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Electronic interactions do not affect electronic decoherence in the pure-dephasing limit

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The relationship between electronic interactions and electronic decoherence is a fundamental problem in chemistry. Here we show that varying the electron-electron interactions does not affect the electronic decoherence in the pure-dephasing limit. In this limit, the effect of varying the electronic interactions is to rigidly shift in energy the diabatic potential energy surfaces without changing their shape, thus keeping the nuclear dynamics in these surfaces that leads to the electronic decoherence intact. This analysis offers a simple and intuitive understanding of previous theoretical and computational efforts to characterize the influence of electronic interactions on the decoherence and opens opportunities to study exact electronic decoherence with approximate electronic structure theories. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5049710>

Understanding the electronic properties of molecules is one of the most important problems in chemistry, fundamental to our ability to characterize, design, and control molecules and materials. Two of the most important factors that influence the nature of the many-electron states are electron-electron interactions¹ and electronic decoherence. The electron-electron interactions, pairwise Coulomb interactions in first-principle treatments, lead to the correlated motion of all electrons in a molecular system.² This correlation determines chemical bonding, the electronic properties of matter, and the many-electron energy eigenstates. In turn, electronic decoherence in molecules arises due to the electron-nuclear interactions.^{3–10} The nuclei act as an environment that induces a loss of phase relationship between the electronic states. Understanding the mechanisms for electronic decoherence is of vital importance for understanding the ground- and excited-state dynamics of molecules,^{5,6,8,9} for developing accurate approximations to model correlated electron-nuclear dynamics^{11,12} and for preserving electronic coherence that can subsequently be used to enhance molecular functions.¹³

A fundamental question that arises in this context is what is the mutual influence of electron-electron interactions and electronic decoherence.¹⁴ More precisely, whether decoherence can induce changes in the electronic correlation and, conversely, whether electron-electron interactions can modify the electronic decoherence dynamics. In a recent exact numerical study of electronic decoherence for the Su-Schrieffer-Heeger (SSH) Hamiltonian amended by the Hubbard electron-repulsion term,⁶ it was shown that while the electron-electron interactions can induce a significant change of the electronic decoherence by introducing and modifying avoided crossings among the Potential Energy Surfaces (PESs), they do not

influence the decoherence when the dynamics is pure-dephasing in nature. That is, when the nuclei do not introduce significant transitions among electronic diabatic states. This is so provided that the dynamics involves the same electronic states as modified by varying the electronic interactions. This surprising observation is consistent with a previous theoretical analysis¹⁴ which states that, for pure-dephasing dynamics, the electron-electron interactions do not influence the electronic decoherence. However, this theory is based on a fictitious process in which the full interacting state for the composite electron-nuclear system is adiabatically connected to one without the electron-electron interaction part that cannot be physically realized.

In this paper, we present an alternative, physically intuitive, analysis of the influence of electron-electron interactions on the electronic decoherence. Specifically, we demonstrate that, in the pure-dephasing limit, varying the electron-electron interactions only induces a rigid shift in the energy of the Diabatic Potential Energy Surfaces (DPESs) involved in the electron-nuclear dynamics, without changing their shape, thus leaving the electron-nuclear entanglement that leads to decoherence intact. For this, we first show that the pure-dephasing dynamics is determined by the nuclear wavepacket dynamics on DPESs. Then we analyze how the nuclear wavepacket dynamics is affected by varying electron-electron interactions.

We consider a general molecular Hamiltonian of the form $H = H_S + H_B + H_{SB}$, where H_S is the purely electronic Hamiltonian, $H_B = T_B + V_B$ is the nuclear component consisting of the nuclear kinetic energy operator T_B and a common nuclear potential V_B , and H_{SB} is the electron-nuclear couplings. Here, $H_{SB} \equiv H_{SB}(\mathbf{r}; \mathbf{R})$ is defined as the residual electron-nuclear interactions that arise when the nuclear geometry deviates from a given reference configuration (e.g., the minimum energy geometry in the ground electronic surface), where \mathbf{r} and \mathbf{R} denote the electronic and nuclear coordinates, respectively.

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In this context, the pure-dephasing condition is expressed as $[H_S, H_{SB}] = 0$. Under this condition, the Hamiltonian can be written in a simplified form that is convenient for this discussion. By defining the electronic diabatic states $\{|\sigma\rangle\}$ (or crude adiabatic states¹⁵) as the eigenstates of H_S at a fixed nuclear geometry $H_S|\sigma\rangle = E_\sigma|\sigma\rangle$, the molecular Hamiltonian can be represented as

$$H = \sum_{\sigma} (E_{\sigma} + V_{\sigma}(\mathbf{R}) + H_B)|\sigma\rangle\langle\sigma| + \sum_{\sigma \neq \sigma'} V_{\sigma\sigma'}(\mathbf{R})|\sigma\rangle\langle\sigma'| \\ \equiv \sum_{\sigma} H_{\sigma}|\sigma\rangle\langle\sigma| + \sum_{\sigma \neq \sigma'} V_{\sigma\sigma'}(\mathbf{R})|\sigma\rangle\langle\sigma'|, \quad (1)$$

where $V_{\sigma}(\mathbf{R}) = \langle\sigma|H_{SB}|\sigma\rangle_{\mathbf{r}}$ with $\langle\cdots\rangle_{\mathbf{r}} = \int \cdots d\mathbf{r}$ and $H_{\sigma} = T_B + \mathcal{V}_{\sigma}(\mathbf{R})$ is the nuclear Hamiltonian corresponding to electronic state $|\sigma\rangle$ with DPES $\mathcal{V}_{\sigma}(\mathbf{R})$. In turn, $V_{\sigma\sigma'} = \langle\sigma|H_{SB}|\sigma'\rangle_{\mathbf{r}}$ is the off-diagonal electron-nuclear couplings. The pure-dephasing approximation amounts to neglecting these off-diagonal couplings which immediately leads to the condition $[H_S, H_{SB}] = 0$. The molecular Hamiltonian in the pure-dephasing limit reads

$$H = \sum_{\sigma} H_{\sigma}|\sigma\rangle\langle\sigma|. \quad (2)$$

Using the diabatic representation instead of the adiabatic representation is convenient to understand electronic decoherence because the diabatic states are a purely electronic basis with no dependence on the nuclear coordinates. By contrast, the adiabatic (Born-Oppenheimer) states contain a parametric dependence on the nuclear coordinates that makes it difficult to isolate purely electronic coherence properties.⁹

Strictly speaking, the pure-dephasing condition is not satisfied by molecules. However, in practice, it is a good approximation when the vibrational dynamics do not induce significant electronic transitions. It has been found to be useful in studies of quantum molecular dynamics, decoherence, and optical spectroscopy.^{3,6,7,16,17}

To quantify the electronic decoherence due to electron-nuclear entanglement, a well-defined basis-independent measure is required. Here we employ the purity $\mathcal{P} = \text{Tr}[\rho_e^2] \leq 1$, where ρ_e is the electronic density matrix obtained by tracing out the nuclear degrees of freedom (dof) from the full density matrix ρ of the electron-nuclear system, i.e., $\rho_e = \text{Tr}_B[\rho]$, where Tr_B denotes a trace over the nuclear states. The purity is $\mathcal{P} = 1$ for pure states and $\mathcal{P} < 1$ for a statistical mixture of states. For a maximally entangled state, the reduced density matrix becomes $\rho_e = \frac{1}{N} \sum_{n=0}^{N-1} |\sigma\rangle\langle\sigma|$, where N is the number of electronic states $\{|\sigma\rangle\}$ that span the chosen Hilbert space, and the purity reaches its minimum value $\mathcal{P} = \frac{1}{N}$.

In the interest of clarity of presentation, we will focus on molecular systems with two DPESs, i.e., $\sigma = \{g, e\}$. However, cases with more than two electronic surfaces can be analyzed in a similar way with identical conclusions. Throughout we employ atomic units ($\hbar = 1$).

When the electron-nuclear dynamics is pure dephasing, the decoherence dynamics is determined by the nuclear wavepacket dynamics on the DPES. Due to the absence of electronic transitions induced by nuclear motion in the pure dephasing dynamics, the electron-nuclear dynamics can be

understood through nuclear wavepacket dynamics on different electronic surfaces.^{3,6,18}

To show this, consider the pure-dephasing vibronic Hamiltonian [Eq. (2)] and an initially separable vibronic state,

$$|\Psi(t=0)\rangle = (c_g|g\rangle + c_e|e\rangle)|\chi_0\rangle, \quad (3)$$

where $|\chi_0\rangle$ is the initial nuclear state and c_g, c_e are the electronic amplitudes. Clearly, at initial time, the electrons are in a pure state because they are not entangled with the nuclear dof. In this molecular system, the nuclear wavepackets move independently on the corresponding DPES. The vibronic state at a later time t becomes

$$|\Psi(t)\rangle = c_g|\chi_g(t)\rangle|g\rangle + c_e|\chi_e(t)\rangle|e\rangle, \quad (4)$$

where $|\chi_{\sigma}(t)\rangle = U_{\sigma}(t)|\chi_0\rangle$ is the nuclear wavepacket in the σ -th surface and $U_{\sigma}(t) = e^{-iH_{\sigma}t}$ is the corresponding nuclear evolution operator. Tracing out the nuclear dof yields the reduced density matrix for the electrons which in matrix form is

$$\rho_e(t) = \begin{bmatrix} |c_g|^2 & c_g c_e^* \langle\chi_0|U_e^{\dagger}(t)U_g(t)|\chi_0\rangle \\ c_g^* c_e \langle\chi_0|U_g^{\dagger}(t)U_e(t)|\chi_0\rangle & |c_e|^2 \end{bmatrix}. \quad (5)$$

Introducing the decoherence function¹⁹

$$\Gamma(t) = \ln |\langle\chi_0|U_g^{\dagger}(t)U_e(t)|\chi_0\rangle|^2, \quad (6)$$

the electronic purity can be written as

$$\mathcal{P}_e(t) = \text{Tr}_e\{\rho_e^2(t)\} = |c_g|^4 + |c_e|^4 + 2|c_g|^2|c_e|^2 e^{\Gamma(t)} \\ = 1 + 2|c_g|^2|c_e|^2 (e^{\Gamma(t)} - 1), \quad (7)$$

where in the last step, we have taken into account that $|c_g|^2 + |c_e|^2 = 1$. The decoherence is thus caused by the decay of the nuclear wavepacket overlaps due to nuclear dynamics in alternative DPES.²⁰

The decoherence function, characterizing the overlap between nuclear wavepackets on different PESs, is of significant importance in chemistry as it also enters into the spectral line shape theory¹⁷ and non-adiabatic and vibrational transition rates in condensed phase environments.^{18,21} This overlap can also be understood as the nuclear wavepacket evolution through a closed time contour where it propagates forward in time on the excited state surface to time t , makes a jump to the ground state surface, and propagates backward in time until the initial time, i.e.,

$$\langle\chi_g(t)|\chi_e(t)\rangle = \langle\chi_0|U_g(-t)U_e(t)|\chi_0\rangle. \quad (8)$$

Such a closed time loop is akin to that used in defining the Loschmidt echo in the study of quantum chaos.²² In this picture, the decoherence function measures how sensitive the nuclear wavepacket dynamics is to the change of the electronic surface. If the nuclear dynamics is very sensitive to the change of DPES, the probability that the wavepacket goes back to the initial state after the time loop is small leading to a fast decoherence.

Having established that in the pure-dephasing limit the decoherence dynamics is determined by nuclear wavepacket dynamics on the DPES, we now discuss how the electronic

interactions change the decoherence function. Let us start by parameterizing the electronic Hamiltonian as $H_S(\lambda) = H_0 + \lambda V_S$, where V_S is the two-body component of the electron-electron interaction that is not included in the reference Hamiltonian H_0 . This parametrization of H_S is not unique, and the choice of H_0 is a matter of convenience. For example, one can choose H_0 as the Hartree-Fock (HF) Hamiltonian and then V_S becomes the electronic correlation. In fact, the following argument remains valid for any separation of H_S provided that H_0 defines the same Hilbert space as H_S . The parameter λ characterizes the strength of the two-body electronic interactions. In this context, the diabatic states, $\{|\sigma(\lambda)\rangle\}$, defined as the eigenstates of the electronic Hamiltonian

$$H_S(\lambda)|\sigma(\lambda)\rangle = E_\sigma(\lambda)|\sigma(\lambda)\rangle, \quad (9)$$

depend on the value of λ . Conceptually, by choosing a diabatic basis that changes with λ , it is supposed that both the initial state [Eq. (3)] and the Hamiltonian change with the electron-electron interactions. That is, the dynamics always involve the same pair of electronic states adiabatically connected as λ is varied. The Hamiltonian for nuclear dynamics associated with the electronic state $|\sigma(\lambda)\rangle$ [cf. Eq. (2)] becomes $H_\sigma = H_B + V_\sigma(\mathbf{R}, \lambda) + E_\sigma(\lambda)$, and the DPES becomes $\mathcal{V}_\sigma(\mathbf{R}) = V_B + V_\sigma(\mathbf{R}, \lambda) + E_\sigma(\lambda)$. At first glance, it would seem that changing the degree of electronic interactions will change the shape of the diabatic surfaces because of $V_\sigma(\mathbf{R}, \lambda)$. Surprisingly, this term does not depend on λ . To show this, we differentiate it with respect to λ to yield

$$\begin{aligned} \frac{d}{d\lambda} V_\sigma(\mathbf{R}, \lambda) &= \frac{d}{d\lambda} \langle \sigma(\lambda) | H_{SB}(\mathbf{r}, \mathbf{R}) | \sigma(\lambda) \rangle_{\mathbf{r}} \\ &= \left\langle \frac{d}{d\lambda} \sigma(\lambda) \left| H_{SB}(\mathbf{r}, \mathbf{R}) \right| \sigma(\lambda) \right\rangle_{\mathbf{r}} + \text{c.c.} \\ &= 0, \end{aligned} \quad (10)$$

where c.c. stands for complex conjugate. Because for pure-dephasing dynamics $[H_S(\lambda), H_{SB}] = 0$, the diabatic electronic states will also be eigenstates of H_{SB} , that is, $H_{SB}|\sigma(\lambda)\rangle = f(\lambda)|\sigma(\lambda)\rangle$ with real eigenvalues $f(\lambda)$. Furthermore, differentiating the normalization condition $\langle \sigma(\lambda) | \sigma(\lambda) \rangle = 1$ with respect to λ leads to $\langle \sigma(\lambda) | \frac{d}{d\lambda} \sigma(\lambda) \rangle + \text{c.c.} = 0$. These two considerations lead to the nullity of Eq. (10). Therefore, the $V_\sigma(\mathbf{R}, \lambda) = V_\sigma(\mathbf{R})$ do not depend on λ . This implies that even though varying the electron-electron interactions may shift the DPES through $E_\sigma(\lambda)$, it does not change their shape. Therefore, even if the initial nuclear state is chosen to be determined by the shape of the surface (e.g., when it is chosen to be an eigenstate of the nuclear Hamiltonian in a given DPES), it remains the same during the process of varying λ . Expressing H_σ into a sum of the nuclear-dependent part and a λ -dependent part, i.e., $H_\sigma = \mathcal{H}_\sigma(\mathbf{R}) + E_\sigma(\lambda)$, the nuclear evolution operator in the diabatic surface σ becomes

$$U_\sigma(t) = e^{-iH_\sigma t} = e^{-i\mathcal{H}_\sigma(\mathbf{R})t} e^{-iE_\sigma(\lambda)t}. \quad (11)$$

Clearly, the electronic interaction only adds a phase factor into the nuclear evolution operator. Inserting Eq. (11) into Eq. (6) yields the decoherence function

$$\Gamma(t) = \ln \left| \langle \chi_0 | e^{i\mathcal{H}_g(\mathbf{R})t} e^{-i\mathcal{H}_e(\mathbf{R})t} | \chi_0 \rangle \right|^2. \quad (12)$$

As can be seen, the decoherence function does not depend on λ . Therefore, the electronic interaction does not change the decoherence function and, thus, the electronic decoherence.

This conclusion implies that, for a general molecular system, the exact electronic decoherence with full electronic correlation is equivalent to the one obtained using mean-field HF approximation for the electronic structure provided that the dynamics is pure-dephasing with and without the electronic correlation. This corresponds to the case of choosing H_0 as the HF Hamiltonian and V_S as the electronic correlation. We stress that the choice of HF for H_0 ($\lambda = 0$) is not unique. The argument above implies that one can use any other electronic structure theory to define H_0 provided that the corresponding Hamiltonian spans the same Hilbert space as the original electronic Hamiltonian and that the pure-dephasing approximation remains valid for $\lambda = 0, 1$ for the DPES at play.

It is interesting to discuss how this general observation manifests itself in the early-times of purity dynamics^{5,23–25} and the cumulant expansion of the decoherence function,¹⁷ which are the two well-established methods to study decoherence. Up to the second-order in the cumulant expansion,¹⁷ the decoherence function $\Gamma(t)$ can be written as

$$\Gamma(t) \approx -2 \int_0^t ds \int_0^s ds' \langle \delta \mathcal{E}_{eg}(s) \delta \mathcal{E}_{eg}(s') \rangle. \quad (13)$$

Here $\langle \dots \rangle = \text{Tr}_B \{ \rho_B \dots \}$, where $\rho_B = |\chi_0\rangle \langle \chi_0|$ is the initial nuclear density matrix, $\mathcal{E}_{eg} = H_e - H_g$ is the energy gap operator, $\delta \mathcal{E}_{eg} = \mathcal{E}_{eg} - \langle \mathcal{E}_{eg} \rangle$, and $\delta \mathcal{E}_{eg}(t) = U_g^\dagger(t) \delta \mathcal{E}_{eg} U_g(t)$. The early-time behavior of the decoherence function is obtained from the Taylor expansion at initial time to second order, which yields

$$\begin{aligned} \Gamma(t) &= \Gamma(0) + t \dot{\Gamma}(0) + \frac{1}{2} t^2 \ddot{\Gamma}(0) + \mathcal{O}(t^3) \\ &= -\langle (\delta \mathcal{E}_{eg})^2 \rangle t^2 + \mathcal{O}(t^3), \end{aligned} \quad (14)$$

where $\dot{\Gamma}(0) = 0$. Inserting Eq. (14) into Eq. (7) and using $e^x \approx 1 + x$ leads to

$$\mathcal{P}_e(t) = 1 - 2 \langle (\delta \mathcal{E}_{eg})^2 \rangle |c_g|^2 |c_e|^2 t^2 + \mathcal{O}(t^3) = e^{-t^2/\tau_d^2 + \mathcal{O}(t^3)}, \quad (15)$$

where the decoherence time scale is $\tau_d = |c_g|^{-1} |c_e|^{-1} / \sqrt{2 \langle (\delta \mathcal{E}_{eg})^2 \rangle}$. This decoherence time scale developed from the cumulant expansion coincides with the short-time purity expansion in the pure-dephasing limit [see Eq. (15) in Ref. 5]. Clearly, the early-time behavior of the electronic purity is determined by the energy-gap fluctuations, which will not change under rigid shifts in the energy of the DPES. Therefore, varying the electronic interactions does not affect the early-time purity dynamics because it keeps initial fluctuations of operators that enter into H_{SB} intact.

An important question in this context is when will the pure-dephasing mechanism dominate. Some insights can be developed from the displaced harmonic oscillator model. This model consists of two coupled harmonic diabatic surfaces with force constants $\{k_\mu\}$ whose equilibrium configuration is displaced by d_μ along the μ th coordinate R_μ upon $|g\rangle \rightarrow |e\rangle$ electronic excitation. The vibronic Hamiltonian includes non-pure-dephasing contributions of the form

$V_{eg}(\mathbf{R})(|e\rangle\langle g| + |g\rangle\langle e|)$, where $V_{eg}(\mathbf{R}) = \sum_{\mu} g_{\mu} R_{\mu} + \gamma$ and γ and g_{μ} are the coupling constants. Equation (22) in Ref. 5 identifies the contributions of pure-dephasing (first term), electronic transitions (third term), and their interference (second term) to the decoherence time τ_d for initial state Eq. (3). The relative importance of the pure-dephasing contribution of the μ th mode can be obtained by taking the ratio between pure and non-pure dephasing contributions to τ_d^{-2} (neglecting the interference), to yield

$$Q_{\mu} = Q_I Q_S^{\mu}. \quad (16)$$

Here $Q_I = |c_g|^2 |c_e|^2 / (1 - 4|c_g|^2 |c_e|^2 \cos^2 \theta)$ characterize the dependence on the initial state and

$$Q_S^{\mu} = (k_{\mu} d_{\mu} / g_{\mu})^2 \quad (17)$$

solely depends on the Hamiltonian. For $Q_I \neq 0$, when $Q_S^{\mu} \gg 1$, the nuclear wavepacket overlap decay is faster than the onset of electronic transitions and pure-dephasing dominates.

To summarize, we have provided a simple and physically transparent analysis to understand the fundamental connections between electronic interaction and electronic decoherence. We showed that the electron-electron interaction does not affect electronic decoherence because it does not change the shape of DPES when the pure-dephasing limit is a good approximation to the electron-nuclear evolution. This theory explains the previous computational observations for the SSH model amended with the Hubbard term using exact numerical methods.⁶ It further explains the numerically observed rigid shifts with increasing electron-electron interactions of the adiabatic potential energy surface away from the avoided crossings (Fig. 1 in Ref. 6) because in these regions, the adiabatic and diabatic surfaces are expected to be close to each other. These developments reinforce the conclusion in Ref. 14 that the electron-electron interactions can influence the electronic decoherence by modifying and opening paths for electronic transitions among diabatic surfaces induced by the nuclear dynamics and, albeit in the pure-dephasing limit,

also open opportunities to follow *exact* electronic decoherence with approximate electronic structure theories.

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