Quantum equations for vibrational dynamics on metal surfaces.

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A first-principles treatment of the vibrational dynamics of molecular chemisorbates on metal surfaces is presented. It is shown that the mean field quantum evolution of the vibrational position operator is determined by a quantum Langevin equation with an electronic friction. In the mean field limit, the quantum noise and friction are related by the quantum fluctuation-dissipation theorem. The classical limit of this model is shown to agree with previously proposed models. A criterion is presented to describe the validity of the weak-coupling approximation and equations of motion for the dynamics in the presence of strong nonadiabatic coupling to electron-hole pairs are presented.

I. INTRODUCTION

Understanding the nonadiabatic dynamics of molecules has been an important and active area of research for several decades. Several methods have been developed to study nonadiabatic molecular dynamics. Among them, mixed quantum-classical methods have had considerable success in studying nonadiabatic effects in molecular systems. However, fully quantum treatments of nonadiabatic molecular dynamics are few and limited in their applicability. A special class of systems, where the nonadiabatic coupling between electron and molecular degrees of freedom is important, involve the dynamics of molecules chemisorbed on metal surfaces. The motion of molecules in an electron-hole pair bath correspond to a limiting case of nonadiabatic dynamics. Molecular degrees of freedom in these situations are coupled to an infinite reservoir of electronic excitation modes. In contrast, gas phase molecular processes involve nonadiabatic coupling between finite numbers of Born-Oppenheimer potential energy surfaces. Due to the continuum nature of the electron spectrum near a metal surface, the nonadiabatic coupling of molecular vibrational modes to electronic excitations results in the dissipation of vibrational excitations.

The dynamics of a chemisorbed molecule on a metal surface is influenced by many different processes. At low temperatures, a dominant mechanism for energy transfer between the molecule and the surface is the dissipative dynamics induced by electron-hole pair excitations. The nonadiabatic coupling between vibrational and electron-hole pair excitations determines the relaxation rate of vibrational excitations on the surface. Furthermore, this nonadiabatic coupling also influences the dynamical evolution of the vibrational mode on the surface. As a result, electron-hole pair excitations play an important role in chemical processes that take place on the surface.

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Though there has been considerable theoretical and experimental work devoted to understanding the role of electron-hole pair excitations in vibrational relaxation processes on metal surfaces\(^1\)\(^-\)\(^19\), there is no first principles theoretical framework which can be used to systematically analyse the role of electron-hole pair excitations on molecular dynamics. This is true even for the case where electron-hole pair effects on the dynamics enter in a mean field fashion. Previously, attempts have been made to guess the formal descriptions of the vibrational dynamics of the molecular system in the presence of electron-hole pair excitations\(^20\)\(^-\)\(^26\). Intuitively, because of the continuum nature of the electronic spectrum at metal surfaces, the effect of electron-hole pair coupling to vibrational dynamics can be thought to be equivalent to an electronic friction acting on the vibrational modes. Previous attempts to study the reduced classical dynamics of the vibrational modes have used these intuitive ideas to construct Langevin type descriptions of the classical vibrational dynamics. A more rigorous approach has been attempted\(^28\) through the application of the Ehrenfest method of mixed-quantum classical dynamics. In this approach, effective Langevin type equations for the vibrational dynamics of the chemisorbed molecule were derived. However, such mixed quantum-classical descriptions are limited to treating the dynamics with the surface at zero temperature. Consequently, a fluctuation-dissipation relation needs to be imposed on the reduced dynamics of the system. Furthermore, because of the somewhat ad-hoc nature of these formulations, there is no quantitative criterion to determine the range of nonadiabatic electron-hole pair coupling strengths excitations for which such descriptions are valid. As a result, it is desirable to formulate a first principles quantum mechanical formulation of the reduced dynamics of molecular chemisorbates on a metal surface.

This work develops, for the first time, a formal and fully quantum description of the nonadiabatic dynamics of molecular modes in the presence of coupling to electron-hole pair excitations. It is shown that as long as the number of possible electronic excitations around the surface are unlimited, and it is possible to retain a mean field separation between vibrational and electronic excitations, the quantum dynamics of the molecule is governed by a generalized Langevin equation with a quantum noise spectrum. The friction and noise correlation functions are shown to be related to each other by the generalized Callen-Welton fluctuation-dissipation theorem for quantum systems\(^29\),\(^30\). Finally, it is shown that this description of the system dynamics reduces to the mixed-quantum classical Langevin equation derived\(^28\) by Head-Gordon and Tully in the limit that the energy of electron-hole pair excitations are small compared to the temperature of the surface. This paper also provides a quantitative criterion to describe the range of validity of the mean field approximation. When the mean field approximation is no longer valid, the resulting nonlinear equations of motion describe molecular dynamics in an effective electromagnetic field induced by electron-hole pair excitations.

The paper is outlined as follows. In Sec II. the general Hamiltonian of the system is written down in a Born-Oppenheimer basis of wavefunctions, and a transformation is introduced which converts the electron-hole pairs into a collection of bosonic excitations. The Heisenberg equations of motion are then written down and the electron-hole pair excitations integrated out. In Sec.III, a
quantum generalized Langevin equation is derived and the fluctuation-dissipation relations derived. The mixed quantum classical limit is then discussed. Finally, an approximate criterion is presented to estimate the validity of the mean field approximation for a vibrationally excited molecule adsorbed on the surface. Further generalizations of the equations of motion in the regime of strong adiabaticity are then presented. The paper ends with a discussion of the results and future work.

II. THEORY

A. The Hamiltonian

The Hamiltonian for a molecular vibration on a metal surface can be written as

\[ H = \frac{P^2}{2M} + U(R) + H_e(r) + V(r, \vec{R}) \]  \hspace{1cm} (1)

The first two terms on the right hand side correspond to the Hamiltonian for the vibrational modes given by the operator \( R \). \( H_e(r) \) is the electronic Hamiltonian and \( V(r, \vec{R}) \) the coupling between the vibrational and electronic modes. If non-adiabatic effects are weak enough to retain some of the separation in timescales between the vibrational and electronic excitations, they can be treated as perturbations to the adiabatic motion of the nuclear modes. In such a situation a Born-Oppenheimer basis of electron wavefunctions can be defined by

\[ [H_e + V(r, \vec{R})] | \phi_k \rangle = \epsilon_k(\vec{R}) | \phi_k \rangle \]  \hspace{1cm} (2)

The basis of wavefunctions \( \phi_k \) depends adiabatically on the vibrational coordinates \( R \). The vibrational momentum operator is off-diagonal in this basis of wave functions. This off-diagonal coupling is responsible for non-adiabatic corrections to the Born-Oppenheimer solution of the system. In this basis, the total Hamiltonian can be rewritten as

\[ H = \frac{P^2}{2M} + U(R) + \sum_k \epsilon_k(R) | \phi_k \rangle \langle \phi_k | + \sum_{k,l} | \phi_k \rangle \langle \phi_k | \frac{P^2}{2M} | \phi_l \rangle \langle \phi_l | \]  \hspace{1cm} (3)

The off-diagonal coupling of the vibrational kinetic energy can be simplified as

\[ \langle \phi_k | \frac{P^2}{2M} | \phi_l \rangle = -\frac{i\hbar}{M} \langle \phi_k | \nabla_R | \phi_l \rangle \cdot \vec{P} - \frac{\hbar^2}{2M} \langle \phi_k | \nabla_R^2 | \phi_l \rangle \]  \hspace{1cm} (4)

The term which consists of the second derivative of the basis states is neglected and the non-adiabatic coupling simplifies to a term linear in the vibrational momentum. With this approximation the Hamiltonian of the system becomes

\[ H = \frac{P^2}{2M} + U(R) + \sum_l \epsilon_l(R) | \phi_l \rangle \langle \phi_l | + \sum_{k,l} | \phi_k \rangle \tilde{V}_{kl}(R) | \phi_l \rangle \cdot \vec{P} \]  \hspace{1cm} (5)

The off-diagonal coupling \( \tilde{V}_{kl} \) is a matrix whose diagonal elements are zero. It is defined as

\[ \tilde{V}_{kl}(R) = -i\hbar \langle \phi_k | \nabla_R \phi_l \rangle \]  \hspace{1cm} (6)
It is also convenient to define

\[ \bar{D}_{kl}(R) = \langle \phi_k | \nabla_R \phi_l \rangle \]  

(7)

The off-diagonal coupling is a vector operator which couples to the momentum operator. It is equivalent to that of a vector potential acting on the system. Thus, the nonadiabatic effects of the electronic modes appear as magnetic potentials acting on the molecular degrees of freedom.

The rest of the derivation can be sketched out as follows. The Hamiltonian is rewritten in terms of electron-hole pair creation and annihilation operators. The Heisenberg equations of motion are then derived for the vibrational coordinate and the electron-hole pair operators. They are then solved self-consistently for the electron-hole pair operators, and the electronic degrees of freedom are eliminated in a procedure reminiscent of the methods used in Ref. (33), to describe the vibrational dynamics. The equations of motion so obtained are shown to correspond to a generalized quantum Langevin equation\(^{33,34}\).

**B. The Boson Approximation**

The Hamiltonian in Eq.(3) can be rewritten in a second quantized form by introducing creation and annihilation operators to describe electronic states. For a molecule adsorbed on a metal surface, only electronic excitations corresponding to excitations from filled orbitals below the Fermi shell to unoccupied orbitals above the Fermi shell contributes. This implies that only terms with \(k > k_f > l\) contribute to the summation over off-diagonal terms. Thus the effective Hamiltonian for molecular vibrations coupled to electron-hole pair excitations is

\[ H = \frac{\vec{p}^2}{2M} + U(R) + \sum_k \epsilon_k(R) c_k^{\dagger} c_k + \sum_{k > k_f > l} [\bar{V}_{kl}(R) c_k^{\dagger} c_l + \bar{V}_{lk}(R) c_l^{\dagger} c_k] \cdot \frac{\vec{p}}{M} \]  

(8)

For a metallic system, the number of electron-hole pair excitations is much smaller than the number of bulk electrons in the ground state. This is because electron-hole pair excitations depend on the number of electrons close to the fermi surface, which is of an order \(O(1/N)\) in comparison to the total number of electrons \(N\) enclosed by the fermi surface. Consequently, one can ignore the contributions from processes which do not correspond to simple electron-hole pair excitations. Since the energy spectrum of the metal surface near the fermi level is continuous, the number of possible electron-hole pair excitations is for all practical purposes, unlimited. Consequently, fermion pair operators of the form \(c_k^{\dagger} c_l\) with \(k > l\) can be regarded as having an approximately bosonic character\(^{31,32}\). In other words, the pair operators are replaced by

\[ c_k^{\dagger} c_l = \rho_{kl} \]  

(9)

Since the index \(k\) is always greater than the index \(l\), the pair operators obey the commutation relations,

\[ [c_l^{\dagger} c_k, c_n^{\dagger} c_m] = 0 \]  

(10)
Here \( c_n^\dagger c_m \) is another electron-hole pair annihilation operator with \( n < m \). Also, the pair operators approximately satisfy

\[
[c_n^\dagger c_k, c_m^\dagger c_n] = \delta_{kn}\delta_{km} \tag{11}
\]

In terms of the operators \( \rho_{mn} \) the approximate commutation relations become

\[
[\rho_{kl}, \rho_{mn}^\dagger] = \delta_{mk}\delta_{nl} \tag{12}
\]

and

\[
[\rho_{kl}, \rho_{mn}] = 0 \tag{13}
\]

Thus, electron-hole pairs created near the Fermi energy can be expected to behave approximately as Bosons. By approximating the Fermionic pair operators as Bosonic creation and annihilation operators, the Hamiltonian for the vibrational motion coupled to electron-hole pair excitations can be written as

\[
H = H_0(R) + \sum_{k > k_f > l} [\vec{V}_{kl}\rho_{kl}^\dagger + \vec{V}_{lk}\rho_{kl}] \cdot \vec{P} + \sum_k \epsilon_k(R) c_k^\dagger c_k. \tag{14}
\]

The operators \( \rho \) are Bosonic operators which create or destroy electron-hole pair excitations.

### C. Equations of Motion

The time dependent Heisenberg operators now satisfy the equations

\[
\dot{R}(t) = \frac{i}{\hbar}[H, \vec{R}]
\]

\[
\dot{\vec{P}}(t) = \frac{i}{\hbar}[H, \vec{P}]
\]

\[
\dot{\rho}_{kl}(t) = \frac{i}{\hbar}[H, \rho_{kl}(t)]
\]

These equations can be explicitly written out to give

\[
M \dot{\vec{R}}(t) = \vec{P}(t) + \sum_{k > k_f > l} [\vec{V}_{kl}\rho_{kl}^\dagger + \vec{V}_{lk}\rho_{kl}] \]

\[
\dot{\vec{P}}(t) = -\nabla_R U - \sum_k \nabla_R \epsilon_k c_k^\dagger c_k - \sum_{k > k_f > l} [\nabla_R \vec{V}_{kl}\rho_{kl}^\dagger + h.c.] \cdot \frac{\vec{P}(t)}{M} \tag{16}
\]

and

\[
\dot{\rho}_{mn}(t) = -i\omega_{mn}\rho_{mn}(t) - \frac{i}{\hbar}\vec{V}_{mn}(t) \cdot \frac{\vec{P}(t)}{M}
\]

\[
\dot{\rho}_{mn}^\dagger(t) = i\omega_{mn}\rho_{mn}^\dagger(t) + \frac{i}{\hbar}\vec{V}_{mn}^\dagger(t) \cdot \frac{\vec{P}(t)}{M} \tag{17}
\]
The energy of the electron excitation from state \( n \) below the Fermi surface to state \( m \) above it, has an excitation energy given by

\[
h\omega_{mn}(R) = \epsilon_m(R) - \epsilon_n(R) \tag{18}\]

Eq.(16) for the position operator \( R(t) \) is differentiated to give

\[
M \ddot{R}(t) = \dot{\tilde{P}} + \sum_{m>n} [\tilde{V}_{mn}\rho_{mm}^\dagger + \dot{\tilde{V}}_{nm}\rho_{mn}] + \sum_{m>n} [\dot{\tilde{V}}_{mm}\rho_{mn}^\dagger + h.c] \tag{19}\]

This can be further simplified by replacing the time derivatives on the right hand side by the appropriate commutators with the Hamiltonian. The time derivative of the non-adiabatic coupling is given by

\[
\dot{\tilde{V}}_{mn}(R) = \frac{i}{\hbar}[H, \tilde{V}_{mn}] \tag{20}\]

or

\[
\dot{\tilde{V}}_{mn}(R) = \nabla_R \tilde{V}_{mn}(R) \cdot \frac{\tilde{P}(t)}{M} - \frac{i\hbar}{2M} \frac{\nabla_R^2 \tilde{V}_{mn}}{\Delta_R} + \sum_{k$l} \{ \tilde{V}_{kl}\rho_{mn}^\dagger + h.c \} \cdot \nabla_R \tilde{V}_{mn} \tag{21}\]

The time derivative of \( \tilde{V}_{mn} \) is further approximated by ignoring second derivatives of \( \tilde{V}_{mn} \) on the right hand side of Eq.(21) as well as the terms of the form \( \tilde{V}_{kl} \cdot \nabla_R \tilde{V}_{mn} \). This amounts to approximating \( \dot{\tilde{V}}_{mn} \) as

\[
\dot{\tilde{V}}_{mn}(R) \approx \nabla_R \tilde{V}_{mn}(R) \cdot \frac{\tilde{P}}{M} \tag{22}\]

The approximation, Eq.(22) can be substituted into Eq.(19) for the second derivative of \( R(t) \). Within this approximation, the sum of contributions from the time derivative of the non-adiabatic coupling and the corresponding contribution from the derivative of the momentum give rise to a magnetic force term. Thus, the following equation is obtained:

\[
M \ddot{R}(t) = -\nabla_R \tilde{W}(R) - \sum_m \nabla_R \epsilon_m(R)\epsilon_m^\dagger c_m + \sum_{m>n} \{ \dot{\tilde{V}}_{mm}\rho_{mn}^\dagger + h.c \} - \frac{\tilde{P}}{2M} \times \tilde{B} + \tilde{B} \times \frac{\tilde{P}}{2M} \tag{23}\]

Here, an effective magnetic field operator has been introduced. It is defined as

\[
\tilde{B} = \nabla_R \times \sum_{m>k>n} \{ \tilde{V}_{mn}(R)\rho_{mn}^\dagger + h.c \} \tag{24}\]

In the limit where the vibrational coordinate is slowly varying, the derivative of the nonadiabatic coupling can also be assumed to be small compared to the coupling strength, and hence ignored. If this approximation is made, Eq.(23) can be simplified further by substituting Eq.(17) for the derivative of the operators \( \rho \), and ignoring the magnetic field terms. The substitution gives

\[
M \ddot{R} = -\nabla_R \tilde{W}(R) + \sum_{k>l} i\omega_{mn} \{ \tilde{V}_{mn}(t)\rho_{mm}^\dagger(t) - \tilde{V}_{nm}(t)\rho_{mn}(t) \} \tag{25}\]
The Born-Oppenheimer potential operator $\tilde{W}$ in Eq.(25) is defined as
\[
\tilde{W}(R) = U(R) + \sum_k \epsilon_k(R)c_k^\dagger c_k
\] (26)

Eq.(25) corresponds to a mean-field description of the vibrational dynamics of the molecule. The description is a mean-field approximation in the sense that the excitations of electron-hole pairs are assumed to be on a timescale during which the nonadiabatic vibrational coupling is nearly constant. This can occur if the vibrational motion has a low amplitude and the nonadiabatic coupling is otherwise well behaved. The validity of this approximation, and the dynamics in situations where this approximation no longer works will be discussed in further detail in a later section.

The quantum acceleration in Eq.(25) is the sum of two terms. The first term is the gradient of the Born-Oppenheimer potential, and the second term corresponds to off-diagonal hopping terms between Born-Oppenheimer potential energy surfaces. The hopping occurs due to the creation or destruction of electron-hole pair excitations. If the time dependence of the electron-hole pair creation-annihilation operators is explicitly taken into account, a quantum generalized Langevin equation (GLE) which describes the reduced dynamics of the vibrational position operator, can be derived. To do this, Eq.(17) which describes the time dependence of the operators $\rho$ will require to be solved. This is solved and a quantum GLE derived below.

In what follows, the time dependence of the Born-Oppenheimer excitation energy $\epsilon_{mn}(R)$ is neglected. This is mainly for the sake of convenience and this approximation is not crucial to the treatment of the problem. The solution to Eq.(17) can be written as
\[
\rho_{mn}^\dagger(t) = \rho_{mn}^\dagger(0)e^{i\omega_{mn}t} + \frac{1}{M} \int_0^t d\tau e^{i\omega_{mn}\tau} D_{mn}(\tau) \cdot \vec{P}(\tau)
\] (27)

This is substituted into Eq.(25) for the acceleration $\ddot{R}(t)$ to give
\[
M\ddot{R}(t) = -\nabla_R \tilde{W} - \int_0^t d\tau \Gamma(t, \tau) \cdot \vec{P}(\tau) + \vec{\xi}(t)
\] (28)

The "friction" tensor $\Gamma$ is given by
\[
\Gamma^{\mu\nu}(t, \tau) = \sum_{m>n} \hbar \omega_{mn} \{ D_{mn}^\mu(t) D_{nm}^\nu(\tau)e^{i\omega_{mn}(t-\tau)} + c.c \}
\] (29)

The indices $\mu, \nu$ label the components along the various axes of the coordinate system. The "noise" term $\xi(t)$ is given by
\[
\vec{\xi}(t) = \sum_{mn} \hbar \omega_{mn} \{ \vec{D}_{mn}(t) \rho_{mn}^\dagger(0)e^{i\omega_{mn}t} - \vec{D}_{nm}\rho_{mn}(0)e^{-i\omega_{mn}t} \}
\] (30)

The "noise" operator $\vec{\xi}(t)$ is a purely off-diagonal operator. Hence, its average value is zero, i.e.,
\[
\langle \vec{\xi}(t) \rangle = 0
\] (31)

The position operator of the vibrational mode satisfies a generalized Langevin equation. Under certain conditions, this generalized Langevin equation reduces to an equation for quantum Brownian motion in the presence of a frictional bath. The analysis of this equation is taken up in the next section.
III. ANALYSIS

The generalized Langevin equation derived above is an equation relating different quantum operators. The effects of the bath influence the system dynamics through the quantum noise operator $\vec{\xi}(t)$. In addition, surface electron-hole pair excitations act as a frictional drag on the system. Thus, a natural question to ask is whether the fluctuation-dissipation theorem is valid for this problem if the electron-hole pair excitations are at a thermal equilibrium.

The relationship between the noise and friction operators can be clarified as below. Consider the commutator of the noise operator at different times.

$$[\vec{\xi}(t), \vec{\xi}(\tau)] = \sum_{m>n} \omega_{mn}^2 \{ \vec{V}_{mn}(t) \vec{V}_{nm}(\tau) e^{i\omega_{mn}(t-\tau)} - \vec{V}_{nm}(t) \vec{V}_{mn}(\tau) e^{-i\omega_{mn}(t-\tau)} \}$$

(32)

From the definitions, Eq.(29) and Eq.(30) of the noise and friction operators, it is easy to see that Eq.(32) implies

$$[\vec{\xi}(t), \vec{\xi}(\tau)] = i\hbar \frac{d}{dt} \Gamma(t, \tau) + O(W\dot{W})$$

(33)

If, as before, terms of the form $W_{mn}\dot{W}_{mn}$ are neglected, the friction and noise are related as

$$[\vec{\xi}(t), \vec{\xi}(\tau)] \approx i\hbar \frac{d}{dt} \Gamma(t, \tau)$$

(34)

This relation ensures that the operators $R(t)$ and their conjugate momenta satisfy the Heisenberg commutation relations. To integrate over the bath degrees of freedom, the assumption made is that the initial density matrix of the system is a direct product of the bath density matrix and the system density matrix. This means that

$$\sigma_0 \approx \sigma_s \otimes \sigma_e$$

(35)

This assumption amounts to stating that the system and bath are decoupled at some (initial) time in the past, and consequently the density matrix of the combined system and bath is factorizable. For this problem however, the vibrational and electronic degrees of freedom are never completely decoupled. An analogous assumption would be that the vibrational and electronic degrees of freedom are adiabatically separable through the Born-Oppenheimer approximation at some time in the past. This assumption is consistent with the approximations made earlier in this work.

Such an assumption means that the initial electron density matrix $\sigma_e$ is a function of the vibrational coordinates $R$ as below:

$$\sigma_e = \frac{\exp \left( -\beta H(\mathbf{r}, R) \right)}{\text{Tr}_r[\exp \left( -\beta H(\mathbf{r}, R) \right)]}$$

(36)

In terms of an set of Born-Oppenheimer electronic states, the electron density matrix is

$$\sigma_e = \frac{1}{Z(R)} \sum_k | \phi_k \rangle e^{-\beta \epsilon_k(R)} \langle \phi_k |$$

(37)

Thus, averages over the electronic degrees of freedom can be defined as traces over the electron density matrix $\sigma_e$. With this definition, the average of the noise operator over the electron degrees of freedom is given by

$$\langle \vec{\xi}(t) \rangle = Z^{-1}(R) \text{Tr}_e \{ \sigma_e(R) \vec{\xi}(t) \} = 0$$

(38)
Furthermore, the adiabatic part of the electron Hamiltonian can be rewritten as

$$\sum_m \epsilon_m(R)c_m^\dagger c_m = \sum_{m>n} \epsilon_{mn}(R)\rho_{mn}^\dagger \rho_{mn} + \Delta \quad (39)$$

In addition to the constraint $m > n$, the index $m, n$ are such that the corresponding energies are further constrained to be above and below the Fermi energy $\epsilon_f$, i.e. $\epsilon_m > \epsilon_f$ and $\epsilon_n < \epsilon_f$. The first term on the right hand side contains contributions from electronic excitations around the Fermi surface, and the second term $\Delta$ consists of the bulk contribution to the energy from below the Fermi surface. Since the excitations are of order $1/N$ compared to the total bulk electrons, $N$, below the Fermi surface, $\Delta$ can be assumed to be roughly constant. With this assumption, the equilibrium distribution of electron-hole pair excitations is given by

$$\langle \rho_{mn}^\dagger \rho_{kl} \rangle = \frac{\delta_{mk} \delta_{nl}}{e^{\beta \epsilon_{mn}} - 1} \quad (40)$$

With this in hand, the average of the anticommutator of the noise operator can be written as

$$\langle \{ \tilde{\xi}(t), \tilde{\xi}(\tau) \} \rangle = 2 \sum_{m>n} \hbar \omega_{mn}^2 \{ \tilde{D}_{mn}(t)\tilde{D}_{nm}(\tau) e^{i\omega_{mn}(t-\tau)} + c.c \} (N(\omega_{mn}) + \frac{1}{2}) \quad (41)$$

Products of the type $\tilde{D}\tilde{D}$ are to be understood as tensor products of the vectors $D$, i.e the product is a matrix such that its elements are given by, $(\tilde{D}_{mn}\tilde{D}_{nm})_{\mu\nu} = D_{mn}^\mu D_{mn}^\nu$. The matrix elements $D_{mn}$ are given by the overlap of delocalized electronic wavefunctions with their derivatives. The function $N(\omega)$ is the thermal distribution function of the electron-hole pair excitations. Within the approximation that they have a Bosonic character, it is given by

$$N(\omega) = [\exp \left( \frac{\hbar \omega}{k_B T} \right) - 1]^{-1} \quad (42)$$

### A. Fluctuation-Dissipation Theorem

For the sake of simplicity it is assumed that the product of the off-diagonal matrix elements $\tilde{V}_{mn}(t)\tilde{V}_{nm}(\tau)$ is real in the discussion that follows. With this assumption, the electronic friction operator has the form

$$\Gamma(t, 0) = \sum_{m>n} \hbar \omega_{mn} \tilde{D}_{mn}(t)\tilde{D}_{nm}(0) \cos[\omega_{mn}t] \quad (43)$$

The mean-field approximation of the previous section is made that the timescale which governs the rate of change of the nonadiabatic coupling matrix elements $D_{mn}(t)$ is considerably larger than the timescales governing the creation and annihilation of electron-hole pairs. This assumption amounts to asserting that the motion of the molecular degrees of freedom is slow enough to allow for the establishment of a local equilibrium distribution for the electron-hole pair excitations. Under this assumption, the Laplace transform of the friction operator becomes

$$\gamma(s) = \sum_{m>n} \int_0^\infty dt \omega_{mn} \tilde{V}_{mn}(t)\tilde{V}_{nm}(0) \cos(\omega_{mn}t)e^{-st} \quad (44)$$
If it is assumed that the off-diagonal matrix elements $W_{mn}(t)$ are slowly varying in comparison to the function $\cos(\omega_{mn}t)$, then the laplace transform becomes

$$
\gamma(s) = \sum_{m>n} \hbar \omega_{mn} \bar{D}_{mn} \bar{D}_{nm} \left[ \frac{1}{s - i\omega_{mn}} + \frac{1}{s + i\omega_{mn}} \right] \tag{45}
$$

This quantity then satisfies the relation

$$
\frac{1}{2} \langle \{\xi(t), \xi(0)\} \rangle = \frac{1}{\pi} \int_0^\infty d\omega \Re[\gamma(-i\omega + 0^+)]\hbar \omega \coth \left( \frac{\hbar \omega}{2k_B T} \right) \cos(\omega t) \tag{46}
$$

The above relationship is a generalized form of the Callen-Welton fluctuation-dissipation theorem\textsuperscript{29,30} for quantum systems. It is easy to see that it reduces to the classical fluctuation dissipation theorem as $\hbar \to 0$. If the classical limit for the system variables is taken, the relevant quantity in the noise correlation function to be considered is the limiting value

$$
\lim_{\hbar \to 0} \hbar \omega_{mn} (N(\omega_{mn}) + \frac{1}{2}) = \frac{1}{2} k_B T \tag{47}
$$

In this limiting case, the noise correlation function and the electronic friction satisfy the classical fluctuation-dissipation theorem:

$$
\frac{1}{2} \langle \{\tilde{\xi}(t), \tilde{\xi}(\tau)\} \rangle = k_B T \Gamma(t, \tau) \tag{48}
$$

The classical limit here is interpreted to be the condition that the characteristic energy of electron-hole pair excitations $\epsilon_{mn}$ is smaller than the temperature scale, i.e $\epsilon_{mn} \ll k_B T$.

Eq.(46) demonstrates that, given the fairly general assumption of a mean field effect of the electronic modes, the resulting dynamics are of a Langevin type for which the fluctuation-dissipation relations are satisfied. Unlike traditional Langevin theory, the noise and friction are due to a quantum mechanical bath. In the limit where the quantum vibrational position and momentum operators are treated classically, the equations of motion reduce to a generalization of the Langevin form derived in Ref.(28). This is not unexpected because the mean field assumptions made to derive the quantum Langevin equation are physically equivalent to a finite temperature Ehrenfest type dynamics in the mixed quantum-classical limit.

### B. Mean Field Criterion

Violations of the Callen-Welton fluctuation-dissipation relation are expected to occur when the timescale which determines the variation of the non-adiabatic coupling is of the same order of magnitude as the timescale of electron-hole pair excitations. In physical terms, this means that violations of the fluctuation-dissipation theorem occur when the electron-hole pairs created at a given nuclear configuration are unable to relax into the mean field limit, due to the rapidity of nuclear motion. Quantitatively, this criterion amounts to stating that the mean field limit obtains when the change in the nonadiabatic coupling over the characteristic timescale for electron-hole pair creation is small relative to the value of the coupling. In other words, a mean field Langevin description of the noise is retained when

$$
\frac{2\pi}{\omega_{mn}} \left| \frac{\dot{V}_{mn}}{V_{mn}} \right| \ll 1 \tag{49}
$$
for typical values of the nonadiabatic coupling $\vec{V}_{mn}$ and electron-hole pair frequencies $\omega_{mn}$. This
criterion can be simplified by rewriting the derivative of the coupling in terms of the vibrational
velocity. The time period of vibration $2\pi/\omega_{mn}$ can be approximated by the time period corresponding
to the vibrational frequency, $\Omega_0$ of the molecule.

$$ \frac{2\pi}{\Omega_0} | \vec{R} \cdot \nabla R \ln | \vec{V}_{mn} | | \ll 1 $$

(50)

Since this criterion involves time derivatives of the vibrational coordinate, large amplitude vi-
brational motion is more likely to result in violations of the mean-field approximation. A more
meaningful statement of this criterion can be written in terms of the vibrational relaxation rates
from the $n=1$ level to the $n=0$ vibrational energy levels when the local density of states is
smooth.

Within the Fermi golden rule, the vibrational relaxation rate, $\Gamma$ is characterised by the propor-
tionality relation;

$$ \Gamma \propto \sigma(\epsilon_f) \langle | \vec{V}_{mn}(\vec{R}) |^2 \rangle $$

(51)

$\sigma(\epsilon_f)$ is the density of states at the Fermi level. $\langle | \vec{V}_{mn}(\vec{R}) |^2 \rangle$ is the transition strength obtained by squaring absolute values of electron-hole pair transition matrix elements $\vec{V}_{mn}$ and calculating their average weighted with respect to the local density of states for the electron-hole pair excitations.

If the dependence, on the vibrational coordinate $\vec{R}$, of the local density of states $\sigma(\epsilon_f)$ is ignored,
then the mean field criterion for the validity of the Langevin description is

$$ \frac{\pi \nu}{2} \vec{R}_0 \cdot \nabla R \ln \Gamma(\vec{R}) \ll 1 $$

(52)

This inequality depends on the quantum number $\nu$ of the initial vibrational excitation of the
molecule and the amplitude of the vibrational motion $R_0$. This expression is derived by replacing
the vibrational velocity by the root mean squared velocity of the free vibrational motion. The
amplitude of the vibration can be written in terms of the vibrational quantum number to obtain
the criterion for the validity of the mean field approximation to be,

$$ \frac{\pi}{2} \left[ \frac{\hbar}{M\Omega_0} \nu^2 (\nu + \frac{1}{2}) \right]^{1/2} | \nabla R \ln \Gamma(\vec{R}) | \ll 1 $$

(53)

It is to be noted that this criterion can be tested experimentally by measuring the linewidth near
the equilibrium chemisorbate geometry.

The inequality in Eq.(53) is a criterion which provides a quantitative measure of the "weak
coupling" approximation. When Eq.(53) is satisfied, the adsorbate vibrational degrees of freedom
obey a generalized Langevin equation subject to quantum white noise. In the semiclassical limit
(i.e when the nuclear degrees of freedom are treated classically) the quantum GLE reduces to a
standard classical Langevin with an electronic friction.

When the vibrational frequency is sufficiently high to render the mean field approximation
invalid, the dynamics of the molecule gain a strongly nonadiabatic character. In this regime the
approximations wherein the derivatives of the nonadiabatic coupling were ignored are invalid.
However, the formalism presented here can be extended to account for these corrections. Formally,
the derivatives of the coupling enter the equations of motion for the acceleration of the vibrational coordinate. To derive this, the full contribution to the quantum acceleration is retained to give,

\[ M \ddot{\vec{R}} = \dot{\vec{P}} + \sum_{m > \epsilon_f > n} \{ \vec{V}_{mn} \dot{\rho}_{mn}^\dagger + \vec{V}_{nm} \dot{\rho}_{mn} \} + \sum_{m > \epsilon_f > n} \{ \vec{V}_{mn} \rho_{mn}^\dagger + h.c. \} \]  

(54)

Unlike in the mean field treatment, the derivatives of the nonadiabatic coupling \( V \) no longer cancel out of the equation. These derivatives are given by

\[ \dot{\vec{V}}_{kl} = \nabla_R \vec{V}_{kl} \cdot \frac{\vec{P}}{M} + \frac{1}{M} \sum_{m,n} \{ \vec{V}_{mn} \rho_{mn}^\dagger + h.c. \} \cdot \nabla_R \vec{V}_{kl} - \frac{i \hbar}{2M} \nabla^2 \vec{V}_{kl} \]  

(55)

The Hamiltonian of the vibrational degrees of freedom in the presence of nonadiabatic coupling corresponds to that of a charged particle in a magnetic field. The "vector potential" corresponding to this magnetic field is a matrix with matrix elements given by the nonadiabatic coupling amplitudes. It is possible to show, with some algebra, that the derivatives of the nonadiabatic coupling contribute to this magnetic force.

Thus, in the general case, the resulting equation for the quantum acceleration is

\[ M \ddot{\vec{R}} = -\nabla_R \vec{W} + \sum_{m > k_f > n} i \omega_{mn} \{ \vec{V}_{mn} \rho_{mn}^\dagger - \vec{V}_{nm} \dot{\rho}_{mn} \} - \frac{1}{2M} \{ M \ddot{\vec{R}} \times \vec{B} - \vec{B} \times M \dot{\vec{R}} \} \]  

(56)

Eq. (56) must be solved self-consistently with the equations of motion for the electron pair creation-annihilation operators.

The quantum acceleration, Eq. (56), in the strong nonadiabatic coupling regime corresponds to a Langevin equation in the presence of a magnetic field. The first two terms correspond to the mean field contributions to the quantum acceleration. In the mean field limit, the two Lorentz force terms vanish. In this equation, the magnetic field is itself a matrix operator which is a linear combination of electron-hole pair creation and annihilation operators. Physically, this implies that each electron-hole pair excitation is associated with a corresponding magnetic flux. This magnetic flux is generated through the nonadiabatic coupling vector associated with the electron-hole pair. Hence, the motion of the molecular coordinates can be thought of as the motion of a charged particle moving in a fluid (electron-hole pair excitations). As the particle velocity increases, it creates eddy currents due to the magnetic coupling which aid in dissipating the energy of the particle. A clearer interpretation of this is as follows. For sufficiently weak nonadiabatic coupling, the vibrational motion of the molecule causes electrons from near the Fermi energy to be excited and form electron-hole pairs. As the nonadiabatic coupling grows in strength, multiple electron-hole pairs as well as electrons with energies that are farther below the Fermi energy begin to be excited. This is manifested through the magnetic field contribution to the acceleration. For very strong nonadiabatic coupling, the excitations could involve sufficient energy to allow for an electron to escape the metal surface.

Eq. (56) corresponds to a set of nonlinear differential equations for the quantum acceleration. This nonlinearity is due to the coupling of the forces and accelerations corresponding to different directions of the vibrational coordinate. There is also a further source of nonlinearity in that this equation is coupled to the equations of motion for the electron-hole pair operators. Consequently,
a general solution of this set of equations is difficult. A quantitative description of the molecular dynamics in the presence of strong nonadiabatic coupling is currently under investigation.

IV. DISCUSSION

In this work, rigorous quantum equations of motion have been derived to describe the quantum dynamics of molecules on metal surfaces when subject to a coupling to surface electron-hole pair excitations. It is found that as long as the nonadiabatic coupling has a slow time variation relative to the timescale of non-adiabatic excitations, the reduced quantum dynamics of the adsorbed molecules are described by a quantum version of the generalized Langevin equation. Further, within this approximation it has been shown that the quantum noise and friction operators satisfy the generalized version of the Callen-Welton fluctuation dissipation theorem. In the semiclassical limit wherein the molecular modes are treated classically while retaining the quantum mechanical nature of the electron-hole pair bath, the noise and friction operators satisfy the classical fluctuation-dissipation relation.

The classical limit of the Langevin equation is found to obtain if the characteristic energy of electron-hole pair excitations is much smaller than the ambient temperature of the surface. However, at low temperatures, this no longer holds and the dynamics should be described correctly by the quantum Langevin equation. Since dissipative effects due to electron-hole pair excitations are dominant over other mechanisms only at low temperatures, this implies that quantum effects could contribute significantly to molecular motion on the surface. The classical limit also enables a physical interpretation of the Langevin equation. The electronic energy levels of the adsorbed molecule broaden due to interaction with the surface. Due to this, a part of the broadened resonance goes below the Fermi energy and becomes populated with metallic electrons. Molecular vibration causes a dynamical charge transfer because the degree of overlap of the resonance below the Fermi level changes. If the electrons lag the nuclear motion, the resonance can be unoccupied at or below the Fermi level, thus causing an electron-hole pair excitation and resultant dissipation. The connection between the Langevin formulation and the dynamical charge transfer become explicitly clear in the Markovian limit, where the electronic friction kernel becomes proportional to the linewidth of the vibrational excitation given by the Fermi golden rule.

It should be noted that numerical computations of the Langevin equation, even in the classical limit are a challenging task. In addition to the difficulties associated with the simulation of Brownian processes with memory dependent friction, additional problems arise due to the dependence of the friction kernel on the vibrational coordinates. A full solution would necessarily involve a self consistent propagation of the Langevin equation with the vibrational motion. However, the numerical simulation of the equation becomes more tractable in the Markovian limit, where the memory dependence of the friction kernel is dropped. In this situation, approximate values of the friction term can be obtained through the use of density functional theory or other electronic structure methods to estimate the matrix elements of the coupling potential around
the Fermi level and thus evaluating the electronic friction. To obtain full self consistency with
vibrational motion, it is necessary to perform this calculation every few time steps. Thus, full
self consistency requires considerable computational expense and limits the time for which the
vibrational dynamics can be propagated.

A simplification of the generalized Langevin equation, Eq.(28) obtains when the local electron
density of states is smooth and slowly varying. In this circumstance, the surface electronic
structure provides a constant frictional background and the memory dependence of the friction
kernel can be dropped. Thus, under such conditions, the Markovian limit of the GLE is obtained.
However, the presence of sharp features in the local density of states causes the dynamics
to become non-Markovian and the friction kernel becomes memory dependent. This change is
because the friction kernel is a two point sum over non-adiabatic couplings evaluated at vibrational
positions corresponding to different times. If the electron density of states is heterogenous and
sharp around one of the two vibrational positions, the summation over local electronic levels are
different for the two times, and the friction kernel becomes memory dependent. This memory
dependence is in general difficult to treat, however if the sharp features in the density of states
are isolated peaks in a smooth background, approximations could be developed for the numerical
resolution of these difficulties by treating the peaks as perturbations in the Fourier representation
of the classical limit Langevin equation. These and other issues concerning the computational
study of the dynamics within the framework presented here are presently under consideration and
will be discussed in more detail at a later date.

In the regime of strong nonadiabatic coupling, the equations of motion for the vibrational
coordinate become nonlinear, and correspond to the dynamics of a charged particle in the
presence of both electric and magnetic field environments. Contrary to the mean field regime,
a strong nonadiabatic coupling is likely to enable multiple electron-hole pair excitations as
well as electron-hole excitations with high energy. This suggests that the dissipation of en-
ergy in the presence of strong nonadiabatic coupling is likely to be nonexponential, and the
corresponding diffusion of the vibrational coordinate is no longer a purely Brownian process.
This is consistent with the evidence provided by a recent series of experiments\textsuperscript{35--40}. In these
experiments, highly vibrationally excited NO molecules were scattered off a metal surface and
it was observed that the scattering process resulted in the relaxation of the vibrational state by
several vibrational quantum numbers. In one of these experiments, the scattering process was
found to result in the emission of electrons from the surface\textsuperscript{39}. It is therefore suggested that
the equations of motion developed here could be used to quantitatively simulate the dynamics
of high vibrationally molecules on the metal surface and test these possible dissipation mechanisms.

The formalism presented here is quite general and the equations of motion derived here are
rigorous and based on first principles. Furthermore, this method can be easily modified to study
nonadiabatic molecular dynamics in more general contexts. When the nonadiabatic dynamics
occurs with coupling between discrete sets of Born-Oppenheimer states, Eq.(56) remains the same.
However, the electron pair creation operators can no longer be approximated to be bosonic, and will have to be propagated using the exact equations of motion. Since these operators are closely linked to the electron density matrix, the equations of motion can be approximated with Pauli type master equations. Under such circumstances, it is intuitively apparent that existing mixed-quantum classical recipes correspond to different approximate solutions of these master equations. As a natural consequence, when the number of electrons are taken to infinity, different mixed quantum classical methods are likely to converge to the mean field GLE derived here. The methodology presented here can therefore aid in the further development of more refined mixed quantum classical molecular dynamics methods. The application of this methodology to study mixed quantum-classical dynamics will be presented in a future publication.

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