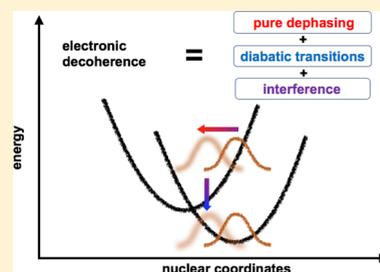


# Generalized Theory for the Timescale of Molecular Electronic Decoherence in the Condensed Phase

Bing Gu<sup>†</sup> and Ignacio Franco<sup>\*,†,‡</sup><sup>†</sup>Department of Chemistry, University of Rochester, Rochester, New York 14627, United States<sup>‡</sup>Department of Physics, University of Rochester, Rochester, New York 14627, United States

## Supporting Information

**ABSTRACT:** We introduce a general theory of electronic decoherence for molecules in the condensed phase that captures contributions coming from pure dephasing effects, electronic transitions among diabatic states, and their interference. The theory is constructed by taking advantage of a recently developed [*J. Phys. Chem. Lett.* 2017, 8, 4289–4294] general expression for decoherence times that is based on an early time expansion of the purity dynamics and extends early electronic decoherence models based on pure dephasing ideas. Using this theory, we construct the decoherence time for the displaced harmonic oscillator model amended with constant and linear diabatic couplings, which is a widely used model of the photoexcited dynamics of molecules. The validity of the short-time expansion is demonstrated by the quantitative agreement of the theory with exact numerical computations of the decoherence dynamics obtained using the hierarchical equation of motion method. These developments offer a rigorous understanding of early time electronic decoherence processes that accompany basic molecular events and demonstrate that electronic transitions among diabatic states play a major role in the decoherence dynamics.



Decoherence arises due to the unavoidable interactions of quantum systems with their environment,<sup>1–4</sup> e.g., molecules interacting with solvent or solar light. During decoherence, a system changes from a pure state  $\sigma(t) = |\psi\rangle\langle\psi|$  to a statistical mixture of states  $\sigma(t) = \sum_i p_i |\psi_i\rangle\langle\psi_i|$  ( $p_i > 0$ ). Such a process reduces the ability of matter to fully exhibit its quantum mechanical features and thus limits the applicability of quantum technologies.<sup>2</sup>

In chemical systems, the state purity of electronic degrees of freedom decays due to electron–nuclear interactions. Understanding electronic decoherence is important for a variety of areas in chemistry including line shape and measurement theory, electron and energy transfer, photochemistry, photo-physics, quantum information, and quantum control.<sup>1,2,5–8</sup> Further, proper treatment of electronic decoherence is essential for developing approximation schemes for the electron–nuclear dynamics of molecules.<sup>9,10</sup>

Despite its ubiquitous and important role in chemical dynamics, the contributions to electronic decoherence remain unclear.<sup>11,12</sup> While important theoretical advances have been made to understand electronic decoherence in condensed phase environments based on two-state models in the pure dephasing limit,<sup>13–17</sup> where the decoherence occurs without energy transfer between the system and environment, it is unclear if those models capture all relevant contributions. In turn, numerically exact computations of electronic decoherence that have been presented necessarily focus on capturing the dynamics of small molecular systems with a few electrons and nuclei as the computational cost of such computations scales exponentially with system size<sup>18–20</sup> and, thus, are not

necessarily representative of large molecules or condensed phase environments (see ref 21 for a potential strategy to circumvent this problem). Furthermore, dynamics methods that are capable of treating large molecular systems<sup>22,23</sup> rely on approximate schemes that do not necessarily accurately capture the decoherence (see ref 10 for a proposed method to test approximations).

In this Letter, we introduce a general theory for electronic decoherence in condensed phase environments and large molecular systems by performing a short-time expansion of the electronic purity dynamics generated by the general Hamiltonian of a molecule. The electronic purity is defined as  $\mathcal{P}(t) = \text{Tr}_S[\sigma^2(t)] \leq 1$ , where  $\sigma(t)$  is the electronic density matrix and the trace is over the electronic degrees of freedom. Purity is a well-defined basis-independent measure of decoherence<sup>24</sup> that quantifies the degree of non-idempotency of the reduced density matrix of the system of interest. The quantity  $\mathcal{P} = 1$  for pure states and  $\mathcal{P} < 1$  for mixed states.

The theory below is based on a recently developed general expression for the decoherence timescale  $\tau_d$  for open quantum systems.<sup>10</sup> It recovers previously identified pure dephasing contributions to coherence loss. In addition, it reveals that electronic transitions among diabatic states introduce an additional important channel for electronic decoherence. Surprisingly, contrary to Bloch equation ideas where dephasing and relaxation effects contribute separately to the decoherence,

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we find that generally the contributions due to electronic transitions (that are also responsible for relaxation) interfere with the pure dephasing effects. To illustrate the validity of the theory in an important model of practical importance, below we also develop a formula for the decoherence time for the displaced harmonic oscillator (or spin-boson) model with constant and linear diabatic couplings. Moreover, to test the applicability of the theory, we contrast the theoretical predictions with numerically exact simulations using the hierarchical equations of motion method.<sup>25</sup>

As shown in ref 10 for a general quantum system ( $\mathcal{S}$ ) coupled to an environment ( $\mathcal{B}$ ) with Hamiltonian  $H = H_{\mathcal{S}} + H_{\mathcal{B}} + H_{\mathcal{S}\mathcal{B}}$ , where  $H_{\mathcal{S}}$  describes the system,  $H_{\mathcal{B}}$  the bath, and

$$H_{\mathcal{S}\mathcal{B}} = \sum_{\alpha} S_{\alpha} \otimes B_{\alpha} \quad (1)$$

the system–bath interactions, the purity decays like a Gaussian  $\mathcal{P}(t) = e^{-t^2/\tau_d^2}$  and the decoherence timescale  $\tau_d$  is governed by initial-time fluctuations of the system  $S_{\alpha}$  and bath  $B_{\alpha}$  operators that enter into  $H_{\mathcal{S}\mathcal{B}}$ . Specifically

$$\tau_d = \hbar \left( 2 \sum_{\alpha\beta} \Delta_{\alpha\beta}^{\mathcal{B}} \times \Delta_{\alpha\beta}^{\mathcal{S}} \right)^{-1/2} \quad (2)$$

where

$\Delta_{\alpha\beta}^{\mathcal{S}} \equiv \langle S_{\alpha} S_{\beta} \rangle - \langle S_{\alpha} \rangle \langle S_{\beta} \rangle$  and  $\Delta_{\alpha\beta}^{\mathcal{B}} \equiv \langle B_{\alpha} B_{\beta} \rangle - \langle B_{\alpha} \rangle \langle B_{\beta} \rangle$  are the crossed fluctuations (covariances) between the system and bath operator. The decoherence time decreases as the initial time fluctuations of  $S_{\alpha}$  and  $B_{\alpha}$  increase. Equation 2 applies to any initially pure system and does not invoke common approximations employed in open quantum system dynamics such as Markovian dynamics, harmonic baths, or rotating-wave approximations. If the long-time limit of the system purity  $\mathcal{P}_{\infty} \equiv \lim_{t \rightarrow \infty} \mathcal{P}(t)$  is known, one can interpolate the short and asymptotic purity behavior as

$$\mathcal{P}(t) - \mathcal{P}_{\infty} \approx (1 - \mathcal{P}_{\infty}) e^{-(1-\mathcal{P}_{\infty})^{-1}(t/\tau_d)^2} \quad (3)$$

This short-time expansion of purity is appropriate to study electronic decoherence in large molecular systems and condensed phase environments where no recurrences in the purity are expected, as has been, in fact, observed in a series of simulations.<sup>18,19,26–28</sup> As noted previously,<sup>10</sup> in a pure-dephasing spin-boson model with Ohmic spectral density, the time in which eq 3 is valid is determined by  $1/\omega_c$  where  $\omega_c$  is the cutoff frequency of the environment. In this context, this time is determined by the period of the fastest vibrational mode that couples to the electronic motion. Such time is that required for the fastest revival, if present, to emerge. If no revivals are present, the early time decoherence captures all relevant dynamics.

To develop an electronic decoherence timescale, we start from the general Hamiltonian for a molecular system

$$H = T_e + T_N + V_{\text{NN}}(\mathbf{R}) + V_{\text{eN}}(\mathbf{r}, \mathbf{R}) + V_{\text{ee}}(\mathbf{r}) \\ = T_N + H_{\text{el}}(\mathbf{r}, \mathbf{R}) \quad (4)$$

Here  $\mathbf{r}$  and  $\mathbf{R}$  denote the electronic and nuclear coordinates and  $H_{\text{el}}(\mathbf{r}, \mathbf{R})$  is the electronic (Born–Oppenheimer) Hamiltonian, which parametrically depends on  $\mathbf{R}$ . In turn,  $T_e$  and  $T_N$  are the kinetic energy operators for electrons and nuclei;  $V_{\text{NN}}$ ,  $V_{\text{eN}}$ , and

$V_{\text{ee}}$  are the nuclear, electron–nuclei, and electronic interactions, respectively. In decoherence language, the electrons are the system of interest, the nuclei are the bath, and their interaction  $V_{\text{eN}}$  leads to electron–nuclear entanglement and thus to decoherence.

A challenge in developing  $\tau_d$  is that eq 2 cannot be directly applied to the Hamiltonian in eq 4 because the Coulomb interaction between electrons and nuclei  $V_{\text{eN}} = \sum_{i,\alpha} -\frac{1}{4\pi\epsilon_0} \frac{Z_{\alpha} e^2}{|\mathbf{r}_i - \mathbf{R}_{\alpha}|}$ , where  $Z_{\alpha} e$  is the charge of the  $\alpha$ th nuclei and  $-e$  the charge of the electrons, is not in the form in eq 1. To overcome this limitation, below we transform the molecular Hamiltonian into a diabatic representation that allows eq 2 to be applied to obtain the electronic decoherence time. The diabatic states provided by the crude Born–Oppenheimer approximation<sup>29</sup> are preferred here to represent the molecular Hamiltonian instead of the alternative adiabatic (or Born–Oppenheimer) states. This is because the electrons and nuclei are already entangled in these adiabatic states,<sup>12</sup> making the discussion of electronic decoherence difficult.

In the crude Born–Oppenheimer basis  $\{\psi_n(\mathbf{r}; \mathbf{R}_0)\}$ ,  $n = 0, 1, \dots$ , the molecular Hamiltonian can be written as

$$H = T_N + \sum_n \mathcal{E}_n |\psi_n\rangle \langle \psi_n| + \sum_{n,n'} V_{n'n}(\mathbf{R}) |\psi_{n'}\rangle \langle \psi_n| \quad (5)$$

where  $\{\psi_n(\mathbf{r}; \mathbf{R}_0) = \langle \mathbf{r} | \psi_n \rangle\}$  is the set of eigenstates of the electronic Hamiltonian of the molecule defined at a fixed reference nuclear geometry  $\mathbf{R}_0$ , i.e.,  $H_{\text{el}}(\mathbf{R}_0) \psi_n(\mathbf{r}; \mathbf{R}_0) = \mathcal{E}_n \psi_n(\mathbf{r}; \mathbf{R}_0)$ . In turn, the electron–nuclear couplings

$$V_{n'n} = \langle \psi_{n'} | H_{\text{el}}(\mathbf{r}; \mathbf{R}) - H_{\text{el}}(\mathbf{r}; \mathbf{R}_0) | \psi_n \rangle_{\mathbf{r}} \quad (6)$$

where  $\langle \dots \rangle_{\mathbf{R}}$  ( $\langle \dots \rangle_{\mathbf{r}}$ ) denotes integration over nuclear (electronic) coordinates only.

From eq 5, it is clear that the electron–nuclear coupling can be identified as

$$H_{\text{eN}} = \sum_{n,n'} V_{n'n}(\mathbf{R}) |\psi_{n'}\rangle \langle \psi_n| \quad (7)$$

The diagonal matrix element of  $V_{n'n}(\mathbf{R})$  represents the diabatic potential energy surface (DPES), and off-diagonal elements are the diabatic couplings. Using eq 7, it is possible to develop a generalized decoherence time by identifying the electronic and nuclear operators in eq 7, computing the crossed fluctuations and inserting them into eq 2. Nevertheless, it is simpler and actually sufficient to focus on few (two and three) level problems as they distill the essence of the dynamics. We first consider the case of two electronic states (i.e., two diabatic surfaces) and then generalize to a three-state model that reveals the effects of adding additional states to the electronic decoherence.

We now specialize eq 5 to the case of two DPES. Let  $|g\rangle$  and  $|e\rangle$  be the electronic ground and excited states. For future convenience, we write the two-surface molecular Hamiltonian as

$$H = \mathcal{H}_g |g\rangle \langle g| + \mathcal{H}_e |e\rangle \langle e| + V_{ge}(\mathbf{R}) |g\rangle \langle e| + V_{eg}(\mathbf{R}) |e\rangle \langle g| \quad (8a)$$

$$= \mathcal{H}_g \otimes \mathcal{I}_e + \mathcal{E}_{\text{eg}}(\mathbf{R}) |e\rangle \langle e| + V_{ge}(\mathbf{R}) |g\rangle \langle e| + V_{eg}(\mathbf{R}) |e\rangle \langle g| \quad (8b)$$

Here  $\mathcal{H}_g = T_N + V_g(\mathbf{R})$  and  $\mathcal{H}_e = T_N + V_e(\mathbf{R})$  denote the nuclear Hamiltonians in ground and excited DPES, respectively,  $\mathcal{I}_e$  is the identity in electronic subspace, and

$\mathcal{E}_{eg}(\mathbf{R}) \equiv \mathcal{H}_e - \mathcal{H}_g$  is the energy gap operator between the ground and excited diabatic surfaces. The quantity  $V_{ge}(\mathbf{R}) (=V_{eg}^*(\mathbf{R}))$  represents the diabatic couplings between DPES, which may be caused by the inherent electron–nuclear couplings or by interaction with external electromagnetic fields. Commonly employed models to understand electron–nuclear dynamics and environment-induced effects, such as the spin-boson and displaced harmonic oscillator models, are of the form in eq 8b. The electronic decoherence time can be obtained by identifying from eq 8b the system–bath (electron–nuclei) coupling as (following the notation in eq 1)

$$\begin{aligned} S_0 &= |e\rangle\langle e| & B_0 &= \mathcal{E}_{eg}(\mathbf{R}) \\ S_1 &= |g\rangle\langle e| + \text{h.c.} & B_1 &= V_{ge}(\mathbf{R}) \end{aligned} \quad (9)$$

where h.c. stands for the Hermitian conjugate and where, without loss of generality, we have taken  $V_{ge}(\mathbf{R})$  to be real. The term  $S_0 \otimes B_0$  is responsible for the pure dephasing effects as it does not introduce electronic transitions, while  $S_1 \otimes B_1$  leads to electron–nuclear entanglement through electronic transitions among DPES.

To define a decoherence time, we suppose that the molecule is initially in a separable electron–nuclear state of the form

$$|\Psi_0\rangle = (c_g|g\rangle + c_e|e\rangle) \otimes |\chi_0\rangle \quad (10)$$

where  $\chi_0(\mathbf{R}) = \langle \mathbf{R} | \chi_0 \rangle$  is the nuclear state. Using this initial state (eq 10), the fluctuations of the system and bath operators (cf. eq 2) are

$$\Delta_{00}^S = |c_g|^2 |c_e|^2 \quad \Delta_{00}^B = \langle \delta^2 \mathcal{E}_{eg}(\mathbf{R}) \rangle \quad (11)$$

$$\Delta_{11}^S = 1 - (c_g c_e^* + c_g^* c_e)^2 \quad \Delta_{11}^B = \langle \delta^2 V_{ge}(\mathbf{R}) \rangle \quad (12)$$

$$\Delta_{01}^S = |c_g|^2 c_g c_e^* - |c_e|^2 c_g^* c_e \quad \Delta_{01}^B = \langle \delta V_{ge}(\mathbf{R}) \delta \mathcal{E}_{eg}(\mathbf{R}) \rangle \quad (13)$$

where  $\delta O = O - \langle O \rangle$ ,  $\delta^2 O = O^2 - \langle O \rangle^2$ , and  $\Delta_{10}^{S/B} = (\Delta_{01}^{S/B})^*$ . The final expression for the electronic decoherence time is obtained by inserting all of the separate contributions into eq 2

$$\begin{aligned} \tau_d^{-2} &= 2\hbar^{-2} (|c_g|^2 |c_e|^2 \langle \delta^2 \mathcal{E}_{eg} \rangle + (1 - 4|c_g|^2 |c_e|^2 \cos^2 \theta) \langle \delta^2 V_{ge} \rangle \\ &\quad + 2(|c_g|^2 - |c_e|^2) |c_g| |c_e| \cos \theta \langle \delta \mathcal{E}_{eg} \delta V_{ge} \rangle) \end{aligned} \quad (14)$$

where  $c_g = |c_g| e^{i\theta_g}$  and  $c_e = |c_e| e^{i\theta_e}$  and  $\theta = \theta_g - \theta_e$  is the angle between  $c_g$  and  $c_e$  in the complex plane. For notational simplicity, we have not included explicitly the nuclear dependence in eq 14.

Equation 14 is the final expression for the electronic decoherence time for a two-level initially pure electronic system. The physical meaning of the terms in  $\tau_d$  is as follows. The first term proportional to  $\langle \delta^2 \mathcal{E}_{eg} \rangle$  is the decoherence due to the energy gap fluctuations between two DPES that represent pure dephasing effects. In turn, the term proportional to  $\langle \delta^2 V_{ge} \rangle$  represents decoherence due to the electronic transitions to other DPES that lead to additional electron–nuclear entanglement. The presence of a third term demonstrates that these two contributions do not operate separately but, in fact, interfere. In terms of the reduced electronic density matrix in the diabatic basis, the pure dephasing induces the decay of the off-diagonal matrix elements without affecting the diagonal matrix elements, while the electronic transitions affect both of them simultaneously, in

analogy to a two-level system interacting with a radiation field. Some observations from eq 14 can be made as follows. When  $|c_g|$  or  $|c_e| \approx 0$ , the pure dephasing contribution and interference can be neglected and the diabatic couplings becomes the dominant contribution. The interference term vanishes when  $|c_g| = |c_e| = 1/\sqrt{2}$  or  $\theta = \{\pi/2, 3\pi/2\}$ . In these cases, the pure dephasing effects and diabatic contribution become additive at the level of  $\tau_d^{-2}$ . The relative importance of these contributions will depend on the specific model under study.

The interference between pure dephasing and the diabatic couplings responsible for energy redistribution including relaxation is a surprising fact that is in stark contrast with the common understanding of decoherence that arises from Bloch models. In these models, the decay of off-diagonal matrix elements between energy eigenstates has independent contributions from pure dephasing and relaxation processes. In fact, the total decoherence rate  $1/T_2$  satisfies<sup>30</sup>  $\frac{1}{T_2} = \frac{1}{T_2^*} + \frac{1}{2T_1}$ , where  $\frac{1}{T_2^*}$  is the decoherence rate due to pure dephasing and  $\frac{1}{2T_1}$  is that due to relaxation. As shown above, this independence of pure dephasing and relaxation is in general not valid for decoherence in non-Markovian environments.

A commonly used expression for electronic decoherence can be recovered in the pure dephasing limit of eq 14. When electronic transitions can be ignored, eq 14 yields

$$\tau_d = \hbar |c_g|^{-1} |c_e|^{-1} / \sqrt{2 \langle \delta^2 \mathcal{E}_{eg} \rangle} \quad (15)$$

Equation 15 relates the decoherence time and the energy gap fluctuations, which is consistent with the observations in refs 13, 15, and 31. For pure dephasing dynamics, it is traditional to introduce the so-called decoherence function to characterize the dynamics of the off-diagonal elements of the reduced density matrix represented with energy eigenstates.<sup>1</sup> Equation 15 recovers the purity computed with decoherence functions at short times for two-level systems.<sup>1</sup> Further simplifications of eq 15 can be introduced using the frozen Gaussian approximation where the bath state is approximated by a set of Gaussian wavepackets to connect the energy gap fluctuations to the Stokes shift.<sup>13</sup>

To understand the effect of additional states in the decoherence, we now generalize eq 14 to a three-level problem. Although the two-state model is adequate for a wide variety of processes, there are cases in which the excited state  $|e\rangle$  couples to other excited states  $|f\rangle$  such that the molecular Hamiltonian can be written as

$$H' = H + \mathcal{E}_{fg}(\mathbf{R}) |f\rangle\langle f| + V_{fe}(\mathbf{R}) (|f\rangle\langle e| + |e\rangle\langle f|) \quad (16)$$

where  $H$  refers to the Hamiltonian as expressed in eq 8b. We focus on the case in which  $|f\rangle$  is initially unoccupied ( $c_f = 0$ ) and the initial state given by eq 10. The third level introduces two additional coupling terms in the Hamiltonian:  $S_2 = (|e\rangle\langle f| + |f\rangle\langle e|)$ ,  $B_2 = V_{fe}(\mathbf{R})$  and  $S_3 = |f\rangle\langle f|$ ,  $B_3 = \mathcal{E}_{fg}(\mathbf{R})$ . The pure dephasing contribution to  $\tau_d$  that could arise due to  $\mathcal{E}_{fg}(\mathbf{R}) |f\rangle\langle f|$  vanishes because  $c_f = 0$  (cf. eq 11). This implies that the only additional contribution is due to possible transitions into the third state. In this case,  $\Delta_{22}^S = |c_e|^2$ ,  $\Delta_{22}^B = \langle \delta^2 V_{fe} \rangle$ , and the new decoherence time

$$(\tau_d')^{-2} = \tau_d^{-2} + 2\hbar^{-2} |c_e|^2 \langle \delta^2 V_{fe}(\mathbf{R}) \rangle \quad (17)$$

Clearly, the presence of a third DPES *accelerates* electronic decoherence for initial states of the form in eq 10 provided that  $\langle \delta^2 V_{je}(\mathbf{R}) \rangle \neq 0$ . However, this conclusion cannot simply be extended to other initial vibronic state where  $c_j \neq 0$ . In that case, the pure dephasing contributions from the third state do not vanish and complicate the analysis. Nevertheless, the above analysis can easily be extended to other initial states and other circumstances in which, for example, the ground state is also coupled to the third state.

We now illustrate the theory in the displaced harmonic oscillator model<sup>32</sup> amended with diabatic couplings. In this model, two electronic diabatic states ( $|g\rangle$ ,  $|e\rangle$ ) are coupled to a set of independent harmonic vibrational modes meant to represent, e.g., the inter- and intramolecular vibrational modes, collective solvent motions, or phonon modes in solids. To capture possible changes in the equilibrium nuclear configuration associated with a change from  $|g\rangle$  to  $|e\rangle$ , the minima of the resulting harmonic DPES are displaced from one another. This model is also known as the spin-boson model if Pauli matrices are used to represent the two electronic states. It has been used extensively in chemistry and physics to study electron transfer,<sup>33</sup> excited state dynamics,<sup>34</sup> energy transfer,<sup>35</sup> non-Markovian decoherence,<sup>36</sup> electronic dephasing,<sup>16</sup> electronic spectroscopy,<sup>32</sup> and quantum dissipation.<sup>37</sup>

For the displaced harmonic oscillator model, the ground DPES can be written as  $\mathcal{H}_g = \sum_{\mu} H_{\mu} = \sum_{\mu} \left( \frac{p_{\mu}^2}{2m_{\mu}} + \frac{m_{\mu}\omega_{\mu}^2}{2} x_{\mu}^2 \right)$ . In turn, the excited DPES consists of the same set of vibrational modes but with displaced equilibrium configuration  $\mathcal{H}_e = \hbar\omega_{eg} + \sum_{\mu} \left( \frac{p_{\mu}^2}{2m_{\mu}} + \frac{1}{2} m_{\mu}\omega_{\mu}^2 (x_{\mu} + d_{\mu})^2 \right)$ . Here  $p_{\mu}$  and  $x_{\mu}$  are, respectively, the momentum and position coordinates of the  $\mu$ th vibrational mode with frequency  $\omega_{\mu}$  and effective mass  $m_{\mu}$ ,  $d_{\mu}$  is the position shift for the  $\mu$ th mode between two surfaces. We consider diabatic couplings of the form  $V_{eg} = \sum_{\mu} g_{\mu} x_{\mu} + \gamma$ , which covers the cases with constant coupling ( $g_{\mu} = 0$ ) and linear coupling ( $\gamma = 0$ ). The constant coupling is usually used in the study of electron transfer,<sup>33</sup> while the linear coupling is often used to model conical intersections<sup>38</sup> and the electron–phonon interaction in solid-state systems (e.g., the Holstein model<sup>39</sup>).

To obtain the decoherence time, the energy gap fluctuation, fluctuation of diabatic couplings, and their interference are required. The energy gap operator for this model is  $\mathcal{E}_{eg} = \hbar\omega_{eg} + \sum_{\mu} \left( \frac{1}{2} m_{\mu}\omega_{\mu}^2 d_{\mu}^2 + m_{\mu}\omega_{\mu}^2 d_{\mu} x_{\mu} \right)$ . We assume that the vibrational modes are initially in thermal equilibrium with inverse temperature  $\beta = 1/(k_B T)$  at the ground DPES, i.e.,  $\rho_N = e^{-\beta\mathcal{H}_g}/Z$ , where  $Z = \text{Tr}_N[e^{-\beta\mathcal{H}_g}]$  is the partition function and the trace is over nuclear coordinates. Taking into account that<sup>40</sup>

$$\langle x_{\mu} | e^{-\beta\mathcal{H}_{\mu}} | x_{\mu} \rangle = \left( \frac{m_{\mu}\omega_{\mu}}{2\pi\hbar \sinh(\beta\hbar\omega_{\mu})} \right)^{1/2} \times \exp\left( -\frac{m_{\mu}\omega_{\mu}^2 x_{\mu}^2}{\hbar \sinh(\beta\hbar\omega_{\mu})} (\cosh(\beta\hbar\omega_{\mu}) - 1) \right) \quad (18)$$

the energy gap fluctuations can be calculated to yield

$$\begin{aligned} \langle \delta^2 \mathcal{E}_{eg} \rangle &= \sum_{\mu} m_{\mu}^2 \omega_{\mu}^4 d_{\mu}^2 \langle x_{\mu}^2 \rangle \\ &= \sum_{\mu} \frac{\hbar m_{\mu} d_{\mu}^2 \omega_{\mu}^3}{2} \coth(\beta\hbar\omega_{\mu}/2) \end{aligned} \quad (19)$$

The fluctuations of  $V_{eg}$  can also be evaluated using eq 18 as

$$\langle \delta^2 V_{eg} \rangle = \sum_{\mu} |g_{\mu}|^2 \langle x_{\mu}^2 \rangle = \sum_{\mu} \frac{\hbar |g_{\mu}|^2}{2m_{\mu}\omega_{\mu}} \coth(\beta\hbar\omega_{\mu}/2) \quad (20)$$

Similarly, the interference between pure dephasing and diabatic transitions is given by

$$\langle \delta V_{eg} \delta \mathcal{E}_{eg} \rangle = \sum_{\mu} \frac{\hbar \omega_{\mu} d_{\mu} g_{\mu}}{2} \coth(\beta\hbar\omega_{\mu}/2) \quad (21)$$

Inserting eqs 19–21 into eq 14 gives the final decoherence time

$$\begin{aligned} \tau_d &= \hbar \left( \sum_{\mu} (|c_g|^2 |c_e|^2 m_{\mu} d_{\mu}^2 \omega_{\mu}^3 \right. \\ &\quad + 2(|c_g|^2 - |c_e|^2) |c_g| |c_e| \omega_{\mu} d_{\mu} g_{\mu} \cos \theta \\ &\quad + (1 - 4|c_g|^2 |c_e|^2 \cos^2 \theta) m_{\mu}^{-1} \omega_{\mu}^{-1} |g_{\mu}|^2 \\ &\quad \left. \times \coth(\beta\hbar\omega_{\mu}/2) \right)^{-1/2} \end{aligned} \quad (22)$$

Equation 22 is the generalized decoherence time for the displaced harmonic oscillator model with diabatic coupling  $V_{eg} = \sum_{\mu} g_{\mu} x_{\mu} + \gamma$ . The physical meaning of each contribution is clear from their dependence of  $g_{\mu}$  and  $d_{\mu}$  as  $g_{\mu}$  enters  $V_{eg}$  while  $d_{\mu}$  determines the energy gap. Importantly, note that all separate contributions have the same temperature dependence, which implies that the relative contribution of the interference between pure dephasing and diabatic transitions does not vanish at high temperature. This observation may provide temperature-robust control of the electronic decoherence through the relative phase  $\theta$ . If  $\theta = \theta_g - \theta_e = 0$ , eq 22 reduces to a simplified form

$$\tau_d = \hbar \left( \sum_{\mu} \frac{(|c_g| |c_e| m_{\mu} d_{\mu} \omega_{\mu}^2 + (|c_g|^2 - |c_e|^2) g_{\mu}^2)}{m_{\mu} \omega_{\mu}} \coth(\beta\hbar\omega_{\mu}/2) \right)^{-1/2} \quad (23)$$

Interestingly, in this case, the diabatic couplings simply renormalize the pure dephasing effects. Because the constant diabatic coupling does not enter the final decoherence time, eqs 22 and 23 are also the decoherence time for the case in which the diabatic coupling  $V_{eg}$  is linear (i.e.,  $\gamma = 0$ ).

Consider now the special case in which the diabatic coupling  $V_{eg}$  is a constant ( $g_{\mu} = 0$ ). In this case, the fluctuations of diabatic couplings vanish  $\langle \delta^2 V_{eg} \rangle = 0$  and the diabatic transitions do not contribute to the decoherence because  $V_{eg}$  is a purely electronic operator that does not introduce additional electron–nuclear entanglement in the short-time expansion. (Note that while the constant diabatic coupling does not directly introduce electron–nuclear entanglement, there are cases in which it affects decoherence dynamics indirectly by changing the electron dynamics; see model 1 in ref 12.) Further, the interference between pure dephasing and

electronic transitions also vanishes. Therefore, the decoherence time is equivalent to the pure dephasing dynamics even when the dynamics itself can have transitions between  $|g\rangle$  and  $|e\rangle$ , i.e.

$$\tau_d = \hbar \left( \sum_{\mu} |c_g|^2 |c_e|^2 m_{\mu} d_{\mu}^2 \omega_{\mu}^3 \coth(\beta \hbar \omega_{\mu} / 2) \right)^{-1/2} \quad (24)$$

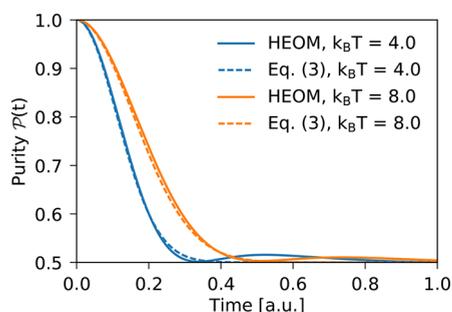
In this limit, we can relate the decoherence time to the reorganization energy at high temperatures. For high temperatures  $\beta \hbar \omega_{\mu} \ll 1$ ,  $\coth(\beta \hbar \omega_{\mu} / 2) \approx \frac{2}{\beta \hbar \omega_{\mu}}$ , the decoherence time reduces to

$$\tau_d = \hbar |c_g|^{-1} |c_e|^{-1} / \sqrt{2\lambda k_B T} \quad (25)$$

where  $\lambda = \sum_{\mu} \frac{1}{2} m_{\mu} d_{\mu}^2 \omega_{\mu}^2$  is the reorganization energy (half of the Stokes shift). Because the reorganization energy can be measured via spectroscopic experiments, eq 25 offers a convenient estimate of the decoherence time.

To demonstrate the validity of the theory and the short-time expansion, we performed numerically exact simulations using the hierarchical equations of motion (HEOM) method. We focus on the case of constant diabatic coupling to a high-temperature Ohmic bath with the Lorentz–Drude cutoff as this is a regime where the HEOM has convenient convergence properties.

Figure 1 shows the exact simulations of the displaced harmonic oscillator model with constant diabatic coupling, in



**Figure 1.** Comparison between eq 3 and exact numerical simulations using the HEOM method for the displaced harmonic oscillator model at different temperatures. The exact quantum dynamics exhibits a Gaussian purity decay in quantitative agreement with eq 3.

comparison with the predictions by eq 3 with  $\tau_d$  given by eq 25. In the model, the effects of the environment are completely characterized by the spectral density  $J(\omega) \equiv \frac{\pi}{2} \sum_{\mu} m_{\mu} d_{\mu}^2 \omega_{\mu}^3 \delta(\omega - \omega_{\mu})$ . Here we use the Ohmic environment with the Lorentz–Drude cutoff  $J(\omega) = 2\lambda \frac{\omega \omega_c}{\omega^2 + \omega_c^2}$ , where  $\omega_c$  is the cutoff frequency of the environment. The parameters are chosen as (in atomic units)  $\lambda = 0.2$ ,  $\omega_c = 2$ ,  $c_g = 1/\sqrt{2}$ ,  $V_{eg} = 0.1$ . The prediction by the present theory is in excellent agreement with the exact numerical simulations. Note that the decoherence dynamics for the chosen model does not exhibit an exponential decay even at high temperatures and is dominated by the early time Gaussian behavior. This validates our choice of short-time analysis for electronic decoherence. In addition to the Gaussian decay, we also observe a slight recurrence of purity in the exact results that cannot be captured by this theory of decoherence.

To understand the range of validity of the theory, we performed additional simulations that explore the effects of changing the cutoff frequency  $\omega_c$  while keeping  $\beta \omega_c$  constant (Figure S1) and changing the electron–nuclear coupling as determined by the reorganization energy (Figure S2). As  $\omega_c$  is increased, the accuracy of the Gaussian interpolation deteriorates because the environment becomes closer to a Markovian environment and the validity range of the short-time expansion becomes smaller. In turn, the Gaussian interpolation offers quantitative agreement with the exact decoherence dynamics for a wide range of system–bath couplings.

In conclusion, we have developed a generalized theory for electronic decoherence in large molecules and condensed phase environments. The final expressions, eqs 14 and 17, recover previously proposed pure dephasing decoherence mechanisms and reveal that electronic transitions among DPES introduce additional important channels for the decoherence. Furthermore, these two effects interfere even in the short-time expression. The theory also indicates that the presence of initially unpopulated diabatic states accelerates the electronic decoherence due to possible transitions into these states. Using this theory, we derived a general decoherence time for the displaced harmonic oscillator model with constant and linear diabatic coupling, which can be used to quantify electronic decoherence during photoexcited dynamics of molecules. Moreover, the validity of the short-time analysis for electronic decoherence was tested by performing exact numerical simulations for the constant coupling model, which show excellent agreement with theory.

These developments can be used to determine molecular factors that lead to electronic coherence loss and to test approximate quantum dynamics schemes for vibronic dynamics. Further, the advances in this Letter illustrate a general strategy of how the universal formula for decoherence times in ref 10 can be applied to develop decoherence times for molecular processes. Future prospects include a quantitative analysis of the importance of the diabatic transitions to electronic decoherence in realistic molecular models and developing decoherence times for additional molecular processes in the condensed phase.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.7b03322.

Figures illustrating the effects of changing  $\omega_c$  and  $\lambda$  on the validity of eq 3 (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: ignacio.franco@rochester.edu.

### ORCID

Bing Gu: 0000-0002-5787-3334

Ignacio Franco: 0000-0002-0802-8185

### Notes

The authors declare no competing financial interest.

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## NOTE ADDED AFTER ASAP PUBLICATION

This paper was published ASAP on February 2, 2018. Equation 22 was updated. The revised paper was reposted on February 5, 2018.