Semiclassical Dynamics of Electron Transfer at Metal Surfaces

Hongzhi Cheng,[1] Neil Shenvi,[2] and John C. Tully[1,2]
[1]Department of Physics, Yale University, New Haven, Connecticut 06520, USA
[2]Department of Chemistry, Yale University, New Haven, Connecticut 06520, USA

(Received 30 January 2007; published 3 August 2007; publisher error corrected 6 August 2007)

In this Letter, we demonstrate that nonadiabatic dynamics of molecular scattering from metal surfaces can be efficiently simulated by semiclassical Gaussian wave packet propagation on a local complex potential. The method relies on the wideband limit decoupling of the nuclear equations of motion on different electronic states. If the continuum diabatic potential surfaces are assumed to be parallel, the number of Gaussian wave packets spawned scales *at most* linearly with propagation time, allowing efficient propagation of nuclear dynamics.

DOI: 10.1103/PhysRevLett.99.053201 PACS numbers: 34.50.Dy, 34.10.+x

Electron transfer underlies a host of important dynamical processes at surfaces, including chemiluminescence, adsorption, inelastic scattering, catalytic bond breakage, and electron-hole pair generation [1–3]. At metal surfaces, electron transfer is ubiquitous because of image charge stabilization. Furthermore, the electron transfer process is usually strongly nonadiabatic; traditional molecular dynamics on the ground state potential energy surface is inapplicable.

Following the classic paper by Newns [4], a number of theoretical treatments of electron transfer in collisions of atoms or molecules with metal surfaces have been reported [1,5]. All of these assume a preassigned trajectory and focus on the electronic evolution. This is not adequate for low-energy (thermal) processes for which the electron transfer event often drastically alters the forces that govern the nuclear motion. Even a self-consistent-field (“Ehrenfest”) trajectory that responds to electron transfer in an average way fails to account for the differing nuclear paths that result from different final electron states [6]. Proper treatment of electronic-state-specific paths of nuclear motion is critical, e.g., to describe low probability events such as dissociative adsorption or distributions of outcomes such as vibrational energy relaxation in molecule-surface scattering, the process we choose as an example below.

In this Letter, we apply a semiclassical approach to nonadiabatic electron transfer dynamics at metal surfaces that, within its regime of validity, properly accounts for electronic-state-specific paths of nuclear motion. This approach is based on two approximations. First, we apply the local potential approximation, which has been studied extensively in the context of electron-molecule collisions [7,8] and electron-stimulated desorption [9,10]. Next, we apply the semiclassical Gaussian wave packet method first derived by Heller [11] and applied to electron-molecule collisions by McCurdy and Turner [12].

To apply these methods to the molecule-surface scattering problem, some modifications must be made. In most gas-phase applications such as vibrational excitation, the scattered nuclear states are bound, allowing the population of a finite number of quantized final states to be considered [12]. However, such an approach is not always possible in molecule-surface scattering, because the final nuclear state may be bound or unbound and a continuum of phonon excitations may occur, so the number of nuclear degrees of freedom is potentially large. On the other hand, in applications such as dissociative attachment or electron-stimulated desorption, the final nuclear state may be unbound, but electronic-state-specific information about the nuclear trajectory is not required [9,10]. Our approach, which treats each electronic continuum diabat independently, efficiently provides electronic-state-specific nuclear information for the scattering problem. We illustrate our approach on a model problem designed to represent inelastic scattering of O_2^- from a metal surface. The probabilities of different final vibrational states of the scattered molecule, representing different nuclear pathways, are compared to the results of numerically exact integration of the time-dependent Schrödinger equation.

The Hamiltonian for a generalized admolecule-metal system is given by

$$H = \sum_i -\frac{\hbar^2\nabla_i^2}{2m_i} + \epsilon_a(\mathbf{x})|a\rangle\langle a| + \sum_k \epsilon_k(\mathbf{x})|k\rangle\langle k| + \sum_k V_{ak}(\mathbf{x})(|a\rangle\langle k| + |k\rangle\langle a|). \qquad (1)$$

Here $|a\rangle$ is the localized adsorbate electronic state, $\{|k\rangle\}$ are the metal electronic states, and $\mathbf{x}$ is the vector of nuclear coordinates. $\epsilon_a(\mathbf{x})$ and $\epsilon_k(\mathbf{x})$ are the electronic diabatic potential energy surfaces (“diabats”) as a function of the nuclear coordinates $\mathbf{x}$, where $\mathbf{x}$ can represent both adsorbate and substrate atom positions. Thus, $\epsilon_a(\mathbf{x})$ is the anionic diabat (i.e., the potential energy surface when the electron is in the adsorbate state $|a\rangle$), and $\epsilon_k(\mathbf{x})$ is the set of neutral diabats (i.e., the potential energy surface when the electron has been transferred to the conduction band state $|k\rangle$). $V_{ak}(\mathbf{x})$ is the coupling between diabats. In the case of an adsorbate-metal system, we can make a useful assumption, namely, that the neutral diabats $\epsilon_k(\mathbf{x})$ are parallel such that $\epsilon_k(\mathbf{x}) = \epsilon_m(\mathbf{x}) + E_k$; i.e., the adsorbate-surface interaction is independent of the specific k state of the conduction electron. Given this assumption, the time-dependent Schrödinger equation yields the coupled differential equations for $|\dot\psi_a(\mathbf{x}, t)\rangle$ and $|\dot\psi_k(\mathbf{x}, t)\rangle$. The local complex potential method allows the nuclear equations of motion on the anionic and neutral diabats $|a\rangle$ and $\{|k\rangle\}$ to be decoupled [8,13] if the bandwidth of the continuum of metal states is large compared to the diabatic coupling strength $V_{ak}(\mathbf{x})$. In this case, the equation for the adatom diabat is

$$i\hbar|\dot\psi_a(\mathbf{x}, t)\rangle = \left(\sum_i \frac{-\hbar^2\nabla_i^2}{2m_i} + \epsilon_a(\mathbf{x}) - i\Gamma(\mathbf{x})\right)|\psi_a(\mathbf{x}, t)\rangle, \tag{2}$$

where $\Gamma(\mathbf{x}) = \pi|V(\epsilon_a(\mathbf{x}))|^2\rho[\epsilon_a(\mathbf{x})]$ is a position-dependent decay term. The solution $\psi_a(\mathbf{x}, t)$ can be obtained by propagating the nuclear dynamics of the initial wave packet using Eq. (2). The solution on each neutral diabat $\psi_k(\mathbf{x}, t)$ can be obtained by solving an inhomogeneous Schrödinger equation using $V_{ka}(\mathbf{x})\psi_a(\mathbf{x}, t)$ as the driving term. Unfortunately, as the number of nuclear degrees of freedom increases, propagation of the full quantum dynamics becomes computationally intractable.

To address this problem, quantum nuclear dynamics can be replaced by semiclassical Gaussian wave packet propagation [11] as described in Ref. [12]. In this scheme, an initial Gaussian wave packet described by the function

$$\begin{aligned}\psi(x, t) = \exp\{&[\mathbf{x} - \mathbf{x}_0(t)][\mathbf{A}(t) + i\mathbf{B}(t)][\mathbf{x} - \mathbf{x}_0(t)] \\ &+ i\mathbf{q}(t)[\mathbf{x} - \mathbf{x}_0(t)] + \delta(t) + i\theta(t)\}\end{aligned} \tag{3}$$

is propagated using Schrödinger's equation. If the potential energy term in the Hamiltonian is expanded to second order in a Taylor series about the point $\mathbf{x}_0(t)$, a set of coupled, nonlinear differential equations is obtained for the parameters $\mathbf{A}(t)$, $\mathbf{x}_0(t)$, $\mathbf{q}(t)$, $\delta(t)$, and $\theta(t)$. To solve for $\psi_a(\mathbf{x}, t)$, we follow the derivations in Ref. [11] except that we allow the potential energy to be *complex*, given by $\epsilon_a(\mathbf{x}) - i\Gamma(\mathbf{x})$. This derivation yields the following equations of motion for the Gaussian parameters:

$$\dot{\mathbf{A}} = -\frac{2\hbar}{m}(\mathbf{AB} + \mathbf{BA}) - \frac{1}{2\hbar}\mathbf{\Gamma}_2, \tag{4}$$

$$\dot{\mathbf{B}} = \frac{2\hbar}{m}(\mathbf{A}^2 - \mathbf{B}^2) - \frac{1}{2\hbar}\epsilon_2, \tag{5}$$

$$\dot{\mathbf{x}}_0 = \frac{\hbar}{m}\mathbf{q} + \frac{1}{2\hbar}\mathbf{A}^{-1}\mathbf{\Gamma}_1, \tag{6}$$

$$\dot{\mathbf{q}} = -\frac{1}{\hbar}\epsilon_1 + \frac{1}{\hbar}\mathbf{BA}^{-1}\mathbf{\Gamma}_1, \tag{7}$$

$$\dot\delta = -\frac{1}{\hbar}\Gamma_0 - \frac{\hbar}{m}\,\mathrm{Tr}[\mathbf{B}], \tag{8}$$

$$\dot\theta = \frac{\hbar q^2}{2m} + \frac{\hbar}{m}\,\mathrm{Tr}[\mathbf{A}] - \frac{1}{\hbar}\epsilon_0 + \frac{1}{2\hbar}\mathbf{q}^T\mathbf{A}^{-1}\mathbf{\Gamma}_1, \tag{9}$$

where ϵ_0, ϵ_1, ϵ_2, Γ_0, $\mathbf{\Gamma}_1$, and $\mathbf{\Gamma}_2$ are the Taylor expansion coefficients of the complex potential energy $\epsilon(\mathbf{x}) - i\Gamma(\mathbf{x})$. Using this semiclassical scheme, we can propagate $\psi_a(\mathbf{x}, t)$, obtaining a trajectory of the parameters $\{\mathbf{A}_a(t), \mathbf{B}_a(t), \mathbf{x}_{0a}(t), \mathbf{q}_a(t), \delta_a(t), \theta_a(t)\}$ and avoiding the difficulties of exact quantum propagation in high dimensions.

Unlike traditional gas-phase approaches, which derive the populations of motion for particular bound *nuclear* states [8,12], we will instead obtain the nuclear wave function on each electronic diabat $|k\rangle$. From Eq. (2), it can be found that the formal solution of $\psi_k(\mathbf{x}, t)$ is

$$\begin{aligned}|\psi_k(\mathbf{x}, t)\rangle = -\frac{i}{\hbar}\int_0^t dt' e^{-iE_k(t-t')/\hbar}U_m^\dagger(t - t') \\ \times V_{ka}(\mathbf{x})|\psi_a(\mathbf{x}, t')\rangle,\end{aligned} \tag{10}$$

where $U_m(t)$ is the propagator on the neutral diabats

$$U_m(t) = \exp\{i[T + \epsilon_m(\mathbf{x})]t/\hbar\}. \tag{11}$$

The integral in Eq. (10) can be evaluated numerically by turning it into a sum to obtain

$$\begin{aligned}|\psi_k(\mathbf{x}, t)\rangle = -\frac{i}{\hbar}\Delta t\sum_{t'=0}^{t} e^{-iE_k(t-t')/\hbar}U_m^\dagger(t - t') \\ \times V_{ka}(\mathbf{x})|\psi_a(\mathbf{x}, t')\rangle.\end{aligned} \tag{12}$$

Equation (10) states that, at each instant t', a new wave packet is spawned on the $|k\rangle$ diabat by the coupling $V_{ak}(\mathbf{x})$ and is then propagated forward to time t by the propagator $U_m^\dagger(t - t')$. The wave function $\psi_k(\mathbf{x}, t)$ is the coherent sum over t' of all of these wave packets. To retain our Gaussian parametrization of the wave packets, we could expand $V_{ak}(\mathbf{x})$ up to second order in a Taylor series and fit the spawned wave packet $V_{ak}(\mathbf{x})|\psi_a(\mathbf{x}, t)\rangle$ to a new Gaussian with modified parameters. Instead, in our semiclassical scheme, we assume that the coupling function $V_{ak}(\mathbf{x})$ varies slowly with respect to the width of the Gaussian wave packet. In this case, $V_{ak}(\mathbf{x})$ in Eq. (12) can be replaced by its value at the center of the $|a\rangle$ diabat wave packet, so that

$$V_{ka}(\mathbf{x})|\psi_a(\mathbf{x}, t')\rangle \approx V_{ka}[\mathbf{x}_{0a}(t')]|\psi_a(\mathbf{x}, t')\rangle. \tag{13}$$

The parameters of the spawned wave packet will then be the same as those of $\psi_a(\mathbf{x}, t')$, up to an overall constant.

For every diabat $|k\rangle$, Eq. (10) could be solved independently. However, here we make a crucial simplifying observation: The dependence of $|\psi_k(\mathbf{x}, t)\rangle$ on k comes only from the phase term $\exp[-iE_k(t - t')/\hbar]$ and the overall scaling factor $V_{ak}[\mathbf{x}_{0a}(t)]$ in Eq. (12). Hence, if we calculate and record the trajectories of the spawned wave packets, we need only perform the phase-weighted sum in Eq. (12) to obtain the wave function on an arbitrary neutral diabat k. In other words, a new Gaussian is spawned on the neutral diabats at every instant t'. We then propagate each of these Gaussians forward in time with $U_m^\dagger(t - t')$ using the semiclassical scheme in Eqs. (4)–(9), yielding a set of trajectories in parameter space $\{\mathbf{A}_m(t;t'), \mathbf{B}_m(t;t'), \mathbf{x}_{0m}(t;t'), \mathbf{q}_m(t;t'), \delta_m(t;t'), \theta_m(t;t')\}$, which completely describes the time evolution on all of the neutral diabats when summed with the appropriate phase factors. If the simulation is performed over τ time steps, then τ wave packets are spawned and propagated. Storing these trajectories [which requires storing $O(\tau^2)$ trajectory points] allows us to calculate $\psi_k(\mathbf{x}, t)$ for any arbitrary k.

To test our method, we applied it to a model problem designed to resemble the vibrationally inelastic scattering of O_2^- from a metal surface. The O_2^- ion was oriented so that its bond was parallel to the surface. The two nuclear coordinates of the system were the O_2^- bond length x and the surface to center-of-mass distance z. At some point in the trajectory, an electron can transfer from the O_2^- molecular anion to the metal surface, creating a neutral O_2 molecule. The anionic electronic states experience an image charge attraction to the metal surface as well as screened Coulombic repulsion, while the neutral states experience only the screened Coulombic repulsion. The parameters for the continuum and the coupling V_{ak} were chosen to be physically reasonable, although not quantitatively representative of any particular metal. For instance, the coupling V_{ak} decays exponentially with z, as would be expected if it were proportional to the overlap of the metal and admolecule orbitals. Similarly, the metal continuum was treated as a uniform band extending from a band minimum of $E_{\min} = -5$ eV up to the vacuum level at $E_{\text{vac}} = 0$, such that the density of states resembles that of copper. The system Hamiltonian was

$$H = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2M}\frac{\partial^2}{\partial z^2} + \epsilon_a(x,z)|a\rangle\langle a| + \sum_k [\epsilon_m(x,z) + E_k]|k\rangle\langle k| + \sum_k V_{ak}(z)(|a\rangle\langle k| + |k\rangle\langle a|), \tag{14}$$

where

$$\epsilon_a(x,z) = U_a(x) - \frac{3.6\ \text{eV}}{z/\text{Å}} + \frac{14.4\ \text{eV}}{z/\text{Å}} e^{-z/\text{Å}}, \tag{15}$$

$$\epsilon_m(x,z) = U_m(x) + \frac{14.4\ \text{eV}}{z/\text{Å}} e^{-z/\text{Å}}, \tag{16}$$

$$V_{ak} = 2\ \text{eV} e^{-z/2\text{Å}}. \tag{17}$$

Here $U_a(x)$ and $U_m(x)$ are the Morse potentials for O_2^- and O_2, respectively, which were fit to gas-phase experimental data [14]. M and μ are the total mass and the reduced mass, respectively, of the O_2 molecule.

The dynamics of the system described above were evaluated using exact dynamics and the semiclassical method. For the exact result, a Gaussian molecular wave packet with an incident velocity of 8.75×10^3 m/s and a width of 0.5 Å was initialized at $z = 8$ Å in the ground vibrational state. The full quantum dynamics were then simulated using split-operator propagation [15–17] with $N = 100$ electronic states used to represent the metal conduction band. The semiclassical method used the same initial wave packet as the exact propagation except that the vibrational state was a Gaussian rather than the exact Morse potential ground state. Because the Hamiltonian in Eq. (14) couples the nuclear and electronic degrees of freedom, the exact nuclear evolution will not be identical on the $|a\rangle$ and $|k\rangle$ diabats. The dynamics were simulated until the electron had been almost completely transferred to the metal at $t \approx 60$ fs.

Figure 1 shows the populations on the different electronic diabats as a function of time using exact and semiclassical dynamics. The semiclassical method is able to accurately simulate the transfer of the electron out of the adsorbate state $|a\rangle$ and onto the metal state $|k\rangle$. However, the semiclassical method is also able to capture the dependence of nuclear observables on the electronic state of the system. Figure 2 shows a plot of the final vibrational energy as a function of the electronic state. The discrepancy between the exact and semiclassical results for low lying states in the metal ($E_k < -2.5$) is due to the low population of these states ($< 10^{-2}$). As shown in the figure, the total vibrational energy of the adsorbate increases as the band energy of the metal state $|k\rangle$ to which the electron is transferred decreases. However, in addition to this expected result, which can be predicted from energy conservation arguments, the semiclassical method also predicts detailed information about the distribution of vibrational energy (e.g., the oscillations in the vibrational kinetic energy shown in Fig. 2). In contrast, a mean-field method such as Ehrenfest dynamics would give only a single average vibrational energy and, thus, would be intrinsically unable to predict the electronic state dependence of the nuclear trajectory, much less the subtle effects

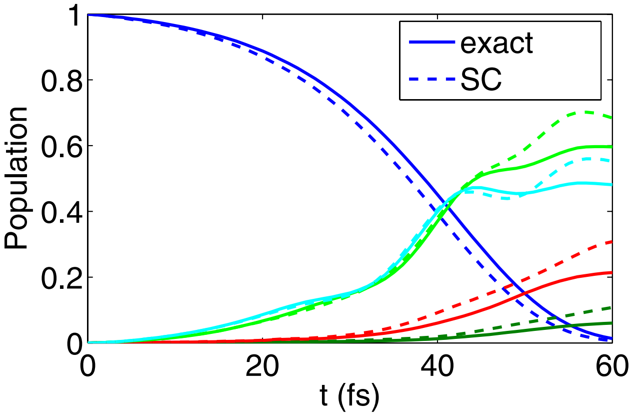

FIG. 1 (color online). The population of the $|a\rangle$ and several $|k\rangle$ diabats versus time as predicted by the exact (solid lines) and semiclassical (dashed lines) methods. The $|k\rangle$ state populations shown here correspond to band energies of $E_k = -2.4$, -2.2, -1.7, and -1.5 eV and are enhanced by a factor of 10 for visibility.

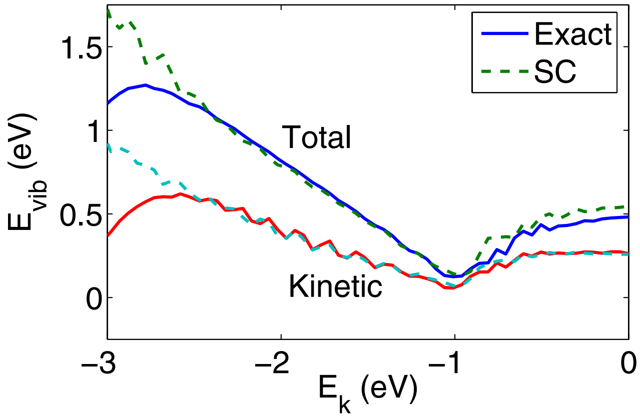

FIG. 2 (color online). The kinetic and total vibrational energy of the scattered molecule at time $t = 60$ fs versus the band energy of the metal electronic state E_k using exact (solid line) and semiclassical (dashed line) dynamics. Discrepancies between the exact and semiclassical results for $E_k < -2.5$ eV are due to the low population of these states; only states with -2.5 eV $< E_k < -1.0$ eV were appreciably populated at $t_f = 60$ fs.

observed here. Finally, it should be noted that the exact dynamics calculations required far more computation time than the semiclassical calculations. On a 3.4 GHz Pentium IV processor, the exact calculation in Fig. 2 required 4 hours of computation, while the semiclassical version required only 21 seconds.

We have shown that electron transfer dynamics at metal surfaces can be efficiently simulated using a semiclassical local complex potential method, appropriately adapted to treat the case of molecule-surface scattering. The critical observation of this adaptation is that newly spawned Gaussians need to be evolved independently on only a single one of the continuum states. Remarkably, different populations and different pathways of nuclear motion on each state arise from the phase interference between the Gaussians. Once a sufficient set of Gaussians has been propagated on a chosen continuum state, motion on any other state can be computed simply by summing with different phase factors. This allows one to select which states to consider and to revise the coarse graining of the continuum after the fact, as needed. Because the semiclassical method avoids the exponential scaling of fully quantum evolution, it is feasible for the simulation of large molecules and multiple adsorbates with the explicit incorporation of large numbers of substrate atoms.

Several areas for future work remain. First, our method relies on accurate diabat energies and coupling matrix elements. In the past, such quantities have been estimated from the excitation of Kohn-Sham orbitals within density-functional theory (DFT) [9]. However, greater accuracy could be obtained from the promising constrained DFT approaches currently being developed [18]. Second, a major limitation of the approach is its applicability only to short time scales, a result of the nonunitarity of the semiclassical Gaussian wave packet propagation procedure. Fortunately, this shortcoming can be overcome by multiplying the Gaussian wave packet by Hermite polynomial factors [12] to extend its validity.

Finally, in realistic metal systems, several complications to electron transfer may arise. At finite temperature, the conduction band of the metal may be partially filled, limiting electron transfer. In certain systems, a narrow *d* band of the metal may couple to the admolecule, yielding coherent oscillation of the transfering electron between metal and admolecule. Even in the absence of a coherent transfer process, multiple incoherent electron transfer events could occur, as electrons hop on and off of the admolecule, generating excited electron-hole pairs. Such a phenomenon is thought to occur in the scattering of NO from Au(111) [19]. For a realistic calculation of scattering, these complications will need to be taken into account.

We are grateful for support of this research by the Department of Energy, Grant No. DE-FG02-05ER15677, the National Science Foundation, Grant No. CHE-0314208, and the Air Force Office of Scientific Research, Grant No. F49620-01-1-0335.

[1] R. Brako and D. Newns, Rep. Prog. Phys. **52**, 655 (1989).
[2] L. Hellberg, J. Strömquist, B. Kasemo, and B. I. Lundqvist, Phys. Rev. Lett. **74**, 4742 (1995).
[3] A. Wodtke, J. Tully, and D. Auerbach, Int. Rev. Phys. Chem. **23**, 513 (2004).
[4] D. Newns, Phys. Rev. **178**, 1123 (1969).
[5] A. R. Canário, A. G. Borisov, J. P. Gauyacq, and V. A. Esaulov, Phys. Rev. B **71**, 121401(R) (2005).
[6] J. Tully, J. Chem. Phys. **93**, 1061 (1990).
[7] T. O'Malley, Phys. Rev. **150**, 14 (1966).
[8] W. Domcke, Phys. Rep. **208**, 97 (1991).
[9] R. E. Walkup, P. Avouris, N. D. Lang, and R. Kawai, Phys. Rev. Lett. **63**, 1972 (1989).
[10] Z. W. Gortel and A. Wierzbicki, Phys. Rev. B **43**, 7487 (1991).
[11] E. Heller, J. Chem. Phys. **62**, 1544 (1975).
[12] C. McCurdy and J. Turner, J. Chem. Phys. **78**, 6773 (1983).
[13] N. Shenvi, H. Cheng, and J. C. Tully, Phys. Rev. A **74**, 062902 (2006).
[14] K. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
[15] J. Bayfield, *Quantum Evolution: An Introduction to Time-Independent Quantum Mechanics* (Wiley, New York, 1999).
[16] R. Kosloff, J. Phys. Chem. **92**, 2087 (1988).
[17] M. Feit, J. Fleck, Jr., and A. Steiger, J. Comput. Phys. **47**, 412 (1982).
[18] J. Behler, B. Delley, K. Reuter, and M. Scheffler, Phys. Rev. B **75**, 115409 (2007).
[19] N. Shenvi, S. Roy, P. Parandekar, and J. Tully, J. Chem. Phys. **125**, 154703 (2006).