# EFFECT OF LATTICE VIBRATIONS ON THE STRUCTURE OF ELECTRONIC STATES IN AMORPHOUS SILICON

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**ABSTRACT**

*The nature of the states near the gap at zero temperature is discussed and especially the way the structure of the states changes for energies ranging from midgap into either band tail (Anderson transition). We then study the effect of lattice vibrations on the eigenstates and find that electronic states near the optical gap can be strongly influenced by thermal modulation of the atomic positions. Finally, we show the structure of generalized wannier functions for amorphous Si, which are of particular interest for efficient ab initio calculation of electronic properties and forces for first principles dynamic simulation.*

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## INTRODUCTION

The electronic states of amorphous semiconductors are of both fundamental and applied interest. In this article we illustrate three aspects of electronic states: we begin by discussing the zero temperature (equilibrium) electronic structure of a-Si. We do this for a model of a-Si in pleasing agreement with structural, vibrational, and electronic/optical properties at the same time. The nature of the electron states near the gap is elucidated by direct calculation, and we find that the states are very complex. These visualizations enable a qualitative understanding of the Anderson transition: in simple terms this amounts to understanding how the structure of the electron states evolves from localized (near the middle of the gap) to extended (well into either conduction or valence bands). Next, we put the electrons and classical lattice vibrations together; we show that the electronic band tail states experience a very large electron – phonon coupling that strongly affects the transport and optical properties of the material. Finally, we present detailed calculations for Wannier – like functions that are well localized in real space, and that span the occupied electronic subspace for the amorphous silicon models. These functions have special importance for current computational techniques (since they enable far more efficient calculations than are achieved by working directly with eigenstates, which are typically extended throughout the model).

## THERMAL EFFECTS ON THE ELECTRONIC STATES

In this section we add thermal disorder to the structural disorder and investigate the resulting fluctuations in the electron states, the structure of which is modulated by the lattice vibrations.[1] These fluctuations in structure of the eigenstates occur *only* if there are localized energy states adjacent both within energy (meaning within a few tenths of an electron volt), and real space, and such that the thermal disorder at a given temperature is sufficient to occasionally bring the energy eigenvalues of the adjacent states very close together. These conditions are often met in realistic models of a-Si for states near the Fermi level at room temperature. Thus, the picture that emerges is one in which the energy eigenvalues and sites where those eigenstates are localized change rapidly and drastically in a quasi oscillatory (but not periodic) manner. Further, the sites where a state is most localized may form wandering string like structures or columns where no two favored sites are nearest neighbors. However, in a variety of physically relevant temperature and energy ranges states never form a static structure, and often a spherical approximation for their geometry would be inappropriate. This is very different from the prevailing view.. While we have limited the current study to a-Si, there is every reason to believe

that the qualitative picture we present here is suited to any disordered insulator, such as glasses.[2] Unfortunately it is very difficult to directly connect these results to experiments because the time scales are very short; yet the ideas contained here are important to constructing proper theories of transport and optical effects.

This work complements an important body of existing theory work. Phenomenological theories of defect dynamics and kinetics (the defect pool model[3]) and transport have solved outstanding problems in their respective areas in a-Si and glasses. A value of the present work is to elucidate the foundations of these approaches by describing *explicitly* the nature of the electron states and their short-time dynamics. It is hoped that this will enhance and extend the value of these theories, and perhaps enable *"ab initio"* input to the phenomenological models.

In this section we employ the approximate local basis *ah initio* molecular dynamics scheme of Sankey and Niklewski. The method is tested for Si in many forms and is quite reliable. As in previous sections, we start with relaxed versions of the supercell structural models of Djordjevic et al., which are currently the most realistic models of a-Si extant since they are the only ones to our knowledge that simultaneously reproduce structural, electronic/optical,[4] and vibrational properties of a-Si. In this section we o 216- and 512-atom models.

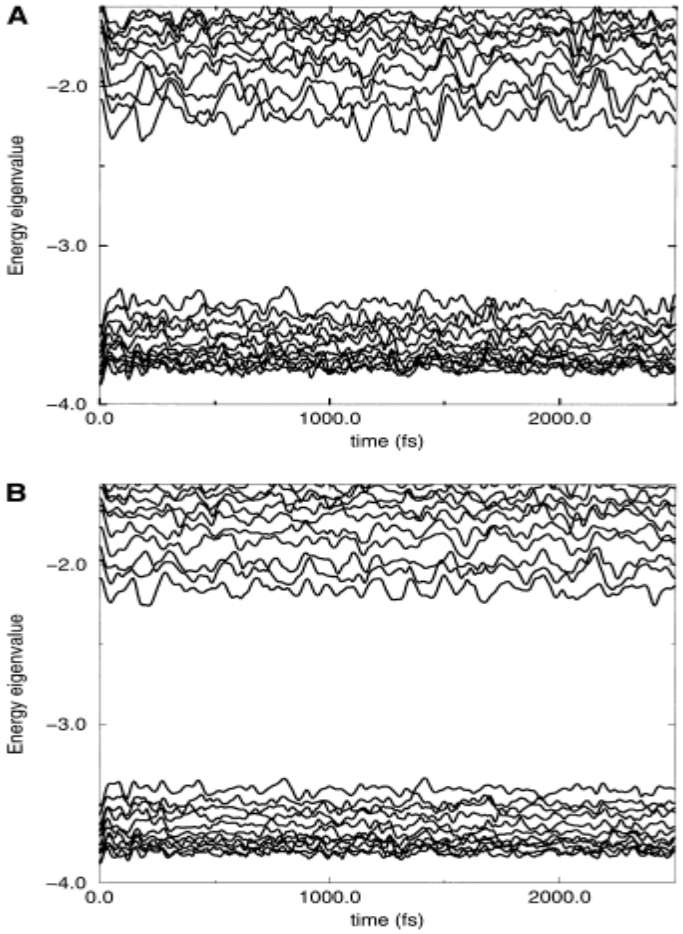


Figure2.Approximate LDA energy eigenvalues plotted against time (femtosecond) for 216-atom model[2] 300K thermal simulation. The Fermi level is in the middle of the optical gap (-2.7 ev). Note the large thermal fluctuations in the eigenvalues near the gap, and the occasional close approach of neighboring energy eigen values a) Simulation at 300K b)150 K

In Figure 2 we indicate the time dependence of the LDA eigenvalues in the vicinity of the optical gap. The Fermi level is near the middle of the gap and several states near the Fermi level are appropriately described as band tail states. These are much like the states that would be responsible for conduction in doped a-Si:H. Figure 2a and b illustrates the effect for a simulation at 300 and 150 K, respectively. As in earlier work[5]L[6] there is a roughly linear relation between RMS temporal fluctuation and temperature. As expected, the higher temperature simulation leads to larger excursions in the positions of the energy eigenvalues.1\lote for Figure 2a (300 K) that the lowest unoccupied molecular orbital (LUMO) fluctuates in time by about -0.3 eV, much larger than thermal energies (-1·0 meV). States deeper into either the valence or conduction bands show progressively less thermal modulation because they are less localized (we have noted[2] a very strong correlation between

the rms fluctuation in the energy eigenvalues due to thermal disorder and the inverse participation ratio, a simple measure of localization in the $T = 0$ model). The localization "amplifies" the electron-phonon coupling. Also, the conduction states fluctuate more than the valence states (suggesting that the conduction tails are more sensitive to thermal disorder than the valence tails, which originate primarily from structural disorder), in pleasing agreement with total yield photoemission experiments'" and earlier theory work.[7]

The key conclusions of this article can be inferred from Color Plate 2, in which we illustrate "snapshots" of a particular electronic eigenvector (the LUMO state) extracted from a 300 K simulation of a-Si[8.] In Color Plate 2, different colors indicate different levels of charge on a given atom (the ordering is red, green, blue, gray, white; see the caption to Color Plate 2 for detail). There is a clear tendency for the LUMO state to alternately "accumulate" on a strained part of the network, sometimes becoming strongly localized (Color Plate 2a), but also occasionally developing a substantially more extended "stringlike" character (Color Plate.2b). These are not the only two recognizable structures, but recur most frequently.9 The time between "characters" is not predictable, although it is on the order of tens of hundreds of femtoseconds.

In Figure 3, we reproduce the 300 K temporal fluctuations of the LDA eigenvalues near the gap for a larger (512-atom) model of a-Si also made by Djordjevic et al.,and also in excellent uniform agreement with experiments. This larger model illustrates some additional points.[10] Although the LUMO energy level fluctuates considerably, the structure of its conjugate eigenvector is much more "static" than the LUMO state of Color Plate 2. Even though there is obviously a large electron-

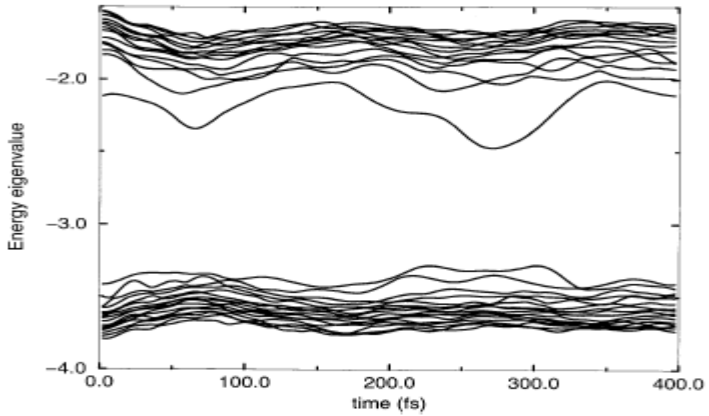


*Figure 3. Approximate LDA energy eigenvalues plotted against time (in femtoseconds) for 512-atom model[2] for 300 K thermal simulation. The Fermi level is contained in the gap (near -3.0 e0.)*

phonon coupling (because of the large fluctuations in energy), the state does not approach closely enough to the next conduction state in energy to exhibit strong mixing and therefore markedly change its structure.[11] This emphasizes the point that a large electron-phonon coupling by itself is not sufficient to cause major changes in the structure of the relevant eigenvector. In Color Plate 3, we illustrate the highest occupied molecular orbital "HOMO" state and snapshots in analogy with Color Plate 2. By inspection of the time development of this state from Figure 3, there are two "close approaches" of this state to the next valence tail state. Indeed, we find that the qualitative behavior of this state is similar to that from Color Plate 2, "snapshots" with color coding identical to Color Plate 2 are presented as Color Plate 3a and b, illustrating compact cluster and chainlike character, respectively. In the short simulation for the 512-atom model (400 fs), we also saw a. distinctive structure involving three rather separated clusters. We conclude that the phenomenon is qualitatively similar for occupied levels such as this or for unoccupied states (the LUMO of Color Plate 2).[12]

We have argued earlier[16] that structural disorder in a-Si gives rise to localized states with energies in the band tails. This work showed that it is useful to view localized energy eigenstates in a-Si as either pure or mixed "cluster states." Cluster states are localized eigenstates of an idealized system that stem from some structural irregularity such that there is no overlap with energetically degenerate clusters. Such cluster states can be difficult to realize in isolation in real a-Si, since structural defects can occur with similar local electron energies, which would cause the system energy eigenvectors to consist of mixtures of the resonant defect clusters if the defects are in adequate spatial proximity to allow overlap between cluster states. We have explained this in Ref. 16. The "simple physics" of this article is that the strong electron-phononcoupling for localized band tail states is sufficient to cause strongly time/temperature-dependent quantum mechanical mixing of cluster states when the thermal disorder is "just right" to make their energies nearly degenerate provided that they have some overlap in real space.[13] Strong mixing of course implies less localization and thus better prospects, at least while the more extended state survives, for conductivity and optical transitions. This work shows that transport and optical calculations based only on $T = 0$ results can be quite misleading.

The consequences of this work can be stated another way. If |i>(|f>) are initial (final) electronic states with energy $E_i$ ($E_f$), then for an electronic transition in a-Si, a Fermi golden rule argument leads quickly to the conclusions that the transition rate is proportional to

$|<i|T|f>|^2\delta(E_f - E_i - \hbar w)$ where 1' is a perturbation inducing the transition (to first approximation a momentum operator) and a) is the frequency of an external probe. Both the energies in the 8 function and the transition matrix elements are sensitive to the instantaneous details of the structural disorder, and as such transition probabilities are also strongly dependent on the time and temperature. The consequences of this to transport are under investigation; the discussion here is based on first-order time-dependent perturbation theory, which for the very strong electron--phonon coupling we discuss, could be inadequate. )

## CONCLUSION

In this article we have shown the structure of typical current electronic structure calculations for a-Si. Then, we showed that the band tail states are very sensitive o additional disorder from lattice vibrations. This is very important for optical and transport calculations, and the defect pool model.

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