, the evolution operator in eq 3 must not change the degree of entanglement between electrons and nuclei. For this to happen, U_{el} must be of the form

$$U_{\text{el}}(0, -\infty) = U_{\text{el}}^{\text{S}}(0, -\infty) \otimes \mathbb{I}^{\text{B}} \quad (10)$$

where U_{el}^{S} is a purely electronic operator and \mathbb{I}^{B} is the identity operator in the nuclear Hilbert space. Under these conditions, and in light of eq 7, $\hat{\rho}^{\text{u}}(t) = \sum_{i,j} \sqrt{\lambda_i \lambda_j} |s'_i\rangle |b_j\rangle \otimes \langle b_j| \langle s'_j|$, where $|s'_i\rangle \langle s'_j| = \lim_{\epsilon \rightarrow 0} U_{\text{el}}^{\text{S}}(0, -\infty) |s_i\rangle \langle s_j| U_{\text{el}}^{\text{S}\dagger}(0, -\infty)$. Since the Schmidt coefficients for $\hat{\rho}^{\text{u}}(t)$ are the same as those of $\hat{\rho}(t)$ (cf. eq 7), the purity of the two states is identical. For U_{el} to be of the form in eq 10, $V_1(\tau)$ must be a purely electronic operator, i.e., $V_1(\tau) = \hat{O}^{\text{S}}(\tau) \otimes \mathbb{I}^{\text{B}}$, where \hat{O}^{S} is an operator in the Hilbert space of the electronic subsystem. This is guaranteed when eq 9 is satisfied. Specifically,

$$V_1(\tau) = -e^{i\tau H^{\text{S}}/\hbar} e^{i\tau(H^{\text{B}}+H^{\text{SB}})/\hbar} V^{\text{S}} e^{-i\tau(H^{\text{B}}+H^{\text{SB}})/\hbar} e^{-i\tau H^{\text{S}}/\hbar}$$

where we have used the fact that $[H^{\text{S}}, H^{\text{B}}] = 0$ and the condition in eq 9. We arrive at the desired form

$$V_1(\tau) = -e^{i\tau H^{\text{S}}/\hbar} V^{\text{S}} e^{-i\tau H^{\text{S}}/\hbar} \otimes \mathbb{I}^{\text{B}} = \hat{O}^{\text{S}}(\tau) \otimes \mathbb{I}^{\text{B}} \quad (11)$$

by taking into account that $[V^{\text{S}}, H^{\text{B}}] = 0$, and the fact that $[V^{\text{S}}, H^{\text{SB}}] = 0$ for Coulombic systems since V^{S} and H^{SB} are both functions of the position operators.

The correlation energy also becomes independent of H^{SB} when the commutation relations in eq 9 are satisfied. To show this, we contrast E_{cor} with the correlation energy $E_{\text{cor}}^{(0)}$ that would have been obtained if H^{SB} is not allowed to influence the response of the system as V^{S} is adiabatically turned off in eq 3. Specifically,

$$E_{\text{cor}}^{(0)}(t) = \text{Tr}[\hat{\rho}(t)\mathcal{H}] - \text{Tr}[\hat{\rho}_{(0)}^{\text{u}}(t)\mathcal{H}_0] \quad (12)$$

where the reference state $\hat{\rho}_{(0)}^{\text{u}}(t) = \lim_{\tau_0 \rightarrow -\infty, \epsilon \rightarrow 0} [U_{\text{el}}^{\text{S}}(0, \tau_0) \hat{\rho}(t) U_{\text{el}}^{\text{S}\dagger}(0, \tau_0)]$ is obtained by setting $H^{\text{SB}} = 0$ throughout the adiabatic process, i.e., $U_{\text{el}}^{\text{S}}(0, -\infty) = U_{\text{el}}(0, -\infty)|_{H^{\text{SB}}=0}$. The interaction potential $V_1'(\tau)$ in $U_{\text{el}}^{\text{S}}(t, -\infty)$ is given by

$$V_1'(\tau) = V_1(\tau)|_{H^{\text{SB}}=0} = -e^{i\tau H^{\text{S}}/\hbar} V^{\text{S}} e^{-i\tau H^{\text{S}}/\hbar} \otimes \mathbb{I}^{\text{B}} \quad (13)$$

where we have used the fact that $[H^{\text{S}}, H^{\text{B}}] = [V^{\text{S}}, H^{\text{B}}] = 0$. If $E_{\text{cor}}(t) = E_{\text{cor}}^{(0)}(t)$, the correlation energy is independent of H^{SB} . For this to happen, the identity $V_1(\tau) = V_1'(\tau)$ must be satisfied such that $\hat{\rho}_{(0)}^{\text{u}}(t)$ and $\hat{\rho}^{\text{u}}(t)$ coincide. Since $V_1'(\tau)$ is identical to the limiting $V_1(\tau)$ in eq 11, by the same argument employed to

arrive at eq 11 we conclude that $E_{\text{cor}}(t) = E_{\text{cor}}^{(0)}(t)$ when eq 9 is true.

From the perspective of the correlation energy, when eq 9 is satisfied E_{cor} is purely determined by the electronic subsystem. This is because $\langle H^{\text{SB}} + H^{\text{B}} \rangle$ remains constant as V^{S} is turned off adiabatically (as can be seen by writing the Heisenberg equations of motion for $H^{\text{SB}} + H^{\text{B}}$). From the perspective of the purity, eq 9 guarantees that the effect of the bath will be the same for the correlated system and its uncorrelated counterpart, thus eliminating a possible V^{S} dependence in the decoherence dynamics. Note that even for stationary Born–Oppenheimer (BO) states, it is not possible for decoherence and correlation to be uncoupled unless eq 9 is satisfied. This is because even when stationary BO states are not entangled, the corresponding uncorrelated state generally will be.

The pure dephasing condition (eq 9) is generally violated by molecules and materials, indicating that the connection between electronic correlation and decoherence is ubiquitous in matter. Nevertheless, pure dephasing dynamics can arise when the frequencies associated with nuclear motion are far detuned from the electronic transitions such that the nuclear dynamics does not lead to electronic transitions in the correlated and uncorrelated system, as can be the case in semiconducting quantum dots.^{29,30} Under such conditions, $H^{\text{SB}} \approx \sum_n F_n \otimes |E_n\rangle \langle E_n|$, where $\{|E_n\rangle\}$ are the eigenstates of H^{S} , and the F_n are nuclear operators defined such that $[V^{\text{S}}, H^{\text{SB}}] = 0$.

We now quantitatively illustrate this connection using a neutral two-site, two-electron, Hubbard–Holstein model with zero net spin as an example;¹ a minimal molecular model that violates the commutation relations in eq 9 and satisfies $[V^{\text{S}}, H^{\text{SB}}] = 0$ as is expected for molecules. Here the electrons are described by the Hubbard Hamiltonian

$$H^{\text{S}} = -t_0 \sum_{\sigma \in \{\uparrow, \downarrow\}} (\hat{d}_{1\sigma}^\dagger \hat{d}_{2\sigma} + \hat{d}_{2\sigma}^\dagger \hat{d}_{1\sigma}) + U(\hat{n}_{1\uparrow} \hat{n}_{1\downarrow} + \hat{n}_{2\uparrow} \hat{n}_{2\downarrow}) \quad (14)$$

where $\hat{d}_{i\sigma}^\dagger$ (or $\hat{d}_{i\sigma}$) creates (or annihilates) an electron on site i with spin σ and satisfies the usual anticommutation relations $\{\hat{d}_{i\sigma}, \hat{d}_{j\sigma'}^\dagger\} = \delta_{ij} \delta_{\sigma\sigma'}$. The quantity $\hat{n}_{i\sigma} = \hat{d}_{i\sigma}^\dagger \hat{d}_{i\sigma}$ is the number operator, t_0 is the hopping parameter, and U is the energy penalty for having two electrons on the same site. The Hubbard Hamiltonian can be decomposed into a Hartree–Fock component $H_0^{\text{S}} = -t_0 \sum_{\sigma \in \{\uparrow, \downarrow\}} (\hat{d}_{1\sigma}^\dagger \hat{d}_{2\sigma} + \hat{d}_{2\sigma}^\dagger \hat{d}_{1\sigma}) + 2U \sum_{i,\sigma} \hat{n}_{i\sigma} \langle \hat{n}_{i-\sigma} \rangle - U \sum_{i,\sigma} \langle \hat{n}_{i\sigma} \rangle \langle \hat{n}_{i-\sigma} \rangle$, and a two-body term $V^{\text{S}} = H^{\text{S}} - H_0^{\text{S}}$, where the expectation value $\langle \hat{n}_{i\sigma} \rangle = 1/2$ is over the equilibrium thermal state. The nuclei are described as four baths of N_b^m harmonic oscillators, with Hamiltonian

$$H^{\text{B}} = \sum_{m=1}^4 \sum_{j=1}^{N_b^m} \left(\frac{p_{mj}^2}{2} + \frac{1}{2} \omega_{mj}^2 x_{mj}^2 \right) \quad (15)$$

where x_{mj} is the mass-weighted displacement away from equilibrium for the j th harmonic oscillator in the m th harmonic bath, p_{mj} is the momentum conjugate to x_{mj} , and ω_{mj} is its oscillation frequency. We assume that each set of harmonic oscillators couples to an independent electronic configuration of zero net spin. Specifically, we choose

$$H^{\text{SB}} = F_1 \hat{n}_{1\uparrow} \hat{n}_{1\downarrow} + F_2 \hat{n}_{2\uparrow} \hat{n}_{2\downarrow} + F_3 \hat{n}_{1\uparrow} \hat{n}_{2\downarrow} + F_4 \hat{n}_{1\downarrow} \hat{n}_{2\uparrow} \quad (16)$$

where $F_m = \sum_{j=1}^{N_b^m} c_{mj} x_{mj}$ is a collective bath coordinate of bath m . The effective electron–nuclear coupling is specified by the

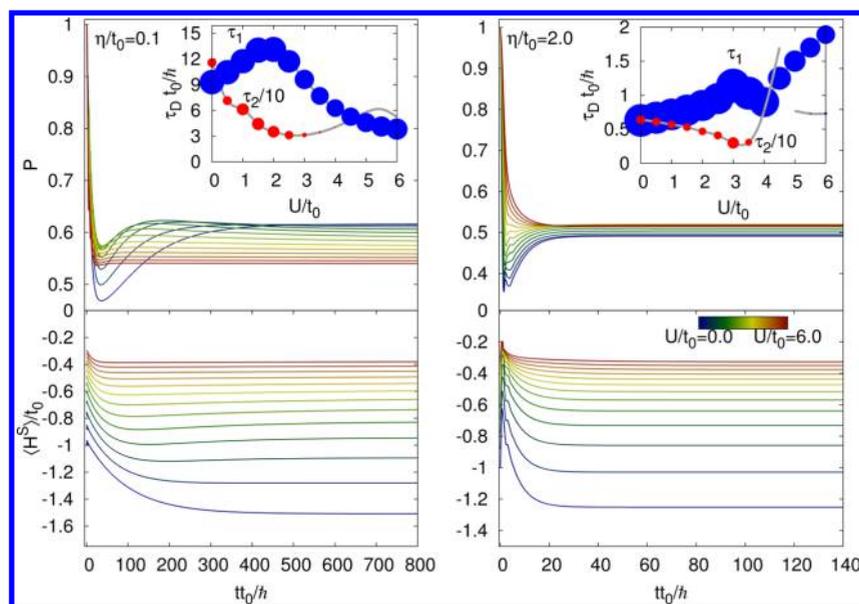


Figure 1. Purity and electronic energy during the evolution of the Hubbard–Holstein molecule ($\beta = 1/t_0$, $\hbar\gamma = 0.3t_0$). The inset shows characteristic time scales in $P(t)$ obtained from an exponential fit $P - P_{\text{thermal}} = \sum_{i=1}^3 a_i \exp(-t/\tau_i)$ (see SI). The dot size measures the magnitude of $|a_i|$ (blue, $a_i > 0$; red, $a_i < 0$; a_3 is small and not shown). Note how increasing U can enhance or suppress the decoherence.

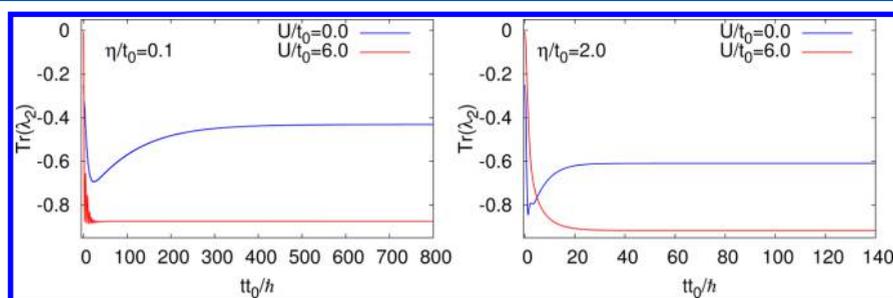


Figure 2. Two-particle cumulant during the evolution in Figure 1.

spectral density $J_m(\omega) = \frac{\pi}{2} \sum_{j=1}^{\Lambda_m^B} \frac{c_{mj}^2}{\omega_{mj}} \delta(\omega - \omega_{mj})$, which is assumed to be the same for all the states and of Debye form $J(\omega) = \eta \frac{\gamma\omega}{\omega^2 + \gamma^2}$. Here γ is the characteristic frequency of the bath, and the parameter η effectively determines the electron–nuclear coupling strength.

The electronic dynamics generated by this model is propagated exactly using the Hierarchical Equations of Motion approach,^{31–34} a nonperturbative and non-Markovian theory of reduced system dynamics. As an initial state, we consider a separable electron–nuclear state $\hat{\rho}(0) = \hat{\rho}_e(0) \otimes \hat{\rho}_n(0)$, where the nuclei are initially at thermal equilibrium $\hat{\rho}_n(0) = \exp(-\beta H^B) / \text{Tr}_B\{\exp(-\beta H^B)\}$ with inverse temperature β , and the electrons $\hat{\rho}_e(0) = |\Psi\rangle\langle\Psi|$ in a superposition $|\Psi\rangle = \frac{1}{\sqrt{2}}(|E_1\rangle + |E_2\rangle)$ between the ground and first excited state.

Figure 1 shows the dynamics of the purity and the electronic energy for different electronic interactions U and effective electron–nuclear couplings η (inset: characteristic decay time scales τ_i in $P(t)$). The fact that eq 9 is violated is reflected by the energetic relaxation of the electrons. The purity observes a sharp initial decay on a τ_1 time scale, followed by a slower dynamics on a τ_2 time scale that asymptotically leads the electronic subsystem to a state of thermal equilibrium. In the presence of electronic correlations, varying U strongly

modulates the decoherence and relaxation dynamics. By contrast, in the Hartree–Fock approximation, the purity for this model is independent of U and equal to the one for $U = 0$. For $U \leq 3t_0$, the decoherence is determined by τ_2 . In turn, for $U \geq 4t_0$, the importance of τ_2 in the dynamics (as characterized by the dot sizes in Figure 1) is diminished, and the decoherence time is determined by τ_1 . Note how increasing U can enhance or suppress the rate of electronic decoherence. Specifically, for $\eta = 0.1t_0$, increasing U leads to a decrease in the decoherence time. By contrast, for $\eta = 2.0t_0$, increasing U leads to a decrease followed by an increase in the decoherence time. As expected, the rate of decoherence is faster in the stronger η case.

The molecular mechanisms at play in Figure 1 can be identified by examining the effect of changing η and U on the potential energy surfaces (PESs). As detailed in the SI, increasing U brings the ground and first excited state closer together in energy, and reduces the difference in curvature between their PESs. The first effect increases the decoherence rate because it increases the nonadiabatic couplings between the two states. Excitation by an incoherent bath leads to decoherence.³⁵ Thus, the enhanced excitation of the electrons by the thermal nuclei increases the decoherence rate. The second effect, by contrast, slows down the decoherence. To see this, recall that for a general vibronic state $|\Psi\rangle = \sum_n |E_n\rangle |\chi_n\rangle$ the electronic density matrix is given by $\hat{\rho}_e = \sum_{nm} \langle \chi_n | \chi_m \rangle |E_n\rangle \langle E_m|$. The coherences between electronic states $|E_n\rangle$ and $|E_m\rangle$ are thus

determined by the nuclear wavepacket overlap $S_{mn} = \langle \chi_m | \chi_n \rangle$.^{12,36} By making the PESs look more alike, increasing U slows down the decay of S_{mn} for each member of the initial ensemble due to wavepacket evolution in alternative PESs. It is the nontrivial competition between these two effects that leads to the intricate dynamics in Figure 1.

Note that the nonadiabatic couplings between the ground (singlet) and first excited (triplet) state that are responsible for the first decoherence mechanism arise due to the $F_3 \hat{n}_{1\uparrow} \hat{n}_{2\downarrow}$ and $F_4 \hat{n}_{1\downarrow} \hat{n}_{2\uparrow}$ terms in H^{SB} . By contrast, the second decoherence mechanism is determined by all four terms in H^{SB} and survives even in the absence of singlet–triplet couplings. In this limit, increasing U protects the electrons from the decoherence.

Does decoherence help us reduce the complexity of the many-body electron problem? Figure 2 shows the evolution of the two-particle cumulant ($\text{Tr}[\lambda_2] = \text{Tr}[(^{(1)}\Gamma)^2 - (^{(1)}\Gamma)]$), where $(^{(1)}\Gamma)$ is the one-body electronic density matrix), which measures the importance of two-body contributions to $\hat{\rho}_e$ that cannot be decomposed in terms of $(^{(1)}\Gamma)$.²⁵ For an uncorrelated closed electronic system $(^{(1)}\Gamma)^2 = (^{(1)}\Gamma)$ and $\text{Tr}[\lambda_2] = 0$. As shown, instead of reducing the complexity, in this case increasing η (and U) enhances the importance of higher order r -body electronic density matrices to the BBGKY hierarchy.³⁷

In conclusion, we have shown that the correlation among electrons and the degree of quantum coherence of electronic states are strongly coupled in matter. For arbitrary states, only when the system-bath dynamics is pure dephasing such that eq 9 is satisfied can correlation and decoherence be considered as uncoupled physical phenomena. Investigating the consequences of this fundamental, ubiquitous, and previously overlooked connection constitutes an emerging challenge in electronic structure and molecular dynamics.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b00467.

Plots for the evolution of the electronic density matrix, the PESs for representative examples, and a discussion of the mechanisms at play in Figure 1 (PDF)

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Notes

The authors declare no competing financial interest.

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