

Electron hopping between localized states: A simulation of the finite-temperature Anderson problem using density functional methods

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We present a simulation of the dynamics of electron packets in *a*-Si at finite temperature by integrating the time dependent Schrödinger equation using a first-principles Hamiltonian in conjunction with thermal simulation of ion dynamics. The mechanism of diffusion of localized states is thermally modulated resonant mixing with extended or localized states adjacent in energy and real space. For a specific localized state, there exists a critical temperature, beyond which the localized state undergoes a transition to diffusive state.

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I. INTRODUCTION

It is of fundamental interest to develop a deeper understanding of transport in disordered materials. For metals, a simple qualitative relation between the conductivity σ and the diffusion coefficient D of a mobile entity is given by Einstein's relation $D \propto \sigma$. Only diffusive states will contribute to the metallic transport. For amorphous semiconductors, transport theory requires a different foundation. In celebrated work, Anderson,¹ using a random lattice model, proved that without thermal activation no diffusion takes place for a sufficiently disordered one-band model. Sophisticated hopping theory²⁻⁴ proposes that the quantum jump of electrons is the essential transport mechanism through the localized states, in which thermal-induced delocalization is the driving mechanism. This picture is essentially correct, but highly incomplete, since it does not incorporate known information about the topological disorder in materials and to date has not used highly accurate descriptions of electronic states.

In this paper, we explore electron dynamics with the time-dependent Schrödinger (Kohn-Sham) equation, while using realistic models of *a*-Si and a suitable approximate density functional Hamiltonian of Harris form⁵ due to Sankey. We elucidate in microscopic detail the process of hopping or "phonon-induced delocalization." The hopping⁶ we describe is correctly between "cluster states" as described by Dong and Drabold. The exact spatial nature of these states depends critically upon the material and the energy of the state. We view *a*-Si as generically representing a disordered insulator—the physical processes we discuss are salient to *any* amorphous, glassy or insulating polymeric material. Our nonadiabatic approach to the electronic dynamics is also potentially valuable for nonadiabatic transport studies for molecular electronics with its intrinsically localized molecular orbitals and strong electron-phonon couplings.⁷

In a conventional *ab initio* MD simulation, the interatomic forces are obtained from the electronic structure of the system at a given instant (with the electrons in their instantaneous ground state). This is the celebrated "Born-Oppenheimer" (BO) approximation. For many problems, certainly including *a*-Si as we discuss here, this leads to reliable ion dynamics as verified by comparison of vibrational state densities and other experiments. The BO approximation

is of very limited utility for studies of electron dynamics. To properly model electron dynamics, the most fundamental approach is to integrate the time-dependent Schrödinger equation. From such a calculation it is possible to compute the time-dependent single-particle (Kohn-Sham) orbitals and the interatomic forces. Work along these lines has been proposed by other authors.⁸

For a system with disorder the physical processes are especially rich. In general such systems have extended states, strongly localized defect states, and intermediate "band tail" states. Depending upon the position of the Fermi level, different states become relevant to hopping, transport and optical properties. Our work can also be interpreted as a direct simulation of the finite-temperature Anderson localization problem in a "real" material, and with far fewer empirical "inputs" than previous computations.

In the simplest picture, thermal disorder modulates the energies of states through the electron-phonon coupling. This induces close approaches or possibly crossings of states. When the electron-phonon coupling makes the two electronic levels resonant, strong mixing results as in Landau-Zener⁹ tunneling. Thus, system eigenvectors become mixtures of localized states at this point. Such mixed states are a superposition of only a small number of neighboring localized states and are therefore more extended than the original orbitals from which they were built. This is the essence of thermally driven hopping and diffusion in these materials.

II. METHOD

The ionic trajectory at various temperatures was simulated from conventional Born-Oppenheimer (BO) dynamics,⁶ and individual electron packets of interest were tracked from the TDSE. One can understand the thermal disorder as inducing transitions between the one-electron orbitals. We make the approximation of decoupling the ionic motion from the effects of the electronic diffusion; a fully coupled solution¹⁰ is possible in principle, but too difficult for the large systems we study here (in this paper we are interested in the dynamical behavior of a single carrier). Moreover, there is no reason to expect that the ionic motion would be very different anyway for a system near the ground state. In conventional BO dynamics one diagonalizes \hat{H} anew at each

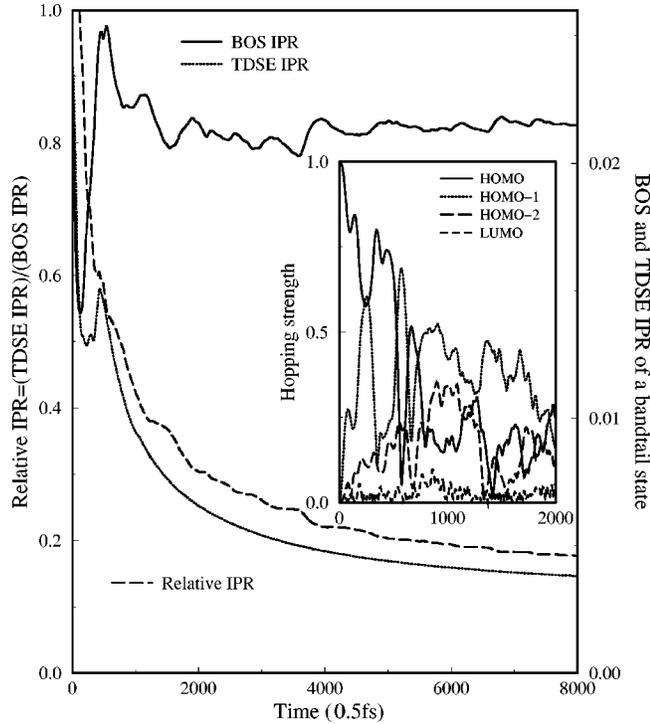


FIG. 1. The evolution of IPR of a bandtail HOMO state in a 216-atom *a*-Si model at 300 K. The inset indicates the spectral leakage into adjacent (energy) states: Γ_{α} . BOS means “Born-Oppenheimer Snapshot” (see text).

time step, computes the density matrix and forces, moves the atoms and so on, thus always working with “pure” one-electron states. For systems with a gap this produces reliable ion dynamics. It is tempting to study the eigenstates of \hat{H} so computed (for each instantaneous ionic conformation) and use them to study electron dynamics.¹¹ We call this BO snapshot electron dynamics “BOS” below.

We begin with the time-dependent Schrödinger equation

$$i\hbar \partial/\partial t \Psi(t) = \hat{H}(t)\Psi(t). \quad (1)$$

Here Ψ is the wave function of a single electron and \hat{H} is the one electron (density functional) Hamiltonian for the host (here, models of *a*-Si) by Fireball96.⁶ For sufficiently small step τ , we use the Crank-Nicholson scheme¹² to evolve the state

$$\hat{U}(\tau) = (1 + i\tau\hat{H}/2\hbar)^{-1} (1 - i\tau\hat{H}/2\hbar). \quad (2)$$

For any τ , $\hat{U}(\tau)$ is unitary. With the Löwdin transformation¹³ we express the wave function $\Psi(t)$ in matrix form as a vector \mathbf{C} over basis ψ_i , $\Psi(t) = \sum C_i(t)\psi_i$ (here, ψ_i are eigenvectors of \hat{H} at time $t=0$). Then the time-dependent state vector is given by $\mathbf{C}(\tau) = \mathbf{U}(\tau)\mathbf{C}(0)$ (for discussion of the suitability of the Löwdin orthonormalization for time-dependent problems, see work of Tomfohr and Sankey¹⁴). We decreased the ionic MD time step to be short enough to also track the electron dynamics from Eq. (1). By limiting ourselves to starting packets which were initially eigenstates with energies near zero (by construction), a time

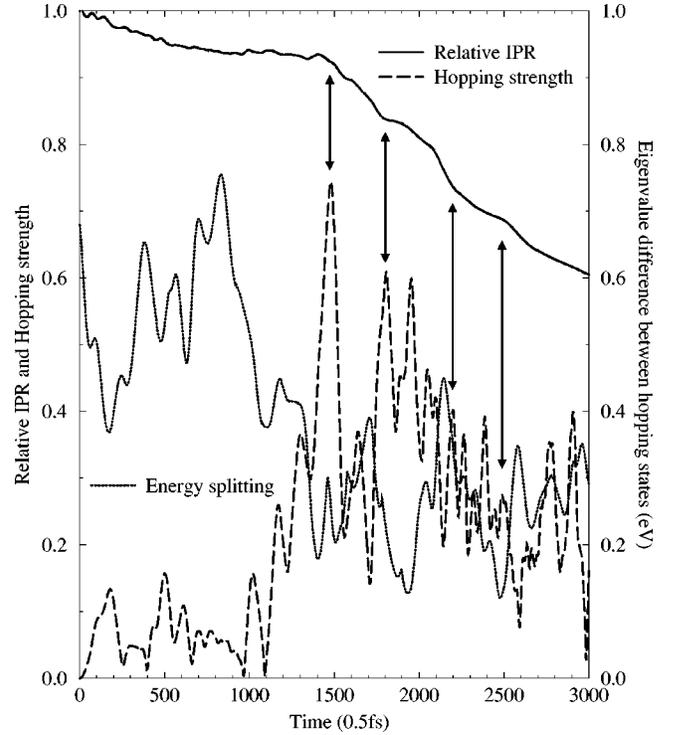


FIG. 2. Delocalization due to hopping from a midgap LUMO state to its nearest unoccupied bandtail state (LUMO+1) in a 216-atom *a*-Si model at 300 K. Each significant change (indicated by the arrows) in the relative IPR, coincides with the surge of hopping strength $\Gamma_{\text{LUMO}+1}$. From perturbation theory (see text), the increase of $\Gamma_{\text{LUMO}+1}$ coincides with the decrease of the energy splitting $\Delta_{\text{LUMO,LUMO}+1}$.

step of 0.5 fs (for both ions and electrons) was adequate. This time step appears to be *very* long; the reason it is acceptable is the proximity of the eigenvalues of localized states to zero energy reference. If we began with a general wave packet built from the full spectral range of the basis, *or* if the starting packet spread across a large spectral range, a far smaller τ would be required.

We performed simulations on two 216-atom and one 64-atom *a*-Si models.¹⁵ Only the Γ point was used for Brillouin zone sampling. Two localized states, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), were chosen to study the delocalization process. These edge states are localized on several atoms in the 216-atom and 64-atom models and are either bandtail or midgap states as we discuss separately for each model. The concentration of localized states in the range of mobility edges in our models is crudely of order 10^{20} cm^{-3} , in line with the experimental estimation.¹⁶

We introduce the time integrated inverse participation ratio (IPR) to study the global evolution of the state in volume as $\text{IPR} = (1/t) \int_0^t \sum_i C_i^4 d\tau$. (This definition gives a smoother, easier to recognize trend than the usual IPR.¹⁷) The range of IPR is between homogeneous extended states $\sim N^{-1}$ (N , the number of basis) and for support solely on a single atomic-like orbital, ~ 1 . Fig. 1 presents 4 ps of time evolution of a bandtail HOMO state from a 216-atom model at 300 K. A

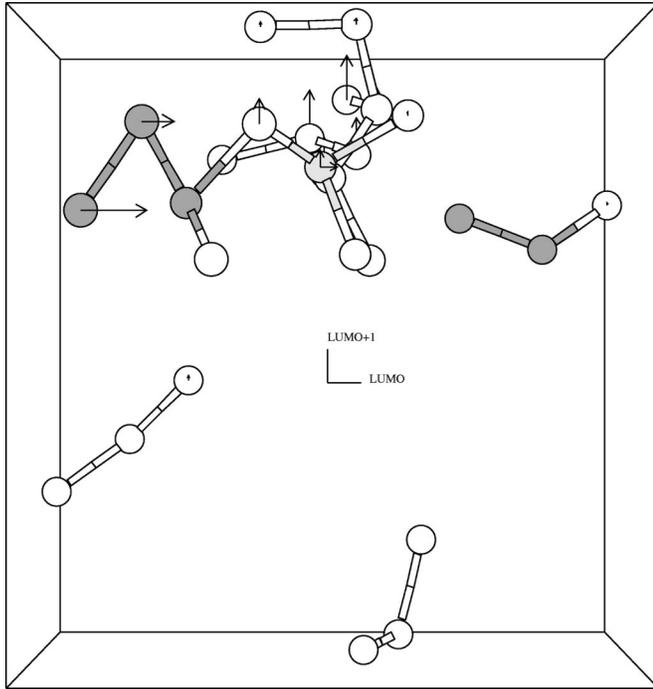


FIG. 3. Charge portrait of TDSE LUMO of Fig. 2: the first significant hopping event. Dark balls represent original LUMO group and the white balls original LUMO+1 group. The magnitude of the arrow on an atom in the LUMO group is proportional to the loss of charge, and on LUMO+1 group is proportional to a gain of charge from phonon-induced scattering. The intermediate grey atom is in both groups.

comparison is made between the TDSE solution and BOS. Room temperature is evidently sufficient to cause spatial diffusion of the original localized states. After 500 fs, the TDSE IPR approaches a homogeneous diffusive state indicating complete delocalization. The relative IPR, defined as a ratio of the TDSE IPR and BOS IPR, reveals the difference of the two solutions. The long time behavior of the relative IPR in Fig. 1 exhibits a diffusive $\sim t^{-1}$ dependence. In the inset of Fig. 1, we unfold the spectral dependence of the diffusion by projecting out to the time-dependent spectral leakage into neighboring states.

III. RESULTS AND DISCUSSION

We analyze delocalization by tracking $\Psi(t)$. In real space, the electron hops from one group of atoms to another neighboring group (the “cluster states” of Dong and Drabold¹⁸) via quantum mechanical mixing. Thermal motion adds a perturbing term $H_T(t)$ to the initial electronic Hamiltonian and may induce transitions from the initial state $|0\rangle$, to $|\alpha\rangle$. The hopping strength Γ_α , is the transition probability for finding the system in eigenstate $|\alpha\rangle$, which we project from the TDSE solution $\mathbf{C}(t)$ as $\Gamma_\alpha(t) = |\langle \alpha | \mathbf{C}(t) \rangle|$. Here, the dominant factor is proportional to $|\langle \alpha | H_T | 0 \rangle|^2 / (\Delta_{\alpha,0} - \omega_p)^2 \sin^2[(\Delta_{\alpha,0} - \omega_p)t/2]$, in first order time-dependent perturbation theory. $\Delta_{\alpha,0}$ is the energy splitting between $|\alpha\rangle$ and $|0\rangle$ and ω_p is the phonon frequency. Figure 2 depicts a typical delocalization process involving hopping between a mid-

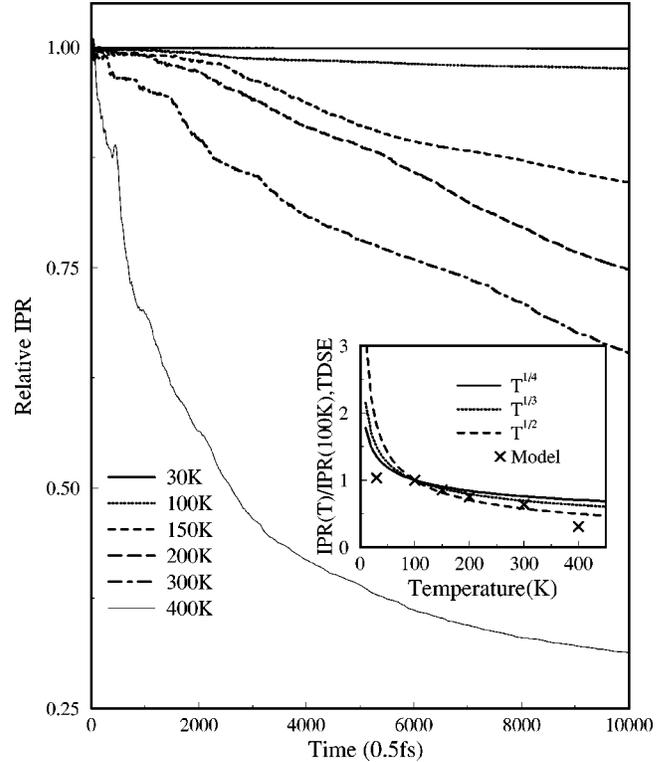


FIG. 4. The temperature dependence of the relative IPR of a midgap state in a 64-atom *a*-Si model. The inset gives each asymptotic TDSE IPR as a ratio to the one at 100 K. Our study shows a temperature dependence between $T^{-1/2}$ and $T^{-1/3}$, comparing to Mott’s $T^{-1/4}$ dependence.

gap state and its nearest neighboring bandgap state in a 216-atom *a*-Si model. Figure 3 provides the atomic view of the charge transfer during such a phonon-scattering event in Fig. 2. In summary, the delocalization process is governed by three factors: (1) the short-range interaction between the localized state and its neighboring states, which depends on the energy splitting and the overlap; (2) the stability of the local conformation of hopping states at the given temperature; (3) the density of available hopping states rendered accessible by thermal modulation. In simple terms one views the thermal disorder as “tuning” the localized electronic energies into and out of resonance. The resonant mixing naturally leads to less localized states and this may continue until the packet has diffused throughout the simulation cell. A graphical representation of the time-dependence of the LUMO and HOMO charge in a small (64 atom) model is given in Ref. 17.

The hopping is selective rather than random at a given temperature. The relative IPR in Fig. 2 reveals a different shape from the diffusive pattern of Fig. 1. This is because the midgap state in Fig. 2 has fewer hopping channels than the bandtail states of Fig. 1 at the same temperature. The concentration of bandtail states is much higher than the midgap states (this is model dependent). A corollary is that one may observe a series of delocalization patterns if we control the activation of hopping channels by temperature (higher T provides access to more channels). Figure 4 provides an explicit, atomistic example of temperature-dependent delocalization.

Below 100 K, the diffusion can be ignored. No significant hopping can be activated in the model system. Between 100–300 K, the relative IPR has a linear shape, in which we observed one hopping channel activated as in Fig. 2. This linear region may be very important in the conduction through a molecule,¹⁴ where a linear excess of charge is induced by external electric field through the isolated molecular orbital. At 400 K, the relative IPR becomes diffusive (Fig. 1) due to activation of multiple hopping channels. This tentatively suggests (for this state) that there exists a critical temperature between 300 and 400 K. Beyond it the localized state undergoes an aggressive diffusion; this is a dynamical transition to diffusive states.

In three dimensions Mott's variable-range hopping (VRH) model¹⁹ proposed a $T^{-1/4}$ dependence of the resistivity. An essential idea in his model is to assume a spherical volume dependence of the admixture of hopping states. In the inset of Fig. 4, we examine the temperature dependence of the asymptotic TDSE IPR, which is a measure of the admixture of hopping states. Comparing to Mott's $T^{-1/4}$ trend we observe that for hopping between 100–300 K, the admixture shows a dependence between $T^{-1/2}$ and $T^{-1/3}$. This may be attributed to the spatial dependence of hopping in a direct atomistic simulation; not the ideal three dimensionally isotropic case indicated in Fig. 3. Instead, it is between a linear and planar dependence, an issue on the relative orientation between hopping states. Beyond this range, the variable-range hopping may not be suitable due to either too small or too large activating energy.

The quantum coherence of states plays a central role in the TDSE simulation. The phonon-scattering $\langle \alpha | H_T | 0 \rangle$ is irregularly time and volume dependent and when phonon-induced mixing occurs, the BOS fails. The transition to the earlier, more localized state is irreversible, and the localization is decreased. In this case, the electron cannot follow the

motion of ions adiabatically. Instead, the artificial coherence implicit to the BO approximation enforces a “jerk” between BO surfaces: electron will elastically return to the static state, leading to a fluctuation of IPR around the localized state and retaining an artificial and unphysically high localization (Fig. 1).

IV. CONCLUSION

In this paper, we presented a simulation of the dynamics of the localized edge states in *a*-Si under a thermal disturbance by integrating the time-dependent Schrödinger equation. This work identifies in a microscopic and detailed way the requirements for thermally driven hopping, and indicates that there exists a critical temperature through which the localized states will undergo a dynamical transition to diffusive states. While in good qualitative agreement with Mott's VRH theory, the simulation points out the limitations of the simple spherical approximation in real hopping events. Decoherence is a dynamical process and can only be approached by the analysis of electron dynamics. Our work demonstrates in a quantitative and realistic way (1) the nature of thermally induced hopping, (2) the need for spatial and spectral overlap for electronic diffusion, and (3) lays important groundwork for a future theory of nonadiabatic transport in disordered systems.

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