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Atomistic Simulation of the Finite-Temperature Anderson Localization Problem

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We present a simulation of the electron dynamics of localized edge states in amorphous silicon (a-Si) at room temperature by integrating the time dependent Schrödinger equation using a Crank-Nicholson method and a first-principles local basis Hamiltonian. We study the character of the spatial and spectral diffusion of the localized states and directly simulate and reveal the nature of thermally driven hopping. Phonon-induced resonant mixing leads to rapid electronic diffusion if states are available nearby in energy and real-space. We believe that many of the results we obtain are crucial for modeling transport phenomena involving localized states.

1. Introduction

It is of great interest to study the coupling between the lattice and the electron states in disordered materials. This interaction is the root of thermally driven hopping between localized states which is the principal mechanism of conduction for virtually all disordered systems at sufficiently low temperatures. Anderson [1] first pointed out the failure of the conventional defect model for ordered structures to explain transport (for an example of recent work on quantum transport see [2]) phenomena in disordered systems. Using a random lattice model he proved that without thermal activation the mobile entities will be localized and at sufficiently low defect concentrations no diffusion takes place. Thomas [3] argued that an electron starting in some localized state (as for example a donor) will be scattered by phonons and become progressively delocalized. He showed, using an Anderson model, that this "phonon-induced delocalization" is essential to the understanding of transport in amorphous materials.

Previous thermal simulations using Born-Oppenheimer dynamics indicated that there is always a very large electron–phonon coupling for the localized states in the band tails and in the optical gap [4]. The effects of thermal disorder on the quantum coherence of the localized states can only be computed by directly dealing with the electron dynamics from the time-dependent Schrödinger equation.

In this paper, we explore a direct integration of the time-dependent Schrödinger (Kohn-Sham) equation to characterize the dynamics of localized states in a small model of a-Si in the presence of thermal disorder (at $T = 300$ K). We employed the Born-Oppenheimer dynamics for the ions and implemented the Crank-Nicholson [5] method along with the orthogonalization scheme of Tomfohr and Sankey [6] to obtain the time-dependence of a given state. The work discussed here is directly relevant to any disordered system and therefore (potentially) to localized states. It can be understood as a first step towards a "realistic" solution of the finite-temperature Anderson problem [7].

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2. Methods

We begin with the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(t) = \hat{H}(t)\, \Psi(t)\,. \tag{1}$$

Here Ψ is the wavefunction of a single electron and $\hat{H}$ is the one electron (density functional) Hamiltonian for the host (here, the model of a-Si). We explicitly compute the time dependence of the Hamiltonian which arises from the ion motion obtained from the Born-Oppenheimer approximation. At each time step of the conventional quantum molecular dynamics (QMD) one can directly diagonalize the Hamiltonian matrix to obtain the stationary solution of the electronic structure. However, the coherence of the electron state is lost in the solution. For any given initial state $\Psi(0)$, the wave function $\Psi(t)$ at the time t can be obtained by solving the time-dependent Schrödinger equation or, equivalently, operating on the initial state with the time evolution operator $\hat{U}(t)$ such that $\Psi(t) = \hat{U}(t)\Psi(0)$. In the Crank-Nicholson method for sufficiently small step τ,

$$\hat{U}(\tau) = \left(1 + \frac{i\tau}{2\hbar}\, H\right)^{-1} \left(1 - \frac{i\tau}{2\hbar}\, H\right). \tag{2}$$

For *any* τ $\hat{U}$ is exactly unitary. We calculated $U(t)$ using $H(t)$ with a time dependence induced by the thermal simulation of the ionic motion from Fireball96 [8]. Using the Löwdin transformation [9] we can express the wave function $\Psi(t)$ as a vector $\mathbf{C}$ over an orthonormal basis ψ_i, $\Psi(t) = \sum C_i(t)\, \psi_i$. The key properties of localization and coherence do not change when applying the Löwdin transformation. We adopt the approximation of Tomfohr and Sankey that for sufficiently small time steps τ the Hamiltonian can be taken to be constant. Then the equivalent matrix equation becomes

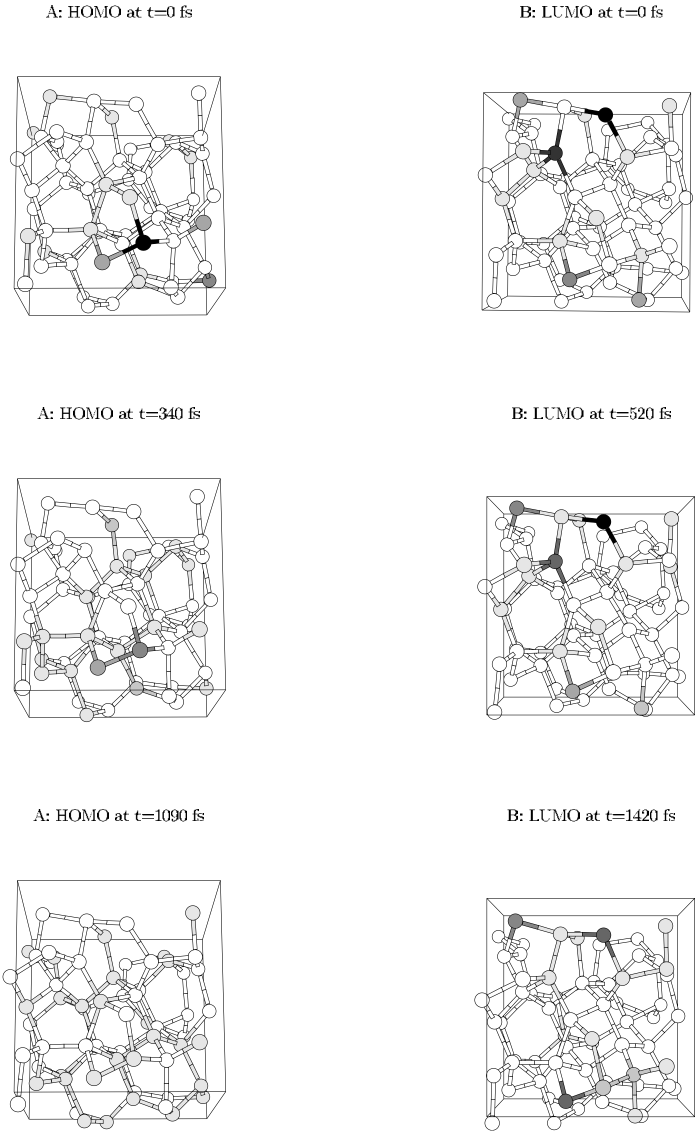
$$i\hbar \frac{\partial}{\partial t} \mathbf{C}(t) = H(t)\, \mathbf{C}(t)\,. \tag{3}$$

At room temperature the results using a time step of 0.5 fs (for both ions and electrons) were found to be close to the results using a finer step of 0.25 fs at the test calculation. So the following results are based on a simulation using a time step of 0.5 fs. This time step appears to be very long; it is, however, acceptable because of the proximity of the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) eigenvalues to zero energy. If we would start with a general wave packet built up from the full spectral range of the basis a much smaller value of τ would be required.

We performed the simulation on a 64-atom a-Si model which has one pair of coordination defects, an undercoordinated dangling bond complex (with energy shifted from mid-gap), and an overcoordinated floating bond. The localized states are associated with the geometrical defects and are located in the band gap. The HOMO is spatially localized around a three fold dangling bond, essentially a *bandtail* state, only 0.1 eV higher in energy than the next occupied orbital and near a dense collection of extended states. The lowest unoccupied molecular orbital (LUMO) is distributed around another small cluster associated with the floating bond. The LUMO of this model is spectrally a *midgap* state, isolated by 0.7 eV from both the lower HOMO and the next unoccupied state. Extended unoccupied states are at least 1.0 eV above the LUMO. We chose both HOMO and LUMO as the initial states to study their dynamics. Only the Γ point was used for Brillouin zone sampling.

3. Results and Discussion

Figure 1 depicts a snapshot of the evolution of charges of the HOMO and LUMO. The diffusion is presented in Fig. 1. It is evident that the thermal disorder is sufficient to cause a spatial diffusion of the originally localized states. This result is very different (this work



A: HOMO at t=0 fs

B: LUMO at t=0 fs

A: HOMO at t=340 fs

B: LUMO at t=520 fs

A: HOMO at t=1090 fs

B: LUMO at t=1420 fs

Fig. 1. The evolution of charges of the original HOMO (A) and LUMO (B). Black indicates a higher concentration than 0.15 electrons. White is the opposite extreme, less than the average (1/64) electron. Between the two extremes the degree of grey indicates a decreasing concentration from the dark to the light. Note the different time scales for the HOMO and the LUMO. After the first 1 ps of evolution the original HOMO state covers almost the whole cell volume while the LUMO state remains somewhat concentrated after a longer 1.5 ps evolution

yielding more extended states) from the results for the "Born-Oppenheimer electron dynamics" (by which we refer to the instantaneous eigenstates of $\hat{H}$ at each ionic configuration) [4], and in which the simulation retains an unphysical coherence in the states as the states are always computed anew at each step and are therefore always pure. More realistically, phonon-induced decoherence accumulates due to repeated phonon scattering events. Thus the time-dependent wave functions $\mathbf{C}(t)$ will show a different behavior compared to those obtained from conventional QMD. We employ the inverse participation ration (IPR) to measure the spatial distribution features, i.e. the localization, of a state: IPR = $\sum C_i^4$. Here C_i is the component of the state vector. For an extended state the IPR approaches $1/N$ where N is the number of the basis. For an ideally localized state the IPR is unity instead.

Figure 2a shows the time development of the IPR of the HOMO in the 5 ps simulation. The time-dependent solution of the HOMO becomes an extended state very

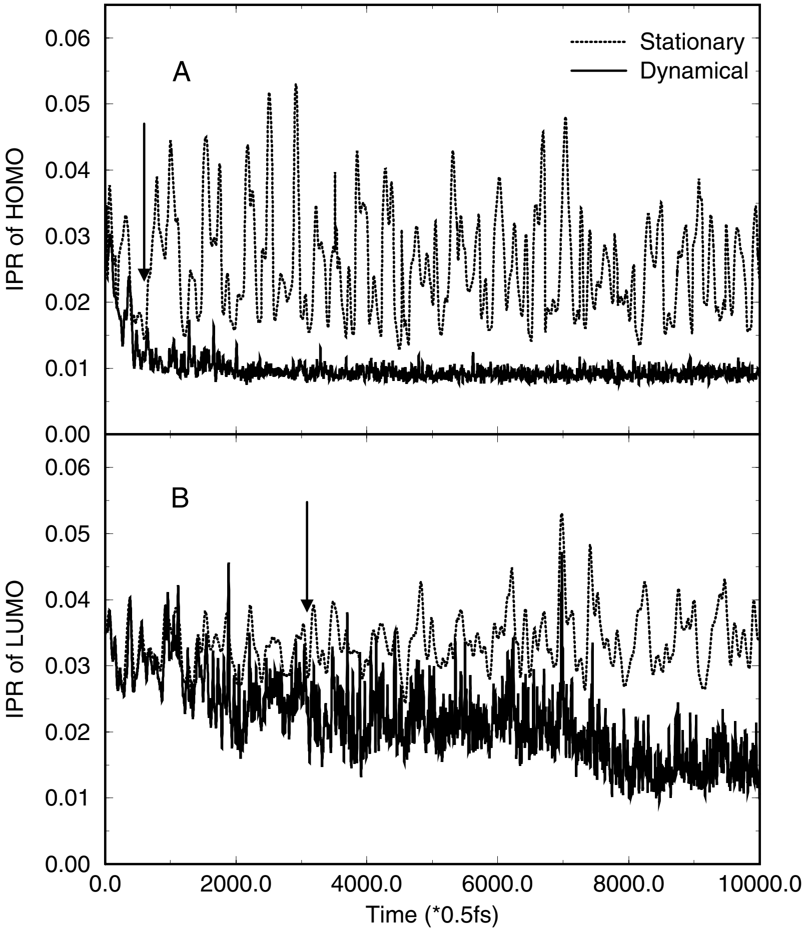


Fig. 2. The evolution of the localization (IPR) of the original a) HOMO and b) LUMO. The dotted line refers to the stationary solution (Born-Oppenheimer) and the solid line to the dynamical (time-dependent Schrödinger equation) solution. The arrows indicate the turning-point at which the dynamical IPR begins to depart from the "Born-Oppenheimer" snapshot dynamics.. The corresponding charge distributions near the turning-points can be found in Fig. 1

quickly. This trend is similar for the LUMO shown in Fig. 2b. The "turning-point" separating the stationary and the dynamical IPR time development occurs near 350 fs for the HOMO state. A similar separation is observed at only 1.5 ps for the LUMO state. A typical charge distribution near the turning-points of the IPR can be found in Fig. 1. The time-dependent solution of the LUMO retains some of its initially localized character after 5 ps of simulation because in comparison to the HOMO at 300 K it is more separated from a reservoir of electronic states with similar energy with which it can mix.

Electronic diffusion is understood qualitatively as a consequence of quantum mechanical mixing when another state gets close in energy (and real-space) to a reference eigenstate whose evolution we are tracking [10]. This mixing naturally leads to less localized states and this continues in principle until the packet has diffused throughout the simulation cell. We now go further to investigate the spectral diffusion of the electron state into nearby (almost resonant) states. Since the structure fluctuates at a fixed moderate temperature the Hamiltonian can be regarded as perturbed around an average H_0. With reference to the initial eigenspace of the Hamiltonian the transition amplitude to the state α is proportional to the probability of finding an eigenvector in the initial eigenspace, i.e.

$$\rho(\alpha) \propto |\langle \mathbf{C}_\alpha(0) \mid \mathbf{C}(t)\rangle|^2 , \tag{4}$$

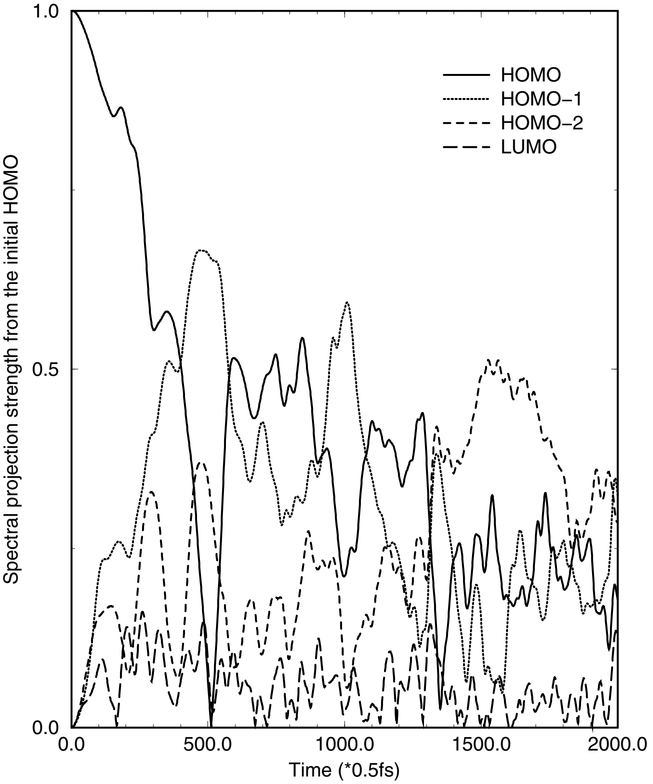


Fig. 3. The spectral evolution of the dynamical HOMO state. Any decrease in the HOMO is accompanied by an increase in the nearby states, a quantum jump between states

where α is the eigenstate label in the initial eigenspace. Here we are interested in the transition to energy states around the gap region which are the most important states for transport and are located near the so-called mobility edges. These edges mark the transition from localized to delocalized states at zero temperature and are destroyed by thermal fluctuations.

Figure 3 depicts the evolution of the transition or hopping probabilities from the HOMO to nearby states during the first 1 ps. The component of the original ($t = 0$) HOMO decreases to zero within 250 fs (which is earlier than the 350 fs IPR turning-point) which indicates that the decoherence is very fast for the HOMO. The valence state just below the HOMO reaches its maximum as the HOMO approaches its first minimum at about 250 fs. The second valence state below the HOMO reaches its maximum at about 750 fs, 0.5 ps later than the first valence state below the HOMO. Spectrally, the original HOMO diffuses into other valence states at a rate related to the thermal activation and splitting from adjacent energy states. Some transitions even occur between HOMO and LUMO. The magnitude of the transition across the gap is far lower than the magnitude of the transition from the HOMO to other valence bands. *This is a quantum effect associated with the huge electron–phonon coupling of the localized states since room temperature (≈ 26 meV) is not high enough to directly induce a transition between the HOMO and LUMO with a gap of 0.6 eV.* Besides the thermal activation the tunneling or spatial overlap between the hopping states may also play an important role in the deeper gap transition. The diffusion of the LUMO to its nearest

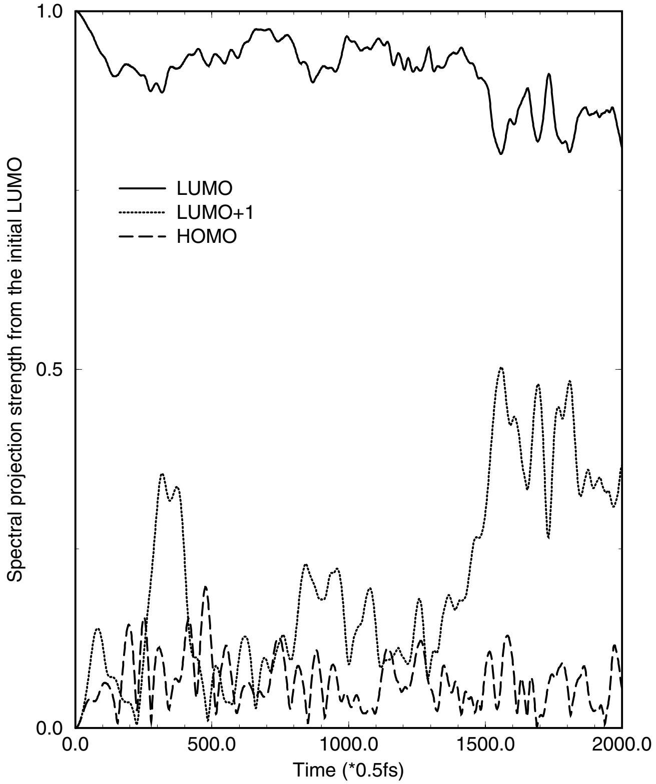


Fig. 4. The spectral evolution of the dynamical LUMO state, similar to Fig. 3 but the initial state is LUMO

unoccupied localized state (0.7 eV above) gives a direct indication of the hopping diffusion in Fig. 4. The character of the LUMO is different from the HOMO. The spectral diffusion of the LUMO is slower than that of the HOMO as shown in Fig. 4. There are, however, similarities: The LUMO diffuses into the neighboring conduction states more easily than across the gap and the spectral diffusion is also strongly dependent on the distance between the LUMO and other conduction states.

We found that these two localized states show a different response to the external thermal manipulation which is in stark contrast to the results obtained by Born-Oppenheimer dynamics. The HOMO is easily delocalized by the thermal disturbance while the delocalizing progress is very slow for the LUMO. In previous Born-Oppenheimer dynamics [4] it has been observed that the eigenvalue of the LUMO shows larger fluctuations than the eigenvalue of the HOMO. However, the time coherence in the dynamical solution reveals the different delocalization process because of the difference in the spectral and spatial “neighborhoods” of the states studied. We found that the delocalization will not occur if the temperature is too close to 0 K.

4. Conclusions

In this paper, we presented a simulation of the dynamics of the localized electronic edge states in a-Si at room temperature by integrating the time dependent Schrödinger equation with a simple Crank-Nicholson method and a first-principles (Fireball96) Hamiltonian. We found that the localized edge states, the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO), are strongly modulated by phonons. Temperature induces a stronger intra-band transition than the inter-band transition across the gap. The simulation indicates a different diffusion mechanism for HOMO and LUMO. We emphasize that the decoherence is a dynamical process and can only be approached by the analysis of electron dynamics. The observed delocalization is also a dynamical effect which will not occur if the adiabatic approach is applied since the memory of the phase of a quantum state is discarded. Our work demonstrates in a quantitative and realistic way (1) the nature of thermally induced hopping, (2) the need of a spatial and spectral overlap for electronic diffusion, and (3) lays important groundwork for a future theory of non-adiabatic transport in disordered systems.

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