

Ehrenfest dynamics with a time-dependent density-functional-theory calculation of lifetimes and resonant widths of charge-transfer states of Li^+ near an aluminum cluster surface

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We present a time-dependent density-functional-theory (TDDFT) Ehrenfest dynamics approach to study the lifetime and the charge neutralization rate of a lithium ion near an aluminum cluster surface. The lifetime of the excited state as a function of the surface-atom distance can be determined, including the effects of level crossings, without prior quantitative information about the coupling between atomic levels and surface states. This method can be used to compute lifetimes of excited atomic states near a surface in both the weak- and the strong-coupling regions and in the avoided crossing region. Because TDDFT Ehrenfest dynamics is a mean-field theory, the wave function consists of contributions from several different excited states during the time propagation. The shortest lifetime is predicted near the region of the avoided crossing between the Li^+ -Al and the Li-Al^+ states.

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Obtaining electronic characteristics of excited states on metal or semiconductor surfaces is crucial for rational design of photoelectronics (e.g., solar cells) and electrophotonics (e.g., organic light emitted diodes). Of great interest are the lifetimes of excited atomic or molecular states near metal or semiconductor surfaces because these short-lived states govern many chemical processes, including charge transfer or injection at interfaces, photochemistry, and surface catalysis. As an atom or molecule approaches a surface, charge transfer will occur, along with broadening of the atomic or the molecular energy levels by the continuum of the surface conduction band. These short-lived charge-transfer states can be characterized by the energy E and the resonant broadening width Γ . The lifetimes of the states are given from the uncertainty principle by $\tau = \hbar/\Gamma$.

A number of methods have been developed to characterize the resonant broadening of a charge-transfer excited adsorbate state as it interacts with a surface. At long surface-atom distances, a jellium model can be used to evaluate atom-surface electron tunneling rates [1–6]. At short surface-atom distances, the interaction is strong, and many approximate methods have been introduced to evaluate the resonant broadening of excited atomic states, including through-bond coupling [7,8], superexchange [9], sequential electron transfer [10], electron and hole transfer [11], electron tunneling currents [12–15], and local density of states approaches [16,17]. These models avoid explicit computations of atom-surface excited states and treat the atom-surface interaction within the perturbative regime. Niedfeldt *et al.* recently introduced a projected density of states (PDOS) method [18] that uses the ground-state density-functional-theory Kohn-Sham (KS) orbitals of the interacting and isolated species. The PDOS method is a first-principles theory that uses single-electron transitions between ground-state orbitals to compute the resonant broadening of an atomic level on a metal surface at any given atom-surface distance. A more accurate but much more difficult approach, as recognized by

the same authors, is using time-resolved quantum-mechanical electron dynamics.

Recently, we developed a nonadiabatic time-resolved time-dependent density-functional-theory (TDDFT) method that can be used for studies of excited states in the strong atom-surface coupling regime [19]. The real-time TDDFT method goes beyond the perturbative regime by including the full interactive potential of the atomic levels and the surface and is able to accurately describe the resonant broadening of atomic levels on surfaces within the Kohn-Sham framework. In this Brief Report, we extend our earlier real-time TDDFT work to include the effects of nuclear motion and present a first-principles time-resolved method to characterize the lifetime of an atomic level on a metal surface in both strong and weak interaction regions and at the avoided crossing of electronic potential-energy surfaces (PESs). We introduce a complete electron-nuclear TDDFT Ehrenfest dynamics approach to characterize the lifetime and the resonant width of a charge-transfer process from an excited state. Using this TDDFT Ehrenfest method, as outlined below, here, we study the charge transfer of a Li^+ atom near an Al cluster (100) surface. A similar approach has been applied to characterize spin transitions during the chemisorption processes [20,21].

The time-dependent single-particle KS equation is

$$i\frac{\partial\phi(\mathbf{r},t)}{\partial t} = \hat{h}\phi(\mathbf{r},t) \quad (1)$$

where \hat{h} is the Kohn-Sham operator with an adiabatic exchange-correlation potential, and orbital $\phi(\mathbf{r},t)$ yields the charge density $\rho(\mathbf{r},t)$. We use the following notation and index conventions throughout this Brief Report: ϕ denotes molecular orbitals in an orthonormal atomic basis; χ denotes orthonormal atomic basis; μ, ν, \dots are atomic basis function indices; and i, j, \dots are molecular orbital indices. Note that a nonorthonormal basis can be transformed into an orthonormal basis by means of Löwdin [22] or Cholesky [23] transformation methods. The one-electron orbital can be expanded in terms of orthonormal atomic basis functions,

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$$\phi_j(r, t) = N_j \sum_{\mu} c_{\mu,j}(t) \chi_{\mu}(r), \quad (2)$$

where N is the molecular orbital occupation. While the basis at fixed nuclear coordinate is time-independent, the current implementation uses an atom-centered basis, which depends on nuclear position and is thus implicitly time-dependent. Assuming the orthonormal basis is unchanged within a short period of time and multiplying both sides of Eq. (1) with χ_{μ} gives

$$\dot{c}_{\mu,j} = -i\varepsilon_j N_j c_{\mu,j}, \quad (3)$$

where ε_j is the energy of the j th Kohn-Sham orbital. Equation (3) indicates that the atomic level χ_{μ} in one-electron orbital ϕ_j oscillates at a frequency ε_j . When the conduction band of the metal broadens an atomic level, the overall evolution becomes

$$\dot{c}_{\mu} = -i \sum_j \varepsilon_j N_j c_{\mu,j} \quad (4)$$

with summation over the atomic levels. Such a time evolution can be captured with time-dependent electronic dynamics. In this Brief Report, we use our recent development of TDDFT Ehrenfest dynamics to obtain the time-resolved electronic dynamics as a function of the atom-surface distance. For a detailed discussion of the algorithm, we refer readers to Refs. [24,25].

The TDDFT Ehrenfest dynamics is integrated with a triple-split operator scheme. The first operator propagates the electronic TDDFT equation in matrix form,

$$i \frac{d\mathbf{P}}{dt} = \mathbf{K}\mathbf{P} - \mathbf{P}\mathbf{K}, \quad (5)$$

where \mathbf{P} and \mathbf{K} are the density and the Kohn-Sham matrices, respectively, in an orthonormal basis. A modified midpoint unitary transformation (MMUT) algorithm with a time step of Δt_e is implemented to integrate Eq. (5),

$$\mathbf{P}(t_{k+1}) = \mathbf{U}(t_k) \cdot \mathbf{P}(t_{k-1}) \cdot \mathbf{U}(t_k), \quad (6)$$

where the propagator \mathbf{U} is constructed from the eigenvalues and the eigenvectors of the Kohn-Sham matrix $\mathbf{C}(t_k) \cdot \mathbf{K}(t_k) \cdot \mathbf{C}(t_k) = \varepsilon(t_k)$ as

$$\mathbf{U}(t_k) = \mathbf{C}(t_k) \exp[i2\Delta t_e \varepsilon(t_k)] \mathbf{C}(t_k). \quad (7)$$

The second operator propagates nuclear degrees of freedom using a velocity-Verlet [26] algorithm with a time step of Δt_N . A third propagator couples electronic and nuclear degrees of freedom by recomputing the TDDFT Hamiltonian every Δt_{Ne} time step. The overall time evolution of the TDDFT Ehrenfest dynamics is given by $\Delta t_N = n\Delta t_{Ne}$ and $\Delta t_{Ne} = m\Delta t_e$.

The development version of GAUSSIAN package [27] is used to compute the necessary integrals, and we use the Becke-Lee-Yang-Parr (BLYP) [28–30] generalized gradient approximation density functional. A 58-atom three-layer fcc cluster of aluminum with a lattice constant of 4.050 Å [31] is used to model the (100) surface. The diameter and the depth of the cluster are 12 and 4 Å, respectively, to ensure that image charge is properly modeled within the electronic

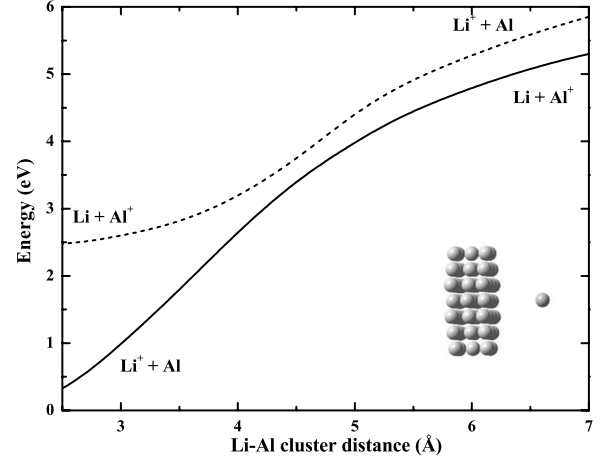


FIG. 1. Linear-response TDDFT potential-energy surfaces of the charge-transfer states of a Li adsorbate on an Al(100) surface. The isolated species energy gap between $\text{Li}^+\text{-Al}$ and Li-Al^+ starts at ~ 1 eV and decreases until the avoided crossing region, which occurs at ~ 4.5 Å at the TDDFT level of theory. The figure inset shows the Al cluster with the Li^+ atom at a distance of 7 Å.

structure description of the cluster when the Li atom is close to the surface. The Li atom is described using the all electron 6-31+G(d) basis set. The nine Al atoms in the interior of the top layer are defined as the collision site. Collision site atoms are modeled with the Los Alamos National Laboratory double- ζ pseudo-core potential (LANL2DZ) [32] basis set, while the Stevens/Basch/Krauss effective core potential minimal basis (CEP-4G) is used for other aluminum atoms. While this work shows a technique for calculating the lifetime and the width of adsorbate charge-transfer states, it should also provide the correct charge-transfer properties of a lithium atom on a bulk aluminum surface. We thus scaled the CEP-4G pseudopotential by a factor of 1.65 for the Al atoms of the cluster, so that the calculated ionization potential of the cluster agreed with the experimental work function of 4.3 eV of a bulk aluminum surface [33]. This scaled pseudopotential scheme introduces an empirical correction to the self-interaction error, which often leads to inaccurate charge-transfer states. The first ionization potential of Li is calculated to be 5.5 eV, while the experimental value is 5.4 eV [34]. TDDFT Ehrenfest dynamics calculations were carried out to 200 fs. Within the dynamic step size control framework [25], the average velocity Verlet time step is 0.1 fs. Within this time step, five steps of midpoint Kohn-Sham and 50 steps of MMUT-TDDFT propagators are used. The total energy of the system is conserved to within 2×10^{-4} eV. The collision site atoms are allowed to be entirely dynamic, while all other Al atoms have fixed positions. The dynamics start with the Li^+ atom at a distance of 8 Å from the Al surface and with an initial kinetic energy of 0.677 eV.

Using linear-response TDDFT theory [35], we plot the PESs of the ground state and the excited state corresponding to the Li-Al surface electron transfer in Fig. 1. At the limit of infinite atom-surface separation, the positively charged atomic state ($\text{Li}^+\text{-Al}$) is ~ 1.22 eV higher in energy than the neutral atomic ground state (Li-Al^+). This energy gap de-

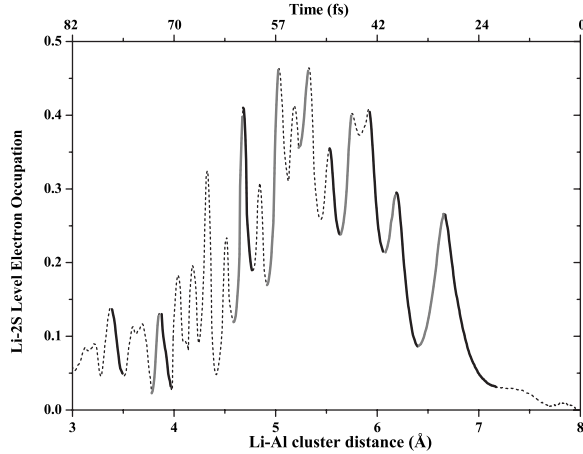


FIG. 2. TDDFT Ehrenfest time evolution of the electron occupation in the Li 2s level. The dynamics start with Li^+ at 8 Å, and the charge is transferred into the Li 2s level from interaction with the Al surface. Highlighted segments are fit to exponential functions to obtain the lifetime and the resonant broadening at a variety of distances. Either side of the oscillation can be used for the fitting, and the light and the dark highlighting is for distinguishing different exponential fits.

creases as the species interact, with PESs experiencing an avoided crossing at $\sim 4\text{--}5$ Å at the time-dependent BLYP (TDBLYP) level of theory. The energy gap between the charge-transfer states is very small in this region. At shorter distances, the ground electronic state shows that Li holds the +1 charge, but there is a strongly localized region of charge buildup on the nearest part of the Al surface due to the interaction of the surface image potential. Using this simple PES analysis, it is difficult to determine if the small energy gap near the avoided crossing or the strong interaction of Li and the Al surface at short distances will have a larger effect on the resonant broadening.

Going beyond the static linear-response picture, we use our TDDFT Ehrenfest dynamics method to resolve the time evolution of the charge on the Li^+ ion near the metal surface including the effects of Al vibration within the collision site of the cluster. We begin the dynamics from the positively charged state, with the Li^+ atom 8.0 Å away from the Al(100) surface. The Li atom reaches a minimum atom-surface distance of 1.6 Å at ~ 100 fs into the dynamics. As the Li atomic levels overlap with Al surface states, the resonant broadening leads to a fast nonradiative relaxation of the excited state to the ground state. Because the ground state of the system corresponds to a neutralized atomic state, such a relaxation process is associated with the charge neutralization rate of a cationic Li on a metal surface. Therefore, by analyzing the characteristic electron occupation in Li 2s level, the lifetime and the resonant broadening of the charged state can be obtained.

Figure 2 plots the TDDFT Ehrenfest time evolution of Li 2s level electron occupation, which shows exponential decay as a result of charge transfer between the Li and the Al clusters. The Li 2p levels do not significantly contribute to the charge-transfer process. Therefore, we concentrate solely on the Li 2s levels. Because of the limited cluster size, the Li 2s charge shows an oscillatory behavior as it bounces

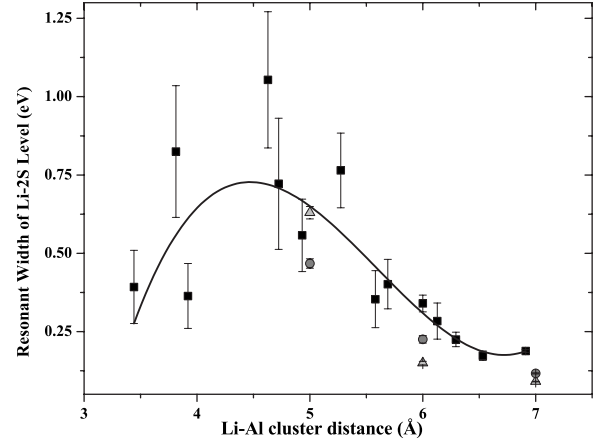


FIG. 3. Resonant width of the Li 2s level as a function of surface-adsorbate distance. Black square points and standard deviation error bars are obtained from exponential fits to the highlighted sections of the TDDFT Ehrenfest Li 2s electron occupation (see Fig. 2). Gray triangles are from exponential fits to real-time TDDFT Li 2s electron occupation, and gray circles are from exponential fits to real-time TDDFT Li 2s electron occupation using a larger Al cluster (see text). The solid line is a least-square fit of a third-order polynomial.

back from the boundary of the cluster. This oscillatory behavior is key to our method of obtaining excited-state lifetimes as a function of adsorbate distance. The charge-transfer rate is a function of both the energy gap between the charge-transfer states and the Li-Al interaction strength or the resonant broadening width of the atomic level, both of which vary with the atom-surface distance. The dynamics start with Li^+ at 8 Å, and the charge is transferred into the Li 2s level from interaction with the Al surface. After the avoided crossing of the $\text{Li}^+\text{-Al}$ and the Li-Al^+ PESs, the Li 2s level begins to lose charge to the Al. The changing charge-transfer rate is reflected in the steepness of the oscillatory curves of the Li 2s level occupation. By fitting multiple sections of the charge oscillation $q(t)$ to the exponential $q(t) = q_0 + A \exp(-t/\tau)$, indicated as solid black and gray lines in Fig. 2, we obtain charge-transfer relaxation processes at different atom-surface distances. The exponential constant τ is the relaxation rate and gives rise to the resonant width Γ of the Li 2s level, $\tau = \hbar/\Gamma$.

The resonant widths of the Li 2s level as a function of the atom-surface distance are shown in Fig. 3. The black squares and error bars correspond to exponential fits to the TDDFT Ehrenfest dynamics Li 2s charge that had 12 or more data points. At long atom-surface distances, the Li 2s atomic orbital does not overlap with surface states extensively. As a result, the neutralization process is very slow and the charged state has a long lifetime and a small resonant width. As the Li atom approaches the surface, the Al surface states start to broaden the Li 2s level. The lifetime of the charged state decreases as the resonant width increases. At the avoided crossing region, formed by the cationic and the neutral Li states (atom-surface distance of $\sim 4.0\text{--}5.0$ Å), the resonant width of the Li 2s orbital reaches a maximum. This suggests that the greatest rate of charge transfer or neutralization on surfaces occurs at the region of the avoided crossing. At

closer distances, when there is a strong localized interaction between the Li and the Al surfaces, the resonant width of the Li $2s$ level slightly decreases, although it is still much larger than those in the long atom-surface distance.

To compare our TDDFT Ehrenfest method to the more established real-time TDDFT method that does not include the effects of nuclear motion [19], we include some additional data points in Fig. 3 for fixed coordinates. The triangles are exponential fits to the Li $2s$ occupation obtained with real-time TDDFT calculations starting with the Li^+ ion at a variety of distances from the surface. The general trend between the two methods is very good at 5, 6, and 7 Å, but it breaks down at closer distances near the avoided crossing region. This is because there is a significant overlap between the Li^+ and the Al clusters, and beginning the dynamics with orthogonal species is no longer an accurate starting wave function. Because TDDFT Ehrenfest dynamics is a mean-field theory, the time-dependent wave function consists of contributions from all excited states of interest during the propagation. By starting the dynamics in an excited pure Li^+ -Al state at large distances and letting the wave function evolve as the Li^+ atom gets closer to the surface, the superposition of electronic states in the TDDFT Ehrenfest theory provides access to the proper mixed states of interest in a single first-principles dynamics calculation. To test the effects of cluster size, also included in Fig. 3 (circles) is the result of the real-time TDDFT dynamics using a larger Al cluster. This cluster contains an additional 20 atoms. The resonant width does not vary much with the larger cluster, showing that the electronic couplings, and thus also the lifetimes and widths, obtained with the smaller cluster are representative of those of a larger system.

In conclusion, a TDDFT Ehrenfest dynamics approach is presented to study the lifetime and the resonant broadening of an atomic adsorbate on a surface. This state-of-the-art method for lifetime determination includes the full electronic coupling between the species, as well as coupling between

electronic and nuclear degrees of freedom. Results are given for the case of a Li $2s$ level on an Al cluster surface. A first-order exponential function is used to fit the charge transfer obtained by the dynamics, and the exponential constant yields the neutralization rate and the resonant broadening of the Li $2s$ level. At long surface-adsorbate distances, the excited adsorbate state corresponds to the cationic Li^+ atom on the neutral Al surface. The charge neutralization rate increases due to the increasing resonant broadening of the atomic level by surface states as the Li atom approaches the surface. The resonant width reaches a maximum value of ~ 1 eV at the avoided crossing region arising from overlapped charged and neutral adsorbate states. At shorter atom-surface distances, the cationic adsorbate state becomes the ground state, and the analysis of charge dynamics gives rise to the lifetime of the neutral adsorbate state. The resonant width of the Li $2s$ level at these shorter distances is smaller than near the region of the state crossings, but greater than at large Li^+ -Al distances.

This Brief Report demonstrates the capability of the TDDFT Ehrenfest method to calculate the resonant broadening of an atomic level on a metal surface in the weak-coupling, strong-coupling, and even avoided crossing regions, within a single TDDFT Ehrenfest dynamics calculation. All interacting potentials are included within the TDDFT framework, without prior quantitative information about the coupling between the atomic level and the surface states. Because the TDDFT Ehrenfest dynamics is a mean-field theory, the wave function consists of contributions from several different excited states of interest, allowing for the description of the mixed state charge-transfer process near the avoided crossing.

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